Nanoscale Properties of Copper Metallization: Real-Time Stress Measurements during Electrodeposition, In-Situ AFM Imaging and Ductility Test Development

A thesis presented to the University of Limerick for fulfilment of the requirements for the award of

Doctor of Philosophy Degree

by

Michael O’Grady, B.Sc.

Department of Physics and Energy

May 2012

Supervisor: Prof. D. Noel Buckley
Declaration

The work presented in this thesis is the original work of the author, under the direction of Prof. D. Noel Buckley and due reference has been made, where necessary, to work of other authors. No part of this thesis has been previously submitted to this or any other University.

______________________________

Michael O’Grady
Acknowledgements

I would like to sincerely thank my supervisor Prof. Noel Buckley for his guidance and advice during the course of my research work. His wisdom and commitment inspired and motivated me. I would also like to extend my thanks to Prof. Nakahara for sharing with me his valuable knowledge and expertise.

I would like to show my gratitude to the department staff, the technicians John Sweeney, John Kelly, Eamonn Campbell and Maria Quinn, and the secretary Josephine Hogan. I particularly would like to thank my fellow postgraduate students for their encouragement and support. I am also grateful for the help and technical support from Dr. Catherine Lenihan and Dr. Shafaat Ahmed.

Finally, I dedicate this thesis to both my family and Maria for their support and patience throughout my work.

This research was carried out both in the Department of Physics and Energy and the Materials Surface Science Institute (MSSI) at the University of Limerick. This work was funded by Science Foundation Ireland (SFI) under grant No. 02/IN1/I217.
‘The best way to have a good idea is to have lots of ideas.’ – Linus Pauling.
Abstract

Copper was electrodeposited on a polycrystalline gold substrate both in the presence and absence of electrochemical bath additives. Stress evolution was monitored in situ using a cantilever beam method and surface morphology was observed using in situ atomic force microscopy (AFM).

Measurements of stress and relaxation behaviour provided adequate data-sets to generate reliable and reproducible plots of local stress in the film. This was possible because (i) the magnitude of stress relaxation upon resumption of deposition was small relative to the stress generated during deposition and (ii) stress upon resuming deposition eventually recovered to its pre-interrupted value.

In-situ stress measurements showed that tensile stress peaked during deposition and eventually reached a relatively constant (plateau) value above a certain thickness (typically > 50 nm). The measured values of plateau stress increased with overpotential, ranging from 25 to 45 MPa for -125 to -200 mV. In-situ AFM imaging showed nucleation of individual copper islands which grew in size and eventually coalesced forming grain boundaries. Coalescence and grain boundary formation coincided with an increase in tensile stress. Surface features smoothened during interruption of deposition and recovered to a roughened configuration upon resumption of deposition. This behaviour coincided with a recovery in stress and this has been attributed to reversible movement of adatoms between the surface and grain boundaries.

Chloride ion significantly reduced tensile stress and produced rougher deposits than without additives. As roughness increased, stress decreased as was observed also for additive-free deposition. PEG alone had no significant effect on stress. However, PEG significantly enhanced stress reduction in the presence of chloride. A flat copper surface with scattered large pyramidal structures was produced.

Three prototypes of ductility testers were developed, the latest of which employed an optical-lever method for determining the displacement of a freestanding nanofilm under load. Several freestanding film structures were fabricated. A commercial AFM microscope was used to generate the load-displacement response of RF-MEMS switches which showed good agreement with FEM simulations.

Publications

1. M. O’Grady, C. Lenihan, D. N. Buckley, 222\textsuperscript{nd} ECS Meeting, Honolulu, Hawaii, Abstract No. TBD, (2012)
TABLE OF CONTENTS

1 INTRODUCTION 1

1.1 Intrinsic Stress in Copper Nanofilms 1

1.2 Calculation of Stress in a Thin Film 3
  1.2.1 General Assumptions 3
  1.2.2 Bending of a Bimetallic Strip 4
  1.2.3 Substrate Curvature during Thin Film Deposition 5

1.3 Overview of Thesis 7

1.4 References 8

2 LITERATURE REVIEW 9

2.1 Introduction 9

2.2 Studies of Intrinsic Stress in Thin Metal Films 9
  2.2.1 Stress Measurement Techniques 11
  2.2.2 In-Situ Stress Measurement during Deposition 13
  2.2.3 Interrupted Deposition 16
  2.2.4 Morphology and Stress 17

2.3 Copper Plating Chemistries: Bath Additives 19
  2.3.1 Effect of Chloride Additive on Copper Electrodeposition 19
  2.3.2 Effect of PEG on Copper Electrodeposition 22
  2.3.3 Effect of PEG with Chloride in Combination 22
  2.3.4 Influence of Additives on the Morphology of Electroplated Copper 25

2.4 Testing Freestanding Nanofilms 28
  2.4.1 Nanoindentation 30
  2.4.2 Bulge Testing 31
  2.4.3 Important Considerations in Testing Freestanding Films 33

2.5 References 34
3 EXPERIMENTAL

3.1 Introduction

3.2 Three-Electrode Electrochemical Cell
  3.2.1 Stress Cell
  3.2.2 AFM Cell
  3.2.3 Reference Electrode
  3.2.4 Counter Electrode
  3.2.5 Working Electrode: Preparation and Fabrication
  3.2.6 Electrolyte
  3.2.7 Electroanalytical Techniques

3.3 In-Situ Stress Measurement System
  3.3.1 Measuring Cantilever Deflection in an Electrolyte
  3.3.2 Optical Lever Configuration
  3.3.3 Data Acquisition and Processing
  3.3.4 Measuring Film Thickness by Coulometry

3.4 In-Situ Electrochemical Atomic Force Microscope (EC-AFM)
  3.4.1 In-Situ EC-AFM Configuration
  3.4.2 Measurement of Surface Morphology
  3.4.3 AFM Data Analysis and Image Processing

3.5 Ductility Measurement
  3.5.1 Nakahara Ductility Tester
  3.5.2 Force-Displacement AFM-based Technique
  3.5.3 Fujikara Arc Fusion Splicer

3.6 References

4 STRESS AND MORPHOLOGY DURING COPPER ELECTRODEPOSITION

4.1 Introduction

4.2 In-situ Stress Measurements and AFM Imaging during Electrodeposition
  4.2.1 Results at -125 mV
  4.2.2 Results at -160 mV
  4.2.3 Results at -200 mV
# 4.3 Interruption of Electrodeposition

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3.1 Results at -125 mV</td>
<td>91</td>
</tr>
<tr>
<td>4.3.2 Results at -160 mV</td>
<td>98</td>
</tr>
<tr>
<td>4.3.3 Results at -200 mV</td>
<td>103</td>
</tr>
</tbody>
</table>

# 4.4 Discussion

107

# 4.5 Conclusions

112

# 4.6 References

113

# 5 EFFECTS OF ADDITIVES

115

## 5.1 Introduction

115

## 5.2 Effects of Chloride on Stress and Morphology

116

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.1 Preliminary Study of Concentration Dependence</td>
<td>117</td>
</tr>
<tr>
<td>5.2.2 Results at -125 mV</td>
<td>123</td>
</tr>
<tr>
<td>5.2.3 Results at -160 mV</td>
<td>130</td>
</tr>
<tr>
<td>5.2.4 Results at -200 mV</td>
<td>136</td>
</tr>
<tr>
<td>5.2.5 Comparison of Results at -125 mV, -160 mV and -200 mV</td>
<td>141</td>
</tr>
</tbody>
</table>

## 5.3 Current Interruption with Chloride Additive

144

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3.1 Results at -125 mV</td>
<td>144</td>
</tr>
<tr>
<td>5.3.2 Results at -160 mV</td>
<td>147</td>
</tr>
<tr>
<td>5.3.3 Results at -200 mV</td>
<td>149</td>
</tr>
<tr>
<td>5.3.4 Comparison of Results at -125 mV, -160 mV and -200 mV</td>
<td>151</td>
</tr>
</tbody>
</table>

## 5.4 Effects of Chloride and PEG in Combination

153

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4.1 PEG</td>
<td>155</td>
</tr>
<tr>
<td>5.4.2 Dependence on Concentration of Chloride Ion and PEG</td>
<td>156</td>
</tr>
<tr>
<td>5.4.3 Stress Results at -200 mV</td>
<td>161</td>
</tr>
<tr>
<td>5.4.4 AFM Results at -200 mV</td>
<td>162</td>
</tr>
<tr>
<td>5.4.5 In-Situ AFM Measurements during Corrosion of Copper Pyramidal Features</td>
<td>164</td>
</tr>
</tbody>
</table>

## 5.5 Summary and Conclusions

167

## 5.6 References

168
6 DEVELOPMENT OF DUCTILITY TESTING OF NANOFILMS 170

6.1 Introduction 170

6.2 Ductility Testing in Macro-Scale Copper Films 173

6.3 Development of a Nanoscale Ductility Tester 177
   6.3.1 First Prototype: MK1 177
   6.3.2 Second Prototype: MK2 182
   6.3.3 Third Prototype: MK3 198

6.4 Fabrication of Cantilevered Microprobes 206
   6.4.1 Fabricating Microprobes with Hemispherical Tips 206

6.5 Fabrication of Freestanding Metal Films 207

6.6 Ductility Measurements of Freestanding Films 208
   6.6.1 Measurements on freestanding copper nanofilms using MK3 tester 208

6.7 Force-Displacement Measurements on RF-MEMS Switches 213
   6.7.1 RF-MEMS Switches 213

6.8 Summary and Conclusions 219

6.9 References 220

7 CONCLUSIONS AND FUTURE WORK 221

7.1 Conclusions 221
   7.1.1 Determination of Local Stress from Force-Thickness Data 221
   7.1.2 Stress and Morphology in the Absence of Additives 221
   7.1.3 Effects of Chloride and PEG 222
   7.1.4 Ductility Testing of Nanofilms 223
   7.1.5 Force-Displacement Measurement of RF-MEMS Switches 223

7.2 Future Work 223
   7.2.1 Island Growth in the Presence of Chloride 224
   7.2.2 Mathematical Model and Experimental Investigation of Stress and Morphology 225
   7.2.3 Other Recommendations for Future Work 225
APPENDICES

A.1 AFM Images with Chloride Additive 227

A.2 Freestanding Film Fabrication 237
   A.2.1 TEM Grid Support 237
   A.2.2 Perforated Copper Foil Support 238
   A.2.3 Silicon Micro-Fabrication of Metal Nanofilms 242

A.3 Bending of a Beam 249

A.4 Bending of a Beam Fixed at One End 253

A.5 Position Sensitive Detector 258

A.6 Annealing Evaporated Gold Films 260
1 Introduction

1.1 Intrinsic Stress in Copper Nanofilms

Thin films deposited on substrates can sustain higher stress levels than their bulk counterpart\(^1\) and this has been the subject of extensive experimental investigation and theoretical analysis. Microelectronic devices and micro-electromechanical systems (MEMS) suffer from reliability issues due to high stresses in thin films, such as cracking, delamination and electromigration.

Stress in thin films is often sensitive to the nature of the materials system, deposition technique, and process parameters. Intrinsic stresses are induced by various physical effects during and after the film growth. Thin films that undergo large temperature cycles in manufacturing processes are subjected to large stresses due to a thermal mismatch between the film and its substrate.\(^2\) Thermal mismatch stresses can be very high if the thermal mismatch is large and the elastic modulus of the film is large, such as is the case for copper films used in integrated circuits. The measurement and understanding of intrinsic stress in thin metal films is a significant challenge.

Electrodeposition is a suitable method for bottom-up filling (or “superfilling”) of high-aspect-ratio trenches in the copper damascene process. Copper has high conductivity, good thermal stability and excellent resistance to stress migration. The deposition conditions and the presence of additives have a considerable impact on micro/nanostructural properties of electrodeposited copper such as stress and morphology. Copper plating baths typically contain additive mixtures with three or four components which facilitate superfilling. Since electrodeposition is a relatively new technology for microelectronics, most work on intrinsic stress has been documented on vapour-deposited films.
Intrinsic stress in nanoscale metal films is most commonly measured using a substrate curvature technique. When metals are deposited under either compressive or tensile stress the substrate material strains and bends accordingly. The amount of bending combined with the thickness of the deposit enables the stress in the film to be estimated. Many modern systems have employed this technique for real-time stress measurement during deposition of metal nanofilms. In Section 1.2 we introduce the theory of a bending beam and its application to intrinsic stress in a deposited film (i.e. Stoney’s equation). 

With time-varying processes occurring in the film during deposition, achieving reliable measurements of intrinsic stress is quite challenging. Deconvoluting these effects has been attempted with growth-interruption experiments, but usually the time variation of the film stress is quite large. It has been extensively documented, both experimentally and theoretically, that intrinsic stress has a strong relationship with the microstructure and the growth processes during deposition. 

Growth processes during electrodeposition are difficult to control due to their stochastic behaviour. Coupling mathematical models with experimental observations is a powerful way of understanding these small-scale phenomena during film growth. The evolution of surface morphology during electrodeposition is typically observed using in-situ atomic force microscopy. Although some authors have used this technique to observe growth during copper electrodeposition, few have coupled this technique with in-situ stress measurement. 

Ductility is an important property in microelectronic devices where the component thin film materials are usually under large strains due to the manufacturing process. A highly ductile film can undergo large strains without reducing the integrity of the material, thus improving the reliability of the device. Measuring ductility is a significant challenge in hardware design, specimen fabrication and handling. Uniaxial tensile testing is the most common technique for measuring ductility. However, biaxial mechanical testing has an advantage in that it can measure ductility in anisotropic films. A simple ductility tester designed by Prof. Nakahara is suitable for metal films on the order of 10 μm in thickness. In Chapter 6, we describe our
work on developing a Nakahara-type tester on the nanoscale. This required not only hardware development but also significant work on specimen preparation.

1.2 Calculation of Stress in a Thin Film

The most common technique for measuring intrinsic stress is the substrate curvature method. Substrate deflection can be measured by optical, capacitive and interference-based methods. Because of its excellent sensitivity, the substrate curvature method has been particularly useful for stress measurement during the very early stages of thin metal film deposition. When metals are deposited under either compression or tension the substrate material strains and bends accordingly. The amount of bending combined with the thickness of the deposit enables the stress under which it is deposited to be calculated. In this section, we apply the theory of a bending beam to a film-on-substrate system to generate Stoney’s equation\(^3\).

1.2.1 General Assumptions

Stoney’s equation\(^3\), which describes the bending of a beam (or substrate), is based on general assumptions. For application of the Stoney equation it is required that the substrate is thick compared to the thickness of the film, but still thin enough that it bends due to stress in the film. Another requirement for application of the Stoney equation is that the film is in a state of plane stress, meaning that in the plane of the film the stress is independent of direction, or in tensor notation:

\[
\vec{\sigma}_f = \begin{pmatrix}
\sigma_f & 0 & 0 \\
0 & \sigma_f & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

No plastic deformation of the film at the substrate interface is allowed, and the force in the film is transmitted directly to the substrate at this interface. Sufficient adhesion is necessary at the interface that the film is not torn loose from the substrate. For convenience of interpretation, it is assumed that each new layer adds a force which is transmitted without change to the substrate. Taking into account these assumptions, the analysis of the bending problem is described as follows.
1.2.2 Bending of a Bimetallic Strip

From Appendix A.3, we showed that bending moment of a film (see Equation A.14) can be expressed as

\[ M_f = \frac{E_f h_f^3 w}{12R} \]  

and similarly for the substrate,

\[ M_s = \frac{E_s h_s^3 w}{12R} \]  

where \( M_f \) is the bending moment of the film, \( M_s \) is the bending moment of the substrate, \( h_s \) is the substrate thickness, \( h_f \) is the film thickness and \( R \) is the radius of curvature.

Combining film and substrate moments, the bending moment \( M \) of the bilayer is

\[ M = M_f + M_s \]  

The ratio of the transverse strain to the axial strain in a strained film is known as the Poisson ratio, \( \nu_f \). In the thin-film approximation (i.e. a thin film on a thick substrate), the average stress on the film can be expressed as

\[ \sigma_f \approx E_{bf} \Delta \varepsilon_0 \]  

where \( E_{bf} \) = biaxial modulus of the film.

\[ E_{bf} = \frac{E_f}{1 + \nu_f} \]

and \( \Delta \varepsilon_0 \) is the lattice mismatch between film and substrate prior to any mechanical relaxation. The biaxial modulus of the substrate is

\[ E_{bs} = \frac{E_s}{1 - \nu_s} \]

where \( \nu_s \) is the Poisson ratio of the substrate. Similarly, in the thin film-film approximation the curvature of a freely bent bilayer
Combining Equations 1.5 and 1.6, we get

$$\frac{1}{R} = \frac{6E_{bf} h_f}{E_{bs} h_s^2} \Delta \varepsilon_0$$  \hspace{1cm} 1.6$$

Therefore,

$$\Delta \varepsilon_0 = \frac{\sigma_f}{E_{bf}} = \frac{E_{bs} h_s^2}{6R E_{bf} h_f}$$  \hspace{1cm} 1.7$$

Substituting for $E_{bs}$, we get Stoney’s Equation

$$\sigma_f = \frac{E_s h_s^2}{6Rh_f}$$  \hspace{1cm} 1.8$$

1.2.3 Substrate Curvature during Thin Film Deposition

A schematic diagram in Fig. 1.1 shows a thin film with thickness $h_{film}$ deposited on a substrate with thickness $h_{sub}$. The width of both the film and substrate is $w$. Fig. 1.2(a) shows the resulting curvature that occurs due to tensional stress in the deposit. The dotted line indicates the neutral axis above which stress is compressive and below which stress is tensile.

![Diagram of thin film and substrate](image)

**Fig. 1.1** Thin metal film with thickness $h_{film}$ deposited on top of a substrate with thickness $h_{sub}$, width $w$, and length $l$.

If the deposit is much thinner than the substrate, the neutral axis will lie within the substrate, as shown by the dotted line in Fig. 1.2(a). The tensile stress in the deposit causes a compressive strain in the substrate above the neutral axis.
Incidentally, the neutral axis shifts to within the deposit itself with sufficient film thickness as shown in Fig. 1.2 (b).

If the deposit is divided up into $N$ layers each with finite thickness $\Delta h$ and width $w$ (see Fig. 1.3), the differential stress $\sigma$ acting on the cross-sectional area of the section is then expressed as

$$
\sigma = \frac{F}{\Delta hw} \tag{1.10}
$$

The average stress $\sigma_{avg}$ in the whole film is expressed as

$$
\sigma_{avg} = \left( \sum_{i=1}^{N} \sigma \right) / N \tag{1.11}
$$

where $N$ is the number of such sections in the film.
The average stress $\sigma_{avg}$ of (a) a thin metal film on a substrate is the sum of the differential stress $\sigma$ in (b) the deposit where each increment has height $\Delta h$ and width $w$.

1.3 Overview of Thesis

In Chapter 2 we present a brief review of the literature on intrinsic stress and morphology in copper metallization. This also describes typical techniques for measuring mechanical properties at the micro/nanoscale. Chapter 3 outlines experimental details. Chapter 4 presents our investigation of stress and morphology in copper nanofilms electrodeposited without the use of any bath. In Chapter 5 we expand this study to include the effect of chloride and PEG additives. Chapter 6 describes our development of ductility testing at the nanoscale. It also describes some stiffness measurements of RF-MEMS switches. Chapter 7 presents a summary of our results and recommendations for future work.
1.4 References

2
Literature Review

2.1 Introduction
The nanoscale mechanical properties of metal films such as intrinsic stress, surface morphology and ductility are of significant interest to the microelectronics industry with regard to the reliability and performance of integrated circuits. Many experimental and theoretical investigations of stress have been carried out on copper nanofilms. While considerable progress has been made in understanding the relationship of stress evolution to the physical processes of film formation, many questions remain. In this chapter, we summarize the literature in the areas of intrinsic stress and morphology, copper plating chemistries, and the mechanical testing of freestanding nanofilm structures.

2.2 Studies of Intrinsic Stress in Thin Metal Films
Thin metal films develop large intrinsic stresses during deposition. High intrinsic stress results in the formation of defects such as voids or hillocks and this significantly affects reliability and lifetime of integrated circuits.\(^1\) Intrinsic stress can arise from lattice-mismatched epitaxial growth\(^2\), nuclei coalescence\(^3\) and grain growth\(^4\) during deposition and incorporation of impurities\(^5\). These sources of stress have a greater impact with reduced film dimension.

It is commonly observed that the microstructure of as-deposited films obtained by sputtering and electrodeposition is not stable at room temperature but changes readily with time,\(^15\) accompanied by recrystallization and grain growth.\(^6\) Stress or stored energy is the driving force for recrystallization in metal films.\(^7\) Recrystallization leads to changes in the electrical, mechanical and microstructural characteristics of deposited copper films.\(^15\) Such changes include a significant drop in resistivity over
time, an evolution of the microstructure by grain growth, changes in texture and stress, and a decrease in micro-hardness.$^{7-14}$

The recrystallization of copper will be greater in regions of high stress and/or dislocation density, i.e. the upper corners of a damascene trench.$^{15}$ Small changes in the microstructure of metal films affect their electrical and mechanical characteristics. Since the degree of strain varies with the deposition conditions, the rate of recrystallization is also expected to vary. For example, the evolution of crystal structure and resistivity is correlated with stress.$^{7,11}$

The recrystallization time is dependent on the plating current density, with significantly longer times at lower deposition current density.$^9$ The high density of crystalline defects acts as the driving force for faster self-annealing.$^4$ When the thickness of an electrodeposited film approaches the grain size, the grain is forced to grow in two dimensions. The stress that is released during recrystallization is remarkably stronger in thinner films.

Annealing is an important step for reducing strain energy during which grain growth and crystallographic development occur.$^{16}$ Annealing results in a decrease in hardness or strength and an increase in ductility.$^7$ However, thermal mismatch between film and substrate can result in cracking of the film.$^{17}$

The effects of interfaces on the intrinsic stresses in polycrystalline films are not completely understood. Densification of a film constrained by a substrate leads to tensile stresses in the film. The grain boundaries in the film can contribute to densification as sinks for excess vacancies, or by eliminating excess boundary volume as a result of grain growth.$^{18}$ Grain boundaries can also play a role in the relaxation of stresses by plastic flow, either as obstacles to dislocations or as sources and sinks in diffusional flow.

The microstructure of electrodeposited copper is strongly related to its electrical properties. It is widely accepted that the resistivity of as-deposited copper exceeds the bulk value of 1.7 $\mu\Omega$-cm by 10-30% and decreases to near-bulk value at room
temperature after some hours.\textsuperscript{15, 19} A 1 \textmu m-thick electroplated copper film can lower its sheet resistance by as much as 19\% within 23 hours at room temperature.\textsuperscript{10} For 100 nm-thick copper films, the resistivity decreases by only 2\% after 50 hours.\textsuperscript{8}

Although the energetics and kinetics of copper deposition from acidic copper sulphate solution are essentially independent of substrate orientation,\textsuperscript{20} the substrate can considerably affect the physical properties of the film (i.e. microstructure, crystallographic texture and morphology).\textsuperscript{21} The difference in strain energy between (111) and (100) oriented grains can change depending on the stress that has developed during grain growth (grain growth-induced stress) or by thermal mismatch between film and substrate during thermal annealing.\textsuperscript{4} The final grain size is the result of minimization of all orientation-dependent driving forces such as surface, interface and strain energies. The difference between surface/interface energies of (100) and (111) orientation is inversely proportional to film thickness.\textsuperscript{4}

An important characteristic of polycrystalline films is that deposited metal atoms bond more strongly with each other than they do with the substrate itself. As a result, atoms tend to join into clusters instead of “wetting” the substrate uniformly.

\subsection*{2.2.1 Stress Measurement Techniques}
In 1909, Gerald G. Stoney\textsuperscript{22} found that when nickel was deposited on to a thin sheet of metal very considerable bending took place. When nickel was deposited under tension it caused the substrate material to strain and bend accordingly. The amount of bending combined with the thickness of the deposit enables the tension under which it is deposited to be calculated. Stoney’s formula calculated the tension in the nickel deposit by considering the following parameters: substrate thickness, deposit thickness, Young’s Modulus, radius of curvature, dimensions of the sample and vertical deflection of the sample. Since Stoney’s work, many experiments involved investigating intrinsic stress during metal deposition using the cantilever beam technique in which the force per unit width as a function of the film thickness was measured. Cantilever deflection is typically measured using optical-lever technique, capacitance measurements,\textsuperscript{23} piezoresistive measurements\textsuperscript{24} and interferometry.\textsuperscript{25}
The cantilevered beam technique is typically used for in-situ stress measurement during metal deposition. Cantilever deflection can be measured by optical, electromechanical and capacitive methods. The optical-lever technique involves measuring cantilever deflection by reflecting a laser on its back-side towards a position sensitive detector (PSD). Using Stoney’s equation, the stress of a film on a substrate can be calculated.

Various cantilever structures have been used as substrates in cantilever deflection experiments. In certain studies, a glass sheet substrate is deposited by a thin adhesion layer, typically titanium, followed by a gold or platinum layer. In other work, silicon micro-fabricated cantilevers are used. A reflective coating (i.e. aluminium on silicon [Gerlach 1998]) is deposited on the backside of the cantilever to obtain laser reflection. In certain experiments, the substrate is annealed to relieve stress and promote (111) crystallographic orientation and grain growth. Substrates with gold on top can be annealed using a hydrogen flame.

Double crystal diffraction topography (DCDT), laser scanning techniques (LST), profilometry and optical interferometry are some of the techniques used to determine curvature of thin film-substrate composites. STM and optical deflection techniques offer a much higher signal-to-noise ratio than interferometric techniques. The strain distribution through a film can be measured using grazing incidence x-ray scattering. Not only is XRD difficult to integrate into a deposition system but its acquisition time is far too long to be considered real time. Raman spectroscopy can be used to determine residual stress in thin films, but cannot perform real time stress measurements during film growth. Reflection high-energy electron diffraction (RHEED) can be used in real time, but it can only measure the surface parameter. Laser interferometric measurement of a curved substrate is useful for observing stress anisotropy of thin films.

In the capacitive technique, the free end of the cantilever is positioned between the anode and cathode of a dielectric capacitor. A change in the position of the cantilever induces a corresponding change in capacitance, which is monitored by a lock-in amplifier. Laser scanning techniques involve scanning a laser over the surface of a sample and measuring its profile using a PSD. One disadvantage with laser scanning
is that oscillation of the laser due to sample vibration may be accidentally interpreted as real curvature changes. During electrodeposition, due to the neglect of the refraction at the optical window may cause an error of 25-30% in the estimation of the stress changes.\textsuperscript{10}

\subsection*{2.2.2 In-Situ Stress Measurement during Deposition}

In a typical experiment, force per unit width of the cantilever $F/w$ is obtained by measuring the product of the biaxial modulus of the film and the difference in coefficients of thermal expansion of the substrate and the film.\textsuperscript{25} Intrinsic stress does not evolve linearly,\textsuperscript{5} but through compressive-tensile or compressive-tensile-compressive (C-T-C) behaviour. During the early stages of deposition (typically 5-10 nm) of a metal film, a small compressive force develops,\textsuperscript{23} beyond which a tensile stress develops with increasing thickness\textsuperscript{23} and eventually becomes net compressive.\textsuperscript{25} The coalescence-induced tensile stress has been associated with islands “zipping” together, driven by a trade-off between free surface and grain boundaries. The existence of the compressive component was ambiguous in the earlier studies but it appeared to be associated with the steady state dynamic surface during deposition. The magnitude of the compressive features in $F/w$ depends on both the species being deposited and the initial surface. Some authors have proposed that compressive stress is a consequence of excess atoms becoming incorporated into the grain boundary,\textsuperscript{33} whereas others attribute it to the surface stress of small nuclei. The tensile component has been attributed to island coalescence during the early stages of layer deposition and grain boundary formation.\textsuperscript{26} The final compressive stage occurs during thickening of the continuous film.

Individual isolated islands nucleate on the substrate during the early stages of deposition. As the islands grow in diameter, they impinge to form a network of islands, eventually coalescing into a continuous polycrystalline film. Tensile stress increases as the islands ‘zip’ together and form a grain boundary at their intersection. Part of the free surface of each island is eliminated resulting in a significant energy reduction. As the grains grow in size tensile stress continues to increase due to the increase in grain boundary volume. Tensile stress reaches a maximum as the film becomes fully continuous. The maximum tensile stress measured during deposition

13
of high mobility materials is typically an order of magnitude lower than that for low mobility materials.\textsuperscript{34}

The growth process that follows nuclei coalescence produces a compressive stress that competes with the initial tensile transient. This tensile-to-compressive transition is typically associated with high-mobility island growth and has been observed in copper deposited from the vapour phase.\textsuperscript{25} In the PVD literature, this post-tensile compressive stress has been attributed to\textsuperscript{33} the non-equilibrium concentration of mobile ad-atoms on the surface which are driven into the grain boundaries. Since a vacancy is assumed to be smaller than an atom, an incoming atom will cause nearby atoms to become compressed as it occupies the vacancy.

The chemical potential on the surface is defined as\textsuperscript{33}

\[ \mu_s = \mu_s^0 + \delta \mu_s \]

where \( \mu_s^0 \) is the chemical potential of the surface adatoms in equilibrium with the solid and \( \delta \mu_s \) is the increase in chemical potential due to impinging deposition flux. The deviation from equilibrium, \( \delta \mu_s \), may result in a supersaturation of adatoms on the surface, nucleation of new clusters, or increase surface step density. It is important to note that \( \delta \mu_s \) corresponds to the difference in the surface chemical potential between equilibrium and growth conditions and not between the surface and the vapour.

Grain boundaries have been shown to play an important role in the generation of compressive stress because it has been observed that films deposited on polycrystalline substrates eventually become compressive while those same films deposited onto single crystal substrates remain tensile.\textsuperscript{33} The incorporation of \( N_{gb} \) atoms into the grain boundary results in a compressive stress in the film. In addition, there is a tensile stress, \( \sigma_t \), that develops as the planes in adjacent clusters grow together to form a grain boundary. This tensile component is approximated as being constant due to the cohesive attraction between atoms at the grain boundary.\textsuperscript{35} The total stress in the film is equal to
\[ \sigma = \sigma_i - \sigma_0 N_{gb} \left( \frac{a}{R} \right) \]

where \( \sigma_0 = Eaa/L \) is the compressive stress, \( a \) is the atomic spacing and \( h \) is the film thickness. \( L \) is the width of the grain, \( E \) is the elastic modulus, and \( \alpha \) is a geometrical shape factor. \( \sigma_0 \) corresponds to the compressive stress that would result if an additional atom were added to each of the atomic planes in the grain boundary without changing the size of the grain.

The growth stresses associated with Volmer-Weber growth from the gas phase have been divided into three distinct modes; low-mobility columnar growth, epitaxial growth, and high-mobility island growth.\(^{34}\) The low-mobility columnar films develop tensile stresses. Epitaxial Volmer-Weber films are completely compressive, while high-mobility films are initially tensile but become compressive as the film thickens. It is generally accepted that the tensile stress in low mobility films is due to the interaction of grain boundaries.

Hoffman’s model\(^5\) for predicting tensile stress as islands coalesce assumes that the islands can slide freely on the substrate, and neglects the effect of mass transport and growth flux. This model does not mention the mechanism for the rise in stress, or whether the material fracture strength is high enough to support the resulting stress. In both single rate depositions and alternating rate depositions in copper and silver, the post-tensile compressive stress decreases with increasing deposition rate.\(^{36}\)

Models by Hoffman\(^5\), Nix\(^{35}\) and Chason\(^{33}\) all neglect the combined effect of deposition flux and mass transport, which must play an important role because the observed stresses vary with the magnitude of the deposition flux. Sheldon’s model\(^{37}\) for the mechanism of tensile stress generation takes into account the competition between growth flux and diffusion. In this model, atoms diffuse to regions of high tensile stress during grain boundary formation, thus relaxing it. If the growth flux, however, is high compared with the rate at which atoms diffuse into the grain boundary, many sites will remain vacant. As a result, the grain boundary develops a tensile stress that should increase with increasing growth flux and decreasing diffusivity and should saturate eventually.
Compressive stress can occur in continuous, single-crystal, epitaxial thin films, which have no grain boundaries.\textsuperscript{38} Other experiments indicate that grain size has little or no effect on the post-coalescence compressive stress.\textsuperscript{39} This suggests that grain boundaries may not be necessary to the stress evolution in metallic thin films.

2.2.3 Interrupted Deposition

Shull observed that when deposition is interrupted, force per unit width ($F/w$) changes with time in the tensile direction regardless of whether the final $F/w$ during deposition is tensile or compressive.\textsuperscript{25} Reversible stress changes in the pre-coalescence and post-coalescence regimes are similar in that: the stress evolves in the tensile direction during growth interruptions, the initial rate of stress evolution is significantly faster when growth is resumed than when growth is first interrupted, and the magnitude of the reversible stress change increases with increasing pre-interruption deposition rate.\textsuperscript{38} Reversible stress changes may be associated with changes in adatom and other surface defect concentrations, corresponding with changes in the growth flux. The change in stress-thickness product with changing film thickness (the instantaneous stress) may be related to the adatom-surface interaction energy.

The initial rate of stress change during a growth interruption is slower than the initial rate of stress change when growth is resumed.\textsuperscript{38} If the reversible insertion of mobile ad-atoms into the grain boundaries is rate-limited by grain boundary diffusion, one would expect the formation and relaxation of the compressive stress to have similar time constants. The magnitude of the reversible stress change is dependent on the deposition rate and not the thickness of the deposit. Consequently, post-tensile compressive stress has been attributed to the concentration of atomic-scale defects on the surface, the formation and removal of which are not kinetically symmetric.

In the early stages of film deposition, less than 50 nm, there is little relaxation. As the deposit thickens, the subsequent interruptions to open circuit result in a stress relaxation in the tensile direction. Stress relaxes exponentially from its steady-state value. The relaxation time constant is dependent on the film thickness and grain size as well as other parameters.\textsuperscript{33}
When deposition resumes, a smaller secondary tensile peak can appear.\textsuperscript{26} This may be due to the creation of the final grain boundaries from the original nuclei or perhaps the result of secondary nucleation on the Cu surface brought about by the new potential pulse. Both tensile relaxation and the subsequent tensile peak diminish as the deposit thickens.

Koch\textsuperscript{32} performed growth-interruption experiments which showed that steady state compressive stress is largely independent of grain size. In addition, the reversible tensile rise upon interruption of deposition increases with film thickness. Koch speculates that when deposition is interrupted, the most recently deposited material on top of the grains (compressive region) moves into the grain boundaries (tensile region). When deposition is resumed, the surface recovers to the original configuration by preferentially collecting impinging atoms at the compressively strained regions.

\subsection*{2.2.4 Morphology and Stress}

There is still some controversy surrounding the mechanism for compressive stress in the pre-coalescence and post-coalescence stages of Volmer-Weber growth.\textsuperscript{35, 40-42} Early stress models have suggested that tensile stresses are produced only when the initial coalescence occurs. More recent models\textsuperscript{43} suggest stress is an inherent part of the growth process when two neighbouring surfaces grow together to form a grain boundary.

There are three known models that give possible mechanisms for the post-coalescence compressive stress. In Cammarata’s model,\textsuperscript{18} the post-coalescence compressive stress is determined by the thickness and the radius at which the islands become firmly attached to the substrate. Individual islands form before significant coalescence has occurred. However, a change in deposition rate during the pre-coalescence stage of growth only changes the density of islands on the substrate. Therefore, in this case, the deposition rate should have no effect on the incremental compressive stress because the radius at which the island attaches to the substrate depends only on the interaction between the depositing species and the substrate and not on the island density on the surface, since in the pre-coalescence stage, each island behaves independently. Since the final grain size does not enter this model, it
has the same predictions for both alternating rate depositions and single rate depositions.

Chason et al.\textsuperscript{33} suggested the post-coalescence compressive stress is associated with the flow of adatoms into non-equilibrium states of grain boundaries due to the flux-induced change of the surface chemical potential. When deposition is interrupted, the atoms move out of the grain boundaries again, thereby relaxing compressive stress. Reversible compressive or tensile stress observed during the pre-coalescence stage (i.e. before grain boundary formation) has been attributed to changes in adatom population.\textsuperscript{44}

Spaepen’s surface ledge model\textsuperscript{36} depends on the interstitial-like atom incorporation between compressive ledges on the surface. An increase in the deposition rate increases the island nucleation rate and hence the density of ledges. Although this increases the number of places where opposing edges offer an opportunity for incorporation of an interstitial, it increases even more the number of regular ledge sites where atoms can be incorporated onto regular lattice sites (by substitution). A deposited adatom, therefore, has a greater chance of reaching a regular lattice site, or, failing that, to participate in the nucleation of a new terrace. The lower fraction of interstitial entrapment thus reduces the compressive stress. Note that the final grain size does not enter into this model, so that the predictions of this model are the same for both alternating and single rate depositions.

In Rajamani’s model,\textsuperscript{43} stress increases to its maximum value as the ratio of the grain boundary length and the height of the grain approaches unity. An important distinction of this model is that the maximum tensile stress does not occur at coalescence but when the grain boundary is fully formed, approaching the thickness of the film. Preferential deposition into the grain boundary (increase in $b/h$) may be due to either as the result of direct deposition or the movement of ad-atoms on the surface, as the material that is added to the boundary reduces the elastic strain associated with bringing the surfaces together.

The equilibrium stress as a function of island-substrate contact angle is related to the island size.\textsuperscript{40} For islands of a given size, the equilibrium stress is strongly dependent
on the contact angle, with the stress decreasing with decreasing contact angle. For a given material, the coalescence stress associated with grain boundary formation may vary significantly for different substrates, depending on detailed differences in wetting behaviour. To quantitatively predict thin film growth stress one must consider the details of the wetting behaviour between the deposited film and the substrate material.

The problem of determining the effect of the deposition rate on the grain size at coalescence is a complicated one since it involves the interplay between the deposition rate, the mobility of the deposited species, and the island nucleation rate. The model developed by Thompson\textsuperscript{45} for random, homogeneous nucleation of islands on a substrate predicts that the grain size at coalescence can decrease or remain constant with increasing deposition rate. Since for islands of hemispherical shape, the island height scales with the island radius, the thickness at film coalescence should show the same dependence on the deposition rate as the grain size at coalescence. Experimental data for copper are consistent with Thompson’s model in that there is no dependence of island size at film coalescence on deposition rate.\textsuperscript{46}

### 2.3 Copper Plating Chemistries: Bath Additives

Deposition of thin films requires conditions that promote lateral overgrowth on the substrate as opposed to continual thickening of the previously deposited metal.\textsuperscript{47, 48} These requirements can be met through control of bath additives and electrodeposition conditions. The nucleation, coalescence and growth of metal films are dependent on the presence of additives in the electrochemical bath.

#### 2.3.1 Effect of Chloride Additive on Copper Electrodeposition

The role of chloride ions as an accelerator (or catalyst) in the acid copper sulphate bath has been long recognized. Chloride ions are usually added at a low level to the acid copper electrolyte bath where they apparently combine with the intermediated cuprous ions, thus suppressing Cu\textsuperscript{+} disproportionation.\textsuperscript{49}
Trace amounts of chloride ions have a catalytic effect on the Cu$^{2+}$/Cu$^{+}$ reaction, but have no effect on the Cu$^{+}$/Cu reaction, i.e. chloride ions shorten the Cu$^{2+}$/Cu$^{+}$ bond length (5-6 Å) at the interface as a result of chloride ion bridging but they do not decrease the Cu$^{+}$/Cu bond length. The overpotential for the deposition reaction decreases with increasing concentration of the chloride ion during galvanostatic plating. In addition, the exchange current density of the Cu$^{2+}$/Cu$^{+}$ reaction increases as a function of increasing chloride ion concentration. This enhancement in reaction rate is attributed to a change in the reaction mechanism from an outer sphere (with a water-water bridge between the hydrated ion) to an inner sphere (involving a chloride ion bridge) at the electrode surface.

Cyclic voltammetry shows that chloride ion results in a larger deposition current.\textsuperscript{50} The shape of the reduction curve in the presence of chloride is similar to that from additive-free solution indicating the presence of chloride leads to an acceleration of the copper reduction current without modification of the mechanism. This acceleration effect is attributed to an increase in the activity of the reaction intermediates and a more facile electron transfer between Cu$^{+}$ intermediates and the electrode surface in the presence of chloride ions.

The potential value of the electrode influences the nature of the response.\textsuperscript{51} At low negative potentials, in the range -0.4 to -0.52 V (SMSE), copper deposition is inhibited and is attributed to the formation of CuCl species which partially blocks the electrode surface. At more negative potentials, -0.52 to -0.6 V (SMSE), copper deposition rate accelerates which is due to the faster reduction of the CuCl. The addition of 50 ppm chloride has little effect on current density in the range (0.2 to 0.0 V) (SCE) while in the range 0.0 to -0.3 V (SCE), chloride causes the current density to decrease (i.e. chloride acted as an inhibitor).\textsuperscript{52}

The effects of chloride ion are concentration dependent. A polarizing (inhibiting) effect is observed if concentrations are ≤ 10 ppm due to the precipitation of CuCl but a depolarizing (accelerating) effect is observed if concentrations are above 40 ppm in a bath containing 0.32 mol dm$^{-3}$ CuSO$_4$ and 1.53 mol dm$^{-3}$ H$_2$SO$_4$. It is suggested that polarization is caused by precipitation of CuCl, when its solubility limit is reached by adding ≥ 10 ppm of chloride to the solution. Other investigations argue
that chloride ion has an inhibiting effect at low concentrations (5 ppm) and an acceleration effect at higher concentrations (20 ppm to 40 ppm). The discrepancies in the results reported by the two different groups are due to different methods of measuring polarization curves.

In the presence of chloride, copper deposits are rough and inhomogeneous in comparison to the smooth, small grains obtained from additive-free solution. A Cu(100) substrate undergoes absorbate-induced roughening/faceting which decreases with decreasing chloride ion concentration in the solution. Faceting is promoted by the presence of chloride ion at low concentrations.

At low concentrations, chloride ions have a negligible effect on the deposition kinetics but significantly affect nodule formation. Few nodules are formed in the absence of chloride ions but their number increases with increasing chloride ion concentration, with a maximum at a few ppm of chloride ions. In the presence of chloride, deposits are smaller and more uniform, and have an increased tendency to facet and develop as pyramidal structures.

Chloride ions affect the tensile strength of copper electrodeposits from acidic plating baths. Small amounts of chloride are essential to promoting ductility of electrodeposits. The presence of chloride ion in the bath results in enhanced elongation (typically 25 %) of the deposits. This effect is attributed to the increased nucleation associated with copper discharge from CuCl.

In the presence of chloride ions, copper clusters and hexagonal CuCl precipitates are produced during electroplating. XRD studies have shown that chloride ion can also affect the crystallographic orientation of the crystal in the deposit. The chloride ion affects the crystallographic orientation of the crystal deposit. The presence of a low chloride ion concentration results in reduced roughness and a higher number of (220) orientation, with the (200) orientation dominating at high chloride concentrations. At higher concentrations of chloride ion, the (111) orientation increases. The addition of 50 ppm chloride improves (100) texture; however, increasing the acid concentration and decreasing the copper sulphate concentration nullifies the substrate orientation effect.
2.3.2 Effect of PEG on Copper Electrodeposition

Polymers employed in electrochemical baths tend to have molecular weights of 200-2000 and contain oxygen in a functional group composed of a repeating ether, alcohol or ketone. The polymer of most interest to the copper electrodeposition process in the microelectronics industry is polyethylene glycol, more commonly known as PEG.

Pseudocrown helix structures, may be formed between PEG and alkali metals due to the interaction of the electron shells of oxygen and metal cations. The form and structure of the ethylene oxide units are strongly influenced by the nature of the solvent.

Depending on their degree of polarization, or above or below a critical potential, PEG adsorption may be weak or strong, hence causing a weak or strong reduction of the rate of discharge of the copper cations. Kelly and West suggested that PEG can be adsorbed in two forms either as rod-like or as spherical PEG molecules. Adsorption of films or monolayers of PEG is also possible. Higher molecular weight polymers caused a greater degree of suppression indicating that the thickness (or density) of the layer increased with PEG molecular weight. The degree of suppression was found to be nearly independent of PEG concentration suggesting a PEG monolayer is formed which acts as a uniform barrier to deposition. Goldbach noted that the reduction of Cu\(^{2+}\) in the presence of the additive LP-1TM (structurally similar to PEG) may be compared to reduction of Cu\(^{2+}\) without the additive but with a reduced active surface of the electrode due to adsorption of LP-1TM. The adsorption of PEG depends on the applied potential. Bonou et al. observed that PEG adsorbs on the copper substrate at least in the potential range where hydrogen evolution reaction occurs.

2.3.3 Effect of PEG with Chloride in Combination

Many authors have agreed that PEG and chloride ions act synergistically and that the combination leads to a strong inhibition of the copper deposition reaction.
Doblohofer et al.\(^{60}\) postulated the formation of an inhibiting PEG-chloride layer on the copper surface which reduces both the \(\text{Cu}^{2+}/\text{Cu}^+\) and the \(\text{Cu}^+/\text{Cu}\) exchange current densities by an order of magnitude. However, the \(\text{Cu}^{2+}/\text{Cu}^+\) reaction still remains the slowest step in the sequence of consecutive reactions \(\text{Cu}^{2+}/\text{Cu}^+/{\text{Cu}}_{\text{metal}}\). Similarly, Goldbach observed\(^{58}\) the measured exchange current density in a LP-ITM chloride-containing solution to be 10 times lower compared to an additive-free solution. This large reduction was also observed by Healy et al.\(^{61}\) with sodium chloride-PEG solutions.

It is assumed that the \(\text{Cu}^+\) ions are bound by the PEG molecules. Each \(\text{Cu}^+\) ion is surrounded by six oxygen atoms of polyethylene oxide forming a positively charged complex of the type \([\text{Cu}^+(\text{EtO})_6]\). In a PEG only containing bath above -0.15 V (\(\text{Cu}/\text{Cu}^{2+}\)) or -0.55 V (SMSE), PEG acts as a highly cationic molecule on the surface and deposition proceeds as \(\text{Cu}^+\) ions are supplied from the solution (\(\text{Cu}^{2+}\)) and the metal (\(\text{Cu}_{\text{ads}}\)) via reduction of \(\text{Cu}^{2+}\) or oxidation of \(\text{Cu}_{\text{ads}}\) respectively. In the potential range more negative than the critical potential, PEG on the copper surface will be deprived of \(\text{Cu}^+\) ions and non-ionic PEG will escape from the surface. In the presence of both PEG and chloride ions, the cationic species interact with chloride ions absorbed on the copper surface. At sufficiently negative potentials, the \(\text{Cu}^+\) oxygen atom bonds break and liberate \(\text{Cu}^+\) ions; copper deposition suddenly commences while PEG returns to the bulk electrolyte, chloride ion will no longer adsorb and hence cupric ion will no longer be stable at the surface. Instead neutral PEG is more likely to adsorb.

Manu\(^{57}\) observed that the barrier layer and thickness of the monolayer of PEG increases as the molecular weight of the adsorbed polymer is increased. Other research groups [88, 122, 123] have attributed the inhibitory effect in part to the homogeneous formation, in aqueous media, of complexes containing polyethers when the number of oxygen atoms is greater than three.

Stoychev\(^{62}\) observed that when both PEG and chloride ion are present in the acid copper electrolyte the simultaneous formation of complexes between both copper ions and ethylene oxide units and copper ions and chloride ion is possible. In
addition to the presence in solution of simple chloride ion complexes of copper, such as CuCl+, CuCl2-, CuCl3-, are also present.

According to Herbert’s model a relationship exists between PEG and chloride in which the PEG surface coverage is determined by that of chloride. The mechanism suggests that the deposition rate is determined by the number of interfacial sites available for cuprous complex formation. They concluded that PEG does not function as a barrier film but instead forms a polymer electrolyte film in which the ions are partially solvated.

West and Kelly assumed on basis of QCM data that inhibition of copper deposition was a consequence of the adsorption of a monolayer of PEG molecules that collapse into a sphere provided chloride ions are present. The adsorption leads to a booking of available surface sites for charge transfer.

A detailed SERS study by Feng et al. provides evidence for the potential dependent interactions between copper, its ions, chloride ions and PEG. In the presence of both additives, the intensity of the Cu-Cl mode decreased with decreasing potential, whereas the polyether mode was found to be only weakly dependent on potential. A strong novel mode at 260 cm\(^{-1}\) (Cl, PEG and Cu ions had to be present) was attributed to a three coordinate PEG/Cl/Cu complex and a peak at 850 cm\(^{-1}\) associated with PEG (which is identical to that of normal Raman spectra of PEG in H\(_2\)O) indicated that PEG is adsorbed on or near the electrode surface.

Bonou et al. observed the disappearance of protuberances from copper surface deposited from a PEG+chloride containing plating solution (protuberances were found to be present on copper surfaces deposited from a PEG-containing plating bath) to disappear and the deposits to become more uniform. XRD diffractograms show that in the additive-free solution, the preferential orientation of the electrodeposited is (220). When both additives are present there is a marked decrease in the (200) orientation and an emergence of the (111) peak.

Fig. 2.1 shows a schematic of the mechanism for copper deposition by a two step process in which Cu\(^{+2}\)\(_{\text{aq}}\) is reduced to Cu\(^{+1}\)\(_{\text{aq}}\) by one electron, followed by a reduction.
to solid copper Cu₅ by a second electron. The Cu₅ adatom is free to diffuse on the surface of the electrode. The intermediate step where Cu⁺¹ₐq is formed can follow a different path when in the presence of Cl⁻ₐq. In this case, a CuClₐds layer can be formed. In the presence of PEGₐq, a PEG-CuClₐds complex is formed. PEG can be desorbed from the complex leaving the CuClₐds layer. Furthermore, Cl⁻ₐq can also desorb leaving a Cu₅ free to diffuse on the electrode surface.

![Diagram](image1)

**Fig. 2.1** A schematic representation of mechanism describing copper electrodeposition in the absence of additives, the presence of chloride with and without PEG.

In the presence of chloride, surface diffusion is increased and thus vertical growth is reduced. Since nucleation is reduced in the presence of chloride, the newly deposited copper diffuses to the nearest copper island. These islands dominate growth which results in a much rougher surface than in the absence of chloride. In the presence of both PEG and chloride, the adsorbed complex layer blocks the current from reaching the electrode surface and deposition is inhibited. Since the complex layer is not perfectly uniform, there will be some regions where the electrode surface is exposed and local current density is high. As a result, regions of high current density will have significant growth in comparison to regions which are blocked by the complex adlayer.

### 2.3.4 Influence of Additives on the Morphology of Electroplated Copper

Scanning probe microscopy has proved to be a useful tool for characterization of the morphology of electrodeposits. SPM maps a sample surface with atomic resolution, revealing information about the deposit such as its crystal structure, the distribution of point defects, adsorbates, and structural defects. *In-situ* SPM allows direct
measurement of textures, and electrochemical and growth processes that occur during deposition, and eliminates problems associated with oxides that may form on the surface following removal from the solution. In-situ SPM allows correlation between morphological and electrochemical information during the deposition process.

The microstructure, morphology and growth processes of electrodeposited copper depend on parameters such as copper sulphate concentration, current density, applied overpotential, and lattice spacing and crystal orientation of the substrate.

During deposition, atoms nucleate to small islands that grow in size and coalesce to eventually form a uniform film. Beyond this, the film thickens and surface grains become coarse. If a grain grows to a size on the order of the films thickness, the grain will intersect with the surface and eventually form a columnar structure.

The nucleation and growth of electrodeposits as a function of overpotential has been the subject of extensive experimental investigation and theoretical analysis. Nucleation can occur instantaneously or progressively. Computational models of nucleation and growth of electrodeposited films have been documented. In certain potential regimes, the nucleation density can increase exponentially with applied potential. High overpotentials produce large quantities of small features and low overpotentials produce small quantities of large features. Similarly, increasing current density decreases the size of crystallites but increases their number density. After the nucleation stage, islands generally begin to grow both laterally and vertically but their numbers do not change significantly beyond the initial nucleation stage.

Copper layers obtained from copper sulphate solution containing sulphuric acid (H₂SO₄) exhibit a rather granular surface that is independent of H₂SO₄ concentration, but grow as large islands in absence of H₂SO₄. The rate of copper deposition, however, appears to be independent of the Cu²⁺ ion concentration. The feature sizes of copper electrodeposits increase with increasing concentration of CuSO₄. The number of copper atoms produced on a substrate is a function of the initial bulk concentration. In low concentration baths, atoms are spaced far apart and have to
travel long distances to form a nucleus. It is more energetically favourable for atoms
to group together with their nearest neighbour which results in the formation of a
large number of small-sized nuclei which, in some cases, can be rough, irregular and
highly porous. In high concentration baths, metal atoms will have more near
neighbours which results in the formation of a small number of large nuclei. In
addition, the size of a given nucleated island will determine the size of its diffusion
zone.

Stress and morphology of electrodeposited copper films is influenced by the
nucleation and growth processes, the structure and chemical nature of the substrate,
the film thickness, and the presence of bath additives in the electrolyte. Additives are
employed in electroplating baths to improve both the levelling and brightness of the
deposit, by promoting grain refinement (< 100 nm), and smoothening the surfaces of
grains. Although the effect of additives on microstructure of thin films has been
investigated extensively, there still remains a gap in our understanding in the effects
of additives on stress in electrodeposited films.

Alkire\textsuperscript{68} described nucleation of copper on a gold substrate with a square array of
copper clusters in the presence of chloride and PEG. Nucleation density increases
with concentrations of chloride and PEG. In the presence of pre-existing copper seed
clusters, however, conditions were favoured with low chloride concentrations, and
moderate PEG concentrations. Experimental observations indicated that as the
chloride concentration was increased from 0.1 ppm to 10 ppm the size of nucleated
features decreased and nucleation density increased.

The nucleation and growth of electrodeposited copper is dependent on the nature of
the substrate. Copper nucleates on Au (111) instantaneously. No additional
nucleation occurs beyond the initial nucleation stage.\textsuperscript{66, 72} The growth centres of
these crystallites are formed on top of the UPD copper monolayer. As the film
thickens, its surface becomes rougher. Perfect epitaxial deposition of bulk copper on
top of a UPD copper layer would lead to highly strained films.

The use of electrodeposition in metallization technology relies on electrolyte
additives that modify the deposition process so as to obtain desirable characteristics
such as superfilling of trenches and vias in the damascene process.\textsuperscript{74, 75} The nature and concentration of additives used in commercial electrodeposition systems is usually proprietary. However, combinations of additives such as chloride ion and polyethylene glycol are frequently used in studies of copper electrodeposition. These additives can have a dramatic effect on film micro/nanostructure and morphology.

The morphology of additive-free deposits remains largely unchanged upon further deposition whereas in the presence of additives pyramidal features are formed.\textsuperscript{72} This phenomenon is attributed to consumption of additives and their incorporation into the deposits. The fast growth rate at exposed areas copper islands leads to much taller features, pyramidal in shape. Higher concentrations of additive increase the amount of charge that is required to form pyramidal features in the deposit. Higher ratios of additive to cupric ions also yield smoother deposits. The combination of SPS, PEG and chloride additives affect the morphology of electrodeposited copper.\textsuperscript{53} SPS, PEG and chloride act together to form a deposit which exhibits some of the inhibitory features of PEG + chloride, but also features the accelerating effect of SPS + chloride.\textsuperscript{53} SPS additive becomes incorporated into copper electrodeposits in the absence of PEG additive. The chloride ion is incorporated in the deposit only in the presence SPS. Depassivation occurs at defects in solutions containing both PEG in and chloride, and the resultant features grow, pyramidal in shape, until a critical size is reached.

Chloride additive influences the geometry, morphology, and growth of electrodeposited copper. Increasing chloride ion concentration causes ridges and polycrystalline deposits to grow. Copper electrodeposits on p-GaAs(100) surfaces in HCl solution develop randomly distributed copper clusters which grow three-dimensionally.\textsuperscript{76} Furthermore, deposition of CuCl pyramidal precipitates can be formed from acidic copper sulphate baths containing chloride additive.\textsuperscript{77}

### 2.4 Testing Freestanding Nanofilms

Experiments for measuring the mechanical properties of thin films fall into two key categories: films tested on a substrate and freestanding thin films. Mechanical testing of thin films on a substrate suffers from effects due to the substrate. In substrate-
based techniques such as nanoindentation difficulties arise when separating the interface and substrate effects, especially at elevated temperatures where interfacial stress develops due to the thermal strain mismatch. In freestanding films, however, substrate-effects are avoided and their properties can be measured directly. In addition, testing of freestanding films leads to simpler stress and deformation distributions that are more easily connected to measured forces and deflections. The conventional tensile test is particularly sensitive to specimen and instrumental factors. In particular, many issues are associated with suffers specimen alignment and gripping. In biaxial tensile testing, the mechanical load can be applied by a pressurized gas or by a probe with a spherical tip. Difficulties associated with bulge testing include specimen preparation and mounting, automated bulge height measurement and the correlation of bulge deformation with the mechanical properties of the thin film.

The load-deflection response of freestanding films is generally influenced by geometrical nonlinearity, plastic deformation and rate-dependent material effects.\textsuperscript{78} In addition, the increasing contact area during indentation and the pre-stretch arising from fabrication both need to be accounted for.

There are many fabrication issues associated with freestanding films. In early work, samples were prepared by simply clamping or gluing the film in a frame. This technique can lead to irreproducible boundary conditions and initial stresses and many of the films of interest are on substrates and too thin to handle. Today, most fabrication processes involve etching away the substrate from the back.\textsuperscript{79} Using an anisotropic wet etchant such as KOH, a micromachined cavity can be etched into a Si substrate creating thin suspended square and rectangular membranes useful as load-deflection specimens. Circular geometries are fabricated onto a silicon substrate using bulk similar micromachining techniques but this is more expensive and harder to accomplish than square and rectangular geometries. Other common configurations involve clamping the sample membrane between two identical rigid grips (i.e. O-rings), thus creating a freestanding diaphragm. Thin metal films can be supported using a sacrificial support structure. Most freestanding metal films are used in microelectronics and in MEMS, but some are known for their use in catalysis.
2.4.1 Nanoindentation

Nanoindentation is arguably the most popular method of measuring mechanical properties of materials. A nanoindenter is capable of measuring small load and displacement with high accuracy and precision. Measuring indentation (using SEM or AFM) can be quite cumbersome so it is important to use an indenter with a geometry known to high precision. Each model of nanoindenter can differ mainly due to tip geometry. Typical geometries include pyramids, wedges, cones, cylinders, filaments and spheres. Indentation sizes can be reduced to ten nanometres or less, which makes possible highly localized studies of the mechanical properties of the microstructure.

![Schematic of a Nanoindenter penetrating a specimen](image)

**Fig. 2.2** Schematic of a Nanoindenter penetrating a specimen.\(^8^0\)

![Schematic of indentation load-depth curve](image)

**Fig. 2.3** Schematic of indentation load-depth curve; data is taken at two different indentation depths (loads).\(^8^0\)

The use of nanoindentation as a tool for measuring mechanical properties, which is prevalent in the literature, does not lend itself to straightforward evaluation of properties such as yield strength or terminal ductility, especially at elevated temperatures, and relies on a significant amount of modelling to give an idea of these values.\(^8^1\) The most significant drawback with nanoindentation is that it strongly depends upon the mechanical properties of the substrate material, thus complicating measurements.\(^8^2\) Stiffness values measured by nanoindentation are systematically
higher than those obtained using the bulge test technique. The difference between measurements is caused by the substrate, which adds significantly to the contact stiffness in the indentation measurements. Another common side-effect with nanoindentation is a specific behaviour called ‘pile-up’ where literally material piles up on the edges of the indent during the indentation process.

Nanoindentation has well known limitations and artefacts including indentation substrate effects, densification, size effects, tip rounding effects, and surface roughness, that can lead to misinterpretation of the results. The densification effect in which indentation contact can collapse pores and inflate the reported elastic modulus may be especially troublesome as porosity is introduced into inter-metal dielectric materials to improve interconnect performance. In addition, characterization of thin films using nanoindentation cannot yield other important information, such as, stress-strain curves and ultimate tensile strength, which are commonly used in finite element simulations and reliability predictions. There is currently no comprehensive model to account for all these effects in a range of materials systems, and nanoindentation is not a viable option for mechanical property measurement for applications in microsystems design at present. However, it can be used for routine process monitoring where it may suffice to check that the same indentation behaviour is obtained for every batch of devices.

2.4.2 Bulge Testing

Bulge testing was originally described by Beams in 1959 and has since been applied in various forms by many investigators. Even today, the bulge test method is considered to be most suitable for testing freestanding films. Before modern silicon fabrication techniques were available, metal films were typically vapour deposited on lacquer layers which had been cemented over the end of a metal tube. After removal of the lacquer layer, air pressure is applied through the tube and the bulge of the film is measured either by a microscope or by light interference. The pressure difference between the two sides of the film and the height of the film are recorded. Most bulges tests are typically performed on circular or elliptical geometries. Some researchers have switched to rectangular bulges with an aspect ratio of at least five. For this rectangular specimen configuration, the film deforms in a plane strain...
manner. A detailed schematic of a bulge produced during a bulge test experiment is shown in Fig. 2.4.

![Fig. 2.4 Schematic of a bulge formed by pressurisation of one side of a freestanding thin film.](image)

In most bulge tests, a freestanding film is pressurized by a gas or liquid and its strain is measured using laser interferometry. The stress-strain characteristics are determined from the following equations:

\[ \sigma = \frac{p a^2}{2 H t} + \sigma_0 \quad 2.3 \]

and

\[ \varepsilon = \frac{2 H^2}{3 a^2} + \varepsilon_0 \quad 2.4 \]

The geometry of the bulge is given by \( t \) the bulge thickness, \( H \) the bulge height and \( a \) the bulge half-width. The pressure appears as \( p \) in Equation (2.5) and \( \sigma_0 \) and \( \varepsilon_0 \) are initial stress and strain values respectively.

Although it is quite common to use spherical bulges geometries, many have often argued whether spherical, elliptical or rectangular bulge geometry is more suitable for bulge testing. Bulge height can be difficult to measure accurately, and some even argue that achieving spherical bulges is virtually impossible.\(^9^2\)

Two major advantages associated with bulge test are the ease of specimen handling and the capability of imposing loading conditions. These advantages are unparalleled by other thin film testing methods such as nanoindentation, substrate-curvature technique, and micro-tensile testing. It is therefore not surprising that bulge test found many applications in the field of materials testing, where dynamic mechanical
tests, creep and viscoelastic tests, and high-temperature tests were reported. The bulge test can eliminate both substrate and densification effects.

### 2.4.3 Important Considerations in Testing Freestanding Films

The load-deflection method is commonly used for measurement of the mechanical properties of thin films. Deflection of a suspended film is measured as a function of the applied load or pressure. Accurate models are essential for the determination of the mechanical behaviour of thin films from load-deflection experiments. Analytical models are desirable for their simplicity, whereas finite element method (FEM) models have the potential to be very accurate.

Analytical models have been developed for rectangular membranes, some of which allow the Young’s modulus and residual stress in thin films to be determined. The stress state in these types of membranes is complex, starting from equal biaxial in the center to plane strain at the edges. Because of the well defined shape of a deflected membrane with rectangular cross-section, it is possible to determine the height of the bulge in the middle of the membrane by measuring the curvature of the bulge. The real bending behaviour is not described accurately with certain analytical models but others do show good agreement with experimental measurements. The membrane shape does not depend on the Young’s modulus of the material, the length of the membrane’s edge, or the thickness of the film.

Some bulge testers measure the curvature of the bulge rather than the height of the bulge. Many researchers have performed mechanical measurements on thin films on substrates, using either x-ray diffraction (XRD) or substrate curvature techniques. Tests on freestanding films are less frequently reported, but are most commonly performed by a uniaxial tensile test. Conventional tensile testing techniques suffer from sample alignment issues, edge effects, slipping, and damage due to gripping. In addition, specimen preparation of thin freestanding specimens and their handling is difficult.

Bulge test models have been developed for square, circular and rectangular membranes. It is important to account for the intrinsic stress and the initial height of the membrane. Freestanding membranes can be fabricated using
anisotropic wet etching techniques. Usually, a sacrificial low pressure chemical vapour deposited (LPCVD) SiN<sub>x</sub> membrane is fabricated first, because of the high selectivity of the Si etchant for SiN<sub>x</sub>. Subsequently, the thin film of interest is deposited on this SiN<sub>x</sub> membrane, and finally the latter is removed by dry etching using fluorine containing gases.

For some time, bulge testers required membranes which were flat. This requirement has limited the use to films grown under tensile stress, since films grown under compressive stress will cause wrinkling of the membrane. More recently, it has been shown that laser scanning technology is suitable for accurate measurement of the curvature of the bulge, without the need for a flat film. Inaccurate Young’s moduli are obtained when samples with nonzero initial bulge heights are tested.

2.5 References

3 Experimental

3.1 Introduction

This chapter describes experimental apparatus, methodology and materials used for in-situ measurements of stress and AFM in electrodeposited copper nanofilms and for ductility measurements of freestanding copper films. In particular, we describe the electrochemical cell design, the cantilever deflection method, and the Nakahara ductility tester.

3.2 Three-Electrode Electrochemical Cell

In this section, we describe the design and configuration of the stress and AFM electrochemical cells, and the materials and electrolyte that were used. The method for preparation and fabrication of the working electrode is also described.

3.2.1 Stress Cell

A conventional three-electrode configuration with a copper-foil counter electrode and a copper-wire reference electrode (Cu/Cu$^{2+}$) in a Luggin capillary is used. The arrangement of the cell is shown in Fig. 3.1. The cantilever is held in a Teflon cell cover by two spring-loaded clips which push the cantilever against a metal contact connected to a potentiostat (CHI 650A). The cell is gastight, the electrolyte is deaerated before introduction into the cell and the gas volume in the cell is maintained air-free by flowing nitrogen gas. The stress cell is glued to a glass block from the back and is held in a mirror mount.

The stress cell is made of pyrex and has an optical flat at the front through which a laser beam passes. A He-Ne laser source is reflected from the metal-glass interface (i.e. from the back face of the electrode) onto a position sensitive detector (PSD). As
copper is deposited on the gold, any bending of the cantilever can be detected with high sensitivity by optical monitoring. This stress measurement system will be described later.

**Fig. 3.1** (a) Photograph and (b) schematic diagram of stress cell (pyrex) containing cantilever working electrode, counter and reference electrodes, N₂ inlet and electrolyte inlet.

### 3.2.2 AFM Cell

Experiments were performed in a custom-fabricated Teflon fluid cell. The cell contains a similar three-electrode configuration as in the stress cell (i.e. a gold working electrode and reference and counter electrodes made of copper). A schematic representation of the AFM electrochemical cell is shown in Fig. 3.2. Due to space restrictions within the AFM, the cell was fabricated with a volume of 2.0 ml (compared to 13 ml for the stress cell). The cell also contains two fluid lines – an inlet for injecting and an outlet for removing electrolyte. The cell was placed in a plastic spill tray and secured to the stage with magnets. Any movement of the cell is not desirable as this causes drift during AFM imaging. To remove the air from the AFM chamber, the chamber was evacuated and backfilled with nitrogen gas to atmospheric pressure. The evacuation-backfill sequence was repeated four times. A
volume of 2.5 ml of electrolyte was then injected with a syringe into the cell (Note: 0.5 ml filled the length of the tubing).

Fig. 3.2 (a) Photograph and (b) schematic representation of the AFM electrochemical cell used for in-situ investigations of electrodeposited copper.

The working electrode was typically cleaved to about half the active length of that used in the stress cell. The backside of the electrode was adhered to a piece of silicon
using conductive silver paste. A sheet of aluminium foil was adhered to the bottom of the cell using lacquer. The backside of the piece of silicon holding the working electrode was adhered to the centre of the aluminium foil using conductive silver paste as shown in Fig. 3.2(a). More silver paste was applied to the edges of the small glass piece so that electrical continuity was made between the gold surface and the aluminium foil. The top of the cell (made of Teflon) was fitted to the base plate and hand-tightened using nylon screws. The working electrode was electrically isolated from other components and made leak-proof using lacquer. Lacquer was applied to the inner part of the cell so that all surfaces (with the exception of the gold surface) are covered completely. The lacquer was allowed to cure for 48 hours at room temperature.

In situ AFM images of copper electrodeposits were obtained in contact mode at a scan rate of 6 Hz. Preliminary experiments carried out under different scan conditions showed that the force exerted by the tip did not disrupt the sample during imaging. To avoid thermal drift issues during image acquisition, imaging was carried out after thermal equilibrium in the cell had been reached (usually 30-45 minutes after the solution had been introduced in the AFM cell). Electrochemical control of the AFM cell was provided by a Chi 650 electrochemical workstation, controlled by a personal computer. Although stirring conditions are more desirable (to reduce boundary layer to increase mass transport), electrodeposition was carried out without any agitation of the electrolyte to avoid disturbing the AFM scan.

In experiments comparing the effect of chloride on surface morphology, it is important to take into account any difference in the deposition rates (with and without chloride), so that similar thicknesses can be compared between both sets of experiments.

The local current density during deposition can vary from point to point on an electrode surface due to (i) the geometry of the system, (ii) the conductivity of the solution and electrodes, (iii) the activation overpotential, (iv) the diffusion overpotential and (v) the hydrodynamics of the system. If the influence of overpotential is negligible, the primary current distribution is determined by the geometry of the system and the conductivity of the solution. Even for a simple
electrode configuration, the calculation of the current distribution is a complex problem and the difficulties further increase with increasing complexity of the geometry, especially if the limiting diffusion current varies over the electrode due to the different geometric and hydrodynamic conditions. Because of this, analytical solutions can be found for some cases (Wagner¹, Newman²).

The current distribution during in the AFM cell during electrodeposition may not be very uniform due to the dimensions of the cell and the close proximity of the cantilever tip holder to the substrate (working electrode). A schematic diagram of this issue is shown in Fig. 3.3. The bevelled edge of the tip holder (region A) impedes some of the current paths in the electric field compared to region B. We later show the discrepancy in current measurements between the stress and AFM cells (see Chapter 4). Examination of the surface morphology at the centre and edge of the working electrode typically show differences between 10-20 %, approximately.

![Schematic diagram of AFM tip scanning the surface of a substrate as viewed from (a) top-down and (b) from the side. The area above which the bevelled edge of the tip is scanning is region A, and outside this region is B.](image)

**Fig. 3.3** Schematic diagram of AFM tip scanning the surface of a substrate as viewed from (a) top-down and (b) from the side. The area above which the bevelled edge of the tip is scanning is region A, and outside this region is B.

In general when current flows in an electrochemical cell, there is a potential drop between the reference electrode and the working electrode. This voltage drop is
caused by the electrolyte conductivity, the distance between the two electrodes and
the magnitude of the current. Using Ohm’s law, the voltage drop can be calculated to
be equal to the product of the current (i) and the resistance (RΩ). The counter
electrode is to be placed far away from the working electrode to minimize the
influence of the current and potential distribution.

For low conductivity media, the resistance can be very high, in the order of several
kΩ and even small currents can lead to large errors in potential. At fast scan rates,
there is a current transient due to the charging and discharging of the double layer.
Therefore, the true potential lags the applied potential according to the following
equation

\[
E_{true} = E_{applied} \left(1 - e^{-\frac{t}{R_Ω C_{dl}}}\right)
\]

where, RΩ is the ohmic resistance, C_{dl} is the double layer capacitance and t is the
time over which the measurement is taken. For fast scan rates, the exponential
approaches 1 and therefore can lead to errors in E_{true} with respect to E_{applied}. For slow
scan rates, the exponential approaches 0 and the errors can be negligible.

Errors can be reduced by increasing the conductivity of the solution, decreasing the
size of the working electrode to decrease C_{dl} proportionally, and moving the
reference electrode as close to the working electrode as possible.

3.2.3 Reference Electrode
The role of the reference electrode is to provide a fixed potential, which does not
vary during the course of the experiment. Since the potential of the reference
electrode remains fixed, differences in the applied potential between the working
electrode and the reference electrode appear across the working electrode/solution
interface. The counter electrode completes the circuit for current flow. A good
reference electrode should be able to maintain a constant potential even if a few
microamps of current are passed through it.

An ideal reference should show the following properties: (a) it should be reversible
and obey the Nernst Equation with respect to some species in the electrolyte; (b) its
potential should be stable with time; (c) its potential should return to its initial value after small currents are passed through the electrolyte (i.e. no hysteresis).

A Cu/Cu$^{2+}$ reference electrode in the form of a copper wire was used. The reaction at the cathode is expressed as

$$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu (solid)}$$

3.2

An insulating (enamelled) layer is on the outside of the copper wire. The wire was cut to expose the cross-section of the copper to the electrolyte. In the stress cell, the wire was inserted into a luggin capillary, which was placed close to the working electrode surface in order to reduce the IR drop. In the AFM cell, the copper wire was positioned approximately 0.5 mm from the working electrode.

3.2.4 Counter Electrode

The current produced by the electrochemical reactions at the working electrode is balanced by a current flowing in the opposite direction at the counter electrode. A 0.25 mm-thick copper foil (99.9% purity) was used as counter electrode. The foil was degreased in acetone and methanol and then etched in 30% H$_2$SO$_4$ for 5-10 seconds before being rinsed in de-ionized water. Finally, the foil was dried with a nitrogen gun.

3.2.5 Working Electrode: Preparation and Fabrication

The working electrode consists of a borosilicate glass cantilever (60 mm x 3 mm x 0.1 mm; Precision Glass and Optics - D263T) on top of which 10 nm of titanium followed by 250 nm of gold was evaporated. Gold is a suitable substrate material as it is inert. Titanium adheres the gold to the glass cantilever. To reduce stress and increase grain size in the substrate$^4$, the gold-coated working electrode was annealed in a quartz-tube furnace at 670 °C for 60 seconds (see Appendix A.6). The as-deposited grain size of the gold is 30-40 nm and the annealed grain size is 500-100 nm. The gold surface is the substrate for electrodeposited copper and this is shown in Fig. 3.4. The procedure for preparation and fabrication of the working electrode is briefly described.
The cantilever glass substrates were stored in concentrated nitric acid for 24 hours. They were then rinsed, sonicated in deionized water, and dried for one hour in a vacuum oven at 120 °C. The cantilevers were gripped between two pieces of silicon wafer wrapped in parafilm. The parafilm ensured adequate gripping of the cantilevers. Titanium and gold sources were added to the tungsten boats. Approximately, 0.42 g of gold is required to deposit a layer 250 nm in thickness.

Before the substrates are placed inside the evaporator, the titanium and gold evaporation sources were added. Two tungsten boats were connected to the electric terminals inside the evaporation chamber. The titanium was added using a spatula. The gold source, which was in the form of a gold wire, was cut to a weight of approximately 0.42 g and added to the other boat. This weight was determined to be the adequate amount of gold to produce a 250 nm-thick deposit. The chamber was evacuated to a pressure < 2 x 10⁻⁶ mbar before evaporation was initiated. A high current flows through the tungsten boat heating the evaporation source to evaporation point. A metal shutter, which was positioned directly underneath the crystal detector (connected to a thickness monitor), was opened after deposition rate became constant. The shutter was closed after the required thickness was deposited and the current was switched off. Titanium was first evaporated, 10 nm in thickness, followed by 250 nm of gold. Air was admitted to the chamber and the substrates were removed.

The thickness of the metal being deposited was monitored in-situ by a thickness monitor (Model IL150) as shown in Fig. 3.5. It measures film thickness and deposition rate by the well-established crystal micro-imbalance technique.
Thickness and deposition rate are calculated from user-supplied data on density and acoustic impedance of the film material. The gold-coated glass cantilevers were annealed at 800 °C for 60 seconds and then placed in a deaerated test tube and stored in a freezer. The substrates were cleaned before experiments in acetone/methanol/de-ionized water.

Preliminary experiments at constant potential showed that the repeatability of current measurements was poor during the first three to four cycles, beyond which the working electrode stabilized and current measurements eventually became very reproducible. One possible explanation of this behaviour is due to changes that occur at the solid-electrolyte interface as a result of the redox reactions. Furthermore it has been reported that, at high overpotentials, when copper electrodeposition is under mass transport control, the cathode coverage by a PEG-Cu-chloride-mediated film becomes either partially or completely detached as the concentration of chloride ions at the negatively charged copper surface diminishes.\textsuperscript{6} If the PEG complex layer is not fully desorbed, it may affect deposition as the number of cycles is increased.

### 3.2.6 Electrolyte

An electrolyte stock of 0.25 mol dm\(^{-3}\) CuSO\(_4\) in 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\) was prepared. The above electrolyte stocks were also prepared with additives - chloride ion and polyethylene glycol (3400 g/mol) at different concentrations. Deionised water greater than 18 M\(\Omega\)-cm was used in solution preparation and for rinsing purposes.

In our investigations of the effect of chloride and PEG, these additives were added into the electrolyte in the stress cell using a syringe. A nitrogen gas line was used to purge the electrolyte. To maintain a constant volume of electrolyte in the cell, the
The same added volume was then removed from the cell. The nitrogen line was removed and positioned above the surface of the electrolyte.

### 3.2.7 Electroanalytical Techniques

Electrodeposition is the process of producing a coating, usually metallic, on a surface by the action of electric current. The deposition of a metallic coating onto an object is achieved by putting a negative charge on the object to be coated and immersing it into a solution which contains a salt of the metal to be deposited.

In our experiments, we used a 650A CH Instruments workstation for parameter control and data acquisition. This comprises a potentiostat with potential control programming and data acquisition capabilities which is interfaced to a computer running appropriate software for parameter control and data acquisition. The potentiostat has a three terminal output, which is connected to the reference, counter and working electrodes of the electrochemical cell.

The potentiostat has a controller circuit that maintains the potential between the working and reference at a predefined value, which may be constant or time varying. The potentiostat reacts to the difference between the control and reference potentials through a negative feedback system, and passes current through the counter electrode circuit so as to reduce the difference to zero.

For experiments involving the potentiostatic deposition of copper followed by removal of the deposit involves the use of a multi-potential step which can be selected in the parameters command option. The main parameters include step potential, step time, sample interval, quiet time and sensitivity.

### 3.3 In-Situ Stress Measurement System

Stress develops in electrodeposited films both during the deposition process and during subsequent aging at room temperature. In this section, an *in-situ* stress measurement system is described. Stoney’s equation\(^7\) (see Section 1.2) is used to calculate stress.
The system is based on a similar apparatus developed by Stafford’s group at the National Institute for Standards and Technology (NIST).\(^4\) It consists of a three-electrode electrochemical cell (in which the working electrode is a gold-coated glass cantilever). A helium-neon laser is directed at the back-side of the cantilever and a position-sensitive detector on an optical bench measures the cantilever deflection.

### 3.3.1 Measuring Cantilever Deflection in an Electrolyte

The curvature of a substrate immersed in electrolyte within a glass electrochemical cell can be monitored using a laser-beam deflection method, as shown schematically in Fig. 3.6. Here we see a typical three-electrode electrochemical cell in which the deflection of the working electrode is monitored by a laser beam deflection method. The front of the cell has a transparent window through which a laser enters and reflects off the back-side of the substrate towards a detector. The refraction of light as it passes through the air/glass/solution interface of the electrochemical cell must be taken into account. The incident beam passes through the air/glass/electrolyte along the normal and is reflected on the backside of the cantilever. Refraction through the electrolyte/glass interface is described as

\[
\eta_{H_2O} \sin A = \eta_{glass} \sin B
\]

Similarly, refraction through the glass/air interface is described as

\[
\eta_{glass} \sin B = \eta_{air} \sin C
\]

Therefore,

\[
\eta_{H_2O} \sin A = \eta_{air} \sin C
\]

Cantilever bending is assumed to be an arc of a circle the radius of curvature is

\[
R = \frac{L}{\theta}
\]

where \(L\) is the distance between the solution level and the reflection point of the laser beam and \(\theta\) is the angle of deflection.
The deflection of a cantilever working electrode substrate during electrodeposition is measured by a laser beam deflection method. The laser is directed at the back-side of the working electrode and is refracted as it travels from (i) electrolyte to (ii) glass and then (iii) air.

When no electrolyte is present in the cell, the angle of deflection of the reflected beam $\alpha$ is simply equal to $2\theta$. But when the cell is filled with electrolyte then, from Snell’s Law, the expression becomes, for small angles:

$$\eta_{\text{air}} \alpha = \eta_{H_2O} 2\theta$$  \hspace{1cm} (3.4)

where $\eta_{H_2O}$ is the refractive index of the electrolyte and $\eta_{\text{air}}$ is the refractive index of air. Combining Equations 3.3 and 3.4, $R$ can be expressed as,

$$R = \frac{2L \eta_{H_2O}}{\eta_{\text{air}} \alpha}$$  \hspace{1cm} (3.5)

At small angles,
\[
\tan \alpha \approx \alpha = \frac{d}{D}
\]

where \(d\) is the deflection of the laser spot on the PSD and \(D\) is the distance from the PSD to the cantilever.

Using Stoney’s formula (Equation 1.9) with Equations 3.5 and 3.6, the force per unit width can be expressed as

\[
\frac{F}{w} = \frac{E_s h_s^2 \eta_{\text{air}} \alpha}{12(1 - v_s) L \eta_{H_2O}} = \frac{E_s h_s^2 \eta_{\text{air}} d}{12(1 - v_s) L \eta_{H_2O} D}
\]

The physical parameters of intrinsic stress in thin films are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force per unit width</td>
<td>(F/w)</td>
<td>N m(^{-1})</td>
<td>(\frac{E_s h_s^2 \eta_{\text{air}} d}{12(1 - v_s) L \eta_{H_2O} D})</td>
</tr>
<tr>
<td>Average Stress</td>
<td>(\sigma_{\text{avg}})</td>
<td>MPa</td>
<td>(\frac{\left(\sum_{i=1}^{N} \sigma_i\right)}{N})</td>
</tr>
<tr>
<td>Differential Stress</td>
<td>(\sigma_i)</td>
<td>MPa</td>
<td>(\frac{F}{hw})</td>
</tr>
</tbody>
</table>

### 3.3.2 Optical Lever Configuration

The optical system is shown schematically in Fig. 3.7. It consists of a helium-neon laser that passes through a beam-splitter, reflects off the back-side of the cantilever working electrode onto a position sensitive detector. Any bending of the cantilever can be detected with high sensitivity. In addition, the whole system is mounted on an optical bench for stability. The beam-splitter is positioned on a prism mount with three orthogonal axes of rotation for adjustment of the beam. The mirror mount is attached to an X-Z translation stage which has micrometer movements with a resolution of 10 \(\mu\)m and maximum travel of 28 mm. The mirror mount can be tilted by means of a high resolution (2.5 \(\mu\)m / division) micrometer.
The PSD used in this case has four electrodes: two cathodes $Y_1$ and $Y_2$ which give output voltages corresponding to the position of the laser spot on the $y$-axis of the PSD. The other two electrodes are the anodes on the $x$-axis of the PSD. The $x$ and $y$ co-ordinates of the beam are proportional to the ratios of these signals as follows:

$$S_x = \frac{L(X_1 - X_2)}{2(X_1 + X_2)}$$  \hspace{1cm} (3.8)

$$S_y = \frac{L(Y_1 - Y_2)}{2(Y_1 + Y_2)}$$  \hspace{1cm} (3.9)

where $X_1$, $X_2$, $Y_1$, and $Y_2$ are the signals at the anodes and cathodes, respectively, and $L$ is the width of the active area of the PSD. $S_x$ and $S_y$ are output voltages proportional to the $x$ and $y$ coordinates, respectively, of the PSD. A bias voltage ($\pm 5$ V) can be applied to the anodes and cathodes of the detector to improve frequency response and signal collection. The PSD outputs were connected to an OT-231DL position sensing amplifier and signal processing circuit, which gives position-sensitive voltage outputs ($S_x$ and $S_y$ above) independent of light intensity. The
voltage output of the OT-231DL is monitored by an Agilent 34970A data acquisition unit interfaced to a personal computer.

The PSD was calibrated in darkness as follows. A laser was directed at the PSD and its position was adjusted in 0.5 mm increments by a one-dimensional translation stage. The output voltage of the PSD was recorded at each position. The PSD was displaced by 23.5 mm in total. A plot of the PSD voltage signal versus the PSD position is shown in Fig. 3.8. The active length of the PSD is 20 mm. The PSD shows excellent linearity within 90 % of the active length. The calibration slope of the PSD was measured in the linear region as 1.11 V/mm. The PSD was only used to measure laser beam deflection within the PSD’s linear region as highlighted by the red points shown in Fig. 3.8.

![Fig. 3.8 PSD signal voltage as a function of the position of coalescence by a laser on the active length of the PSD.](image)

3.3.3 Data Acquisition and Processing

The PSD is connected to an amplifier circuit, the output of which is connected to a data acquisition card interfaced to a personal computer. A 2.0 Ω (± 0.1 %) resistor is connected between the counter electrode (CE) and the CE terminal on the potentiostat. The voltage drop across the resistor was recorded using the data acquisition system and the deposition current was determined by Ohm’s Law.
The voltages across the resistor and the voltage output on the PSD (and corresponding times) were recorded *in situ* during the electrodeposition of copper on gold. Each data point was automatically acquired in the following sequence: \( t_{\text{PSD}} \), \( V_{\text{PSD}} \), \( t_{\text{res}} \) and \( V_{\text{res}} \).

When a single data point was recorded for each parameter, the data acquisition sequence is automatically repeated. Table 3.2 shows a typical set of raw data. We can see that the data was acquired at a sample interval of 142 ms, approximately.

<table>
<thead>
<tr>
<th>( t_{\text{PSD}} ) (s)</th>
<th>( V_{\text{PSD}} ) (V)</th>
<th>( t_{\text{res}} ) (s)</th>
<th>( V_{\text{res}} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.054</td>
<td>-7.53</td>
<td>0.101</td>
<td>-40.1</td>
</tr>
<tr>
<td>0.196</td>
<td>-7.53</td>
<td>0.243</td>
<td>-40.7</td>
</tr>
<tr>
<td>0.337</td>
<td>-7.52</td>
<td>0.385</td>
<td>-40.1</td>
</tr>
<tr>
<td>0.48</td>
<td>-7.52</td>
<td>0.527</td>
<td>-41.5</td>
</tr>
</tbody>
</table>

The potential was held at +200 mV during the first 20 s, after which the potential was switched in polarity. The positive and negative potential regions will be referred to as \( V^+ \) and \( V^- \), respectively. The data acquisition software (Agilent Benchlink Data Logger) was switched on at 5-10 s before the change in polarity and the current and deflection were recorded. A plot of a typical raw data curve for current and deflection is shown in Fig. 3.9. Neither \( V_{\text{res}} \) nor \( V_{\text{PSD}} \) changed significantly in the \( V^+ \) region.

The average \( V_{\text{res}} \) within the \( V^+ \) region was calculated and this average was set as the initial data point at \( t = 0 \) s as shown in Fig. 3.10. All \( V_{\text{PSD}} \) data in the \( V^- \) region was referenced to the value at the switch in polarity and this is also shown in Fig. 3.10. A rapid jump in the current appears at the onset of deposition causing the cantilever to bend in the tensile direction. The jump occurs within the sample interval time of 142 ms. The magnitude of initial deflection is significantly smaller than that observed during subsequent deposition. Thus, the effects of switching potential at the interface are assumed to be negligible.
The active area of the electrode was measured using a vernier calipers and the current density was determined by dividing the current in the 2.0 Ω resistor by this active area. The force per unit width of the cantilever $F/w$ was determined by Equation 3.7. A plot of the time dependence of current density and $F/w$ is shown in Fig. 3.11.

Fig. 3.9 Time dependence of (a) $V_{res}$ and (b) $V_{PSD}$ within the (i) $V^+$ and (ii) and $V^-$ regions.

Fig. 3.10 Time dependence of (a) $V_{res}$ and (b) $V_{PSD}$ in the $V^+$ region.
3.3.4 Measuring Film Thickness by Coulometry

Faraday’s 1\textsuperscript{st} law of electrolysis\textsuperscript{10} states that the mass of a substance altered at an electrode during electrolysis is directly proportional to charge transferred at that electrode. Faraday’s 2\textsuperscript{nd} law of electrolysis states for a given quantity of electric charge, the mass of an elemental material altered at an electrode is directly proportional to the element’s equivalent weight. The equivalent weight of a substance $m_{dep}$ is expressed as follows:

$$m_{dep} = Q \left(\frac{M}{nF}\right)$$ \hspace{1cm} (3.10)

where $Q$ is the total charge passed, $n$ is the number of electrons transferred per ion, and $F$ is Faraday’s constant (96,485 C mol\textsuperscript{-1}). The density of a deposited material is expressed in terms of the mass $m_{dep}$ and volume $V$ of the deposit as follows

$$\rho = \frac{m_{dep}}{V} \equiv \left(\frac{M}{V_m}\right)$$ \hspace{1cm} (3.11)

where $M$ is the molar mass and $V_m$ is the molar volume of the deposit. The volume of a given deposit is

Fig. 3.11 Time dependence of (a) current density and (b) $F/w$ within the $V^+$ region.
\[ V = h_c A \]  
where \( h_c \) is the coulometric thickness and \( A \) is the area of the deposit. Therefore, the mass of a deposit is

\[ m_{dep} = \rho h_c A = \left( \frac{M}{V_m} \right) h_c A \]  

3.13

The coulometric thickness of a deposit is then

\[ h_c = \frac{m_{dep}}{A} \frac{V_m}{M} \]  

3.14

3.4 In-Situ Electrochemical Atomic Force Microscope (EC-AFM)

The use of in-situ AFM to study the electrodeposition of metals has very considerable advantages over traditional ex-situ methods. In-situ techniques allow the structure of the surface to be measured directly, without the need for removal of the electrode from solution, thereby avoiding any morphological changes that may occur on drying. Also, changes in the properties of a single area as a function of time may be studied.

Current transient analysis is the standard way of determining nucleation rates and saturation nucleation densities. It is an indirect method in the sense that it relies on comparison of the experimental transients with theoretical expressions for the current density. In-situ AFM is a suitable technique for observing dynamic growth processes during electrodeposition and comparing this behaviour with current transient analysis.

3.4.1 In-Situ EC-AFM Configuration

The Enviroscope can be equipped with a specialized tip holder that permits operation under fluid, as shown in Fig. 3.12(a). The fluid tip holder interchanges with the standard tip holder quickly and easily. It consists of a small glass assembly with a wire clip for holding an AFM cantilever substrate. The glass surfaces provide a flat, bevelled interface so that the AFM laser beam may pass into the fluid without being
distorted by an unstable fluid surface. The four sockets located on the top of the fluid tip holder are used to attach the top holder to the four pins at the end of the scanner tube.

A rubber protective skirt in Fig. 3.12 (b), also called a “splash guard”, is used to protect the EnviroScope scanner from getting liquid on it. Splash guards allow greater movement of the stage while minimizing evaporation. It is recommended that a splash guard be used with all wet samples. In addition, tips should not be immersed in fluids deeper than 2 mm.

Experiments were performed in a Veeco Enviroscope AFM operating in contact mode. Standard silicon nitride probes (Veeco model DNP), having a force constant of approximately 0.32 N m$^{-1}$ were used.

The electrochemical cell should be secured to the stage with magnets and the AFM chamber door closed. If the sample tray was not properly secure to the stage during evacuation, there was a risk of the tray moving towards the cantilever tip. As a precautionary measure to avoid the sample tray crashing into the cantilever tip, the stage was moved away from the engage point by at least 2 mm prior to switching on the roughing pump. During evacuation, the chamber pressure was monitored on the pressure display unit. At 5 x 10$^{-1}$ Torr chamber pressure, the roughing pump was switched off remotely and the chamber was back-filled with nitrogen gas. The
evacuation and back-fill sequence was repeated 4 more times. The stage was then returned to the engage position. The roughing pump was switched off. Purged electrolyte solution (2.5 ml) was injected into the AFM electrochemical cell. To achieve a stable laser signal, the electrolyte was given 20 minutes for it to reach thermal equilibrium with the AFM tip. If any further drift was observed, it was either due to the substrate itself or the fact the sample tray was not secured properly. Difficulties with engaging the AFM tip can be due to a number of possibilities such as (a) any part of the cell obstructing movement of the AFM head, (b) the AFM tip being too close/far from the surface, or (c) damage to AFM tip itself.

3.4.2 Measurement of Surface Morphology

The surface morphological evolution of electrodeposited copper can be observed in-situ using electrochemical AFM (Atomic Force Microscopy). A schematic representation of an AFM cantilever probe scanning in contact mode across the surface of a deposit is shown in Fig. 3.13(a). The vertical heights of the copper islands are measured with reference to the lowest point measured during the scan. Once the AFM cantilever has touched the substrate during a scan, it will reference the substrate from which the thickness of the deposit can be accurately determined. However as the deposit gets thicker, as shown in Fig. 3.13(b), the AFM cantilever probe will no longer be able to reference the substrate, but will now reference the lowest point that the probe can access. This means that the heights of the surface features above this point are measured. The lateral dimensions of the visible surface, however, can be measured accurately regardless of film thickness.

The coulometric thickness \( h_c \) represents the thickness of the deposit if all the material was uniformly deposited on the substrate. Fig. 3.13 (a) and (b) shows a line indicating \( h_c \). The coulometric thickness during the early stages of deposition is small and some of the heights of the copper islands are large relative to this value. During the later stages of deposition the deposit covers the entire substrate.

The setpoint is essentially a measure of the force applied by the AFM tip to the sample. In contact mode, this setpoint (or applied force) represents a certain deflection of the cantilever. This deflection is maintained by the feedback electronics so that the force between the tip and the sample remains constant. A large force
Fig. 3.13 Schematic representation of the reference point for the AFM probe tip (a) before and (b) after full coverage is achieved. The dashed line represents the coulometric thickness $h_c$ of the film.

applied to the sample will often produce better imaging, but the tip and/or sample will wear more easily. The setpoint should only be increased slowly so the tip/sample is not damaged.

A proportional-integral-derivative controller (PID controller) is a commonly used loop controller that calculates an “error” value as the difference between a measured process variable and a desired setpoint. The controller attempts to minimize the error by adjusting the process control inputs. To control the feedback of the tip, the proportional and integral gains on the PID controller can be adjusted. Increasing the gains increases the amount of input signal from the photodetector which is fed back into the output signal (the z-piezo). Higher gains produce a faster reaction by the AFM to changes in topography in the sample. However if the gains are set too high, feedback oscillations will result. One should maximize the gains while avoid producing oscillations in the image. Typically, the integral is increased first followed
by the proportional gain. The PID values, setpoint, scan size and scanning speed are all interrelated and can affect the tracking of the AFM on the sample.

3.4.3 AFM Data Analysis and Image Processing

A typical AFM raw data file contains 512 x 512 data points. After the AFM tip has finished scanning the surface of the sample, the software finds the lowest data point and uses it as a reference for the whole dataset. However in each new scan, a new point of reference is determined based on the lowest measured point. This is an issue if the surface being scanned is changing with time. If the substrate is completely covered by a deposited copper film within the scan area, the heights of the features can no longer be accurately referenced to the substrate. In this case, we can only measure the surface morphological features and how they change with time (or thickness).

Typical AFM topography images in (a) 2-D and (b) 3-D are shown in Fig. 3.14. The heights of the features in (a) are depicted by a color scale, where dark colours represent low regions and bright colours represent high regions. The 3-D image in (b) gives a rendition of what the surface topography actually looks like. That is, data displayed in the x y and z axis.

![AFM topography images](image)

**Fig. 3.14** A typical AFM topography image of the surface of electrodeposited copper on gold.

AFM images usually have some degree of surface curvature that is not representative of the real surface. This apparent curvature can be introduced from the x-y-z scanner.
Several algorithms that can be used for “levelling” the images include: line-by-line and three-point techniques. In line-by-line levelling, a single line in an image is fit to a polynomial equation, and then subtracted from the image line. Then, the average height of each line is set equal to the previous line. In the three-point method, three points on an image are selected. These three points define a plane which is then subtracted from the image. The three-point method is particularly useful for levelling an electrodeposited film when some area of the substrate is exposed during the initial stages of the scan.

3.5 Ductility Measurement

Ductility is the ability of a solid material to deform under tensile stress. Uniaxial and biaxial tensile testing techniques can be used to characterize the ductility of freestanding films. One example of measuring ductility in metal films is that described by Nakahara.¹²

3.5.1 Nakahara Ductility Tester

The specimen is held rigidly between two metal plates with circular openings while a metal ball is slowly pushed upwards until the metal film ruptures. The distance the metal ball travels between where it first makes contact with the film and that where the film ruptures is observed.

A schematic of the ductility tester devised by Nakahara is shown in Fig. 3.15. It consists of a micrometer; a brass spindle extension with a steel ball; a pair of circular brass plates, each with a round opening at the centre. The extension rod is about 25 mm long and has the same diameter as the micrometer spindle. These two elements are cemented with epoxy resin and electrically isolated from one another. The micrometer and the lower brass plate are screw-mounted on a thick brass stand for ruggedness. To measure ductility, a film specimen is first placed over the O-ring that is held in the circular groove of the lower plate, and the upper and lower plates are clamped tightly together with two screws. The specimen is then slowly pushed upward by turning the micrometer. The distance the steel ball travels between contacting the specimen and the specimen’s rupture is read on the micrometer.
Nakahara defines the percentage elongation based on biaxial tensile deformation rather than on uniaxial deformation. Consider the case in which the steel ball is large, with its diameter approaching that of the opening in the brass stage. The cross-sectional profile of the film in this case is represented in Fig. 3.16. The profile consists of two linear segments $AB$ and $CD$ (non-contact regions) with length $m$, and a circular segment $BC$ of length $l$ (contact region). For a thin film, bending stresses are assumed to be negligible.

The lengths of the contact and non-contact regions, which are determined geometrically, are expressed as follows

$$m = \sqrt{(L_0/2)^2 + (r - d)^2 - r^2} \quad 3.15$$

and

$$l = 2r \cdot \tan^{-1} \left[ \frac{rL_0 - 2m(r - d)}{mL_0 + 2r(r - d)} \right] \quad 3.16$$

where $r$ is the radius of the steel ball, $d$ is the vertical displacement of the film at the center, $L_0$ is the diameter of that portion of the film subjected to elongation (gage length). The total length of the film is
\[ L = 2m + l \]  

The percentage elongation, or ductility, is given by

\[ \frac{(L - L_0)}{L_0} \times 100 \]  

---

**Fig. 3.16** Cross-sectional profile of a ball and specimen during testing.

**Fig. 3.17** Cross-section of a small ball pushing against film with a large diameter.

A typical curve relating percentage elongation to \( d \) is shown in Fig. 3.18 for two of several different ball sizes. When the size of the steel ball is small, the profile of that portion of the film not in contact with the ball becomes curved, as illustrated in Fig. 3.17. In this case, it is not difficult to imagine that the strain is localized to a large extent in that area of the film which is in contact with the ball. The percentage elongation measured with a small ball has little physical significance because of the highly localized strain distribution. For these reasons, the lower curve in Fig. 3.18 is
not expected to represent the actual percentage elongation, the error being greater for more ductile films (larger $d$ values).

**Fig. 3.18** Relationship between % elongation and displacement as a function of ball size.$^{12}$

### 3.5.2 Force-Displacement AFM-based Technique

To measure the stiffness of RF-MEMS switches, a force-displacement technique is employed through use of AFM. A SiN AFM cantilever tip (Olympus microcantilever model no. OMCL-AC160TS) is used operating in tapping mode. It has a spring constant of 42 N/m and a tip radius of 10 nm. The $x$, $y$ and $z$ piezos were calibrated against a standard calibration reference having surface features of precisely known dimensions. The known dimensions on the calibration reference’s surface were compared with those estimated by the SPM (Scanning Probe Microscope) software. The calibration parameters were adjusted until the SPM’s dimensions agreed with the true dimensions of the reference.

A laser is reflected from the back-side of the cantilever towards a position sensitive detector indicating its position. The cantilever is calibrated with respect to the $z$-piezo by pushing it against a hard surface and measuring its deflection in volts. The cantilever sensitivity, which is the slope of the linear region on the force calibration plot, allows conversion of the cantilever deflection from volts to nanometers. Three
important parameters for performing force measurements are trigger threshold, ramp size and dwell time. The trigger threshold defines the maximum force applied to the sample. The ramp size sets the total range for the z-piezo movement which was scaled along the horizontal axis of the force plot. In general, the ramp size is limited by the full range of the Z piezo. The dwell time is the duration the nanoindenteter maintains with the specimen before withdrawing. Without ramp delay, the tip is retracted immediately after the indentation has complete.

Fig. 3.19 A plot of the tip deflection against the z piezo position during a loading-unloading cycle.

Fig. 3.19 shows a typical plot of load versus displacement. The tip-to-sample interaction can be described in 7 stages:

1. The z-piezo extends; and the tip descends. No contact is yet made with the sample surface.
2. The tip is pulled down to the surface by van der Waals force.
3. As the tip presses down into the surface, the cantilever bends upward.
4. The z piezo retracts and the tip ascends until the upward force cancels the surface attraction. The probe is momentarily at its original deflection state (step 1).
5. As the z piezo continues retraction, the tip ascends further. The probe bends down as surface attraction holds onto the tip.
6. As the tip continues its ascent, it finally breaks free from surface attraction. The probe rebounds sharply upward.
7. As the z piezo continues retracting, the probe tip continues its ascent. There is no further interaction with the sample surface during this cycle.

*Note: The z piezo has a maximum displacement of approximately 2 µm.*

### 3.5.3 Fujikara Arc Fusion Splicer

Fusion splicing is the act of joining two optical fibres end-to-end using heat from an electric arc source. The splicing process begins by preparing each fibre end for fusion. Fusion splicing requires that all protective coatings be removed from the ends of each fibre. The fibre is then cleaved so that its end-face is perfectly flat and perpendicular to the axis of the fibre. In fusion splicing, the two end-faces of the fibres are aligned, then fused together. However, in this study, the ARC fusion splicer is used for a different purpose – the fabrication of probes with micro-spherical tips.

The optical fibre used in this study is a single-mode fibre and shown schematically in Fig. 3.20. It consists of four component materials - core (8 µm), cladding (125 µm), buffer (250 µm) and jacket (400 µm).

**Fig. 3.20** A typical single mode optical fibre showing the component layers. Their respective diameters are given as: (A) Core ~ 8 µm, (B) Cladding ~ 125 µm, (C) Buffer ~ 250 µm and (D) Jacket ~ 400 µm.

A Fujikura ARC Fusion Splicer\(^\text{13}\) model no. FSM-30SF (see Fig. 3.21) is used to fabricate microspherical tips at the end of optical fibres. The arc fusion splicer has two electrodes that stimulate an electric arc and heats up the fibre. The fibre end is heated by absorbing the electric arc discharging power. If enough energy is absorbed
the temperature will be high enough to cause excessive fibre-end deformation and change the glass geometry, forming a microsphere at the end of the fibre tip.

Fig. 3.21 Top-down optical image of the Fujikura ARC fusion splicer.

The fibre is placed along the v-groove and the fibre-end is centered between the two electrodes and locked down. The menus are navigated by pressing [up, down], and values are selected by pressing ENT. To position the fibre using the motor, select Motor Move, followed by ZL Motor. The fibre can be positioned by operating the [up, down] keys. To return to the main menu, select MENU 3 times. To turn on the arc, press and hold ARC. The diameter of a heated tip depends on the distance between the electrodes and tip, arc voltage and arc time.

3.6 References

3. Metrohm, Autolab Application Note EC03.
8. M. Veeco, DLS-20 Dual Lateral Position Sensitive Detector, UDT Sensor
12. Manual, Fujikura ARC Fusion Splicer model no. FSM-30SF
4 Stress and Morphology during Copper Electrodeposition

4.1 Introduction

Thin metal films deposited on a substrate are usually in a state of intrinsic stress, and this has been the subject of extensive experimental investigations and theoretical analysis.\textsuperscript{1-3} Electrodeposited thin films of copper are important for metallization technology in microelectronics applications and stress in such films can have considerable impact on device reliability.\textsuperscript{4, 5} While considerable progress has been made in understanding the relationship between stress evolution and the physical processes of film formation, many questions still remain. It is commonly observed that the microstructure of as-deposited films obtained by sputtering and electrodeposition is not stable at room temperature but changes readily with time, accompanied by recrystallization and grain growth.\textsuperscript{6} One of the main challenges with understanding stress in thin films is the deconvolution of such time variation.

Although several studies have investigated stress\textsuperscript{1, 7-10} and morphology\textsuperscript{11-21} of electrodeposited copper, few studies have shown \textit{in-situ} measurements of both. \textit{In situ} stress measurement allows continuous measurements of stress evolution in the film as it is deposited.\textsuperscript{1, 10, 22} \textit{In-situ} electrochemical AFM is a powerful technique for observing surface morphological evolution of electrodeposited materials which our group has previously demonstrated.\textsuperscript{22-24} In this chapter, we combined both \textit{in-situ} measurement techniques to investigate stress and morphology under various deposition conditions. We employ an “interrupt method” to observe changes in surface morphology during deposition, open circuit, and resumed deposition and compare these observations with corresponding \textit{in-situ} stress measurements.
4.2 *In-situ* Stress Measurements and AFM Imaging during Electrodeposition

To characterize the cathodic current over a range of overpotentials for the electrodeposition of copper on gold, a potential sweep experiment was performed. Fig. 4.1 shows a linear sweep voltammogram (LSV) for the electrodeposition of copper on the gold-coated cantilever in the stress cell (see Section 3.2.1 for details). As the potential was scanned in the negative direction, a cathodic current corresponding to the electrodeposition of copper was observed at -36 mV. The current increased through the reaction controlled region and eventually saturated at a value of ~ 3.6 mA cm\(^{-2}\) (the diffusion-limited region).

![Fig. 4.1 LSV for the deposition of copper on gold in 0.05 mol dm\(^{-3}\) CuSO\(_4\) in 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\) at 0.5 mV s\(^{-1}\). The dashed lines represent overpotentials of (i) -125 mV, (ii) -160 mV, and (iii) -200 mV at which subsequent constant-potential experiments were performed.](image)

It is clear from Fig. 4.1 that current changes rapidly at potentials lower (less negative) than -100 mV (kinetic control region). At higher (more negative) potentials, it approaches diffusion control. The overpotentials chosen for detailed experiments at constant potential (i) -125 mV, (ii) -160 mV, and (iii) -200 mV, are indicated by dashed lines in Fig. 4.1. These potentials were chosen based on the reproducibility of preliminary experiments. At potentials lower than -125 mV...
experiments were more difficult to reproduce. This was attributed to the strong
dependence of current on potential (as seen in Fig. 4.1) and consequent run-to-run
variations due to small potential changes (stability of reference electrode, surface
state of substrate etc.). These three overpotentials were used throughout the studies
presented in this chapter.

At each potential, we performed in-situ stress measurements during copper
electrodeposition and compared these measurements with in-situ AFM observations.
Both stress measurement and AFM imaging were carried out in three-electrode cells
with similar electrodes and electrolyte but with different geometry. A standard
electrolyte of 0.05 mol dm$^{-3}$ CuSO$_4$ in 0.1 mol H$_2$SO$_4$ was used throughout this
study. The working electrode in each cell was a gold-coated glass cantilever. Further
details regarding the experimental conditions of this work are shown in Chapter 3.

4.2.1 Results at -125 mV

In a typical experiment, the electrode potential was stepped directly from +200 mV
to a constant overpotential (in this case -125 mV). (Note: The magnitude of the
change in stress due to switching potential was significantly smaller than that which
had occurred during deposition [see Fig. 3.11]). The current and laser-beam
deflection due to cantilever bending were simultaneously monitored over time. The
current density was calculated as described in Section 3.3.3. Typical plots showing
the time dependence of current density and coulometric film thickness $h_c$ at an
overpotential of -125 mV are shown in Fig. 4.2. The current density, (a), (which we
will hereafter refer to as current) increases rapidly to a peak, beyond which it decays
to reach a constant value (or plateau). The coulometric thickness (b) was obtained
from the current-time curve (as explained in Section 3.3.4).

As copper was deposited on the cantilever substrate, it bent accordingly (see Section
1.2.3). The direction of bending depends on the stress (compressive or tensile) in the
deposit. The force per unit width $F/w$ of the cantilever was calculated from the laser-
beam deflection using Equation 3.7. The plots of (a) $F/w$ and (b) current taken from
Fig. 4.2 are shown in Fig. 4.3; positive values of $F/w$ correspond to tensile force.
Force increased in the tensile direction during deposition. The $F/w$ curve changes
very slowly with time during the early stages of deposition but begins to increase significantly in the tensile direction after 50-100 s.

![Graph](image1.png)

**Fig. 4.2** Time dependence of electrodeposition current (a) after a potential step to -125 mV for the gold-coated glass cantilever in additive-free electrolyte. The coulometric thickness $h_c$ estimated from the current-time curve is shown in (b).

![Graph](image2.png)

**Fig. 4.3** Plot of force per unit width of cantilever ($F/w$) during electrodeposition after a potential step to -125 mV, corresponding to the current-time plot in Fig. 4.2. The values of $F/w$ were determined from the cantilever deflection as described in Section 3.3.1. (b) Current-time plot as in Fig. 4.2 (a).
For a redox reaction, such as Cu/Cu$^{2+}$, the current measured depends on the rate at which copper ions diffuse to the electrode (diffusion control). During the initial stages of electrodeposition, nucleation can occur either instantaneously or progressively. Instantaneous nucleation occurs only when nucleation rate is high enough to occupy all available active sites on the electrode surface in a very short time period. The Scharifker-Hills model$^{17}$ can be used to calculate the nuclei population density of instantaneous nucleation mechanisms from the peak coordinates on a current transient.

$$N_0 = 0.065 \left( \frac{1}{8 \pi C_0 V_m} \right)^{1/2} \left( \frac{nFC_0}{i_{\text{max}}t_{\text{max}}} \right)^2$$

where $n$ is the number of electrons involved, $F$ is Faraday's constant, $C_0$ is the concentration of species in the bulk, $V_m$ is the molar volume, $t_{\text{max}}$ is the peak time and $i_{\text{max}}$ is the peak current.

Fig. 4.4(a) shows the $F/w$ data in Fig. 4.3 re-plotted against the thickness (from Fig. 4.3). The $F/w$ curve represents the sum of the stress forces in the film in the direction parallel to the cantilever plus any additional components of force at the interface (per unit width of cantilever). Assume that the forces at the interface remain approximately constant as deposition proceeds and that stresses within the film do not change significantly with time post deposition (these assumptions will be discussed and justified later). Then, for an incremental change $dh$ in thickness the corresponding change $dF/w$ represents the sum of the stress forces (parallel to the cantilever) in the newly-deposited lamina of copper of thickness $dh$ and so the stress in that lamina is

$$\sigma = \frac{dF/w}{dh}$$

Thus, within the assumptions above, the slope of the $F/w$ plot at any given thickness represents the local stress in the film deposited at that thickness. We will hereafter refer to the slope of the $F/w$ versus thickness plot as the differential stress $\sigma$.

The slope of the $F/w$ curve (a) in Fig. 4.4 was determined by numerically differentiating the $F/w$ data with respect to thickness. However, in doing this, small
amounts of scatter in the data become greatly amplified in the differentiation process. This scatter has been reduced somewhat by applying a moving average (i.e. preliminary investigations showed that 40 consecutive data points was the ideal size increment for averaging. A step size of one was used until the end of the dataset was reached). The average stress \( c \) in Fig. 4.4 over the entire film is

\[
\sigma_{avg} = \frac{F/w}{h}
\]

Neither differential nor average stress change significantly until 50 nm has been electrodeposited, at which point the differential stress becomes more tensile and eventually saturates at approximately 25MPa. The coulometric thickness of the film at which \( \sigma \) begins to saturate is approximately 150 nm. The stress curve is a useful approximation to stress in the local layer when time variation is considered to be small. If time effects are large, however, then stress measurements are not as reliable.

![Fig. 4.4](image)  
(a) Force per unit width \( F/w \) of cantilever plotted against film thickness \( h_c \) (from Fig. 4.3); (b) differential stress \( \sigma \) obtained from the slope of (a); and (c) average stress \( F/(w h_0) \).
Based on the assumption of a uniform film, Stoney’s equation can be used only to measure stress along the plane of the film. In very rough films where this assumption no longer holds, small error may be introduced.

To examine the surface morphology corresponding to these stress measurements, we repeated the same electrodeposition experiment in the AFM cell. The AFM cell had a similar three-electrode cell configuration as the stress cell. However, there were a number of differences between the two cells (as detailed in Section 3.2). The AFM cell held a smaller volume of electrolyte (2 ml compared with 13 ml in stress cell). In addition, the geometries of the two cells were different. The substrate used in the AFM cell was half the length of that used in the stress cell. Both stress and AFM measurements were performed under the same deposition conditions, however. AFM imaging was performed in contact mode, as described in Section 3.4.

The current measured in the AFM cell during deposition is compared with the current measured in the stress cell in Fig. 4.5. The current measured in the stress cell (ii) increased rapidly to a peak and eventually decayed to a plateau value. In general, the current in the AFM cell (i) was slightly higher. The current in the AFM cell had a double peak during the early stages of deposition and this may be due to a non-uniform current distribution because of the reduced dimensions of the AFM cell and the close proximity of the AFM scanner during electrodeposition (as described in Section 3.4.1). With the exception of an initial double peak, the current measured during electrodeposition in the AFM cell and stress cell are similar. The corresponding coulometric thickness curves are also shown in Fig. 4.5 and are in reasonable agreement. In general, the current measured in the AFM cell shows close agreement with that measured in the stress cell beyond the initial stages of deposition and this is typical in all of our experiments, in this chapter.

The regions marked AFM(a) to AFM(d) in Fig. 4.5 indicate the times during which the surface morphology was observed by AFM. A typical AFM image obtained during the beginning stages of deposition [Region AFM(a)] at -125 mV is represented in four different ways in Fig. 4.6. A grey-scale map of the z-deflection (height) data is shown in (a). The same data is represented as a shadow image in (b) and as three-dimensional representations at aspect ratios (height to width) of 1:1 and
4:1 in (c) and (d) respectively. The black arrow on the time axis indicates the direction of time progression during the scan. Each scan took 84 s. The potential was stepped to -125 mV at point “A” in the scan. Since the AFM scans were taken in situ while the copper was being electrodeposited, the resulting images show the time progression of the growth over the 84 s scan period (i.e. features which appeared at the beginning of deposition showed the early stages of deposition compared with the later stages of deposition observed at the bottom of the scan). When the AFM tip reached the bottom of the scan area ($h_c = 91$ nm), it returned to the top and repeated the scanning process.

Fig. 4.5 Current-time curves measured in (i) AFM cell and (ii) stress cell after a potential step to -125 mV at time = 0. The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (d) correspond to the times during which the AFM images in Fig. 4.6 and Fig. 4.8 were obtained. The stress cell data in (ii) and (iv) are from Fig. 4.2.
Fig. 4.6 Images obtained from an in-situ AFM scan during electrodeposition of copper after a potential step to -125 mV. (a) Grey-scale map of the z-deflection (i.e. height data); (b) shadow image; (c) and three dimensional images at aspect ratios (height-width) of 1:1 and 4:1, respectively. The line L1 represents the position of the line scan shown later in Fig. 4.7. The scan time was 84 s. On each image, the point at which the potential was applied is marked ‘A’ and represented as zero on the time axis which shows the progression of time during the scan.
A line scan is a height profile in any direction along the \( x-y \) plane. Line scans in the \( x \)- and \( y \)-directions yield different information about the deposit. Since the time axis points along the \( y \)-direction, any line scan taken along the \( y \)-axis will show the time-progression of the surface morphology. On the other hand, line scans along the \( x \)-direction will show the surface morphology at approximately a single instance in time. A single line scan is not, however, representative of the entire surface as it is taken over a very small portion of the surface and, thus, it must be closely compared with the AFM image of the entire surface. An example of a horizontal (\( x \)-direction) line scan is shown in Fig. 4.7 at height-width aspect ratios of 1:1 and 4:1; (a) and (b) correspond to the dashed lines in Fig. 4.6(c) and (d), respectively.

![Fig. 4.6 (c)](image)
![Fig. 4.6 (d)](image)

**Fig. 4.7** AFM line scans at L1 in (a) Fig. 4.6(c), and (b) Fig. 4.6(d).

As discussed previously in Section 3.4, if the substrate is completely covered by a deposited copper film within the entire scan area, the heights of the features can no longer be accurately referenced to the substrate. Although we cannot measure the thickness of a continuous film with AFM, we can however observe changes in the surface morphology of the deposit with time. We regularly refer to coulometric thickness and not the thickness measured by the AFM when describing AFM measurements. The coulometric thickness \( h_c \) is shown in each AFM image.
A time series of AFM images taken over the same surface region during electrodeposition at -125 mV is shown in Fig. 4.8. Each AFM scan was performed continuously and the time delay between each scan was less than a second. In addition, the same surface region was measured during each scan. The coulometric thickness $h_c$ at the beginning and end of each subsequent scan is shown in the image. The image in (a) shows the evolution of surface morphology during the first 56 nm of deposition. The entire gold surface appears to have been covered by protruding copper features with certain features growing to a larger size. Referring to Fig. 4.4, we observed no increase in stress within the first scan up to $h_c = 56$ nm. In the second scan between 57 and 135 nm, shown in (b), many copper features have coalesced on their near neighbours. The corresponding increase in tensile stress, which we observed earlier in Fig. 4.4 at this thickness, coincides with this island coalescence. In the third scan (136 to 214 nm) it appears that most islands are in contact with their near neighbours. The increase in size of the islands is not as dramatic with further deposition. We would expect that at a constant deposition rate the amount of material deposited on any given island decreases as surface area increases. Our results suggest that the increase in tensile stress in the deposit is due to island coalescence and the associated increase in grain boundary volume. Tensile stress appears to saturate when most islands are in contact, i.e. when their boundaries have formed.
Fig. 4.8 Sequence of AFM images obtained in situ during electrodeposition after a potential step to -125 mV at 0 s on the time axis shown. Image (a) corresponds to that in Fig. 4.6. Images (b), (c) and (d) follow sequentially at the times corresponding to AFM(b), AFM(c) and AFM(d) in Fig. 4.5. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
Fig. 4.9 shows (a) line scans taken from Fig. 4.8 and (b) the corresponding stress curve taken from Fig. 4.4. Each line scan is shown with a 1:1 height-width aspect ratio. The first line scan $L_1$ was taken from the first AFM scan at $h_c = 29$ nm. Each subsequent line scan corresponds to the same position but at increased thicknesses. We can clearly see a dramatic change in the surface morphology of the deposit between $L_1$ and $L_2$ (30 nm to 80 nm). Stress is negligible during the early stages of deposition when features are small and isolated (region A). The features grow laterally and vertically in size (L2) and as they coalesce and form boundaries (region B), tensile stress increases in the stress curve. Tensile stress increases further as the islands grow vertically and laterally in size (L3). We can also see evidence of trench-filling (region C). Tensile stress approaches saturation when the evolution of surface morphology occurs more slowly (L4). In addition, some features develop facets and this becomes more apparent as the features grow in size. For an isolated island (region D), the island shows growth along specific directions as indicated by the arrows.

Our results show that stress does not increase during the first 50 nm of deposition, during which the majority of large copper features remain isolated. The onset of island coalescence (> 50 nm) coincides with the increase in tensile stress seen in Fig. 4.8. The measured tensile stress appears to saturate when the majority of island boundaries have formed. Earlier work in our group has attributed the increase in tensile stress to grain boundary formation\textsuperscript{22}. This was based on the observation that as nucleation density increased with overpotential tensile stress also increased. Our observations are also in agreement with theoretical models\textsuperscript{25-29} described in the literature.

4.2.2 Results at -160 mV

We have already presented in-situ stress and AFM measurements at an overpotential of -125 mV. We repeated these experiments at higher overpotentials of -160 mV and -200 mV, to determine if potential has an effect on stress or morphology. The results for -160 mV are presented here. Those for -200 mV are presented in the next section.
Fig. 4.9 (a) AFM line scans at L1, L2, L3 and L4 in Fig. 4.8. The coulometric thicknesses $h_c$ are 29 nm, 107 nm, 186 nm and 264 nm, respectively. (b) Corresponding stress curve is taken from Fig. 4.4.
Fig. 4.10  (a) Plots of (i) current and (ii) $F/w$ against time after a potential step to -160 mV. (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$.

The time dependence of current and $F/w$ at -160 mV are shown in Fig. 4.10(a). The $F/w$ curve increases in the tensile direction during deposition. Both current and $F/w$ are higher than at -125 mV. Fig. 4.10(b) shows the thickness dependence of stress...
and $F/v$ during the first 400 nm of deposition. Tensile stress rapidly increases to a peak at 100 nm, beyond which it decays reaching a relatively constant value (40 MPa) at ~ 200 nm. Previously at -125 mV (Fig. 4.4), we observe that tensile stress reached a maximum at approximately 150 nm. Comparing the measurements at -160 mV and at -125 mV, we can see that the thickness at which tensile stress reaches a peak increases with potential (or deposition flux). The difference in tensile stress between these two potentials is smaller during the later stages of deposition (i.e. in the plateau region).

To examine the surface morphology, we again carried out AFM measurements in situ during deposition. Fig. 4.11 shows the current-time plot obtained in the AFM and stress cells. The current in the corresponding stress experiment (from Fig. 4.10) is also shown as are the thicknesses derived from these curves. Again, it can be seen that there is reasonable agreement although (as observed at -125 mV) the current is slightly higher in the AFM cell. The current and thickness curves are similar to that observed at -125 mV, but are higher in magnitude.

![Current-time curves measured in (i) AFM cell and (ii) stress cell after a potential step to -160 mV at time = 0. The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (d) correspond to the times during which each AFM image was captured. The stress cell data in (ii) is from Fig. 4.10(a).](image)

**Fig. 4.11** Current-time curves measured in (i) AFM cell and (ii) stress cell after a potential step to -160 mV at time = 0. The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (d) correspond to the times during which each AFM image was captured. The stress cell data in (ii) is from Fig. 4.10(a).
Fig. 4.12 Sequence of AFM images obtained in situ during electrodeposition after a potential step to -160 mV at 0 s on the time axis shown. Images (a), (b), (c) and (d) correspond to AFM(a), AFM(b), AFM(c) and AFM(d) in Fig. 4.11. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
A time series of AFM images taken during electrodeposition at -160 mV is shown in Fig. 4.12. As previously observed at -125 mV, the largest change in the deposit occurs within the thickness range of the first scan (i.e. $h_c < 84$ nm) and this again coincides with an increase in tensile stress in the deposit (Fig. 4.10). The surface is much flatter at this potential than at -125 mV.

**Fig. 4.13** AFM line scans at L1, L2, L3 and L4 in Fig. 4.12. The coulometric thicknesses $h_c$ are 45 nm, 150 nm, 248 nm and 343 nm, respectively.

Horizontal line scans in Fig. 4.13 show the surface morphology at different stages of deposition. It is possible that at -160 mV, significant grain boundary formation has occurred at a much earlier stage. However, we can see very little change in the surface morphology during deposition at this potential since growth is occurring too rapidly for the AFM to resolve. In general, surface morphology did not change
significantly beyond 84 nm. The surface of the deposit is much flatter than that observed at -125 mV. One explanation for this tensile stress behaviour (Chason’s model\textsuperscript{30}) will be described later in the chapter.

**Fig. 4.14** (a) Plots of (i) $F/w$ and (ii) current against time after a potential step to -200 mV. (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
4.2.3 Results at -200 mV

Having observed stress and morphology at both -125 mV and -160 mV, we repeated these measurements at -200 mV and present the results in this section.

Fig. 4.14(a) shows a plot of the time dependence of current and \( F/w \). Both current and \( F/w \) are higher than at lower potentials. Thus, tensile stress increases with deposition flux. The increase in tensile stress during the first 50 nm of deposition may be a result of grain boundary formation. Fig. 4.14(b) shows the thickness dependence of stress and \( F/w \) during the first 450 nm of deposition. The peak is much larger than previously observe at lower potentials. Since the presence of this peak is not completely understood, it can be difficult to reliably compare measurements within the early stages of deposition. It is more reliable, however, to compare stress measurements within the plateau region, where stresses are not varying as much.

![Diagram showing current-time curves and thickness dependence of stress and F/w](image)

**Fig. 4.15** Current-time curves measured in (i) AFM cell and (ii) stress cell after a potential step to -200 mV at time = 0. The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (d) correspond to the times during which each AFM image was captured. The stress cell data in (ii) is from Fig. 4.14(a)
To examine the surface morphology at -200 mV, we again carried out AFM measurements in situ during deposition. Fig. 4.15 shows the current-time plot obtained in the AFM and stress cells. The current in the corresponding stress experiment (from Fig. 4.14) is also shown as are the thicknesses derived from these curves. As observed at lower potentials, the current in the AFM cell is slightly higher overall than that in the stress cell and exhibits an initial double peak. The current and thickness curves are similar to that observed both at -125 mV and -160 mV, but are higher in magnitude.

A time series of AFM images taken during electrodeposition at -200 mV is shown in Fig. 4.16. Similar to that observed at -160 mV, the largest change in the deposit occurs again within the thickness range of the first scan (i.e. \( h_c < 84 \) nm) and this again coincides with an increase in tensile stress in the deposit (Fig. 4.14). The surface appears to be a little flatter at this potential than at -160 mV and is much flatter than that observed at -125 mV.

In Fig. 4.17, horizontal line scans (obtained from Fig. 4.16) show the surface morphology at different stages of deposition. The surface appears somewhat rough during the first scan (~ 50 nm). Trench features appear filled in by the second scan (~ 179 nm). We can see very little change in the surface morphology during deposition beyond the second scan. In general, surface morphology did not change significantly beyond 84 nm. The surface of the deposit is much flatter than that observed at lower potentials. AFM images and line scans have shown that the surface morphology is flatter at higher potentials.

Comparing these observations with stress measurements, we can see that tensile stress is higher in flatter films. The trenches between each copper feature are filled in more quickly than the top surface of the features, resulting in greater tensile stress due to zipping. These observations will be quantified in terms of surface roughness later in Section 5.2.5.
Fig. 4.16 Sequence of AFM images obtained in situ during electrodeposition after a potential step to -200 mV at 0 s on the time axis shown. Images (a), (b), (c) and (d) correspond to AFM(a), AFM(b), AFM(c) and AFM(d) in Fig. 4.11. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
As discussed previously, the differential stress values presented correspond to the local stress in the film only if (i) film stress does not change significantly post-deposition and (ii) interfacial forces remain relatively constant during deposition. In the next section we report experiments where deposition is interrupted. The results of these experiments provide a basis on which to assess the validity of these assumptions.
4.3 Interruption of Electrodeposition

In general, intrinsic stress in copper nanofilms is a difficult property to deconvolute. Intrinsic stress and its behaviour during (and after) deposition is dependent on many deposition and relaxation processes, and other physical effects such as interplay between film and substrate. To understand such effects, measurements of stress and surface morphology during deposition, open circuit and resumed deposition were carried out. By interrupting the deposition, we can observe both the time-dependent behaviour of stress relaxation in the film and the corresponding surface morphological evolution. By resuming the deposition, we can determine if interruption to deposition has an effect on how stress and surface morphology behaves compared with depositions without any interruption to deposition.

In Section 4.2, we presented in-situ measurements of stress and surface morphology during the electrodeposition of copper on gold at three different overpotentials (i.e. -125, -160 and -200 mV). We repeated these experiments with intermediate interruptions to the deposition. Deposition was interrupted by opening the circuit. Stress and surface morphology were observed continuously over time during deposition, open circuit and resumed deposition. We present the results in this section.

4.3.1 Results at -125 mV

A current-time plot measured at an overpotential of -125 mV where the deposition was interrupted (at A) after 200 s and the potential re-applied (at B) after a further 200 s is shown in Fig. 4.18(a). Initially, the current increased rapidly to a peak and then decayed to a plateau value as observed during continuous deposition experiments in previous sections. (Note: The peak in current appears very early. This is possibly due to the rapid nucleation on the previously deposited copper). When potential was re-applied after the interruption, the current reached a peak instantly. The magnitude of the peak, however, was much higher than the initial peak observed pre-interruption. The current then decreased, eventually reaching its pre-interrupted value after approximately 50 s and remained constant thereafter.
Fig. 4.18  (a) Plot of (i) current and (ii) $F/w$ against time during electrodeposition after a potential step to -125 mV. (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
The $F/w$ curve increased in the tensile direction during deposition. Although no relaxation of tensile stress was observed in the film during the first instance at open circuit, relaxation was observed during the second instance. The magnitude of the relaxation during open circuit, however, was small. The $F/w$ curve recovered approximately its pre-interrupted values when deposition was resumed.

The thickness dependence of stress and $F/w$ are shown in Fig. 4.18(b). A small section of the processed data upon resumption of deposition was lost at the expense of the data fitting and averaging process. For this reason, a small break in the $\sigma$ curve can be seen between the point of interruption and resumption of deposition.

![Fig. 4.19](image)

**Fig. 4.19** Plot of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$ during continuous (dashed line) and interrupted (solid line) electrodeposition after a potential step to -125mV.

The interruption had little effect on stress in the deposit, as observed in the stress curve. Since little time variation was observed in the $F/w$ curve at open circuit at -125 mV, the stress curve could be assumed to be a reliable measurement of stress in the surface layer (or newly deposited material) if the pre-interruption and post-resumption values of $F/w$ match those taken during continuous deposition at this and at higher potentials.
To determine if interruption effects $F/w$ (i.e., to examine the reversibility of film stress), an overlay of the $F/w$ and stress curves for continuous and interrupt depositions at -125 mV is shown in Fig. 4.19. We can see that stress during resumed deposition deviates slightly from that during the first 50 nm of continuous deposition. After resuming deposition, stress recovers to approximately the same value as that upon interruption. More importantly, the recovery of stress to the uninterrupted value suggests that our measurements are a reliable and representative of stress in the local surface layer.

The change in $F/w$ during interruption is small compared with that during deposition indicating low-mobility Volmer-Weber growth. High-mobility films usually undergo a compressive-tensile-compressive trend in stress. One possible explanation for the reversible stress behaviour is proposed by Chason’s model which describes reversible movement of surface adatoms to/from the grain boundary. During deposition, tensile stress increases due to island zipping. When deposition is interrupted, the higher chemical potential at the surface (due to the excess adatom population) acts as a driving force causing movement of surface adatoms into the grain boundaries, thus increasing compressive stress. Since electrodeposited copper has low mobility at room temperature, the rate of incorporation of adatoms into the grain boundaries is much slower than the rate of increase in tensile stress due to zipping. When deposition is resumed, the process is reversed as an excess chemical potential in the grain boundaries forces movement of adatoms back onto the free surface.

To examine the surface morphology, we again carried out AFM measurements in situ during deposition. Fig. 4.20 shows the current-time plot obtained in the AFM and stress cells. The current in the corresponding stress experiment (from Fig. 4.18) is also shown as are the thicknesses derived from these curves.
Fig. 4.20  Current-time curves using *interrupt method* at -125 mV measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (c) correspond to the times during which each AFM image was captured

The regions marked AFM(a) to AFM(d) in Fig. 4.20 indicate the times during which the surface morphology was observed by AFM. The coulometric thickness $h_c$ of each deposit is shown at the beginning and end of each scan. The location of the scan when the circuit was opened is labelled “OFF” and when the potential was re-applied is labelled “ON”. The surface morphological evolution of the deposit was observed during all stages.

Because little time variation occurs in the deposit at -125 mV while at open circuit [see Fig. 4.18(a)] we would not expect a significant change in the surface morphology. We do, however, observe very subtle changes on the surface of the deposit. The surfaces of the copper features appeared slightly rough (or faceted) during deposition. When deposition was interrupted, the surface appeared to have a smoother appearance. During resumed deposition the surface returned to a more roughened configuration.
Fig. 4.21  Sequence of AFM images obtained in situ during electrodeposition after a potential step to -125 mV at 0 s on the time axis shown. Images (a), (b) and (c) follow sequentially at the times corresponding to AFM(a), AFM(b) and AFM(c) in Fig. 4.20. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
According to Chason’s model\textsuperscript{30}, we would expect an excess population of surface adatoms on resumption of deposition (which would produce a relatively rough surface). When deposition is interrupted, the excess adatoms are driven into the grain boundaries (producing a smoother, relaxed surface). As deposition is resumed, the excess adatoms in the grain boundaries move onto the surface. The surface recovers to a roughened configuration as a result of the newly deposited material.

AFM line scans obtained at L1, L2 and L3 in Fig. 4.22 show the surface features undergoing some subtle smoothing during open circuit and roughening during resumed deposition. Both changes in surface morphology and $F/w$ [see Fig. 4.18(a)] are negligible during open circuit.

Our measurements have shown that, at -125 mV, current during resumed deposition attained its pre-interrupted value after approximately 50 s and remained constant thereafter. The magnitude of the change in stress during open circuit was small.
4.3.2 Results at -160 mV

Having observed stress and morphology at -125 mV during interrupted deposition, we repeated these measurements at an overpotential of -160 mV and present the results in this section.

A current-time plot measured at an overpotential of -160 mV during interrupted deposition is shown in Fig. 4.23(a). The current behaves in much the same way as that described at -125 mV (see Fig. 4.18), except at a higher magnitude. $F/w$ during open circuit, however, relaxes more in the compressive direction than it did at -125mV. This suggests that the magnitude of relaxation in the deposit increases with deposition flux. Nevertheless, the magnitude of the change in $F/w$ during open circuit is much smaller than that measured during deposition. The $F/w$ curve recovers its original value during resumed deposition.

The thickness dependence of stress and $F/w$ is shown in Fig. 4.23(b). Deposition was interrupted at approximately 200 nm film thickness. We can see that tensile stress recovers to the uninterrupted value within 100 nm of resumed deposition. The magnitude of stress upon resuming deposition is greater at -160 mV than that observed at -125 mV.
To examine the surface morphology, we again carried out AFM measurements \textit{in situ} during deposition and interruption. Fig. 4.24 shows the current-time plot obtained in the AFM and stress cells. The current in the corresponding stress experiment (from
Fig. 4.23) is also shown as are the thicknesses derived from these curves. The current and thickness curves are similar to that observed at -125 mV, but are higher in magnitude.

![Diagram showing current and thickness curves](image)

**Fig. 4.24** Current-time curves using interrupt method at -160 mV measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (c) correspond to the times during which each AFM image was captured.

The corresponding series of AFM images taken during electrodeposition are shown in Fig. 4.25. As observed at -125 mV, the magnitude of the change in $\frac{F}{w}$ [see Fig. 4.23(a)] during open circuit is small and, as expected, the change in surface morphology is very subtle. Again we observe slight smoothing during open circuit and surface roughening during resumed deposition.
Fig. 4.25 Sequence of AFM images obtained in situ during electrodeposition after a potential step to -160 mV at 0 s on the time axis shown. Images (a), (b) and (c) follow sequentially at the times corresponding to AFM(a), AFM(b) and AFM(c) in Fig. 4.24. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
Fig. 4.26 Lines scans during deposition (L1), open circuit (L2), and resumed deposition (L3) obtained from AFM images in Fig. 4.25.

AFM line scans in Fig. 4.26 (obtained at L1, L2 and L3 in Fig. 4.25) show the surface features undergoing some subtle smoothing during open circuit and roughening during resumed deposition. Both changes in surface morphology and $F/w$ [see Fig. 4.23(a)] are negligible during open circuit. This observation is consistent with that at -125 mV.

Our results at -160 mV show that, similar to that observed at the lower potential, upon resumption of deposition, stress recovered its pre-interrupted value. The magnitude of relaxation during open circuit was small relative to the stress that was generated during deposition. The magnitude of stress upon resuming deposition was larger at the higher deposition flux. Stress recovers its pre-interrupted value when deposition was resumed. We have observed surface smoothing at open circuit and recovery of surface roughness during resumed deposition.
4.3.3 Results at -200 mV

Having observed stress and morphology at -125 mV and -160 mV during interrupted deposition we repeated these measurements at an overpotential of -200 mV and present the results in this section.

A current-time plot measured at an overpotential of -200 mV during interrupted deposition is shown in Fig. 4.27(a). The current behaved in much the same way as that described at lower potentials except the peak and plateau values of the current were higher. The $F/w$ curve once again shows that the magnitude of relaxation in the deposit increases with overpotential. The magnitude of relaxation is small relative to the stress increase during deposition. We again find that $F/w$ recovers its original value during resumed deposition.

The thickness dependence of stress and $F/w$ are shown in Fig. 4.27 (b). Deposition was interrupted at approximately 225 nm film thickness. Comparing continuous and interrupted depositions, at any given thickness (beyond the peak in tensile stress) the interrupted film eventually recovered the differential stress measured in the continuous film. We observe this recovery at all potentials. The magnitude of the peak in tensile stress upon resuming deposition and the rate of recovery in stress increases with potential.

To examine the surface morphology, we again carried out AFM measurements in situ during deposition. Fig. 4.28 shows the current-time plot obtained in the AFM and stress cells. The current in the corresponding stress experiment (from Fig. 4.27) is also shown as are the thicknesses derived from these curves. The current and thickness curves are similar to that observed both at -125 mV and -160 mV, but are higher in magnitude.
Fig. 4.27 (a) Plot of (i) current and (ii) $F/w$ against time during electrodeposition after a potential step to -200 mV for continuous (dashed line) and interrupted (solid line) deposition. (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
Fig. 4.28  Current-time curves using *interrupt method* at -200 mV measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (c) correspond to the times during which each AFM image was captured.

The corresponding series of AFM images taken during electrodeposition are shown in Fig. 4.29. We again see slight smoothing during open circuit and surface roughening during resumed deposition.

AFM line scans in Fig. 4.30 shows the surface features during deposition were pointed (faceted) and became more rounded during open circuit. The surface features recovered to a similar pointed shape as that observed during pre-interrupted deposition.
Fig. 4.29 Sequence of AFM images obtained in situ during electrodeposition after a potential step to -200 mV at 0 s on the time axis shown. Images (a), (b) and (c) follow sequentially at the times corresponding to AFM(a), AFM(b) and AFM(c) in Fig. 4.28. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
4.4 Discussion

One of the key achievements from these experiments is that stress in the plateau region is very reproducible for each of the three potentials. To the best of our knowledge no one has yet demonstrated \textit{in-situ} stress data in which the time-variation in the deposit is small and compared it with \textit{in-situ} AFM.\textsuperscript{31} We carried out interruption experiments where stress recovered to the same value as its uninterrupted counterpart. This method is particularly useful for demonstrating the validity of our measurements in continuous depositions.

Furthermore, interrupt measurements of stress and morphology for electrodeposited films have not been documented in the literature. Thompson\textsuperscript{31, 32}, however, has performed interrupt experiments with vapour-deposited copper films.\textsuperscript{30, 31} Regarding his data, Thompson comments that a true steady-state $F/w$ evolution in which the differential stress is time-invariant was not achieved. We have shown sufficiently good data of stress in that the variation of time during open circuit was small (due to low mobility of electrodeposited copper at room temperature).
Fig. 4.31(a) shows a plot of current and $F/w$ during electrodeposition at overpotentials of -125 mV, -160 mV and -200 mV. The characteristic feature of each curve is that it increases in tensile stress to a peak. At low potentials the peak is smaller and the stress eventually reaches a saturated value with increasing thickness. At higher potentials, tensile stress increases to a peak followed by a decrease towards a constant value (or plateau). Since we did not perform interruptions before the peak in tensile stress, we cannot adequately interpret the peak. It is possible that the peak is related to the formation of grain boundaries in the deposit or alternatively, it could be related to the stress at the interface.

Development of a tensile stress during island coalescence is widely regarded as being due to the process of grain boundary formation.28, 29 Our results show [Fig. 4.31(b)] that tensile stress increases with overpotential and this is in agreement with the literature.33 AFM observations show that density of nucleated islands also increases with overpotential. The general understanding in the literature is that tensile stress results from a strain between islands as they coalesce.

A comparison of the plateau stresses Fig. 4.31(b) where $h_c = 250$ nm for each overpotential is shown in Fig. 4.32. Although we only investigated three overpotentials, we can clearly see that tensile stress increases with overpotential.
Fig. 4.31  (a) Plot of $F/w$ (dashed line) and current (solid line) against time during continuous electrodeposition after a potential step to (i) -125 mV, (ii) -160 mV and (iii) -200 mV. (b) Corresponding plots of $F/w$ (dashed line) and differential stress (solid line) against coulometric thickness $h_c$. 

(b)
The time dependence of current and $F/w$ during interrupted deposition is shown Fig. 4.33(a). The current at each potential upon resumption of deposition is initially high, but decays rapidly reaching the same value as pre-interrupted deposition. The corresponding thickness dependence of $F/w$ and stress at each potential is shown in Fig. 4.33(b).

It is also important to consider the effects of ripening of the deposit at room temperature. It has been well documented in the literature that the microstructure of electrodeposited copper changes dramatically over a period of hours to days or weeks. This has a considerable reduction in film stress as the grains grow in size. Intrinsic stress acts as a driving force for recrystallization. At high deposition overpotentials where nucleation density is high, a larger intrinsic stress is generated in the deposit. Therefore, we would expect a greater degree of microstructure evolution in films deposited at high overpotentials.
Fig. 4.33  (a) Plot of current (solid line) and $F/w$ (dashed line) against time during interrupted electrodeposition after a potential step to (i) -125 mV, (ii) -160 mV and (iii) -200 mV. (b) Corresponding plots of $F/w$ (dashed line) and differential stress (solid line) against coulometric thickness $h_c$. 
4.5 Conclusions

We have monitored stress *in situ* in copper nanofilms and have showed that the time variation of stress is small after interruption of electrodeposition. This shows that the time-variation of stress due to relaxation is small on the time-scale of electrodeposition. Therefore differential stress was shown to be a valid representation of local stress as a function of thickness $h$. We further showed that our time-series of $F/\nu$ and simultaneous current measurements provided an adequate data-set to generate reliable and reproducible plots of stress $\sigma_h$ versus thickness $h$.

Our interruption experiments have also shown that film stress recovers approximately to the original value when deposition is resumed (post interruption) and becomes approximately constant with increasing film thickness. This constant value increases with overpotential. The film becomes levelled and tensile stress increases with overpotential.

While the stresses generated in the formation of the first few nanometres of film were not determined in this study, beyond this thickness, stress was found to be tensile. The evolution of stress with increasing film thickness followed a similar pattern at all potentials investigated and eventually reached a relatively constant (plateau) value of tensile stress above a certain thickness. The measured plateau values of stress increased with increasingly negative overpotential, ranging from 25-45 MPa for -125 to -200 mV.

The increase in tensile stress in the early stages coincided with the coalescence of protruding surface features observed by *in-situ* AFM. We also observed that at a higher deposition flux, islands were smaller and occurred at a higher density. We observed the coalescence of these smaller features followed by trench filling. We deduced that the coalescence of small features resulted in higher grain boundary volume. Since the highest stress coincided with the presence of smaller features we conclude that the increase in tensile stress is caused by grain boundary filling.

At the higher potentials (-160 mV and -200 mV), the decrease in local stress after the peak may be explained by a decrease in the rate of grain-boundary formation.
Evidence for this is provided by the AFM which shows a flatter surface at higher thicknesses at these potentials as compared to -125 mV.

4.6 References

5 Effects of Additives

5.1 Introduction

The use of electrodeposition in metallization technology relies on electrolyte additives that modify the deposition process so as to obtain desirable characteristics such as superfilling of trenches and vias in the damascene process.\textsuperscript{1,6} The nature and concentration of additives used in commercial electrodeposition systems are usually proprietary. However, combinations of additives such as chloride and polyethylene glycol (PEG) are frequently used in the electrodeposition of copper.\textsuperscript{7,8}

The action of organic additives on copper electrodeposition has been empirically characterized and have been shown to have a dramatic effect on micro/nanostructure and morphology.\textsuperscript{9} In addition some studies have been carried out on the effect of additives on intrinsic stress in the deposited film.\textsuperscript{10} However, few experimental investigations have been documented in comparing both morphology and stress in the presence of these additives.\textsuperscript{9,11}

The role of chloride in acidic copper sulphate baths has long been recognized.\textsuperscript{4,12-14} Chloride behaves as a surface stabilizing agent and promotes epitaxial growth.\textsuperscript{15} Although the concentrations of additives used in industry are proprietary, a literature survey suggests the typical concentration used for effective superfilling is the region of ~ 1 mM.\textsuperscript{4,14,16,17} At low chloride concentrations, copper deposition is inhibited and this has been attributed to the formation of a CuCl species which partially blocks the electrode surface.\textsuperscript{18} At high chloride concentrations, copper deposition is accelerated. To the best of our knowledge no work has been published on the effect of chloride on stress in electrodeposited copper nanofilms.
PEG is usually added to electroplating baths to inhibit deposition by impeding the transport of copper ions from bulk electrolyte\textsuperscript{19} and suppressing surface diffusion of copper atoms.\textsuperscript{12} PEG alone has only a small effect on electrode kinetics.\textsuperscript{19} It is generally understood that chloride ions and PEG have an interactive effect and that their combination leads to a strong inhibition of the copper deposition reaction.\textsuperscript{20} In the presence of chloride, PEG acts as a suppressor, adsorbing on the cathode and exhibiting a blocking effect with respect to the cupric ions in the electrodeposition process.\textsuperscript{21, 22} Many studies have investigated the mechanism for the inhibitive behaviour of PEG in the presence of chloride,\textsuperscript{21-24} and their combined effect on the morphology\textsuperscript{8, 25-27} of copper electrodeposits. In the presence of PEG and chloride the onset of copper deposition occurs at a potential which depends on the chloride ion concentration.\textsuperscript{7, 13, 28, 29}

In Chapter 4 we used an “interruption method” to demonstrate that differential stress is a reliable measurement of local stress in the layer. We also showed AFM measurements that suggest grain boundary formation results in an increase in tensile stress in the deposit. In this chapter, we extend that study to the effects of additives (chloride ion and PEG) on stress during copper electrodeposition and compare these measurements with observations of surface morphology.

5.2 Effects of Chloride on Stress and Morphology

In this section, we present the results of our investigation of chloride as an additive. In Section 5.2.1, we present preliminary experiments aimed at identifying a suitable concentration. In subsequent sections, we describe stress and AFM results at each of three constant potentials (-125 mV, -160 mV and -200 mV). These experiments were carried out without any interruption of deposition (continuously). Experiments where the deposition was interrupted will be described later in Section 5.3.
5.2.1 Preliminary Study of Concentration Dependence

Before investigating in detail the effect of chloride on stress and morphology we carried out preliminary experiments to identify the most suitable concentration of chloride for our studies of stress and morphology. The results of preliminary potential sweep experiments are presented in Section 5.2.1.1 and the results of preliminary constant potential experiments are presented in Section 5.2.1.2.

5.2.1.1 Preliminary Potentiodynamic Sweep

Fig. 5.1 shows LSVs for the electrodeposition of copper on gold in 0.05 mol dm\(^{-3}\) CuSO\(_4\) in 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\) in the presence of chloride at various concentrations. The potential was scanned from +200 mV to -400 mV (Cu/Cu\(^{2+}\)) at 0.5 mV s\(^{-1}\). For comparison, current was measured initially during deposition without the presence of chloride, and this is indicated by the black (dashed) line shown in Fig. 5.1. Each of the six concentrations (ranging from 0.0036 ppm to 360 ppm) is indicated on the plot. For each concentration of chloride, when deposition was finished the copper film was removed from the gold by applying a potential at +200 mV (Cu/Cu\(^{2+}\)). The concentration of chloride was then increased before the potential was re-applied. The LSV measurement was repeated for each added concentration. It is clear from Fig. 5.1, that current is inhibited in the presence of chloride at potentials lower than ~ -160 mV. It appears that while chloride has a large effect at potentials lower than ~ -160 mV (kinetic control), at higher potentials (diffusion control) its effect is not as obvious. The three overpotentials, which were used previously in studies in the absence of additives (Chapter 4), were also used throughout the constant-potential studies in this chapter. These were (i) -125 mV, (ii) -160 mV, and (iii) -200 mV and are indicated by dashed lines in Fig. 5.1.

The concentration dependence of current on chloride is demonstrated by plotting the current data (taken from Fig. 5.1) against the log of the chloride concentration at different overpotentials (see Fig. 5.2). It is clear that while chloride strongly inhibits current at potentials lower than ~ -160 mV, this strong inhibition is only observed at concentrations > 1 ppm, approximately. The effect of chloride at larger potentials is not as significant.
Fig. 5.1 LSV for the deposition of copper on gold in 0.05 mol dm$^{-3}$ CuSO$_4$ in 0.1 mol dm$^{-3}$ H$_2$SO$_4$ with various concentrations of chloride at 0.5 mV s$^{-1}$. The dashed lines represent overpotentials of (i) -125 mV, (ii) -160 mV, and (iii) -200 mV at which subsequent constant-potential experiments were performed.

Fig. 5.2 Concentration dependence of chloride on current during potentiodynamic electrodeposition of copper on gold at various overpotentials in 0.05 mol dm$^{-3}$ CuSO$_4$ in 0.1 mol dm$^{-3}$ H$_2$SO$_4$. The measured current values are taken from the LSV shown in Fig. 5.1.
Fig. 5.3 (a) Time dependence of current density during electrodeposition at an overpotential of -200 mV in the presence of various concentrations of chloride. (b) Corresponding $F/w$ curves.
5.2.1.2 Preliminary Potentiostatic Measurement at -200 mV

Having determined the effect of chloride under potentiodynamic conditions, copper was electrodeposited on gold at a constant potential of -200 mV potential (Cu/Cu$^{2+}$) following a potential step from +200 mV (Cu/Cu$^{2+}$). Concentration of chloride was increased in a similar manner to that described in Section 5.2.1.1.

The current-time curve at each concentration of chloride is shown in Fig. 5.3(a). In the absence of chloride, current rapidly increases to a peak and decays to reach a relatively constant value (plateau), as usual. Similar to the potential sweep experiments, chloride does not greatly affect current until at least 1 ppm chloride is added. The effect of chloride approaches saturation at concentrations greater than 3 ppm.

The corresponding time-dependence of $F/w$ is shown in Fig. 5.3(b). In the absence of additives, $F/w$ increases in the tensile direction during deposition. With the addition of chloride the $F/w$ curve does not change significantly until 1 ppm chloride is added. Tensile stress then reduces with increasing concentration of chloride; saturating at > 10 ppm concentration.

The corresponding measurements of differential stress (as described Section 1.2.3) are shown in Fig. 5.4. In the absence of chloride, tensile stress increases rapidly reaching a peak at 40-50 nm, beyond which it decays reaching a plateau at approximately 200 nm.

A minimum of 1 ppm chloride was required to reduce stress in films thicker than 80 nm. While in thinner films a concentration of 10 ppm of chloride reduced stress by half, a concentration of 1 ppm reduced stress by a lesser but still significant amount. Chloride is known to reduce nucleation and increase surface diffusion. Since a rougher surface is produced, i.e. less grain boundary formed, the grain-boundary-induced tensile stress is expected to be reduced.
Fig. 5.4  Thickness dependence of $\sigma$ in copper nanofilms electrodeposited at $-200$ mV potential ($\text{Cu/Cu}^{2+}$) in the presence of various concentrations of chloride.
To determine the dependence of stress on chloride concentration in the plateau region the average stress over the 200-300 nm thickness range was determined for each concentration of chloride and these are plotted versus the log of concentration in Fig. 5.5. The horizontal dashed line represents the film stress (49 MPa) in the absence of chloride. Tensile stress reduces approximately linearly with the log of concentration between 0.3 and 10 ppm, and approaches saturation thereafter. We chose a 3 ppm concentration within the linear region, as we wished to observe the effect of chloride on stress before saturation. This concentration of 3 ppm was used hereafter for all experiments involving chloride.
5.2.2 Results at -125 mV

In Chapter 4, we presented in-situ measurements of stress and surface morphology on electrodeposited copper nanofilms in the absence of additives. We repeated these measurements at different overpotentials in the presence of 3 ppm chloride. In this section, we present the results at -125 mV.

The time dependence of current and $F/w$ are shown in Fig. 5.6(a). The current increases initially for ~ 60 s to reach a constant value of ~ 2.5 mA cm$^{-2}$ and then decays slightly after ~ 160 s. The onset of increase in the $F/w$ curve occurs at ~ 80 s. The corresponding thickness dependence of $F/w$ and $\sigma$ are shown in Fig. 5.6(b). Small fluctuations appear quite large on the scale of this graph. The general trend in the stress curve, however, is approximately zero stress until 125 nm at which point stress increases in the tensile direction and appears to saturate at a value of approximately 3 MPa beyond 250 nm.

The results in Fig. 5.6 are re-plotted in Fig. 5.7 along with the corresponding results (from Fig. 4.3 and Fig. 4.4) at -125 mV in the absence of additives. It can be seen from Fig. 5.7(b) that the stress is dramatically reduced from a plateau value of ~ 28 MPa in additive-free electrolyte to a value of ~ 3 MPa in the presence of chloride (i.e. almost an order of magnitude reduction). Comparing the currents [Fig. 5.7(a)], it is clear that, although chloride inhibits the current significantly in the early stages of deposition, it has rather little effect on the current after ~ 40 s. This strongly suggests that the presence of chloride ion affects stress directly. If the chloride ion had caused a large reduction in current, it might have been suspected that the reduced stress simply reflected the reduced current. However, over most of the range of time examined, the current is slightly higher in the presence of chloride. Thus, it appears that chloride directly causes a large reduction in tensile stress.
Fig. 5.6 (a) Plot of (i) current and (ii) $F/w$ against time during electrodeposition after a potential step to -125 mV in the presence of chloride. (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
Fig. 5.7 (a) Plot of current (solid line) and $F/w$ (dashed line) against time during electrodeposition after a potential step to -125 mV in (i) the absence (black line) and (ii) the presence of chloride (red line). (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
To examine the effect of chloride on the surface morphology, we carried out AFM measurements \textit{in situ} during deposition. Fig. 5.8 shows the current-time plot obtained in a typical AFM experiment. The current in the corresponding stress experiment (from Fig. 5.7) is also shown as are the thicknesses derived from these curves. The current measured in the AFM cell is somewhat lower than in the stress cell for reasons discussed in Section 3.2.2.

![Current-time curves at -125 mV in the presence of 3 ppm chloride measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions marked AFM(a) to AFM(d) correspond to the time intervals during which each AFM image was captured.](image)

**Fig. 5.8** Current-time curves at -125 mV in the presence of 3 ppm chloride measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions marked AFM(a) to AFM(d) correspond to the time intervals during which each AFM image was captured.

A time series of AFM images taken during electrodeposition at -125 mV in the presence of 3 ppm chloride is shown in Fig. 5.9. Small copper islands appear during the first few seconds of deposition. The distribution in size of the islands is very narrow during the first 29 nm of deposition. Between thicknesses of 29 and 82 nm, some islands coalesce and their size distribution becomes larger. The majority of islands remain isolated however. We can see that with further deposition the change in surface morphology is not as dramatic as that observed at the earlier stages.
Fig. 5.9 Sequence of AFM images obtained in situ during electrodeposition in the presence of 3 ppm chloride after a potential step to -125 mV at 0 s on the time axis shown. Images (a), (b), (c) and (d) correspond to AFM(a), AFM(b), AFM(c) and AFM(d) in Fig. 5.8. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
By comparing the series of AFM images for chloride (Fig. 5.9) and for no additives (Fig. 4.8) we can comment on the differences between their surface morphologies. In both cases, the most dramatic change in the surface morphology occurs during the earlier stages of deposition (see Fig. A.1). The island density is higher and their heights of the individual features are somewhat smaller. In the absence of chloride, it appears that some islands remain small and isolated while others have coalesced forming larger features, leading to a wider size distribution. In the absence of chloride, islands eventually coalesce forming large features. Coalescence is not as widespread in the presence of chloride but the islands are much shorter in height. Comparing these observations with stress measurements at similar thicknesses [see Fig. 5.7(b)], it becomes more apparent that the increase in tensile stress coincides with island coalescence. It is possible that chloride has reduced the amount island coalescence, thus reducing stress in the deposit.

AFM images during the later stages of deposition 150-319 s are also for chloride (Fig. 5.9) and no additives (Fig. 4.8). In the presence of chloride, it appears that the number of islands is greater and the coalescence of large-sized clusters is reduced. It is clear that surface morphology, in the absence of additives, evolves quite dramatically up to approximately 200 nm. Within a similar thickness range in the presence of chloride, the surface changes very slowly and very few islands coalesce. Since less grain boundary has formed, tensile stress is expected to be lower.

The effect of chloride on the surface morphology of electrodeposited copper has been documented in the literature. Although no work has been published on the effect of chloride on stress in electrodeposited copper nanofilms using the cantilever beam method, many authors have examined the interaction of islands during growth. The general understanding in the literature is that tensile stress increases during the grain boundary formation.\textsuperscript{30, 31} Since it has been reported that chloride reduces island density and increases the average size of features in electrodeposited copper films,\textsuperscript{32} we would expect a reduction in tensile stress. Although our observations at -125 mV do not agree with the literature, we do see features of similar size in both the presence and absence of chloride.
Fig. 5.10  (a) Plot of current (solid line) and $F/w$ (dashed line) against time during electrodeposition after a potential step to -160 mV in (i) the absence (black line) and (ii) the presence of chloride (red line). (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
5.2.3 Results at -160 mV

In Section 5.2.2, we presented in-situ measurements of stress and surface morphology on electrodeposited copper nanofilms at an overpotential of -125 mV in the presence of 3 ppm chloride. We repeated these measurements at an overpotential of -160 mV and present the results in this section.

The time dependence of current and $F/w$ in the presence and absence of chloride are shown in Fig. 5.10(a). The current follows a similar trend to that observed at -125 mV (see Fig. 5.7), but at a higher magnitude. Even though the currents are in reasonable agreement we observe a significant reduction of tensile stress in the $F/w$ curve. The corresponding thickness dependence of $F/w$ and $\sigma$ are shown in Fig. 5.10(b). Tensile stress increases more rapidly than that observed at -125 mV. Chloride reduces tensile stress in the plateau region from ~ 38 MPa to ~ 8 MPa. This reduction is not as dramatic as that previously observed at -125 mV. This suggests that the chloride caused a greater reduction in stress at a lower overpotential.

If we consider that the film deposited in the presence of chloride is rougher, it will have a larger surface area than that without the presence of additives. The current density, therefore, would be lower and the amount of copper deposited per unit area would be less. Hence, we would expect that copper material deposited on a rough surface to have lower stress.
Fig. 5.11 Current-time curves in the presence of 3 ppm chloride at -160 mV measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (d) correspond to the times during which each AFM image was captured.

To examine the effect of chloride on the surface morphology, we again carried out AFM measurements in situ during deposition. Fig. 5.11 shows the current-time plot obtained in the AFM and stress cells. The current in the corresponding stress experiment (from Fig. 5.10) is also shown as are the thicknesses derived from these curves.

A time series of AFM images taken during electrodeposition at -160 mV in the presence of 3 ppm chloride is shown in Fig. 5.12. We can see that nucleated copper islands during the early stages of deposition grow in size and coalesce more rapidly than that observed at -125 mV (Fig. 5.9). It is possible that this increased rate of island coalescence (and boundary formation) has caused a higher tensile stress at this potential.
Fig. 5.12 Sequence of AFM images obtained *in situ* during electrodeposition in the presence of 3 ppm chloride after a potential step to -160 mV at 0 s on the time axis shown. Images (a), (b), (c) and (d) correspond to AFM(a), AFM(b), AFM(c) and AFM(d) in Fig. 5.11. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
Fig. 5.13 Sequence of AFM images obtained in situ during (150-319 s) electrodeposition in (a)-(b) the presence of 3 ppm chloride and (c)-(d) the absence of additives after a potential step to -160 mV at 0 s on the time axis shown. Images (a) and (b) are taken from Fig. 5.11, and (c) and (d) from Fig. 4.12. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
In Fig. 5.13, we directly compare the AFM images taken in the presence and absence of chloride during the later stages (150-319 s) of deposition. The difference in the surface morphology between deposits in the presence and absence of chloride is dramatic. In the absence of additives, the surface is very flat. In the presence of chloride, however, the surface is significantly rougher with many copper islands and exposed regions of what appears to be the substrate (alternatively it could be a thin film of deposited copper). The effect of chloride at roughening the deposit appears more dramatic at this potential than that observed previously at -125 mV [with chloride (Fig. 5.9) and without additives (Fig. 4.8)].

It is clear from the line scans shown in Fig. 5.14 that the surface of electrodeposited copper is flat in the absence of additives. In the presence of chloride, the surface of the deposit is much rougher.

**Fig. 5.14** AFM line scans taken at L4 in the absence (Fig. 4.13) and presence (Fig. 5.12) of 3 ppm chloride.
Fig. 5.15  (a) Plot of current (solid line) and $F/w$ (dashed line) against time during electrodeposition after a potential step to -125 mV in (i) the absence (black line) and (ii) the presence of chloride (red line). (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
5.2.4 Results at -200 mV

Having examined *in-situ* explorations of stress and surface morphology on electrodeposited copper nanofilms at -125 mV and -160 mV in the presence of 3 ppm chloride, we repeated these measurements at an overpotential of -200 mV.

The time dependence of current and $F/w$ in the presence and absence of chloride are shown in Fig. 5.15(a). The current follows a similar trend to that observed at -125 mV (see Fig. 5.7) and -160 mV (Fig. 5.10) but at a higher magnitude. The tensile stress in the $F/w$ curve reduces dramatically in the presence of chloride. Since the currents are in reasonable agreement, it suggests that the reduction in tensile stress is not due to the current but chloride itself. The corresponding thickness dependence of $F/w$ and $\sigma$ are shown in Fig. 5.15(b).

The corresponding thickness dependence of $F/w$ and $\sigma$ are shown in Fig. 5.15(b). Tensile stress increases more rapidly than that previously observed at lower potentials. Chloride reduces tensile stress in the plateau region from ~ 45 MPa to ~ 20 MPa. These measurements once again show that chloride is not as effective at reducing stress at a higher overpotential.

To examine the effect of chloride on the surface morphology, we again carried out AFM measurements *in situ* during deposition. Fig. 5.16 shows the current-time plot obtained in the AFM and stress cells. The current in the corresponding stress experiment (from Fig. 5.15) is also shown as are the thicknesses derived from these curves. The current shows better agreement at this potential than at the lower overpotentials shown previously.
Fig. 5.16 Current-time curves in the presence of 3 ppm chloride at -160 mV measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (d) correspond to the times during which each AFM image was captured.

A time series of AFM images taken during electrodeposition at -200 mV in the presence of 3 ppm chloride is shown in Fig. 5.17. We can see that nucleated copper islands during the early stages of deposition grow in size and coalesce more rapidly than that observed at -125 mV (Fig. 5.9) and -160 mV (Fig. 5.12). This observation supports the possibility that the rate of island coalescence (and boundary formation) is related to the increase in tensile stress.
Fig. 5.17 Sequence of AFM images obtained *in situ* during electrodeposition in the presence of 3 ppm chloride after a potential step to -200 mV at 0 s on the time axis shown. Images (a), (b), (c) and (d) correspond to AFM(a), AFM(b), AFM(c) and AFM(d) in Fig. 5.16. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
Fig. 5.18 Sequence of AFM images obtained \emph{in situ} during (150-319 s) electrodeposition in (a)-(b) the presence of 3 ppm chloride and (c)-(d) the absence of additives after a potential step to -200 mV at 0 s on the time axis shown. Images (a) and (b) are taken from Fig. 5.16, and (c) and (d) from FIG. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
In Fig. 5.18, we directly compare the AFM images taken in the presence and absence of chloride during the later stages (150-319 s) of deposition. The difference in the surface morphology between deposits in the presence and absence of chloride is obvious, but not as dramatic as that observed at -160 mV (Fig. 5.13). Chloride dramatically increases surface the roughness of a deposit as many copper islands are large in size before impinging.

![AFM line scans taken at L1, L2, L3 and L4 in the absence (Fig. 4.17) and presence (Fig. 5.17) of 3 ppm chloride during electrodeposition at an overpotential of -200 mV.](image)

**Fig. 5.19** AFM line scans taken at L1, L2, L3 and L4 in the absence (Fig. 4.17) and presence (Fig. 5.17) of 3 ppm chloride during electrodeposition at an overpotential of -200 mV.

It is clear from the line scans shown in Fig. 5.19 that at -200 mV the surface of electrodeposited copper is much flatter in the absence of additives. In the presence of chloride, individual features grow in size and less coalescence occurs. This result is consistent with that observed at -160 mV.
5.2.5 Comparison of Results at -125 mV, -160 mV and -200 mV

In this chapter, we have shown *in-situ* stress and AFM measurements during continuous deposition each at three different constant potentials in the absence and presence of chloride. We compare these results in this section.

Previously in Chapter 4, we showed that plateau stress is a very reproducible measure of the stress in the deposit (as indicated in interrupt experiments by the recovery of stress to the plateau value). The peak in tensile stress, however, is not completely understood as it may be indicative of film growth processes, stresses at the interface, or both. Thus, we rely on the plateau stress region as measure to examine the effects of chloride on film stress.

Fig. 5.20(a) shows the thickness dependence of stress during continuous electrodeposition at each potential in the absence (solid lines) and presence (dashed lines) of chloride. The average value of the differential stress in the plateau regions (between 200 and 300 nm) in each curve was determined and plotted versus overpotential in Fig. 5.20(b). In the absence of additives, stress increases with overpotential. Tensile stress is reduced at all overpotentials in the presence of chloride. By comparing the relative magnitude of reduction at each potential, it is clear that chloride is more effective at reducing stress at lower potentials.

The surface roughness of each deposit was determined for each potential, with and without the presence of chloride and these are plotted against thickness in 5.2.1(a). We can see that surface roughness decreases with increasing potential. By taking the RMS roughness within the plateau region [i.e. at 150 nm in Fig. 5.20(a)], and plotting stress against it, we find that stress decreases as surface roughness increases both in the presence and absences of chloride.
Fig. 5.20 (a) Thickness dependence $\sigma$ during continuous electrodeposition at overpotentials of -125 mV, -160 mV and -200 mV both in the presence (dashed line) and absence (solid line) of chloride. (b) Corresponding $\sigma$-values at plateau (225 to 275 nm) regions.
Fig. 5.21 (a) Thickness dependence of RMS roughness at overpotentials of -125 mV, -160 mV and -200 mV in the presence and absence of chloride. (b) Corresponding RMS roughness dependence of stress in the plateau region, taken at 150 nm in (a) for no additives (solid line) and chloride (dashed line).
In Chapter 4, we showed that the differential stress in the plateau region is representative of local stress in the film. Interruption experiments demonstrated that film stress does not change significantly post-deposition and interfacial forces remain relatively constant during deposition. In the next section we report interruption experiments in the presence of chloride additive to assess the validity of our continuous measurements.

5.3 Current Interruption with Chloride Additive

To examine the behaviour of stress and morphology in the presence of chloride during open circuit and resumed deposition, we carried out interruption experiments at the same three overpotentials (-125 mV, -160 mV and -200 mV) and present the results in this section.

5.3.1 Results at -125 mV

The time dependence of current and $F/w$ during interrupted deposition is shown in Fig. 5.22(a). The current increases initially for ~ 60 s to reach a constant value of ~ 2.5 mA cm$^{-2}$. The $F/w$ curve increased in the tensile direction during deposition. During interruption, $F/w$ continues momentarily to increase by a small magnitude in the tensile direction for ~ 20 s at which point it transitions in the compressive direction. Upon resuming deposition, a similar tensile rise in $F/w$ is observed until it eventually continues horizontally with time, suggesting that no net stress is being generated in the deposit. Upon interrupting deposition for the second time (at 600 s), $F/w$ dramatically increases in the tensile direction before eventually saturating after ~ 100 s and continuing horizontal thereafter. We can see that stress is negligible during pre-interrupted and post-interrupted deposition. One explanation for the sudden increase in $F/w$ is the out-diffusion of vacancies from the deposit.\textsuperscript{33} It is possible this change was not observed in the absence of additives since it may have been overwhelmed by the magnitude of stress in the film during deposition. Since chloride reduces stress significantly at low overpotentials (as shown in Section 5.2) $F/w$ during deposition is negligible, however, these subtle changes in $F/w$ at open circuit can be more easily observed. Although the out-diffusion of vacancies is a possible explanation for tensile stress generation at open circuit, the time scale over which it
is known to occur is generally much longer than changes observed in the $F/w$ curve. The corresponding thickness dependence of $\sigma$ and $F/w$ is shown in Fig. 5.22(b).

**Fig. 5.22** (a) Plot of current (solid line) and current (dashed line) against time during electrodeposition after a potential step to -160 mV for interrupted deposition.(b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 

145
Fig. 5.23  (a) Plots of current (solid line) and $F/w$ (dashed line) against time during electrodeposition after a potential step to -125 mV for interrupted deposition in (i) the absence (black line) and (ii) the presence of chloride (red line). (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
The results in Fig. 5.22 are re-plotted in Fig. 5.23 along with the corresponding results (Fig. 4.18) at -125 mV in the absence of additives. In Fig. 5.23(a), the behaviours of \( F/w \) are similar during the first interruption, but are the opposite during the second interruption. The \( F/w \) curve moves in the compressive direction without additives and momentarily in the tensile direction in the presence of chloride. It can be seen from Fig. 5.23(b) that the stress is dramatically reduced. Both in the presence and absence of chloride, stress does not vary significantly after resuming deposition.

Earlier in Chapter 4, we showed that the magnitude of relaxation during open circuit in the absence of additives was small. This small relaxation coincided with a subtle smoothing of the surface. Recovery of stress during resumed deposition also coincided with a subtle reversible surface roughening. AFM observations were carried out during interrupted deposition in the presence of chloride. No obvious change in the surface morphology was observed during open circuit or resumed deposition.

5.3.2 Results at -160 mV

Having observed stress and morphology during interrupted deposition at -125 mV in the presence and absence of chloride, we repeated these measurements at -160 mV and present the results in this section.

The time dependence of current and \( F/w \) during interrupted deposition in the presence and absence of chloride are shown in Fig. 5.24(a). The current follows a similar trend to that observed at -125 mV (see Fig. 5.23), but at a higher magnitude. The \( F/w \) curves in the presence and absence of chloride have somewhat opposite behaviours during open circuit. Without additives, the \( F/w \) curve moves in the compressive direction. In the presence of chloride, \( F/w \) initially moves in the tensile direction followed by a transition in the compressive direction during the first interruption. During the second interruption, however, \( F/w \) continues horizontally beyond the initial tensile rise.

The corresponding thickness dependence of \( F/w \) and \( \sigma \) are shown in Fig. 5.24(b). In the absence of additives, tensile stress is initially high during resumption of deposition. Chloride has significantly reduced the magnitude of tensile stress upon
Fig. 5.24  (a) Plots of current (solid line) and $F/w$ (dashed line) against time during electrodeposition after a potential step to -160 mV for interrupted deposition in (i) the absence (black line) and (ii) the presence of chloride (red line). (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
resuming deposition. As a result, tensile stress recovers much more quickly in the presence of chloride and this is consistent with our observation at -125 mV (see Fig. 5.23).

AFM observations carried out during interrupted deposition in the presence of chloride showed no clear change in the surface morphology either during open circuit or resumed deposition.

5.3.3 Results at -200 mV

Having observed stress and morphology during interrupted deposition at -125 mV and -160 mV in the presence and absence of chloride, we repeated these measurements at -200 mV and present the results in this section.

The time dependence of current and $F/w$ during interrupted deposition in the presence and absence of chloride are shown in Fig. 5.25(a). The tensile rise during open circuit, which was observed at lower potentials, is not as obvious at this potential. In fact, the $F/w$ curves appear to show a change in the compressive direction but at a lower magnitude than that at the lower potentials. By comparing the open circuit behaviour in the presence and absence of chloride with those corresponding to -160 mV (Fig. 5.24) and -125 mV (Fig. 5.23), we see that the magnitude of tensile rise decreases with increasing potential. In Chapter 4, we showed that the magnitude of the compressive change in $F/w$ during open circuit increased with potential. Thus, it appears that two stress generating mechanisms are competing. At a low deposition potential, one stress mechanism causes a tensile rise in the $F/w$ curve during open circuit which dominates the opposing mechanism. On the other hand, this tensile rise becomes overwhelmed by the opposing mechanism at high deposition potentials.

The corresponding thickness dependence of $F/w$ and $\sigma$ are shown in Fig. 5.25(b). Chloride significantly reduces the magnitude of tensile stress upon resuming
Fig. 5.25  (a) Plots of current (solid line) and $F/w$ (dashed line) against time during electrodeposition after a potential step to -200 mV for interrupted deposition in (i) the absence (black line) and (ii) the presence of chloride (red line). (b) Corresponding plots of (i) $F/w$ and (ii) differential stress against coulometric thickness $h_c$. 
deposition and this was also observed at previously at -160 mV (Fig. 5.24). At all potentials we have observed a rapid recovery in tensile stress in the presence of chloride.

No significant change in the surface morphology was observed in the presence of chloride either during open circuit or resumed deposition at any of the three potentials.

5.3.4 Comparison of Results at -125 mV, -160 mV and -200 mV

One or the main purposes of Section 5.3 was to assess the validity of the continuous deposition experiments in Section 5.2. In this section, we compare continuous and interrupted depositions both in the absence and presence of chloride additive.

Fig. 5.26 shows a comparison summary of the stress measurements during continuous and interrupted depositions both in the presence and absence of chloride. It is clear that at all three potentials, stress recovers to the same value as its uninterrupted counterpart and this is observed both in the absence and presence of chloride. The recovery of stress in all cases demonstrates the validity of the stress measurements within the plateau region. It is clear that chloride not only reduces tensile stress during deposition, but it also reduces the peak in tensile stress upon resumption of deposition.
Fig. 5.26 Thickness dependence of $\sigma$ during continuous (red lines) and interrupted deposition (black lines) at overpotentials (a) -200 mV, (b) -160 mV and (c) -125 mV in the presence (dashed line) and absence (solid line) of chloride additive.
5.4 Effects of Chloride and PEG in Combination

Having established a reliable method for measurement of stress to determine the effect of additives on stress, we repeated the same measurements in the presence of chloride and PEG at a single potential (i.e. -200 mV) and present the results in this section.

In section 5.4.1, we present preliminary experiments aimed at first understanding the effect of PEG alone on current and stress. Following this, we identify a suitable concentration of PEG to incorporate with chloride for the subsequent constant-potential experiment at -200 mV. We continued to use chloride at 3 ppm concentration as this was used in our previous study of chloride alone (Section 5.2).

It has been well documented that PEG in combination with chloride interact and inhibit current more than chloride alone. This inhibition may affect the stress in the deposit. However, to our knowledge no studies have compared \textit{in-situ} stress and AFM measurements in the presence of both chloride and PEG. Before investigating the effect of PEG and chloride in combination on film stress and morphology, we examined the effect of PEG alone on current and stress.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.27.png}
\caption{LSVs for the deposition of copper on gold in 0.05 \text{ mol dm}^{-3} \text{ CuSO}_4 in 0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 with various concentrations of PEG.}
\end{figure}
Fig. 5.28 (a) Time dependence of current density during electrodeposition at an overpotential of -200 mV in the presence of various concentrations of PEG (i.e. 0.1, 1, 2, 5 and 50 ppm). (b) Corresponding F/w curves.
5.4.1 PEG

To characterize the effect of PEG on current, we performed potentiodynamic electrodeposition of copper on gold in the presence of PEG. Fig. 5.27(a) shows LSVs for the electrodeposition of copper on gold in 0.05 mol dm\(^{-3}\) CuSO\(_4\) in 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\) with various concentrations of PEG with an average molecular weight of 3400 g mol\(^{-1}\). The potential was scanned from +200 mV to -400 mV (Cu/Cu\(^{2+}\)) at 0.5 mV s\(^{-1}\). PEG has a small inhibiting effect particularly in the potential region -75 to -160 mV. However, the magnitude of this inhibition is significantly smaller than that observed when chloride alone is present (see Fig. 5.1).

Copper was electrodeposited in the presence of PEG at a constant potential of -200 mV. The current and \(F/w\) measurements are shown in Fig. 5.28. The corresponding stress curves in Fig. 5.29 show PEG has no significant effect on stress.

![Fig. 5.29](image-url) Thickness dependence of \(\sigma\) during continuous electrodeposition in the presence of various concentrations of PEG (i.e. 0.1, 1, 2, 5 and 50 ppm).
5.4.2 Dependence on Concentration of Chloride Ion and PEG

Having showed that PEG alone has no significant effect on current and stress, we examined the concentration dependence of PEG in the presence of 3 ppm chloride. To characterize the interaction effect of PEG and chloride on current, we performed potentiodynamic electrodeposition of copper on gold using linear sweep voltammetry (LSV). Fig. 5.30 shows LSVs for the electrodeposition of copper on gold in 0.05 mol dm$^{-3}$ CuSO$_4$ in 0.1 mol dm$^{-3}$ H$_2$SO$_4$ in the presence of 3 ppm chloride with various concentrations of PEG. The potential was scanned from +200 mV to -400 mV (Cu/Cu$^{2+}$) at 0.5 mV s$^{-1}$. The working electrode that was used in the preliminary study of chloride concentration was again used in this experiment. During the chloride study, copper was deposited and removed repeatedly and this process may have deteriorated of the substrate (i.e. aging and dissolution of copper into the gold). The surface of the substrate during the chloride-PEG study would not be comparable to that during the chloride study. Therefore, we have not made any comparisons between the two studies. A potentiodynamic sweep was performed in the absence of additives. Chloride (3 ppm) was added and the potential sweep was repeated. After each deposition, the copper deposit was removed by applying an overpotential of +200 mV. PEG was added in a sequence of 1 ppm, 2 ppm, 5 ppm and 300 ppm and each of their characteristic potential sweeps were measured.

In the absence of additives, the current shows a slight kink at about 150 mV. It is possible this is related to the surface condition of the substrate, as already mentioned. With the addition of 3 ppm chloride, current decreases. The addition of 1 ppm PEG has a little effect on current. The current decreases dramatically with 2 ppm PEG and decreases a little further with 5 ppm PEG. Current does not change significantly with the addition of 300 ppm PEG. It appears that the interactive effect of chloride (3 ppm) and PEG occurs at low concentrations on the order of a few ppm. Since PEG began to have an effect at 2 ppm, we chose a slightly higher value of 5 ppm for potentiostatic electrodepositions in which the interactive effect of chloride and PEG on surface morphology and stress could be observed.
In Fig. 5.31, the current and $F/w$ curves for constant potential (-200 mV) show that current is inhibited more when PEG is present. The thickness dependence of $\sigma$ in the presence of various concentrations of chloride with 5 ppm PEG is shown in Fig. 5.32. We can see that no significant change in stress occurs until 1 ppm chloride is added and this is similar to that observed previously in the presence of chloride alone (see Fig. 5.3). Comparing the current and $F/w$ curves for depositions with 3 ppm chloride alone and in combination with 5 ppm PEG, we see that PEG and chloride do have an interactive effect. Stress is reduced in the film at thickness > 80 nm. The relatively small reduction in stress (see Fig. 5.32) with the presence of PEG suggests that chloride plays the most important role in reducing film stress and the effect of PEG not as great. Examining the concentration dependence of chloride on current in the presence of PEG, we can see that chloride has a similar concentration effect in that current becomes significantly inhibited at concentrations > 1 ppm.
Fig. 5.31  Time dependence of (a) current and (b) $F/w$ during deposition at -200 mV in the presence of no additives, 3 ppm chloride alone and chloride with PEG (0.01, 0.1, 0.3, 1, 3, 10 ppm).
Fig. 5.32 Thickness dependence of $\sigma$ at -200 mV in the presence of no additives, 3 ppm chloride alone and with various concentrations of PEG (0.01, 0.1, 0.3, 1, 3, and 10 ppm).

Fig. 5.33 Concentration dependence of chloride in the presence of 5 ppm PEG, corresponding to Fig. 5.32.
Fig. 5.34 Time dependence of (a) current and (b) $F/w$ at potential of -200 mV in the presence of no additives, 3 ppm chloride alone and chloride with 5 ppm PEG.
5.4.3 Stress Results at -200 mV

In this section, we examine the effect of chloride and PEG on stress and surface morphology. Fig. 5.34(a) shows the current-time curves (taken from potentiostatic experiments in Section 5.4.2) at -200 mV for electrodeposited copper on gold in no additives, 3 ppm chloride alone and with 5 ppm PEG. In the absence of additives, current increased to a peak and decayed to a plateau. In the presence of 3 ppm chloride, the current is higher during the first 80 s of deposition, beyond which it becomes strongly inhibited. When PEG is added to the chloride, the current becomes even more inhibited. Although the peak in current is slightly reduced, the current beyond the first 25 s of deposition is reduced by far more. The current continues to decrease until 100 s, at which point it remains relatively constant with further deposition.

Fig. 5.34(b) shows the time-dependence of $F/w$ during deposition. Chloride alone reduces tensile stress. PEG in combination with chloride reduces tensile stress even further. The corresponding stress curves in Fig. 5.35 also show that tensile stress is reduced to zero for a film $> 100$ nm in thickness.

Fig. 5.35 Thickness dependence of $\sigma$ during deposition at -200 mV in the presence of 3 ppm chloride and 5 ppm PEG corresponding to Fig. 5.34.
5.4.4 AFM Results at -200 mV

A full series of AFM images taken during electrodeposition at -200 mV in the presence of 3 ppm chloride and 5 ppm PEG is shown in Fig. 5.36(a)-(c). The growth behaviour of copper features on the surface is remarkably different to that observed with chloride alone (see Fig. 5.17). We see that a four-sided pyramid structure has formed surrounded by a very flat copper layer. We examine both the growth of the pyramid and the flat surrounding layer during deposition. The copper deposit in the regions surrounding the pyramid is much more uniform and flatter in the presence of chloride with PEG than in the absence of additives or presence of chloride alone.

A four-sided pyramid indicates that the substrate surface comprises a (100) plane, whereas a three-sided pyramid indicates that the substrate comprises a (111) plane. An example of a fairly symmetric four-sided pyramid structure is shown in Fig. 5.36(a). The area surrounding the pyramids comprises flat coalesced features typical of what is seen in Fig. 4.16 at -200 mV with no additives. A smaller neighbouring structure of similar shape appears in (b), and the large pyramid develops four very smooth facets with their edges showing a terraced structure. A high-magnification view of the top of the pyramid is show in Fig. 5.36(d). We can see that the top of the pyramid does not have a single-pointed shape, but appears to have a small recess and numerous surrounding terraces on the surface, as indicated by the arrows.

Fig. 5.37 shows an overlay of horizontal-direction line scans over the centre of the pyramid obtained from each set of AFM scans in Fig. 5.36. The pyramid grows quite rapidly during the early stages but grows more slowly as it increases its surface area. It is possible that stress was relieved through the formation of pyramid structures and this stress-relieving mechanism has been reported in the literature for Ge/Si systems. In this case the Ge film, a microscopically rough surface of small triangular is formed and defect-free pyramids develop in a pseudomorphic growth regime up to 8 monolayers. As soon as the pyramids are completed and start to coalesce, strain relieving defects are created at their base and eventually arrange to the dislocation network. After the overgrowth of the dislocations the surface smoothes again showing a much larger terrace length. The periodic dislocation network at the interface gives rise to an elastic deformation of the surface.
Fig. 5.36  *In-situ* AFM images of pyramid island growth at different stages [shown in (a) to (c)] during electrodeposition of copper at potential -200 mV in the presence of 3 ppm chloride with 5 ppm PEG. (d) Close view of the top of the copper pyramid after deposition.

An alternative explanation for the formation of isolated pyramidal and dome-like features is based on the effect of the adsorbed PEG-Cu-chloride complex on current. This complex layer is known to block current paths and inhibit deposition. The PEG adlayer typically has defects and in certain regions the adlayer does not cover the substrate. As a result large current local densities will be present resulting in growth of isolated features.
Previously in Section 5.2, we showed that chloride alone produces a rough deposit. PEG in combination with chloride has a desirable effect in that it levels the film and reduces tensile stress even further than chloride alone. To further understand the growth of the copper pyramid, we carried out corrosion experiments.

5.4.5 In-Situ AFM Measurements during Corrosion of Copper Pyramidal Features

The factors which control the sizes and shapes of self-assembled copper islands are not completely understood. The positions at which islands nucleate are difficult to predict due to the spontaneous nature of island formation. It is known that lattice mismatch between the deposit and the substrate plays an important role in the formation of islands.\textsuperscript{34} The copper pyramid presented in Section 5.4.3 (deposited in 3 ppm chloride and 5 ppm PEG) was corroded to further understand the growth processes that were involved.

Fig. 5.36 shows a low magnification image of the copper deposit containing scattered large pyramidal structures. We can see that not all features are pyramidal, but most are multi-faceted. The area highlighted in the image is the area that was examined during deposition in Fig. 5.36.

The time sequence of the pyramid during corrosion is shown in Fig. 5.39. As the deposit is corroding in (b), the facets in the small pyramid have revealed prominent
terraces whereas in the large pyramid terracing is not as dramatic. One explanation for this difference is that for the same amount of copper removed, facet layer removal in the smaller pyramid. Corrosion appears to be occurring along the plane of each facet. In the surrounding area, corrosion is roughening the surface. We can see in (c) further progression of facet removal and roughening of the surrounding region. Comparing the large pyramid in (d) with that before corrosion was initiated in (a), we can see strong evidence of preferential etching in that copper has mostly been removed from the top and bottom planes. In the surrounding region, the copper has been corroded significantly exposing large areas of the substrate. We can see that the remaining copper is in the form of individual islands of different sizes. With further corrosion, as is seen in (e) and (f), the surrounding region of copper is virtually removed and the pyramid shape disappears (within the time-scale of the scan) revealing smaller faceted features on an almost bare gold substrate.

**Fig. 5.38** AFM images of pyramidal structures formed after electrodeposition of copper at potential -200 mV (Cu/Cu²⁺) on a gold-coated glass cantilever in 0.05 mol dm⁻³ CuSO₄ in 0.1 mol dm⁻³ H₂SO₄ containing 3 ppm chloride in 5 ppm PEG.
Fig. 5.40 shows an overlay of horizontal-direction line scans over the centre of the pyramid obtained from each set of AFM scans in Fig. 5.39. Preferential removal of the facet layer is clearly seen along the direction of A, but not until a later scan at which point the majority of the surrounding copper has been removed. The profile of the pyramid beyond the peak (region C) is exaggerated due to the fast scan rate by the AFM.

**Fig. 5.39** *In-situ* AFM images of copper pyramid island at different stages during *corrosion* at potential +50 mV (Cu/Cu$^{2+}$).
5.5 Summary and Conclusions

Tensile stress in electrodeposited was reduced significantly with the addition of 3 ppm of chloride and this effect is greater at a lower potential. Interruption experiments have demonstrated that tensile stress upon resuming deposition recovers to the uninterrupted value, both in the absence and presence of chloride. Chloride increased the surface roughness of the deposit and appeared to have larger island features on coalescence. It is possible that the increase in feature size has resulted in the observed decreased in tensile stress. In general, a direct correlation was determined between stress and roughness. Stress decreased with increasing surface roughness, both in the absence and presence of chloride. PEG alone has no significant effect on stress. The reduction in tensile stress is enhanced when chloride is in the presence of PEG. Four-sided pyramidal structures surrounded by a flat copper surface are formed during electrodeposition in the presence of 3 ppm chloride and 5 ppm PEG. AFM measurements during deposition and corrosion show that pyramids grow preferentially along certain planes.
5.6 References

6 Development of Ductility Testing of Nanofilms

6.1 Introduction

It has been well established that the mechanical properties of thin film materials can be very different from those of their bulk counterpart. For example, an increase of the yield stress as the grain size decreases is customarily expressed by an inverse power law known as the Hall-Petch\(^1, 2\) relation. The validity of this relation at the nanoscale is a topic of considerable interest and current investigation.\(^3-5\) In addition to theoretical considerations, the importance of nanostructured materials in today’s nanoscale devices has accentuated this interest.

Controlling the mechanical behaviour of materials at the nanoscale is a significant benefit for applications such as the fabrication of micro/nanomechanical parts with complex shapes, and the improvement of performance and reliability of materials in microelectronic devices. Metal films in both microelectronic and MEMS devices experience loads due to operational and environmental conditions and may suffer failures such as cracking, delamination and void/hillock formation under stress.\(^6, 7\) In MEMS devices, where components may be in constant motion or under large loads, the mechanical behaviour of the materials is of great importance. Designing to avoid such failures requires an understanding of the fundamental mechanism of material deformation and fracture on the micro/nanoscale. While good data is available for mechanical properties of bulk metals, these have not been shown to extrapolate to the nanoscale. Thus, the measurement of micro/nanoscale properties is an important and challenging problem.
Many different approaches have been employed in research on the measurement of micro/nanomechanical properties of thin films and these are described in several reviews.\textsuperscript{5, 8} Techniques investigated include tension tests, bend tests (including axisymmetric plate bending, microbeam bending, bulge tests, electrostatic beam bending and wafer curvature tests), dynamic (resonant tests), and the fabrication of passive strain sensors. Each of these techniques has some useful applications but all of the techniques suffer from significant limitations as regards the mechanical properties that can be measured, the type of structures that may be examined, the ease of specimen fabrication and fixturing, the availability of instrumentation, measurement sensitivity, and computational requirements for data reduction.

Considerable efforts have been made to develop nanoindentation techniques to measure mechanical properties at the nanoscale and commercial instruments have been developed. Using these techniques it is possible, in principle, to estimate values of Young’s modulus, residual stress, yield strength and fracture strength.\textsuperscript{9-11} However the application of nanoindentation to thin films is complicated by several factors including substrate effects and pile-up of materials around the indentor and the surface roughness of the specimen.\textsuperscript{8} Thus, although nanoindentation may be used for routine process monitoring where it may suffice to check that the same indentation behaviour is obtained for every batch of devices, it is presently not a viable option for micro/nanomechanical property measurement for applications such as microsystems design.

In order to avoid the difficulties in deconvoluting film properties from substrate effects, it is desirable to use freestanding films. Freestanding films have been investigated by uniaxial tension tests, and by biaxial bulge tests, but these are limited by issues such as specimen gripping and alignment. Moreover, the fabrication of freestanding metal films is quite challenging where, for example, the quality and reliability of freestanding films suffer from manufacturing processes such as etching, temperature and humidity.

Over 30 years ago, Professor Shohei Nakahara invented a simple and ingenious method of measuring the ductility of metal films (see Section 3.5.1). The specimen is held rigidly between two metal plates with circular openings while a metal ball is
slowly pushed upwards until the metal film ruptures. The distance the steel ball travels between contacting the specimen and the specimen’s rupture is read on the micrometer, giving a measure of the ductility. The Nakahara ductility tester was designed as a simple alternative to earlier more elaborate techniques such as hydrostatic bulge testers. Nakahara’s ductility tester was applicable to films with thickness typically in the range 10-100 µm.

We first carried out experiments on thick copper films using Nakahara’s macroscopic ductility tester. The tester was used to obtain data on the ductility (percentage elongation to fracture) of thick electrodeposited copper films and to show the effect of surface microstructure on ductility in thick films. Moreover, it provided a basis for comparison of the measurement methodology between the macroscale and the micro/nanoscale versions of the test.

The main goal of our work was to extend Professor Nakahara’s ductility tester to the nanoscale. This work addresses the development of hardware and methodology suitable for measuring the load-deflection profile of freestanding nanofilms. This work specifically addresses the suitability of a variety of mechanical probes, and the collection and analysis of stress-strain data. By generating stress-strain curves, the method has been able to determine not only ductility but other mechanical properties such as elasticity, plasticity and film stiffness. The development and construction of our nanoscale ductility tester is described through three key stages of its development and its capabilities are demonstrated by testing the behaviour of circular freestanding thin metal films under load. In addition this work addresses the suitability of deposition and handling of specimen nanofilms on suitable support jigs. Ductility measurements on copper nanofilms using the latest version of the ductility tester are shown.

Radio frequency (RF) MEMS switches are low-power low-cost RF components for high-frequency applications. Understanding the mechanical properties of RF-MEMS switches is important for performance and reliability purposes. We use an AFM operating in nanoindentation mode to measure the load characteristics of RF-MEMS
switches and compare the capabilities of the AFM with our ductility measurements system.

6.2 Ductility Testing in Macro-Scale Copper Films

In this Section, we determined the repeatability of Nakahara’s ductility tester (see Section 3.5) and examined the fracture that occurs in thick copper films using this instrument. In addition, we demonstrated the importance of microstructure on ductility in copper films.

The Nakahara ductility tester has advantages such as mechanical stability during deformation and ease of sample preparation. The specimen is held rigidly between two metal plates with circular openings while a metal ball is slowly pushed upwards until the metal film ruptures. The distance the metal ball travels between where it first makes contact with the film and that where the film ruptures is observed. The reproducibility of the Nakahara ductility tester in measuring displacement was determined by testing thick copper films (with 7.8 µm thickness). An SEM image of the copper foil is shown in Fig. 6.1. The surface microstructure shows grains approximately 1 µm in length and 200 nm in width. Grains are elongated primarily along one direction due to the rolling process during fabrication. The ball radius $r$ (see Section 3.5) was measured to be 3.17 mm.
Eleven experimental measurements yielded an average displacement $d$ of approximately $0.419 \pm 0.039$ mm (i.e. $\pm 9.3\%$). The ductility of the 7.8 $\mu$m-thick unannealed copper foil was $0.51\%$, calculated using Equations 3.15 to 3.18.

Fig. 6.2 also shows a typical set of optical images for a specimen before and after testing. The ruptured sample shows three fracture lines which originated from the weakest point, near the centre of the film. The ductility of the film (which is a measure of the % elongation of the film) was determined using the equations described in Section 3.5.1.
Fig. 6.2 Images of the copper foil (from Fig. 6.1) are shown in (a) before and (b) after ductility testing in the Nakahara tester.

To show the importance of microstructure on ductility of electrodeposited copper, we electrodeposited copper at different electrolyte stirring rates. Both mechanical properties\textsuperscript{12} and morphology\textsuperscript{13} of electrodeposited metals as a function of stirring conditions have been described in the literature. Increases in microhardness with stirring speed have been attributed to grain refinement.\textsuperscript{12} Others also describe the influence of the stirring speed on the thickness of the diffusion layer, where at high stirring rates deposition becomes kinetically controlled.\textsuperscript{13, 14} Each film was electrodeposited galvanostatically on the copper foil substrate with the same coulometric thickness of 23.4 µm. Fig. 6.3 shows a plot of % elongation of the deposits at rupture versus electrolyte stirring speed in (a) and corresponding SEM images of the deposits in (b). The stirring rate of the electrolyte was controlled using a magnetic stirrer. Each film was electrodeposited at a different electrolyte stirring rate.
Fig. 6.3  (a) Percentage elongation (or ductility) for 23.4-µm-thick copper galvanostatically electrodeposited at a current density of 30 mA cm$^{-2}$ at stirring rates of (i) 118, (ii) 157, (iii) 196 and (iv) 237 cm s$^{-1}$. The corresponding SEM images of the surface of each deposit are shown from (b) to (e).
The speed of the electrolyte at the liquid-solid interface of the working electrode was determined by the distance of the working electrode from the centre of the cell and the stirring rate of the electrolyte and by the RPM speed of the stirrer. We can see that highly ductile electrodeposits are produced at stirring speeds faster than 120 cm s\(^{-1}\), as expected. At low stirring speeds (120 cm s\(^{-1}\) and below), surfaces exhibit a rough powdery surface. At higher stirring speeds, deposits are smooth with finer grains. Our results show that the ductility of electrodeposited copper has a strong dependence on the microstructure of the deposit. Highly ductile films had small grains in the deposits, whereas brittle films had large powdery surface features.

In summary, we have shown that the error in measurement of %elongation in a 7.8 \(\mu\)m-thick copper foil using the Nakahara ductility tester was within 10%.\(^{15}\) In addition, we have demonstrated a typical ductility test in which a copper foil was deformed bi-axially, and fractured along three directions from a single point. The ductility in electrodeposited copper films (23.4 \(\mu\)m in thickness) has a strong dependence on the grain size in the deposit. These investigations show that Nakahara’s ductility tester is robust and capable of measuring ductility in micro-scale films. In Section 6.3, we describe our attempts to design and construct an instrument for testing ductility in freestanding metal films at the nanoscale.

6.3 Development of a Nanoscale Ductility Tester

We have extended the Nakahara ductility tester to the nanoscale in three stages: \textit{MK1}, \textit{MK2}, and \textit{MK3}. The goal of our work was to develop a ductility tester that can test freestanding films 100 times thinner than those in Nakahara’s tester. This work involved reducing the scale of the test probe and improving measurement capabilities (i.e. resolution, and sensitivity).

6.3.1 First Prototype: \textit{MK1}

Since the Nakahara tester does not have any force feedback mechanism in place, the identification of fracture is quite subjective and as a result measurement of the true elongation of a specimen is not very reliable. The simple addition of a high-magnification lens allowed closer examination of fracture events during testing. A lens system with adjustable magnification was mounted on top of the tester, as
shown in Fig. 6.4, above which a video camera was positioned and interfaced to a personal computer, thus allowing real-time observation of the film during loading.

![Fig. 6.4 Schematic of Nakahara ductility tester with adapted real-time video imaging.](image)

The approach to extending Nakahara’s ductility tester to the nanoscale was performed by examining the scalability of Nakahara’s tester. This work involved redesign, miniaturization and implementation of the ball-specimen jig configuration.

We fabricated a miniaturised spherical probe by simply gluing a stainless steel ball (0.8 mm in diameter) to the end of a flat-polished stainless steel pin. The opposite end of the pin was inserted into a short and flat Teflon rod that fitted in the Nakahara tester. However, the Teflon rod did not fit perfectly into the tester and as a result there was some undesirable movement in the probe.

The next stage of the development addressed the support and fixturing of freestanding film specimens. Visual inspection of two mild steel plates (3 mm thickness with 60 mm diameter) in contact usually revealed tiny gaps indicating non-uniform flatness in the plates. In this case, the metal plates were not suitable for supporting freestanding films. Nakahara avoided the issue by holding a given test specimen between a set of 8.0-mm rubber O-rings and squeezing them together by two screw-tightened metal plates.

(a) Macro-probe fabrication: We fabricated a new, smaller specimen-jig (similar to Nakahara’s) for supporting freestanding metal films. A 2.0-mm through-
hole was drilled in two flat steel plates. A recess to hold a 2.5-mm O-ring was machined in each plate using a lathe. The specimen-jig was mounted on top of the Nakahara tester and positioned using a set of screws. The specimen was squeezed between 2.5-mm O-rings using two screws at opposite ends. A schematic of the modified specimen-jig configuration is shown in Fig. 6.5. Displacement of the spindle extension holding the probe was operated using the linear micrometer on the Nakahara tester.

Attempts to modify the Nakahara tester to achieve smaller film span and probe diameter were successful but not without some drawbacks. The main drawbacks were the method of film fixturing and in the implementation of a miniature probe to the Nakahara tester. The squeezing of O-rings usually generated a tensile stress in the film whose magnitude was dependent on the force between the O-rings. Thus, the use of O-rings to support films as thin as 100 nm was not a viable option. In addition, the use of a miniature probe in Nakahara’s tester was complicated by the rotational motion of the probe as it was displaced vertically, and this was not desirable. To use a micrometer that moves linearly and without any rotation would avoid undesirable
twisting of the film while the probe is in contact during loading. The accuracy of measurement was also dependent on the resolution of the micrometer. Implementing small components into a robust structural configuration is challenging. At shorter length scales, the control of motion and loading conditions becomes increasingly difficult and cannot be achieved by conventional means.

Although Nakahara’s tester showed some limitations in its design, its principle remains viable as a model for further development. The modifications to the Nakahara tester demonstrated the importance of implementing a solid, rigid probe for accurate mechanical measurement and the use of suitable fixturing for supporting freestanding films.

(b) Micro-probe fabrication: A new design of test-probe was fabricated from a 100 µm optical fibre. The tip of the optical fibre was rounded using a commercial arc fusion splicer. Based on the principles of arc discharging energy absorption and the surface tension phenomenon, a microsphere was formed at the tip of the optical fibre. The plastic cladding of a single mode optical fibre (80 to 125 µm in diameter) was softened with acetone (applied with cotton buds) and removed mechanically using a stripper (Miller). The fibre was gently wiped with lens paper to remove any remaining cladding or debris. The fibre was cleaved using a commercial fibre cleaver (PK Technology FKII). The operation of the fusion splicer and fibre cleaver are described in Section 3.5.3.

The end of an aluminium rod was machined leaving a section protruding, as shown in Fig. 6.7. The fibre-probe was carefully handled with a fine-tip tweezers and double-sided sticky tape. The microprobe was adhered to the flat protruding section of the rod with a very small drop of epoxy and care was taken to avoid contaminating the tip.
Fig. 6.6 Schematic diagram of the microprobe holder used in the MK1 ductility tester. The aluminium rod has a section protruding with a V-groove, which allows secure placement of the microprobe during application of the epoxy.

Fig. 6.7 Schematic diagram of MK1 ductility tester.

Having fabricated a probe with tip diameter ~ 100 µm, it was attached to the holder and fitted to the top of the test rig (see Fig. 6.7). The frame of the rig is a microscope stand and it was exploited for both its 3-axis stage motion, and its strong structural integrity.
The stage has x-y translation and its z-axis control has resolution of ~ 1 µm. An x-y-z micro-position controller was screwed to the stage and was used for positional adjustment of the specimen before testing. The z-axis control on the microscope enabled movement of the specimen towards the probe.

Deformation of the specimen by the probe was viewed through a 10 X optical lens oriented at a 45° angle to the specimen. The control has 200 divisions per full revolution. The displacement of the stage after 100 revolutions of the control was measured as 21.0 mm with vernier calipers. Thus, the resolution of the controller was calculated as 1.05 µm/div. Since the resolution of the calipers is 0.1 mm, the error in measurement was less than 0.5 % (i.e. 0.1 mm / 21.0 mm).

The MK1 tester measures ductility of a specimen in the same way as Nakahara’s tester. Measurement accuracy of film displacement was affected by the resolution of the micrometer and mechanical effects such as backlash and stiction. However, the main source of error was the measurement of the initial point of contact.

In the Nakahara tester, contact was observed by means of an LED that illuminates when an electric current passes between ball and specimen and this is not a suitable method for establishing initial contact in the MK1 tester since the probe (glass) is non-conductive. A conventional method for measuring initial contact involves the use of a probe with load feedback. An atomic force microscope, for example, uses a cantilever probe to sense the surface as it engages, and causes a sudden deflection in the cantilever. Our next step in development of the ductility tester (MK2) involved design and implementation of an “optical-lever” method so that the initial point of contact between probe and specimen could be accurately determined. In addition, the load-displacement profile of a specimen could be measured using an optical-lever method.

6.3.2 Second Prototype: MK2

In this section we describe the design of the ductility tester MK2 and its improvement over the MK1 prototype. A schematic diagram and a photograph of the MK2 tester are shown in Fig. 6.8 and Fig. 6.9, respectively. The optical-lever system consists of
a cantilevered probe (Section 6.5), laser source, beam-splitter cube and position sensitive detector (PSD). The load is applied by a cantilever tip, which is attached to the end of a substantially rigid L-plate. The force applied to the sample is proportional to the cantilever deflection. The cantilever probe was cleaved from a silicon wafer and a glass microprobe was attached to its end. The sample was mounted on an x-y-z micro-stage and its alignment with respect to the tip was monitored by a long-working-distance optical microscope. The z-axis stage control was calibrated as described in Section 6.3.1. The 1 mW semiconductor diode laser (Maplin Model No. LE07H) has a 670 nm wavelength and a 1 mm spot size. The one-dimensional PSD (Hamamatsu S8543) has a 24 mm active length and a 1 mm active width.

![Schematic of the nanoductility tester (MK2).](image)

**Fig. 6.8** Schematic of the nanoductility tester (MK2). The setup consists of a silicon cantilever beam with a manually operated three-dimensional stage, a position sensitive detector, laser and beam splitter.
In general, the mechanical properties of a test specimen and the geometrical configuration of an optical-lever system must be considered before selecting a cantilever. The ideal cantilever will allow complete measurement of a specimen’s load-deflection characteristics until failure without exceeding the cantilever’s bending limit for measurement of its deflection.

Choosing a less rigid (or longer) cantilever permits a larger range of motion in the cantilever, thus optimizing its load-measurement resolution. A silicon wafer, 100 mm in diameter and 500 µm in thickness, was cleaved to the required length and width. Attaching a microprobe perpendicular to the surface of a cantilever beam was performed using micromanipulation techniques, as we now describe.

Once the microsphere probe was fabricated, the fibre shaft was cut to approximately 5 mm in length. A square piece (side length 1 cm) of 1 mm-thick glass slide was cleaved. A piece of double-sided tape was placed over one face of the glass slide. The glass slide (sticky-side down) was placed into the holder of the 3-axis x-y-z micromanipulator and tightened using screws. The micro-probe was held using a
fine-tip tweezers, and the spherical side of the probe was attached to the sticky face of the glass slide and allowed to freely hang downwards. Using a fine wire, a small amount of quick-drying epoxy was applied to the end of the cantilever beam. Using the x-y-z controls, the probe was guided into contact between the epoxy and the cantilever surface. Care was taken to ensure the probe pointed perpendicular to the cantilever surface.

Fig. 6.10  Schematic of technique used to attach a micro-probe to the end of a cantilever beam.

Fig. 6.11  Side-view photograph of (a) 300 µm glass and (b) 2.5 mm stainless steel spherical-tip probes attached to the end of silicon cantilever beam.

The angle of the probe with respect to the cantilever was adjusted using the x-y controls. The cantilever-probe was cured in air at room temperature for approximately 20-30 minutes before the sticky tape was carefully removed. The bond between the probe and the cantilever was further strengthened by applying additional epoxy to the base of the probe shaft and this ensured the probe did not buckle under mechanical load. A schematic diagram of the process is shown in Fig. 6.10. An optical view of (a) a glass micro-probe with a 300-µm tip and (b) a 2.5-mm stainless steel ball attached to the end of a silicon cantilever beam are both shown in Fig. 6.11.
Tight gripping at the fixed end of the cantilever minimized fixed-end deflection, ensuring good stability during loading. The accuracy and sensitivity of measurement in cantilever deflection was dependent on the distance between the cantilever and PSD, and the resolutions of both the PSD and the z-axis stage motion. The PSD and beam-splitter cube (12 mm side length) were both supported by separate L-plates which both shared the same 2.5 mm-thick stainless steel sheet clamped to the microscope stand. Different clamping arrangements were used for gripping cantilevers including micromanipulator grips, and L-plate clamps. We found the best clamping was achieved using a rigid L-clamp.

The system needed to be re-calibrated if any changes were made to the optical-lever configuration. The system was aligned before calibration. Alignment was difficult to perform with the MK2 design. Each system component was adjusted manually and their exact position and orientation were not easily controlled. Any slight change in position or orientation of any component misaligned the setup. In addition, the setup was restricted to small changes in optical-lever configurations (i.e. PSD-cantilever distance, and beam-splitter position).

### 6.3.2.1 Position Sensitive Detector (PSD) Calibration

The PSD was mounted on a one-dimensional micrometer so that its position could be controlled during calibration. The laser was positioned at different points along the length of the active area by adjusting the PSD position using the micrometer. Measurements of the PSD output voltages are performed in darkness and in ambient light. Voltages $V_A$ and $V_B$ are proportional to the output currents $I_A$ and $I_B$ at the anodes A and B, respectively of the PSD. Voltages $V_A$ and $V_B$ are recorded and plotted as a function of the laser position, as shown in Fig. 6.12. While the laser moves from anode A to anode B, (see Fig. 6.12) $V_A$ decreases and $V_B$ increases. Both $V_A$ and $V_B$ change almost linearly within the measured range with respect to the position of the laser.
**Fig. 6.12** Plot of voltage at anode A and anode B as a function of the laser position on a one-dimensional PSD, in darkness.

**Fig. 6.13** Plot of the fractional position of the laser (measured by the PSD) as a function of its position on the photodiode (measured by the micrometer). Measurements were taken both in (a) darkness and (b) ambient light.

The position of the laser on the PSD can be described by Equation A.34. The fractional position of the laser (see Section A.5) was measured in ambient light and in darkness, as shown in Fig. 6.13. The slope of each plot is 0.083 mm\(^{-1}\) in darkness.
and 0.075 mm\(^{-1}\) in ambient light. From the measured slopes, we can see the slope decreases by \(\sim 9\%\) when ambient light is switched on. Performing measurements in darkness eliminated effects of ambient conditions.

### 6.3.2.2 Cantilever Calibration

A typical calibration experiment involves applying a load to the fixed end of the cantilever and measuring its deflection using a laser beam deflection method. From this we can determine the cantilever sensitivity. A rigid block was pushed against a cantilever-probe using the z-axis stage control and this caused the cantilever to deflect. The cantilever was 39 mm in length, 20 mm in width, and 0.5 mm in thickness. According to beam theory\(^{16}\) (see Equation A.32), the theoretical stiffness of this cantilever was 1.686 N/m.

The fractional position of the laser on the PSD was measured as a function of the cantilever deflection, and this graph is shown in Fig. 6.14(a). Cantilever sensitivity was calculated by measurement of the slope, which equals 0.451 mm\(^{-1}\). The stiffness of a cantilever is calibrated with a set of calibrated weights and its deflection measured with the PSD. The stiffness of the cantilever was measured by slope of the graph in Fig. 6.14(b) and is equal to 1.744 N/m. The measured stiffness of the cantilever shows close agreement with its theoretical value.

We then tested a 600 nm-thick copper film with 1.6 mm diameter. The cantilever deflection versus stage displacement is shown in Fig. 6.15(a). A Type-A glass probe of diameter 0.8 mm was used. Film displacement is controlled using the stage and cantilever deflection is measured using the PSD. The stage displaces by 1.560 mm and the cantilever deflects by 1.292 mm before the film fractures. By subtracting the cantilever deflection from the stage displacement, we know the film has displaced by 268 \(\mu\)m before it fractures. A plot of cantilever deflection versus film deflection is shown in Fig. 6.16. The cantilever deflection has a non-linear relationship with film deflection.
Fig. 6.14  (a) Fractional position of laser on PSD versus stage displacement during the loading of a cantilever on a steel block. (b) Corresponding applied load versus cantilever deflection. A silicon cantilever was used with a Type-A glass probe of diameter 0.8 mm.
Fig. 6.15 Cantilever deflection versus stage displacement for a 600 nm-thick circular freestanding copper film with 1.6 mm diameter under load. A silicon cantilever was used with a Type-A glass probe of diameter 0.3 mm. The arrow indicates the point of fracture.

Fig. 6.16 Cantilever deflection versus film displacement for a 600 nm-thick circular freestanding copper film with 1.6 mm diameter under load (from data in Fig. 6.15). A silicon cantilever was used with a Type-A glass probe of diameter 0.8 mm.
We calculated the applied load using Hooke’s Law. A plot of applied load versus % elongation of the film is shown in Fig. 6.17. In this experiment, we used a probe with a diameter of 0.8 mm. The arrow indicates the film fractured at a stage displacement of 1.6 mm. Film elongation is dependent on the diameters of both the film and the probe, and on the displacement of the film. Film ductility (or % elongation) is calculated using Nakahara’s Equations (Section A.12). The maximum applied load on this film before failure is 100 mN. The film fractured after 5.6 % elongation.

6.3.2.3 Ductility Testing using the MK2 Prototype

In this section, we investigated the load-deflection and load-elongation profile of freestanding films as a function of their span (i.e. diameter of freestanding circular section). A 7.8-µm-thick copper foil was clamped between two o-rings over different diameter holes (3.0, 4.0 and 8.0 mm) in an aluminium plate and tested with a 2.5 mm steel probe. Fig. 6.18 shows (a) load-deflection and (b) load-elongation measurements of the copper foil. These samples are representative of a typical sample measured under the conditions described above. A comparison of load, film displacement, and % elongation are shown in Table 6.1.
Table 6.1  A comparison of maximum load ($P_{\text{max}}$), film displacement ($d_{\text{film}}$), and % elongation as a function of film span in 7.8 µm-thick copper foil using a steel probe of diameter 2.5 mm.

<table>
<thead>
<tr>
<th>Film Span (mm)</th>
<th>$N_{\text{samples}}$</th>
<th>$P_{\text{max}}$ (mN)</th>
<th>$d_{\text{film}}$ (µm)</th>
<th>% elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>11</td>
<td>1257 ± 198</td>
<td>203 ± 44</td>
<td>1.0 ± 0.5</td>
</tr>
<tr>
<td>4.0</td>
<td>11</td>
<td>1187 ± 183</td>
<td>247 ± 29</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>8.0</td>
<td>11</td>
<td>1066 ± 191</td>
<td>278 ± 82</td>
<td>2.3 ± 0.2</td>
</tr>
</tbody>
</table>

Fig. 6.18  Plots of load versus (a) film displacement and (b) film elongation of 7.8 µm-thick copper foil with spans 3.0, 4.0 and 8.0 mm. A silicon cantilever was used with a steel probe of diameter 2.5 mm.
We would expect that if the diameter of a film is reduced, the load required to rupture the film will be greater. Similarly, if the diameter of the probe is too small, the load becomes localized in the centre of the film where probe contact is made.
Fig. 6.20  Plots of load versus (a) film deflection and (b) film elongation of 1.6 mm-span circular freestanding copper films with thickness 300, 400 and 600 nm. A silicon cantilever was used with a steel probe of diameter 2.5 mm.

6.3.2.4 Measurements on Annealed Copper Nanofilms

In this section, we investigate the effect of annealing on Type F2 freestanding copper films (see Section 6.5 for fabrication details) by measuring their load-deflection and
load-elongation response. Copper films were annealed at 450 °C for 1 hour in a 5% H$_2$/Ar atmosphere. Annealed copper films, with 1.6 mm span, were tested. Load-displacement and load-elongation as a function of film thickness 300, 400 and 600 nm, are shown in Fig. 6.21. Measurements are also shown as a function of film span in Fig. 6.22.

![Fig. 6.21 Plots of load versus (a) film displacement and (b) film elongation of annealed (450 °C 1 hour) 600 nm-thick circular freestanding copper films with spans 0.8, 1.2 and 1.6 mm. A silicon cantilever was used with a Type-A glass probe of diameter 0.3 mm.](image-url)
Both load at fracture and elongation increase with film thickness but no clear dependence is observed as a function of film span. Both load to fracture and elongation are lower in annealed films.

**Fig. 6.22** Plots of load versus (a) film displacement and (b) film elongation of annealed (450 °C 1 hour) 1.6 mm-span circular freestanding copper films with thickness 300, 400 and 600 nm. A silicon cantilever was used with a Type-A glass probe of diameter 0.3 mm.
6.3.2.5 Repeatability

The accuracy of measurement of the applied load, film displacement and % elongation in freestanding copper films was investigated. A summary of measurements on as-deposited copper films is shown in Table 6.2. The average deviation in the applied load of all the samples was \( \sim 8.5 \, \text{mN} \). The average deviation in the film displacement of all the samples was \( \sim 47 \, \mu \text{m} \). The large deviation in the measured film displacement was mostly due to the stochastic behaviour of the film under load, and not the capabilities of the measurement technique.

<table>
<thead>
<tr>
<th>h (nm)</th>
<th>2a (mm)</th>
<th>n</th>
<th>( P_{\text{max}} ) (mN)</th>
<th>( \delta_{\text{max}} ) (( \mu \text{m} ))</th>
<th>% elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.6</td>
<td>4</td>
<td>31 ( \pm 1 )</td>
<td>132 ( \pm 27 )</td>
<td>1.4 ( \pm 0.6 )</td>
</tr>
<tr>
<td>400</td>
<td>1.6</td>
<td>3</td>
<td>53 ( \pm 3 )</td>
<td>209 ( \pm 11 )</td>
<td>2.4 ( \pm 0.4 )</td>
</tr>
<tr>
<td>600</td>
<td>1.6</td>
<td>6</td>
<td>113 ( \pm 10 )</td>
<td>286 ( \pm 82 )</td>
<td>6.7 ( \pm 3.7 )</td>
</tr>
<tr>
<td>300</td>
<td>1.2</td>
<td>5</td>
<td>31 ( \pm 10 )</td>
<td>134 ( \pm 52 )</td>
<td>2.8 ( \pm 1.8 )</td>
</tr>
<tr>
<td>400</td>
<td>1.2</td>
<td>5</td>
<td>66 ( \pm 8 )</td>
<td>202 ( \pm 22 )</td>
<td>5.7 ( \pm 1.2 )</td>
</tr>
<tr>
<td>600</td>
<td>1.2</td>
<td>3</td>
<td>167 ( \pm 20 )</td>
<td>206 ( \pm 14 )</td>
<td>5.9 ( \pm 0.8 )</td>
</tr>
<tr>
<td>400</td>
<td>0.8</td>
<td>4</td>
<td>55 ( \pm 6 )</td>
<td>168 ( \pm 93 )</td>
<td>10.4 ( \pm 11.5 )</td>
</tr>
<tr>
<td>600</td>
<td>0.8</td>
<td>2</td>
<td>208 ( \pm 10 )</td>
<td>234 ( \pm 73 )</td>
<td>17.3 ( \pm 9.7 )</td>
</tr>
</tbody>
</table>

6.3.2.6 Discussion of MK2

A one-dimensional position sensitive detector is suitable for measuring the deflection of a laser from the back-side of a cantilever. However, the PSD showed sensitivity to ambient light source and therefore should only be operated in darkness.

We have described the calibration of a cantilever and have shown a typical experiment in which the applied load was measured as a function of the elongation in a copper film.
We have shown measurements of load-deflection and load-elongation of films as a function of both film diameter and thickness. For a given probe diameter, small-diameter films required a larger load before failure was observed. Film displacement was greater in films with large diameters.

The clamping force of the specimen by the O-rings had a significant effect on film deflection. In contrast, the effect of clamping on the maximum observed load was relatively small. Films with large pre-tension failed sooner during testing.

Our measurements have shown that ductility increased with film thickness, as expected. Since the displacement of the stage was controlled manually, measurements were not as reliable. The stability of the system was not adequate with all components being mounted on the same bracket. In addition, the resolution of each curve was not suitable for measuring ductility reliably. To overcome these issues, a third prototype was developed – MK3.

6.3.3 Third Prototype: MK3

The MK1 tester highlighted the importance of establishing an accurate measurement of the initial point of contact between probe and specimen. Although miniaturization of probe size and jig size is relatively simple, a significant challenge remained in achieving reliable and accurate measurements of displacement in thin film specimens under load. The MK2 tester demonstrated the optical-lever system was a suitable technique for establishing initial contact between probe and specimen. However, it was not deemed reliable for alignment purposes and thus impacts the repeatability of measurements. The MK3 tester overcomes these alignment and repeatability issues by isolating the main components and replacing the microscope stage with a high-resolution micro-actuated control. Isolating the components onto individual rods has enabled an increased range of motion control for components during positional alignment. The MK3 tester demonstrates more accurate measurements of the load-deflection response of metal films as thin as 100 nm.

Similar to the MK2 tester, the MK3 tester has four main components - laser module, cantilever probe, beam-splitter and position sensitive detector (PSD). A schematic diagram and a photograph of the setup are shown in Fig. 6.23 and Fig. 6.24,
respectively. The laser module, as before, is a 1 mW semiconductor diode with 670 nm wavelength and 1 mm spot size. The x-y-z position of the laser module is set using the adjustable stand and its tilt is set using an adjustable cylindrical holder, as shown in Fig. 6.23. The laser beam is reflected from the cantilever towards the PSD (see Section A.5). The voltage signals from the two anodes on the PSD were collected by a multiplexer and a data acquisition card connected to a personal computer. The voltage signals were recorded using Labview. An image of the graphical user interface is shown in Fig. 6.25(a). The x- and y-axis stage positions were controlled using translation stages with 13-mm travel ranges. The z-axis stage position was controlled by a 25 mm motorized actuator, which was driven by a single channel DC servo motor connected to a personal computer via USB. The DC servo motor was compact and allowed for manual and/or automated control. The APT (Advanced Positioning Technology) software, which operated the DC servo motor and micro-actuator, allowed manual control of motor parameters such as velocity, acceleration and step size. An image of the APT main user interface is shown in Fig. 6.25(b). The stage can also be sent to a home/zero position, and enabled or disabled. A stage sequence can be automated using the “move sequence” panel, where for example, travel distance, velocity and acceleration can be set.
Fig. 6.23  Schematic representation of the MK3 ductility tester. This image shows the cantilever beam, laser source, beam-splitter and PSD.

Fig. 6.24  Optical image of the MK3 ductility tester is shown in (a). A schematic of the clamping arrangement for the cantilever probe is shown in (b).
Fig. 6.25 Images of (a) an interface on a Labview program designed for capturing output voltages of the PSD and (b) the interface of APT software used for controlling the DC motor controller manually.

Fig. 6.26 Image of Move Editor window used for inputting a move command. Parameters include distance, acceleration and maximum velocity.

The setup consists of three adjustable stands, one for the beam-splitter and PSD, one for the laser module, and another for the cantilever probe. Each stand consists of a stainless steel rod, 22 mm in diameter, sitting on a flat aluminium base plate, 7 mm in thickness. The base plate has two elongated holes that allow for positional adjustments of the component. Each component is attached to the steel rod by means of a square aluminium block, approximately 30 mm in width, and adjustable screws. Each block has a through hole allowing positional adjustment of any component in the z-direction, and is tightened by adjustable screws.

The fixed-end position of the cantilever is clamped to a steel L-plate, as shown schematically in Fig. 6.24(b). Thin rubber sheeting is placed on both sides of the cantilever where it is gripped to prevent slippage and cracking. A 10 mm-thick steel block is screwed to the L-plate using two M6 screws, thus tightening the position of the cantilever. This clamping arrangement permits changes in cantilever conditions (i.e. length, width, thickness and choice of material), which is useful in experiments where the cantilever stiffness or sensitivity needs to be changed. The free end of the cantilever (with attached probe) hangs over the stage, underneath which a sample is
placed. Because all the controlling and monitoring components are isolated from the cantilever probe, vibration and noise is reduced during testing.

In general, the MK3 ductility tester was set up and operated in the following manner:
   a) The cantilever probe was inserted into the L-plate grips, as shown schematically in Fig. 6.24(b).
   b) The beam-splitter was positioned close to the cantilever so that full deflection of the cantilever was measured by the PSD.
   c) The laser was switched ON and the system was aligned as follows:
      a. The laser was aligned to the optical bench by adjusting its height and tilt.
      b. The orientation of the beam-splitter was adjusted so that the reflected part of the beam returned to the laser module. The beam-splitter was also positioned close to the cantilever.
      c. The orientation of the cantilever was adjusted until the laser beam passed through the beam-splitter and returned to the laser module.
      d. Finally, the orientation and position of the PSD were adjusted so the laser hit one end of the PSD’s active length.
   d) The PSD was activated for at least 15 minutes (performed in darkness).
   e) The sample was placed on the stage underneath the probe and centered using the xy-translation control. The entire system was covered with a box and all light sources were switched OFF.
   f) Using APT software, the stage was programmed to approach the sample slowly (typically at a rate of 0.01 mm/s) and after approximately 3 mm of travel from the point of initial contact the cantilever was retracted. The fractional position of the laser on the PSD using Labview.
   g) If the sample did not rupture during loading, the cantilever was replaced with a stiffer cantilever. Similarly if the sample ruptured too soon, the cantilever was replaced with a softer cantilever. This ensured that maximum resolution of measurement in cantilever deflection was achieved.
Calibration and testing is performed in darkness, with the setup covered by a box to reduce signal noise due to ambient light. The stability of the PSD is characterised by monitoring its drift signal with time. The laser is reflected from the stationary cantilever towards the PSD. The voltage signals from the PSD are recorded as a function of time after its initial activation. The signal (fractional position) drifts by 0.001 for the first 750 seconds of activation (as indicated by the dashed line) and stabilizes thereafter (<< 0.001), as shown in Fig. 6.27. Before calibration and/or testing is performed, it is important to activate the PSD for at least 15 minutes to allow it to stabilize.

The cantilever was loaded against a solid steel block for calibration. The cantilever sensitivity was dependent on the geometrical configuration of the system, i.e. cantilever length and distance between cantilever and PSD. A typical calibration plot of the fractional position of the laser on the PSD as a function of cantilever position is shown in Fig. 6.28. The cantilever deflection remained constant during approach (Region A), and increased during loading (Region B). As the cantilever was retracted, the cantilever deflection decreased (region C) until it retracted from the stage (region D).
Fig. 6.28 Fractional position signal of the laser versus cantilever position during (A) approach, (B) loading, (C) unloading and (D) retraction. The cantilever was loaded against a steel block.

The data from the loading cycle in region B was re-plotted as fractional position versus cantilever deflection. The cantilever sensitivity (mm\(^{-1}\)) was determined by simply measuring the slope of the line normally shows good repeatability (usually within 1% variation).

Having set up the system a sample was tested. A sample was centred underneath the probe using the x-y translation stage. During loading, the sample was displaced from its initial position. The displacement of a freestanding film, \(d_{\text{film}}\), under load is simply calculated as:

\[
d_{\text{film}} = Z_{\text{stage}} - C_{\text{def}}
\]  

where \(Z_{\text{stage}}\) is the stage displacement and \(C_{\text{def}}\) is the cantilever deflection. \(C_{\text{def}}\) is calculated as:

\[
C_{\text{def}} = F_{\text{pos}} \times S
\]

where \(F_{\text{pos}}\) is the fractional position of the laser on the PSD, and \(S\) is the calibrated cantilever sensitivity.
In most cases, the sample was displaced towards the probe at a rate of 0.01 mm s\(^{-1}\) and the voltage data from the PSD is captured at sampling intervals of 165 ms. An example of a typical plot of cantilever deflection as a function of film displacement is shown in Fig. 6.29(a). The cantilever deflection (or load) increased rapidly with film displacement and this is expected according to beam theory (see Section A.4).
The load (calculated by Hooke’s Law) is plotted in Fig. 6.29(b) as a function of ductility or % elongation, which is calculated using Nakahara’s geometric Equations (as described in Section 3.5). In this case, the film fails after an elongation of 1.47%.

6.4 Fabrication of Cantilevered Microprobes

Although a wide variety of tip shapes and dimensions are commercially available, it is more cost effective to custom-fabricate micro-probes to suit test conditions. To reduce the localized deformation, the smoothness of the loading top surface is critical. In addition, a tip with a relatively large surface area will avoid stress concentration and premature failure of fragile specimens. A spherical tip is required for the purpose of implementing the Nakahara tester on the nanoscale. A series of methods to fabricate probes tips with diameters from 2.5 mm down to 0.1 mm and their attachment to the end of a cantilever beam were described in Section 6.3.2.

6.4.1 Fabricating Microprobes with Hemispherical Tips

We have already described the fabrication of probes (see Section 6.3.2) using a commercial arc fusion splicer and another technique involving the attachment of a stainless steel ball to the end of a pin. An alternative technique is described here.

Micro-probes can be fabricated from glass rods using a common glass drawing technique. A schematic representation of the process is shown in Fig. 6.30. This simple technique involves heating a glass rod at its centre with enough rotation to distribute heat uniformly. As the glass softens, the glass rod is pulled from both ends to the required distance. The further it is pulled the narrower the fibre that is produced. The fibre is cut into sections using a glass-cutter and their tips are rounded in the flame for a short time (usually around 1 second). The dimensions of the tip can then be measured using an optical microscope, as shown in Fig. 6.31. When a probe is subjected to larger loads, the width of the shaft becomes more critical.
Fig. 6.30 Heating-drawing technique for producing narrow glass fibres. The fibres are cut with a glass-cutter and their tips are rounded in the flame.

Fig. 6.31 Optical images of glass probes with measured diameters (a) 586 µm and (b) 1080 µm.

6.5 Fabrication of Freestanding Metal Films

We investigated various methods of fabricating free-standing copper films for ductility measurements. We developed and optimized four different techniques.

The first of three of these used a perforated metal matrix to support the free-standing nanofilms. In each of these, a sacrificial lacquer of polymeric material was used to support the metal nanofilms during deposition. This was then removed leaving free-standing nanofilm supported by the perforated metal structure. The three techniques used are summarized here. The detailed procedures can be found in Appendix A.2.

(1) Film type TG: A transmission electron microscopy (TEM) grid was used as the support structure. The TEM grid supported on the flat surface of a polishing stub was in-filled with polymethylmethacrylate (PMMA). This was
then polished flat, a suitable copper film was evaporated on its and the
PMMA was dissolved leaving the free-standing film.

(2) Film Type F1: Holes ranging in diameter from 0.3 to 1.6 mm were in-filled
with lacquer which was then polished flat, a suitable layer of copper was
evaporated on it and the lacquer was then dissolved leaving the free-standing
film.

(3) Film Type F2: These films were prepared as in (2) except that the in-filled
structures were not polished before metal evaporation.

The fourth technique for preparation of freestanding films (Type S) used a
lithographic process to define holes which were wet-etched through a silicon
substrate, with a thin layer of SiNₓ/SiOₓ. Copper was then deposited and the
SiNₓ/SiOₓ in the holes removed by etching.

6.6 Ductility Measurements of Freestanding Films

In this section, we measured load-displacement of copper films using the MK3 tester.
We performed these experiments on copper, gold and aluminium films with
thicknesses 100, 300 and 500 nm and with diameters from 0.1 to 1.0 mm. These
copper nanofilms are created using silicon microfabrication techniques, as described
in Section A.2.3.

6.6.1 Measurements on freestanding copper nanofilms using MK3 tester

Copper films, 100 nm in thickness, have been constructed using microfabrication
techniques. An optical image of a 100 nm-thick copper film is shown in Fig. 6.32.
The load-deflection and load-elongation profiles of 100 nm-thick copper films with a
1.0 mm span are shown in Fig. 6.34, respectively. The five films tested exhibit a
mean maximum load of 199 ± 104 mN and mean maximum film displacement 34 ±
15 µm. Due to issues with the fabrication process, not all SiOₓ films are entirely
removed from underneath the copper films. This will result in higher loads than
expected and may affect repeatability of measurement.
The corresponding load-deflection and load-elongation of a 100 nm-thick circular copper film with a 1.0 mm span is shown in Fig. 6.33. The Type-A glass probe with a diameter of 540 μm was used on a silicon cantilever with a stiffness of 391 N mm\(^{-1}\) is used. The % elongation (ductility) of the film was determined by Nakahara’s Equations (Section 3.5).

In Fig. 6.33(a) load increases rapidly during the first 25 μm of film displacement or 0.12% elongation. Beyond 20 μm film displacement, the cantilever deflection increases at a constant rate. The film may be cracking under load as observed by the sudden increases in film displacement at ~ 40 μm. These events increase in number once again beyond 60 μm of film displacement. Finally, film failure occurs after 80 μm displacement. In Fig. 6.33(b) we can see the corresponding % elongation to failure is ~ 1.55%.
Fig. 6.33 Plots of load versus (a) film deflection and (b) film elongation of 100 nm-thick evaporated copper with 1.0 mm span. A silicon cantilever was used with a Type-A glass probe of diameter 0.54 mm.
Similarly, the load-deflection and load-elongation profiles of 100 nm-thick copper films with a 0.7 mm span are shown in Fig. 6.35, respectively. The same 540 µm diameter probe is used. The five films tested exhibit a mean maximum load of 177 ± 82 mN and mean maximum film displacement 32.4 ± 10.8 µm.
Fig. 6.35 Plots of load versus (a) film deflection and (b) film elongation of 100 nm-thick copper with 0.7 mm span. A silicon cantilever was used with a Type-A glass probe of diameter 0.54 mm.

Despite decreasing the film span (or span-probe diameter ratio) from 1.0 mm to 0.7 mm, the mean values of maximum load and maximum film displacement did not change significantly. In fact, the ductility of films with 1.0 mm spans is smaller than films with 0.7 mm spans, by a factor of 0.6. If the diameter of the probe is too small, the load becomes localized in the centre of the film where probe contact is made. However, as the probe diameter approaches the span of the film, stress becomes distributed over a larger portion of the film. This allows the film to undergo larger
average strains, thus resulting in larger measured values in ductility. In most cases
the films ruptured at their edges where they make contact with the substrate. It may
be possible that the bending stresses at the edge of the film are too large at this
thickness scale, thus causing failure in this region. This failure mechanism suggests
that loads required to instigate rupture in the centre of the film may far exceed the
load required for rupture in the edge of the film. In addition, the integrity of the
film’s edge-substrate region may deteriorate due to residual stresses formed as a
result of the fabrication process.

6.7 Force-Displacement Measurements on RF-MEMS Switches

At the outset of this project, the use of an AFM with an appropriate tip to measure
the ductility of free-standing nanofilms was considered. However, it is now clear that
the displacements necessary to measure the ductility of films in the 100-nm thickness
range exceeds the capability of a typical commercial AFM. However, during the
course of our study, we found that an AFM could indeed be used to obtain load
versus displacement data in a related application, namely the investigation of
radiofrequency (RF) microelectromechanical system (MEMS) switches. In this
section we present the results of this investigation.

6.7.1 RF-MEMS Switches

A major challenge to the successful commercialization of RF MEMS capacitive
switches is achieving a high reliability and this is currently the subject of intense
research. Electrical and mechanical characteristics impact both the reliability and
performance of RF MEMS capacitive switches. The key parameters of RF MEMS
switches such as pull-in voltage, contact and restoring forces strongly depend on the
mechanical properties of the bridge. Capacitive fixed-fixed beam RF MEMS
switches suffer from issues such as dielectric charging beam stiction and humidity
induced beam stiction. The design, fabrication process and loading conditions can all
affect the mechanical properties of RF MEMS switches. Degradation of the stiffness
in MEMS switches is a key issue. If stiffness is too low, there is a risk of buckling. If
it is too high, the pull-in voltage will be too large. In this work, the load-
displacement characteristics of RF MEMS switches are measured using an AFM SiN
cantilever tip and their spring constants are determined.
Fig. 6.36  (a) SEM image of a 100 µm x 100 µm membrane supported by meander suspensions. (b) A fully processed and released RF MEMS switch (not to scale). (Tyndall National Institute).

Fig. 6.37  Optical image of six RF MEMS configurations: Left column contains 100 µm x 100 µm membranes and right column contains 200 µm x 200 µm membranes. Membranes are supported by different suspensions – (a) meander (top row), (b) straight (middle row) and (c) spiral (bottom row). (Tyndall National Institute)
The capacitive switch, shown in Fig. 6.36(a), is made of a 1 µm-thick square aluminium membrane suspended at its four corners by an aluminium structure. When a biasing voltage is applied, the membrane is pulled down, and the transmission line is short-circuited. A schematic cross-section of a fully processed capacitive switch is shown in Fig. 6.36(b). Six different RF MEMS configurations are shown in Fig. 6.37, each consisting of a different type of suspension (meander, straight, and spiral) which support a square membrane (100 or 200 µm) in air. The air gap height is typically between 2 and 4 microns but can vary from device to device.

The force-displacement technique is described in Section 3.5.2. Fig. 6.38(a) shows a typical measurement of the cantilever deflection, $\Delta_{\text{deflection}}$, versus the displacement of the $z$ piezo, $\Delta_{\text{piezo}}$, during loading against a 200 µm RF-MEMS switch with straight suspension. The displacement of the switch, $\Delta_{\text{film}}$, is determined by the following relationship:

$$
\Delta_{\text{film}} = (\Delta_{\text{piezo}} - z_0) - \Delta_{\text{deflection}}
$$

where $z_0$ is the point of initial contact between tip and sample.

The nominal stiffness for the cantilever is 42 N m$^{-1}$. The load exerted by the cantilever can be calculated using Hooke’s Law. The applied load as a function of film displacement is shown in Fig. 6.38(b). The stiffness of the each RF MEMS structure is determined by measurement of slope of the elastic region. Table 6.3 shows a comparison between theoretical and measured stiffness’s of each membrane.

The load-deflection profile of each RF MEMS switch was modelled by the MEMS group in Tyndall National Institute using a finite element method (FEM). The model makes the following assumptions:

1. All devices have the same air gap height
2. The membrane is under biaxial stress
3. A parallel plate model exists
In reality, the surfaces of membranes will be non-uniform and possibly buckle as a result of the fabrication process. The height of the air gap will depend on the sensitivity of the suspension and its mechanical properties will be influenced by process-induced stress. From the experimental results summarised in Table 6.3, we can determine the following:

1. In general, there is good agreement between theoretical and experimental measurements of the RF MEMS stiffness.
2. The 100 µm membranes have a higher stiffness than 200 µm membranes.

3. For 200 µm membranes, the straight suspension has the highest average stiffness (at 3.68 N/m) followed by the meander suspension (at 1.44 N/m) and then by the spiral suspension (at 0.44 N/m). The loading cycles for all membranes on sample 2 are shown in Fig. 6.39.

Table 6.3  A comparison between theoretical and measured values of stiffness values for each RF MEMS switch.

<table>
<thead>
<tr>
<th>Membrane I.D.</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
<th>(E)</th>
<th>(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane Size (µm)</td>
<td>100</td>
<td>200</td>
<td>100</td>
<td>200</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Suspension Type</td>
<td>Meander</td>
<td>Meander</td>
<td>Straight</td>
<td>Straight</td>
<td>Spiral</td>
<td>Spiral</td>
</tr>
<tr>
<td>Sample 1, k (N/m)</td>
<td>1.74</td>
<td>1.27</td>
<td>4.49</td>
<td>2.87</td>
<td>5.02</td>
<td>0.51</td>
</tr>
<tr>
<td>Sample 2, k (N/m)</td>
<td>2.75</td>
<td>1.60</td>
<td>18.1</td>
<td>4.49</td>
<td>10.1</td>
<td>0.44</td>
</tr>
<tr>
<td>Experimental Average, k (N/m)</td>
<td>2.25</td>
<td>1.44</td>
<td>11.3</td>
<td>3.68</td>
<td>---</td>
<td>0.44</td>
</tr>
<tr>
<td>FEM Simulations, k (N/m)</td>
<td>3.63</td>
<td>2.35</td>
<td>15.6</td>
<td>12.5</td>
<td>0.67</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Fig. 6.39  A plot of the applied load versus displacement of the film for membranes A to F (sample 2).

In addition, the load-deflection characteristics of the membranes are measured under two more dwell-time conditions (i.e. the cantilever is held against the switch for a fixed period of time). The dwell conditions are described as follows:
1. The dwell time equals zero. (All membranes are tested, as in Table 6.3)
2. The dwell time is increased in increments up to 200 s. (Only membranes A and C are tested).
3. The dwell time is held at 200 s, and the measurements are ‘cycled’ 400 times. (Only membranes A and C were tested).

Table 6.3 shows a comparison between stiffness in the 100 µm meander and straight suspensions for all the above cases. From this table, we make the following observations:

1. Loading appears to briefly increase the membrane stiffness (i.e., from 1.74 to 3.27 N/m in the 100 µm meander membrane); this may be due to some work hardening in the suspension.
2. Membrane stiffness has degraded after a relaxation time of approximately one day. The rate of degradation is unknown and needs to be investigated further.
3. Overall, the 100 µm straight membrane has a larger degradation in stiffness (4.49 to 2.74 N/m) than the 100 µm meander suspended membrane (1.74 to 1.58 N/m). This may have been due to differences in their relaxation times.
4. Stiffness does not appear to be significantly influenced by the number of cycles (up to 400 in this case), although some degradation was measured in the 100 µm meander suspended membrane beyond 100-150 cycles. This degradation was not observed in the 100 µm straight membrane. In both membranes, however, the membrane stiffness was most sensitive up until approximately the first 10 cycles. Beyond 10 cycles, the stiffness remained constant.

### Table 6.4
Stiffness values of 100 µm RF MEMS switches, A and C (sample 1).

<table>
<thead>
<tr>
<th>Membrane Description</th>
<th>k (N/m): Ramp: 0 s</th>
<th>k (N/m): Post Incremental Loading</th>
<th>k (N/m): Pre Cyclic Loading</th>
<th>k (N/m): Post Cyclic Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meander</td>
<td>1.74</td>
<td>3.27</td>
<td>1.60</td>
<td>1.58</td>
</tr>
<tr>
<td>Straight</td>
<td>4.49</td>
<td>8.2</td>
<td>3.77</td>
<td>2.74</td>
</tr>
</tbody>
</table>
6.8 Summary and Conclusions

We developed a ductility measurement system which employed an optical-lever method for determining the displacement of a freestanding film under load. This technique can apply load in the micro-newton to milli-newton range by displacement control. Our system demonstrates that challenges such as reduction of probe size, and accurate control and measurement of the motion of the probe relative to the sample can be overcome.

The fabrication of suitable free-standing nanofilms for test structures poses an even more difficult challenge. We demonstrated two different classes of technique. The first class employs the infilling of openings in metal templates with a soluble resin. The second class of techniques employs silicon microfabrication techniques.

We measured the stiffness of a range of RF-MEMS switches using a commercial AFM microscope operating in nanoindentation mode. In this study, we measured the stiffness of a range of RF-MEMS devices. In general, our experimental results showed good agreement with FEM simulations carried out at Tyndall National Institute.
6.9 References

7
Conclusions and Future Work

7.1 Conclusions
This thesis presents an *in-situ* study of the interrelationship of intrinsic stress and morphology in electrodeposited copper nanofilms. We have combined AFM imaging with high-resolution measurements of stress during electrodeposition of copper. We also developed and constructed a ductility measurement system based on Professor Nakahara’s design and implemented it at the nanoscale for copper films.

7.1.1 Determination of Local Stress from Force-Thickness Data
Using a substrate curvature method to monitor stress *in situ*, we showed that the time variation of stress is small after interruption of electrodeposition in acidic CuSO$_4$. This shows conclusively that the inherent time-variation of stress due to relaxation effects is small on the time-scale of electrodeposition under these conditions. Thus, the rate of variation of tensile force with thickness can be used to obtain a valid estimate of local stress $\sigma_h$ as a function of thickness $h$. In other words, the first derivative with respect to $h$ of the experimental $F/w$ curve gives a valid plot of $\sigma_h$ versus $h$. We further showed that our time-series of $F/w$ and simultaneous current measurements provided an adequate data-set to generate reliable and reproducible plots of stress $\sigma_h$ versus thickness $h$.

7.1.2 Stress and Morphology in the Absence of Additives
We used this methodology to measure stress during electrodeposition at overpotentials of -125, -160 and -200 mV. While the stresses generated in the very early stages of deposition were not determined in this study, stress was always found to be tensile under the conditions of our experiments on the thickness scale examined. The evolution of stress with increasing film thickness followed a similar
pattern at all potentials investigated. The tensile stress eventually reached a relatively constant (plateau) value above a certain thickness. The measured plateau values of stress increased with increasingly negative overpotential, ranging from 25 to 45 MPa for -125 to -200 mV.

At the early stages of deposition, stress increased in the tensile direction with increasing film thickness at all overpotentials. In experiments at -160 mV and -200 mV, the stress peaked before decreasing to the plateau value. The thickness at which this occurred was typically > 50 nm. The peak stress was higher at -200 mV than at -160 mV; at -125 mV there was no significant peak, but rather the stress simply increased to a plateau value.

The increase in tensile stress in the early stages coincided with the coalescence of protruding surface features observed by in-situ AFM. AFM also shows that, at higher potential, islands are smaller and occur at higher density. This suggests a higher boundary volume as the islands coalesce and would explain the higher stress observed at higher potentials.

At the higher potentials (-160 mV and -200 mV), the decrease in local stress after the peak may be explained by a decrease in the rate of grain-boundary formation. Evidence for this is provided by the AFM which shows a less rough surface at higher thicknesses at these potentials as compared to -125 mV.

7.1.3 Effects of Chloride and PEG

When chloride was added to the electrolyte, tensile stress was significantly reduced. This reduction was greater at lower potentials. The AFM images showed that the films formed in the presence of chloride were significantly rougher than their counterparts without additives. Thus, roughness directly correlates with stress: as roughness increases, stress decreases as was observed also for additive-free deposition.

PEG alone has no significant effect on stress. However it significantly enhances stress reduction in the presence of chloride. The presence of these two additives in combination produced a flat surface with scattered large pyramidal structures.
Deposition and corrosion experiments determined that these features grow along the plane of the facets.

### 7.1.4 Ductility Testing of Nanofilms

We showed that the Nakahara method of ductility testing can be applied to films of nanoscale thickness. The measurement system which we developed employs an optical-lever method for determining the displacement of a freestanding film under load. This technique can apply load in the micro-newton to milli-newton range by displacement control. Our system demonstrates that challenges such as reduction of probe size, and accurate control and measurement of the motion of the probe relative to the sample can be overcome.

The fabrication of suitable free-standing nanofilms for test structures poses an even more difficult challenge. We demonstrated two different classes of technique. The first class is based on the infilling of openings in metal templates with a soluble resin. The second class is based on silicon micro-fabrication techniques.

### 7.1.5 Force-Displacement Measurement of RF-MEMS Switches

We demonstrated that a commercial AFM microscope can be used in the nanoindentation mode to generate stress-strain data for RF-MEMS switches. In this study, we measured the stiffness of a range of RF-MEMS devices. In general, our experimental results showed good agreement with FEM simulations.

### 7.2 Future Work

The combination of *in-situ* AFM and in-situ stress measurements described in this thesis as well as the methodology of estimating load stress by numerical differentiation of force-thickness curves are both very powerful techniques that can be extended to investigate other aspects of stress in thin films. In this section, we recommend several important areas in which our work can be carried forward.
7.2.1 Island Growth in the Presence of Chloride

An overlay of AFM line scans in Fig. 7.1 shows the evolution of a copper island during electrodeposition in the presence of chloride additive.

At an average (coulometric) thickness of 29 nm, the lateral width and vertical height of the copper island are 400 nm and 100 nm, respectively suggesting the island has grown more quickly in the lateral direction. The surface of the island has a rounded shape which changes as more copper is electrodeposited. At an average thickness $h_c = 112$ nm, the island grows at the approximately the same rate in the vertical and lateral directions. We clearly see that the surface of the island has two large flat surface features (or facets) perpendicular to the direction of the arrows. As more copper is electrodeposited the island continues to grow laterally and vertically and facets become more prominent. The island makes contact with a smaller neighbouring island at 196 nm thickness. At 239 nm thickness, the large island grows over the smaller island and in this region another facet develops. The island continues to grow along the directions of the two main facets.

These line scans show that chloride has the effect of causing preferential growth along specific planes or facets. The shape of a copper island is likely to depend on the energy of the deposited film, and this energy is determined by a number of factors including overpotential.

Examining the growth of an island at a lower overpotentials, as shown in Fig. 7.2, we can see that in the first scan ($h_c = 14$ nm) two neighbouring islands are at the onset of
coalescence. The gap between the two islands is filled in (48 nm) and faceting has appeared. The island grows along the directions of the facets as indicated by the arrows in the figure. However, faceting at -125 mV is not as clearly defined as at -160 mV. The results presented in this section are a preliminary study which will be extended to examine the growth mechanisms of copper deposits both with and without additives.

![AFM line scan of copper island growth during electrodeposition at -125 mV in the presence of 3 ppm chloride. The arrows indicate the direction of faceting. The aspect ratio of the graph is 1:1.](image)

**Fig. 7.2** AFM line scan of copper island growth during electrodeposition at -125 mV in the presence of 3 ppm chloride. The arrows indicate the direction of faceting. The aspect ratio of the graph is 1:1.

### 7.2.2 Mathematical Model and Experimental Investigation of Stress and Morphology

Our work could also be enhanced with the use of mathematical modelling. We recommend a multi-approach study of the early stages of film formation (i.e. nucleation and coalescence of electrodeposited copper). This study would include real-time AFM and stress measurements augmented with mathematical modelling.

### 7.2.3 Other Recommendations for Future Work

Other areas to which the work in this thesis could be extended include study of the early stages of deposition at low overpotentials. One challenge in electrodepositing at low overpotentials is achieving reliable control the potential. To target industrial applications, it is important to investigate higher concentrations of CuSO₄ and H₂SO₄ typical of commercial baths. To further characterize the stress-relieving properties and the effect of additives on microstructure, we need more detailed studies of additive concentrations. Adding additives during deposition could provide an
additional tool with which to investigate the mechanism of additive effect. The system for remote addition of electrolyte which we have implemented with our \textit{in-situ} AFM technique would be particularly useful in such an investigation.
Appendices

A.1 AFM Images with Chloride Additive

In this section, we present AFM images of the surface morphological evolution during copper electrodeposition on gold at overpotentials of -125 mV, -160 mV and -200 mV (Cu/Cu$^{2+}$). We also present corresponding line scans at each potential.

![AFM Images](image)

Fig. A.1 Sequence of AFM images obtained *in situ* during (0-149 s) of electrodeposition in (a)-(b) the presence of 3 ppm chloride and (c)-(d) the absence of additives after a potential step to -125 mV at 0 s on the time axis shown. Images (a) and (b) are taken from Fig. 4.8, and (c) and (d) from Fig. 5.9. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
Fig. A.2 Sequence of AFM images obtained in situ during (150-319 s) electrodeposition in (a)-(b) the presence of 3 ppm chloride and (c)-(d) the absence of additives after a potential step to -125 mV at 0 s on the time axis shown. Images (a) and (b) are taken from Fig. 4.8, and (c) and (d) from Fig. 5.9. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
**Fig. A.3** AFM line scans taken at L1, L2, L3 and L4 in the absence (Fig. 4.8) and presence (Fig. 5.9) of 3 ppm chloride.

**Fig. A.4** Current-time curves in the presence of 3 ppm chloride using interrupt method at -125 mV measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (c) correspond to the times during which each AFM image was captured.
Fig. A.5  Sequence of AFM images obtained in situ during electrodeposition after a potential step to -125 mV at 0 s on the time axis shown. Images (a), (b) and (c) follow sequentially at the times corresponding to AFM(a), AFM(b) and AFM(c) in Fig. A.4. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.

To observe the effect of chloride on the surface morphology during open circuit and resumed deposition, we carried out AFM measurements under similar experimental
Fig. A.6 Sequence of AFM images obtained in situ during (0-149 s) electrodeposition in (a)-(b) the presence of 3 ppm chloride and (c)-(d) the absence of additives after a potential step to -160 mV at 0 s on the time axis shown. Images (a) and (b) are taken from Fig. 4.11, and (c) and (d) from Fig. 5.12. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
conditions. Fig. A.4 shows a plot comparing the time dependence of current (and coulometric thickness $h_c$) in the AFM and stress cells in the presence of chloride.

To observe the effect of chloride on the surface morphology during open circuit and resumed deposition, we carried out AFM measurements under similar experimental conditions. Fig. A.7 shows a plot comparing the time dependence of current (and coulometric thickness $h_c$) in the AFM and stress cells in the presence of chloride.

![Graph showing current-time curves in the presence of 3 ppm chloride using interrupt method at -160 mV measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (c) correspond to the times during which each AFM image was captured.](image)

**Fig. A.7** Current-time curves in the presence of 3 ppm chloride using interrupt method at -160 mV measured in (i) AFM cell and (ii) stress cell. (iii) The coulometric thicknesses from these curves are shown in (iii) and (iv) respectively. Regions (a) to (c) correspond to the times during which each AFM image was captured.

A sequence of AFM images taken during deposition at -125 mV, open circuit and resumed deposition obtained in the presence of chloride is shown in Fig. A.5. We did not observe any significant change in the surface of the deposit at open circuit.
Fig. A.8  Sequence of AFM images obtained in situ during electrodeposition after a potential step to -160 mV at 0 s on the time axis shown. Images (a), (b) and (c) follow sequentially at the times corresponding to AFM(a), AFM(b) and AFM(c) in Fig. A.7. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
Fig. A.9 Sequence of AFM images obtained in situ during (0-149 s) electrodeposition in (a)-(b) the presence of 3 ppm chloride and (c)-(d) the absence of additives after a potential step to -200 mV at 0 s on the time axis shown. Images (a) and (b) are taken from Fig. 4.16, and (c) and (d) from Fig. 5.17. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
To observe the effect of chloride on the surface morphology during open circuit and resumed deposition, we carried out AFM measurements under similar experimental conditions. Fig. A.10 shows a plot comparing the time dependence of current (and coulometric thickness $h_c$) in the AFM and stress cells in the presence of chloride.

A sequence of AFM images taken interrupted deposition at -200 mV is shown in Fig. A.11. We did not observe any significant change in the surface of the deposit at open circuit.
Fig. A.11 Sequence of AFM images obtained in situ during electrodeposition after a potential step to -200 mV at 0 s on the time axis shown. Images (a), (b) and (c) follow sequentially at the times corresponding to AFM(a), AFM(b) and AFM(c) in Fig. A.10. The coulometric thickness $h_c$ at the beginning and end of each scan is shown.
A.2 Freestanding Film Fabrication

A.2.1 TEM Grid Support

This section describes how a TEM structure was used to support freestanding Au nanofilms. An Athene 150-mesh Cu TEM (G201) grid was the chosen structure for supporting Au nanofilms. A schematic of the process is shown in Fig. A.12. A 10-mm-diameter aluminium stub is grinded/polished flat using SiC grinding paper using SiC paper (P300, P600, P1200). The aluminium stub supports the TEM grid during PMMA deposition, polishing and nano-film deposition. Toluene with 2% PMMA (Polymethyl Methacrylate) was prepared at 100K. Two or three drops of the solution were placed on the polished aluminium stub and the TEM grid was immediately placed on top. As the toluene evaporated, the grid adhered to the stub.

The toluene-PMMA solution was placed over the stub entirely covering the TEM grid. The PMMA was cured in air at room temperature followed by 30 seconds curing on a hot plate. The copper TEM grid was tested for electrical continuity using a multimeter to ensure adequate coverage of PMMA (Non-conductive). The PMMA was polished back to the copper TEM grid in a series of steps using a (Struers) spin polisher with 9 µm “MetaDi” monocrystalline diamond suspension. The PMMA was polished for about 2-3 minutes, rinsed, dried and finally checked for electrical continuity. These 4 steps (polish/rinse/dry/continuity) were repeated until electrical continuity was not detected. Polishing times were reduced during approach to the PMMA-stub interface to avoid over-polishing the grid.
A 100 nm-thick gold film was evaporated on top of the copper TEM grid using the Edwards Coating System E306A under UHV conditions. The quality of the gold film was visually inspected using SEM. The films had low yield (< 10 %) and typically exhibited delamination and cracking especially at the edge of the grid holes, as shown by SEM images in Fig. A.13.

![Fig. A.13 Freestanding 100 nm-thick evaporated Au film on top of a Cu TEM grid. The grid-hole diameter and line width are measured at 136 µm and 31 µm respectively. Images are captured at magnifications (a) 150X, (b) 400X and (c) 450X.](image)

**A.2.2 Perforated Copper Foil Support**

An alternative approach to fabricating freestanding copper nanofilms was attempted. Copper nanofilms, 100 to 600 nm thick, were evaporated on 250 µm-thick copper substrates. A copper foil substrate (0.25 mm thickness) was perforated with holes whose diameters range from 400 to 1600 µm. The holes were filled with lacquer from the back-side of the substrate, and the lacquer was cured in air. Copper was evaporated directly onto the back-side of the substrate. After evaporation, the lacquer was chemically removed leaving freestanding copper metal films.
There are several factors that must be considered when drilling holes. Such factors include the material being drilled, the strength of the drill-bit and its dimensions, the speed of the drill and the forces exerted on the substrate by the drill-bit. The ductile nature of copper required a slow and gentle drilling rate. In addition debris was removed regularly and the drill bit was lubricated using oil or water. A pilot hole, $\frac{3}{4}$ the diameter of the final hole, was drilled preventing strain on the drill bit and reducing drilling time. The substrate used was a 250 µm thick copper foil. A typical template used is shown in Fig. A.14. Holes were drilled with diameters 0.4 mm to 1.6 mm. A narrow file was used to remove unwanted burrs and reduce surface roughness on the walls of the hole. Both sides of the hole were polished using SiC grit paper (P300, P600 & P1200). The quality of the holes was visually inspected using an optical microscope.

A standard bottle of nail varnish / lacquer was used to fill holes. The holes were filled with lacquer using two techniques. Technique (1) describes how lacquer was applied to the front-side of a sample 30 x 30 mm substrate and polished back using a series of polishing steps. Technique (2) describes how lacquer was applied to the backside of the substrate but without any polishing steps.

**Technique 1:** A thin layer of lacquer was applied to the backside of a perforated copper substrate and cured in air at room temperature for 15-20 minutes. The backside of the substrate was applied with quick-dry epoxy, making sure not to cover the holes, and adhered to a flat aluminium polishing block. The front-side of the substrate was applied with a thin layer of lacquer and cured in air at room temperature. Once the top lacquer layer was air-cured, the substrate was oven-cured.
at about 80 °C for 1 hour. The lacquer was polished back using a Struers polisher in a series of polishing steps with SiC paper (P600 and P1200) and followed by a 9 µm diamond polishing suspension. If the polishing block is too large, there is a high probability of a non-uniform polish from centre to edge. It is better to use a small flat polishing block. The sample was visually inspected post-polish, post-evaporation and post-lacquer removal using optical microscopy. Fig. A.15(a) shows optical images of the lacquer-holes post polishing. Copper nanofilms, 500 nm in thickness, were evaporated using the Edwards Coating System E306-A. Fig. A.15(b) shows optical images of the copper nanofilms post evaporation. A selection of solvents including methanol, ethanol, iso-propanol, acetone and ethyl acetate were tested for their effectiveness at dissolving the lacquer. In order of effectiveness, ethyl acetate was the most aggressive, followed by acetone. The most effective solution at removing lacquer was a 1:1 mixture of ethyl acetate and ethanol. Fig. A.15(c) shows optical images of freestanding copper nanofilms, i.e. post removal of lacquer. Films that have had the underlying lacquer removed exhibited damage especially at the edges of the holes. This may have been due to the nature of the polishing lines or the cleaning process itself. To identify whether the lacquer removal or polishing process is the root cause for damage in films, an alternative technique without a polishing step was used.

**Technique 2:** This technique was similar to technique 1, but it did not have a polishing sequence. Fig. A.16(a) shows optical images of the lacquer-holes post application. Copper nanofilms, 500 nm thick, are evaporated using the Edwards Thermal Evaporator. Optical images of the of the lacquer film (a) post lacquer application, and the copper films (b) post evaporation, and (c) post lacquer removal are shown in Fig. A.16.

Technique 2 has a significant improvement in yield over technique 1. Technique 2 is used to fabricate all subsequent freestanding copper nanofilms. The lacquer layer profiled using a stylus profilometer, seen in Fig. A.17, shows the dried lacquer is not level with the copper surface. In fact, it dips as low as 80 µm the surface and its base is quite level, within 10-20 µm. These films are not the ideal geometry for supporting copper nanofilms. However, these films exhibit a robustness that is not possible to fabricate using technique 1.
Fig. A.15 Optical images of (a) lacquer post lacquer polish, (b) copper nanofilms post evaporation and
(c) copper nano-films post lacquer removal

Fig. A.16 Optical images of (a) lacquer post lacquer application, (b) copper nanofilms post evaporation
and (c) copper nano-films post lacquer removal.
Freestanding copper films with thickness 300, 400 and 500 nm after the removal of the underlying sacrificial layer are shown in Fig. A.18. The 600 nm-thick copper films was capable of maintaining integrity after processing. However at thickness 400 and 300 nm, the films had a substantial amount of slack. In addition the films may be more vulnerable to processing conditions at lower thickness, as expected.

Fig. A.18  Optical images of freestanding copper films with thickness 300, 400 and 600 nm after removal of the underlying sacrificial layer.

A.2.3  Silicon Micro-Fabrication of Metal Nanofilms

Freestanding circular copper, gold and aluminium nanofilms were fabricated using state-of-the-art silicon fabrication techniques. This work was performed by Tyndall’s MEMS facility in Co. Cork, Ireland and was funded by the National Access Program, (NAP-333). Circular membranes were fabricated on 10 by 10 mm die. These circular membranes ranged between 100 and 1000 µm in diameter and 100 to 500 nm in thickness.
The general fabrication method is described as follows. Circular holes were etched through the back side of a silicon wafer to an end-stop layer. These membranes were metalized and subsequently a protective polymer film was spun-on. The stop layer was removed. The wafers were diced and the polymer layer was removed, leaving freestanding metal membranes.

The circular holes were created by etching through silicon wafers. The method of choice for this was Deep Reactive Ion Etching (DRIE). The DRIE is an anisotropic etch process that uses a pulsed process of 1) an etch step using a SF6 plasma and 2) a passivation step using C4F8 plasma that forms a polymer layer on the side walls. Using DRIE has some disadvantages. A vacuum was used to keep the wafer against the cooling chuck. Therefore, the membranes need to be strong enough to withstand the vacuum. Since Tyndall’s DRIE tool was installed in a CMOS compatible fab, materials such as gold and copper were not allowed in this tool for risk of contamination to other wafers. Finally, the etch rate was dependent on the ratio of the feature to be etched (i.e. smaller holes etched slower than larger holes. If the aspect ratio is stated as diameter over depth, a large aspect ratio has a lower etch rate as it is limited by transport of etching species to and from the hole.

During the DRIE process Tyndall found that the larger membranes were susceptible to breaking. To avoid breaking the membranes, the process wafer was mounted on a second wafer, breaking the vacuum. This did affect the cooling of the process wafer and therefore the etch rate.

The aspect ratio dependent etch resulted in significant thinning of the silicon oxide stop layer before the small diameter holes were etched. Fig. A.19 shows measurements of etch depth as a function of hole diameter for typical processed wafer. All 1000, 700 and 500 μm holes were etched completely, while the 400 μm holes were partially etched.
A stop layer needs to have good selectivity to silicon in the DRIE, and to the metals in the subsequent etch step. Silicon oxide is a suitable material as it has good selectivity in the DRIE process and can be removed without affecting the metal layer. The disadvantage with silicon oxide as an etch stop is that it is deposited at high temperature. The difference in coefficient of thermal expansion results in a stressed layer at room temperature. This stressed layer will cause deformation of the membrane once the underlying material is etched.

The silicon oxide was grown on the wafer by thermal oxidation. This process forms a silicon oxide layer on both sides of the wafer. The DRIE process requires a hard mask on the back side of the wafer with circular features. The silicon oxide on the back side of the wafer was used as a hard-mask.

Copper and aluminium layers were sputtered on a thin Ti adhesion layer. Gold was e-beam evaporated with a thin Cr adhesion layer.

The most challenging step in the process was the dicing of the wafers. Dicing uses a jet of water to cool the diamond blade and this jet may be strong enough to break the membranes. To protect the films during handling and dicing, a polyimide layer was

Fig. A.19 DRIE etch depth as a function of hole diameter in a silicon wafer with silicon oxide etch stop.
spun on the wafer creating a thin flexible film. If too many membranes have popped during processing, it would not be possible to spin on the polymer. Instead, the polymer layer could be sprayed on but this method doesn’t provide good thickness uniformity. The polymer layer was removed by plasma ashing. The ashing process etches polymers very quickly and can easily be performed after dicing at chip level.

A wet etch was not used because etch rate is difficult to control as it can result in sideways under-etching of holes. In plasma etch processes, the holes limit the transport of etch-species and etch-products to and from the stop layer. The silicon oxide stop layer was removed with a Reactive Ion Etch (RIE) with a plasma of CF$_4$ and CHF$_3$. This plasma has good selectivity between oxide and aluminium, gold and copper. However, the oxide was removed using a timed etch and slight over-etching in the metal was expected.

The fabrication process is shown schematically in Fig. A.20 and the steps are detailed in Table A.1.

![Fig. A.20](image)

**Fig. A.20** A schematic representation of the process to fabricate freestanding metal membranes. (Not to scale).

**Table A.1** Process flow for the fabrication of freestanding metal membranes (NAP-333 Tyndall)

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Wafer Side</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thermal oxidation of silicon to form silicon oxide</td>
<td>Both</td>
<td>3 µm</td>
</tr>
</tbody>
</table>
2 Spin photoresist and expose the mask 1: ‘Alignment marks’
   Front 8.7 µm
3 Partial plasma etch front oxide; remove resist
   Front 2 µm
4 Spin photoresist and expose with mask 2: ‘Etch holes’
   Back 8.7 µm
5 Plasma etch back oxide; remove resist
   Back 3 µm
6 DRIE silicon
   Back 525 µm
7 Sputter or e-beam-evaporate metal on oxide membranes
   Front 100 and 500 nm
8 Spin polyimide for protection
   Front 5 µm
9 Reactive Ion Etch oxide
   Back 8.7 µm
10 Dice wafers; plasma ash of polyimide
    Front 5 µm

Each wafer was segmented into 10 by 10 mm die. Each die contained an array of different sized holes. The die layout was shown in Fig. A.0.21. The number of holes per die was determined by the following relationship:

\[ N = \frac{1}{F} \left( \frac{X}{d} - 1 \right) + 1 \quad \text{A.1} \]

where \( X \) is the active length of the chip, \( d \) is the hole diameter and \( F \) is the centre-centre hole spacing factor.

The centre-centre hole spacing, \( k \) is expressed as:

\[ k = F \cdot d \quad \text{A.2} \]
Fig. A.0.21 A typical die layout containing N holes with diameter, d, and centre-centre hole spacing, k, where X is the active length of a chip with full length, L.

The chip layout is shown in Fig. A.22. Each wafer contained a 5 mm periphery region leaving a maximum of 52 full dice available for testing. The number of holes per chip and per wafer is listed in Table 6.
Fig. A.22 Proposed wafer layout containing die with holes size: (■) 1.0 mm, (▲) 0.7 mm, (■) 0.5 mm, (■) 0.4 mm, (▲▲) 0.3 mm, (■) 0.2 mm and (■) 0.1 mm.

Table A.2 Distribution of hole sizes per chip and per wafer calculated using Equation A.1.

<table>
<thead>
<tr>
<th>Hole Diameter (mm)</th>
<th>No. Chips</th>
<th>No. Holes per Chip</th>
<th>No. Holes per Wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>12</td>
<td>9</td>
<td>108</td>
</tr>
<tr>
<td>0.7</td>
<td>12</td>
<td>9</td>
<td>108</td>
</tr>
<tr>
<td>0.5</td>
<td>8</td>
<td>25</td>
<td>200</td>
</tr>
<tr>
<td>0.4</td>
<td>6</td>
<td>36</td>
<td>216</td>
</tr>
<tr>
<td>0.3</td>
<td>6</td>
<td>64</td>
<td>384</td>
</tr>
<tr>
<td>0.2</td>
<td>4</td>
<td>144</td>
<td>576</td>
</tr>
<tr>
<td>0.1</td>
<td>4</td>
<td>529</td>
<td>2116</td>
</tr>
</tbody>
</table>
A.3 Bending of a Beam

Consider a beam of uniform rectangular cross section of thickness $h$ that is bent in a circular arc due to an internal/external force as shown in Fig. A.23. Let the arc AB represent the mid-plane in the beam. The length of AB equals the product of the radius of curvature $R$ and the bending angle $\theta$ (in radians).

$$AB = R\theta$$  \hspace{1cm} A.3

Fig. A.23 A beam with thickness $h$ bending in a circular arc at an angle $\theta$ where $R$ is the radius of curvature and $z$ is the distance of an arc CD from the mid-plane AB.

Choosing another plane in the beam, CD, the radius of curvature is $R + z$. The length of CD is

$$CD = (R + z)\theta$$  \hspace{1cm} A.4

Strain $\varepsilon$ is defined as the change in length per unit initial length:
where \( L \) is the original length and \( \Delta L \) is the change in length.

Taking \( AB \) as the original length \( L \), the strain \( \varepsilon \) in arc CD is

\[
\varepsilon = \frac{CD - AB}{AB} = \frac{(R + z)\theta - R\theta}{R\theta} = \frac{z}{R} \quad \text{A.6}
\]

In this case, strain is a function of \( R \). Young’s modulus \( E \) is related to stress \( \sigma \) and direct strain \( \varepsilon \) for an elastic material as follows

\[
E = \frac{\sigma}{\varepsilon} \quad \text{A.7}
\]

and so,

\[
\sigma = E\varepsilon \quad \text{A.8}
\]

From Equation A.6 and Equation A.7, if follows that stress also varies along the length of the beam depending on the radius of curvature. Since the film stress is related to the position above or below the mid-plane AB, we get

\[
\sigma(z) = \frac{Ez}{R} \quad \text{A.8}
\]

where \( z = 0 \) is the neutral axis where tensile and compressive forces cancel. (Note: The neutral axis is the same as the mid-plane for a homogeneous material.)

Consider a thin transverse slice of the beam (shown in light grey in Fig. A.23) divided into infinitesimally small elements (shown in red and green in Fig. A.24). The width of the beam is \( w \). Any given element within the beam is at a distance \( z \) from the neutral axis, and has a cross-sectional area \( dA \) (highlighted in green).
Fig. A.24 Thin transverse slice taken from Fig. A.23 divided into infinitesimally small elements of area \( dA \) (highlighted by the green area) at a distance \( z \) from the neutral axis.

By integrating over these elements from the bottom to the top of the beam, the force acting on the entire cross-section of the beam is expressed as a scalar quantity of

\[
F = \int_{bottom}^{top} \sigma dA
\]

Substituting Equation A.8, we get

\[
F = \frac{E}{R} \int_{bottom}^{top} zdA
\]

The compressive and tensile forces in the beam produce a bending moment \( M \) about the neutral axis. The bending moment within the entire beam is expressed as

\[
M = Fz = \int_{bottom}^{top} zdF = \int z \frac{Ez}{R} dA = \frac{E}{R} \int z^2 dA
\]
\[ M = \int_{\text{bottom}}^{\text{top}} z \, dF = \int_{\text{bottom}}^{\text{top}} z \frac{Ez}{R} \, dA \quad \text{A.11} \]

Substituting for \( dA = wdz \),

\[ M = \frac{Ew}{R} \int_{\text{bottom}}^{\text{top}} z^2 \, dz \quad \text{A.12} \]

Since \( I = \int_{\text{bot}}^{\text{top}} z^2 \, dA \) is known as the second moment of area, Equation A.12 can be expressed as

\[ M = \frac{EI}{R} \quad \text{A.13} \]

By integrating from the neutral axis to the top of the beam at \( z = h/2 \), the total bending moment produced in the beam (which is twice that in half of the beam) is expressed as

\[ M = \frac{2Ew}{R} \int_{0}^{h/2} z^2 \, dz = \left( \frac{2Ew}{R} \frac{z^3}{3} \right)^{h/2}_0 \]

\[ = \left( \frac{2Ew}{R} \frac{h^3}{2} \right) \frac{3}{3} \]

Therefore, we get

\[ M = \frac{Ewh^3}{12R} \quad \text{A.15} \]

where \( w \) is the width of the sample.

The use of Equation A.15, which describes the moment of a bending beam, is applied in Section 1.2.2 for the bending of a bi-metallic strip. This theory leads to Stoney’s equation which is used for determining the intrinsic stress of a thin metal film. We will next, however, describe the bending of a beam fixed at one end (as this principle applies to our ductility measurement system).
A.4 Bending of a Beam Fixed at One End

A rectangular beam fixed at one end is shown in Fig. A.25(a) with length \( l \), width \( w \), and thickness \( h \). Fig. A.25(b) shows a transverse cross section of the cantilever showing a thin element of thickness \( \Delta h \) at a distance \( z \) from the neutral axis.

The second moment of area (see Equation A.12) of a rectangular beam is determined as:

\[
I = w \int_{-h/2}^{h/2} z^2 \, dz = \frac{w}{3} \left( \frac{h^3}{2} \right)
\]

Fig. A.25  (a) Dimensions of cantilever beam with length \( l \), width \( w \), and thickness \( h \). (b) Cross section of the beam.
Fig. A.26 The free-end position of the cantilever is applied with a force $F$ causing it to deflect a distance $y_{\text{max}}$ in the $y$-direction, where $\alpha$ is the angle of deflection.

Consider now the cantilever beam of length $l$ deflected (by a force acting upward at a distance $x$ from the fixed end).

The curvature of any curve $y(x)$ is given by

$$\frac{1}{R} = \frac{d^2 y/dx^2}{\left[1 + (dy/dx)^2\right]^{3/2}}$$

For small angles, the denominator is equal to 1

$$\frac{1}{R} = \frac{d^2 y}{dx^2}$$  \hspace{1cm} A.17

We can neglect the weight of the beam and only consider the upward force $F$ at the free end of the beam.

$$M(x) = F(l - x)$$  \hspace{1cm} A.18

where $(l-x)$ is the distance over which the force is acting, and where $x$ is the position of the applied force with respect to the free-end of the beam.
From Equation A.13, we get

$$\frac{1}{R} = \frac{M}{EI}$$  \hspace{1cm} \text{A.19}

Combining Equations A.17 and A.19, we get

$$\frac{d^2y}{dx^2} = \frac{1}{R} = \frac{M}{EI} = \frac{F(l-x)}{EI}$$  \hspace{1cm} \text{A.20}

Through integration we get,

$$\frac{dy}{dx} = \frac{F}{EI} \left( lx - \frac{x^2}{2} \right)$$

and

$$y = \frac{F}{EI} \left( lx - \frac{x^3}{2} + \frac{x^3}{6} \right) = \frac{Fx^2}{6EI} (3l-x)$$

Therefore, the deflection of a cantilever at any point is

$$y(x) = \frac{Fx^2}{6EI} (3l-x)$$  \hspace{1cm} \text{A.21}

At $x = l$, the deflection at the fixed-end of the cantilever is expressed as

$$y(l) = \frac{Fl^2}{6EI} (3l-l) = \frac{Fl^3}{3EI}$$  \hspace{1cm} \text{A.22}

The displacement at the end of the beam is proportional to $l^3$. To determine the angle of deflection of the beam:

Since at the fixed end of the beam, $l = 0$

$$M(x) = -Fx$$  \hspace{1cm} \text{A.23}

$$\frac{d^2y}{dx^2} = -\frac{Fx}{EI}$$

$$\frac{dy}{dx} = -\frac{Fx^2}{2EI} + C_1$$
\[ y = -\frac{Fx^3}{6EI} + C_1x + C_2 \tag{A.24} \]

Applying the boundary conditions at \( x = l \), (i.e. \( dy/dx = 0 \)) we get

\[
0 = -\frac{Fl^2}{2EI} + C_1
\]

\[ C_1 = \frac{Fl^2}{2EI} \]

At \( x = l, y = 0 \)

\[
0 = -\frac{Fl^3}{6EI} + \frac{3Fl^3}{6EI} + C_2 \Rightarrow 0 = -\frac{Fl^3}{6EI} + \frac{3Fl^3}{6EI} + C_2
\]

\[ C_2 = -\frac{2Fl^3}{6EI} \]

Substituting \( C_1 \) and \( C_2 \) into Equation A.24, we get

\[
y = -\frac{Fx^3}{6EI} + \frac{3Fl^2}{6EI}x - \frac{2Fl^3}{6EI} \]

\[
y = \frac{F}{6EI}[-x^3 + 3l^2x - 2l^3] \tag{A.25}
\]

\[
\frac{dy}{dx} = -\frac{Fx^2}{2EI} + \frac{Fl^2}{2EI} = \frac{F}{2EI}(l^2 - x^2) \tag{A.26}
\]

At the free-end where \( x = 0 \), we get maximum deflection of the cantilever

\[ \gamma_{\text{max}} = \frac{Fl^3}{3EI} \tag{A.27} \]

For small angles, the slope at this point is:

\[
\frac{dy}{dx} = \tan(\alpha) \approx \alpha \tag{A.28}
\]

where \( \alpha \) is the angle of deflection. From Equation A.26,

\[ \alpha = \frac{Fl^2}{2EI} \tag{A.29} \]

We can experimentally determine the angle of deflection of the cantilever using a laser beam deflection method (see Fig. A.27) where:
\[ \beta = 90^\circ - \alpha \]

\[ \frac{\theta}{2} = 90^\circ - \beta = 90^\circ - 90^\circ + \alpha \]

\[ \Rightarrow \theta = 2 \alpha \]

where \( \theta \) is the double-angle or the angle of deflection of the laser.

**Fig. A.27** The determination of the angle of deflection of a cantilever beam using a laser deflection method. Since the laser deflects at twice the angle of \( \alpha \), it is referred to as the double angle.

We can relate the cantilever deflection and the angle of deflection simply by dividing Equation A.27 by Equation A.29

\[ \frac{y_{\text{max}}}{\alpha} = \frac{Fl^3}{3EI} \cdot \frac{2EI}{Fl^2} = \frac{2l}{3} \]

Therefore, the deflection at the free-end of the cantilever can be also be expressed as:

\[ y_{\text{max}} = \frac{2l\alpha}{3} \quad \text{A.30} \]

or

257
Using Hooke’s Law and Equation A.27, the stiffness of the cantilever is

\[ k = \frac{3EI}{l^3} \quad \text{A.32} \]

**A.5 Position Sensitive Detector**

In our nanoscale ductility tester, we used a one-dimensional lateral effect PSD used (Hamamatsu Model No. S8543) to measuring laser deflection. The PSD has an active area of 24 mm x 0.7 mm, a 140 kΩ inter-electrode resistance and a spectral response range from 320 to 1100 nm. The main advantage of lateral-effect diodes is their wide dynamic range. They can measure the light spot position all the way to the edge of the sensor. They are also independent of the light spot profile and intensity distribution that affects the position reading in the segmented diodes. The input beam may be any size or shape, since the position of the centroid of the light spot is indicated and provides electrical output signals proportional to the displacement from the centre. The devices can be resolved to a position better than A.5 μm.

![Schematic of a cross-sectioned position sensitive detector and electrical circuit diagram containing two anodes, X₁ and X₂, and a common cathode.](image)

When a light spot strikes a position sensitive detector, as shown in Fig. A.28, an electric charge proportional to the light intensity is generated at the incident position. This electric charge is driven through the resistive layer and collected by the output electrodes X₁ and X₂ as photocurrents, shown in Fig. A.29, while being divided in inverse proportion to the distance between the incident position and each electrode. By finding the ratio the difference or ratio of the current at X₁ and X₂, the light input can be obtained irrespective of the incident light intensity level and its changes.
Fig. A.29 Schematic of a one-dimensional PSD with anodes, X₁ and X₂. A laser strikes at a distance X from the centre of the active area, where Lₓ is the total length of the active area.

The position of the laser spot on the active area of the PSD is calculated from the following formula.

\[
\frac{I_{X_2} - I_{X_1}}{I_{X_2} + I_{X_1}} = \frac{2x}{L_x}
\]

A.33

Iₓ₁ and Iₓ₂ are the output currents obtained from electrodes X₁ and X₂, where Lₓ is the total length of the active area. The one-dimensional PSD (S8543) has four pins – two of which are the anodes X₁ and X₂ and two of which are common cathodes.

An op-amp circuit was built (shown in Fig. A.30) and connected the one-dimensional PSD. The first two op-amps in the circuit act as current-to-voltage converters. In this configuration the output voltages at points A and B are summed and subtracted in the second set of op-amps. These two outputs can be divided by a divider in a final stage. A simpler option involves measuring the voltages with a software package which can perform the summation, subtraction and division. The position is given as:
\[ X = \frac{A - B}{A + B} \]

OP-07 op-amps are used in this setup. These devices offer low offset and long-term stability by means of a low-noise, chopperless, bipolar-input-transistor amplifier circuit. Low bias currents and extremely high input impedances are maintained over the entire temperature range (0°C to 70°C). The maximum supply voltage rating is 22 V. This setup uses 15 V supply voltage. \( R_1 \) and \( R_2 \) resistors have a 150 kΩ resistance.

### A.6 Annealing Evaporated Gold Films

A sheet of borosilicate glass, 100 µm in thickness, was evaporated with 10 nm of Ti followed by 250 nm of gold. The gold-coated substrate was annealed under various conditions. Two methods of annealing are compared – flame annealing and furnace annealing. In the case of flame annealing, a sample was annealed for ~ 1 second. Other samples were flame annealed by swiping the sample through a flame (i.e. 10 to 80 swipes). The furnace annealing was carried out at different temperatures (850, 670, 470, 310 and 185 °C) for different times. The surface microstructure of each annealed sample was imaged by scanning electron microscopy at low (10 X) and high (50 X) magnifications. These images are presented in this section.
Fig. A.31 Low magnification (left column) and high-magnification SEM images (right column) of the microstructure of as-deposited, and flame annealed gold (1 s, and 10 swipes). The thickness of the titanium and gold layers are 10 nm and 250 nm, respectively.
Fig. A.32  Low magnification (left column) and high-magnification SEM images (right column) of the microstructure of flame annealed gold (20, 40 and 80 swipes). The thickness of the titanium and gold layers are 10 nm and 250 nm, respectively.
Fig. A.33 Low magnification (left column) and high-magnification SEM images (right column) of the microstructure of furnace annealed gold (850 °C for 5, 10 and 20 s). The thickness of the titanium and gold layers are 10 nm and 250 nm, respectively.
Fig. A.34 Low magnification (left column) and high-magnification SEM images (right column) of the microstructure of furnace annealed gold (850 °C for 30 and 60 s). The thickness of the titanium and gold layers are 10 nm and 250 nm, respectively.
Fig. A.35 Low magnification (left column) and high-magnification SEM images (right column) of the microstructure of furnace annealed gold (670 °C for 30, 60, and 120 s). The thickness of the titanium and gold layers are 10 nm and 250 nm, respectively.
Fig. A.36 Low magnification (left column) and high-magnification SEM images (right column) of the microstructure of furnace annealed gold (470 °C for 1, 2, and 5 minutes). The thickness of the titanium and gold layers are 10 nm and 250 nm, respectively.
Fig. A.37  Annealing temperature versus annealing time profile to produce titanium oxide particles on the surface of the gold.
Fig. A.38 Cross-section SEM images of as-deposited (left column) and annealed gold (450 °C for 1 hour) (right column).
Fig. A.39  TEM cross-section image of (a) as-deposited and (b) annealed (450 °C for 1 hour). Corresponding cross-section EDX map of (i) as-deposited and (ii) annealed gold films; gold, titanium and silicon are represented by the colours yellow, blue, and red, respectively.

Fig. A.40  TEM cross-section image of an annealed (450 °C for 1 hour) gold film showing Ti along the grain boundaries of the gold.