

Perpendicular Growth of Catalyst-free Germanium Nanowire Arrays†

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Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

High yields of single-crystalline Ge nanowires (NWs) were synthesized through the thermal decomposition of diphenylgermane (DPG) in the vapor phase of a high boiling point organic solvent. The NWs were single crystal and ranged from 7 to 15 nm and 0.5-10 μm in diameter and length respectively. Catalyst-free growth only occurred in areas exposed to the organic vapor, with no growth occurring in the liquid phase. NW growth was fully localizable to surfaces heated within a critical nucleation temperature range. High density, perpendicular arrays of Ge NWs were subsequently grown from ITO coated substrates. This approach represents a viable and convenient route toward orientated arrays of catalyst-free Ge NWs for high-performance device applications.

Group IV semiconductor NWs have been incorporated into a variety of novel device architectures including – high performance field effect transistors, lithium ion battery anodes and next generation solar cells – due to their unique size dependent properties.¹ A particular benefit of group IV NWs is their inherent compatibility with CMOS technologies. In recent years the use of Ge in electronic and optoelectronic application has garnered significant interest due to its larger Bohr exciton radius and higher carrier mobility compared to Si.² A variety of techniques – including chemical vapor deposition (CVD), laser ablation and various solution protocols – have been employed in their synthesis.³ The archetypal and best studied approach is the Au nanoparticle seeded route which takes advantage of the low eutectic temperature between Au/Si and Au/Ge.⁴ While this route has been widely adopted in the controlled synthesis of NWs, its viability for device applications has been limited due to inherent Au contamination of the resultant nanostructures,⁵ prompting interest in the use of alternative metal catalysts.^{6, 7} Concurrently, the more recent discovery of routes to Ge NWs grown without metal catalyst particles deemed as ‘unseeded’ or ‘self-seeded’ processes offer even higher purity NW formation.⁸ Ge et al. showed that anisotropic growth of crystalline Ge nanostructures was possible in organic solution.⁹ Zaitseva et al. also reported the solution growth of Ge NWs via decomposition of organometallic precursors in various high boiling point solvents.¹⁰ The different mechanisms responsible for catalyst-free growth can be separated into two categories, namely; catalysis by liquid Ge particles or by organic droplets.

Controlled, high density growth of group IV NWs on substrates offers potential for the realization of a wide range of high-performance, NW-based optical and electronic devices, including solar cells, photodetectors and transistors.¹¹

Catalyst-free approaches for Ge NW growth on substrates at low temperatures have been hampered by the lack of a eutectic alloy to lower the nucleation point and the restriction imposed by the maximum boiling point of the solvent system. Ge NW growth on transparent conducting metal oxides such as ITO is desirable for optoelectronic applications.¹²

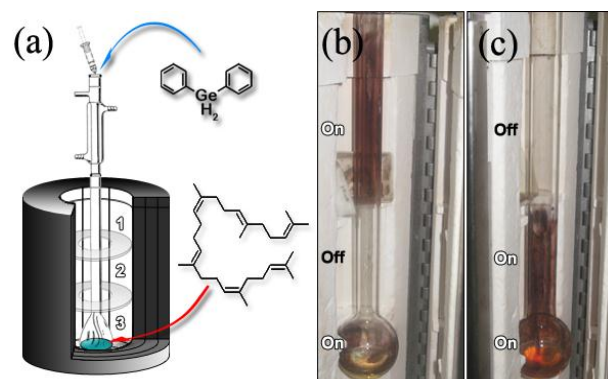


Fig. 1 Schematic (a) outlines the synthetic strategy for catalyst-free growth of Ge NWs. Photographs (b) and (c) show flasks after a typical synthesis where the NW growth was thermally localized.

Vapor phase systems such as CVD are amongst the most widely used and successful routes providing crystalline NW growth.¹³ Previous high boiling solvent based methods have all focussed on liquid phase growth.^{14, 15} Vapor phase growth in high boiling point solvents has been overlooked despite the fact that it represents an attractive, simple alternative to established techniques. Herein, we describe a simple method for catalyst-free Ge NWs growth via the thermal decomposition of an organometallic precursor in the vapor reflux of the high boiling point solvent, squalene. The simple round-bottomed flask based approach is then extended to the perpendicular growth of Ge NWs from ITO coated substrates.

The schematic outlined in Fig. 1a highlights the reaction setup and growth chemistry used in this work. DPG was thermally decomposed by injection into the vapor reflux of the high boiling point solvent squalene to form germane gas which was transported to the heated sidewalls of the reaction vessel (or growth substrate) by the refluxing solvent, allowing self-seeded Ge NW growth. NW growth was clearly evident from the pink coloration of the reaction flask sidewalls post-synthesis (Fig. 1b and c). Growth in the case of this system does not occur in the liquid solution unlike conventional high boiling point solvent synthesis methods.¹⁶ Rather, NW growth is possible across the inner surfaces of heated quartz/pyrex long necked flasks in contact with organic vapor. The organic vapor acts as both a decomposition medium for the DPG and a

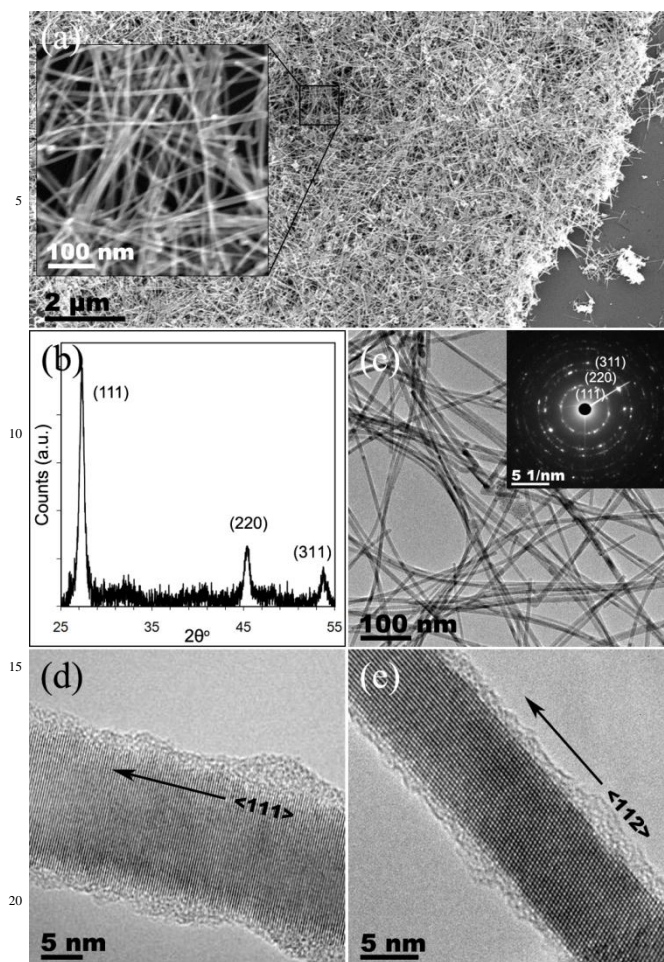


Fig. 2 SEM image (a) of NWs with magnified image inset. (b) XRD pattern for the NWs indicating crystalline Ge. (c) TEM image showing a selection of Ge NWs with the corresponding SAED pattern (inset). (d,e) HRTEM images of NWs exhibiting $\langle 111 \rangle$ and $\langle 112 \rangle$ growth directions.

carrier for the resultant germane gas allowing NW formation. The reaction times necessary for growth were found to be very short, as high NW yields could be achieved after only two minutes, with no significant increase in yield given longer reaction times of up to two hours. Localized heating experiments were conducted where either zone 1 or zone 2 of the furnace was left inactive while the globe of the flask in zone 3 was continuously heated. Post-synthetic photographs of the system (Fig. 1b, c), show that the NW growth could be fully localized, with no growth occurring in the non-heated zones. It can also be seen that no crystalline material was produced in the liquid portion of the high boiling point solution.

The SEM image seen in Fig. 2a shows a dense bundle of Ge NWs sonicated from the sidewalls of a reactor and drop cast onto a Si wafer. The high aspect ratio of the NWs is clearly illustrated from the high resolution micrograph inset, with some possessing lengths in the tens of microns. The dominance of Ge in the samples was confirmed by energy dispersive X-ray spectroscopy (ESI† S1), with Ge oxides, residual solvent and the silicon substrate accounting for the O, C and Si peaks respectively. Fig. 2b shows a powder X-ray diffraction pattern collected from Ge NWs synthesized using

squalene as the solvent. The resultant diffractogram gave strong peak reflections at $2\theta = 27.29^\circ$, 45.43° and 53.81° , corresponding to the (111), (220) and (311) peaks for diamond cubic germanium.

TEM analysis of the NWs showed that they were non-tapered with a diameter range between 7 and 15 nm (Fig. 2c). A small 1-2 nm oxide layer is also visible at the periphery of the NWs. The corresponding selected area electron diffraction (SAED) pattern (Fig. 2c inset) obtained from a collection of NWs, shows a polycrystalline ring pattern from which the maximum intensity rings give d spacings of 0.327, 0.199 and 0.170 nm respectively. These spacings can be matched to the b , $\{220\}$ and $\{311\}$ type planes expected for the diamond cubic crystal structure of Ge and are consistent with the XRD analysis. It was noted that in a typical synthesis, 80% of the NWs exhibited a $\langle 111 \rangle$ growth direction (Fig. 3d) while the remaining 20% showed a $\langle 112 \rangle$ growth orientation (Fig. 3e). The predominance of the $\langle 111 \rangle$ growth over $\langle 112 \rangle$ is consistent with previous reports on both metal catalyzed and catalyst-free techniques.¹⁷

XPS was used to examine the surface chemistry of the NWs. A low-resolution survey scan (ESI†, S2) of the NWs on an oxidized silicon substrate, yielded peak positions for Ge, O, C and Si. The C, O and Si peaks were attributed to the presence of residual organic solvent, surface oxidation of the NW surface and Si oxides on the substrate, and the substrate respectively. The Ge 3d spectrum has two peaks corresponding to Ge and a third peak assigned to O 2s. The Ge $2p_{3/2}$ spectrum is fitted with a peak at 1217.1 eV which corresponds to elemental Ge¹⁸ and the two other component peaks at higher binding energies correspond to GeO_x, due to oxides on the NWs. Raman analysis, (ESI†, S3) also gave confirmation of the presence of nanocrystalline Ge shown by the downshifted peak position of 298.1 cm^{-1} when compared to bulk Ge.¹⁹

Having successfully grown the NWs from quartz and pyrex flasks, the viability of oriented Ge NW growth on substrates was probed. ITO was chosen as a suitable substrate due to its compatibility with solar and optoelectronic applications. SEM cross-sectional analysis shown in Fig. 4a, conducted at a 70° tilt, shows the nature of Ge NW growth on an ITO coated substrates. The circa 150 nm layer of ITO can be readily identified beneath the extremely dense arrays of perpendicularly grown Ge NWs, covering an area of over $10 \mu\text{m}^2$. This highly ordered array grown directly from the substrate is further magnified in Fig. 4b. The NWs can be seen to be individual and freestanding up to approximately $1 \mu\text{m}$ from the substrate before becoming intertwined into a dense mesh. High resolution imaging found the NWs to be untapered along their length from root to tip, with no evidence of metallic seed particles being identified.

XPS analysis was used to examine the surface and interfacial chemistry of the Ge NWs on the ITO growth substrate in an effort to investigate potential seeding of the NWs by elemental In as highlighted in previous studies.⁷ The high resolution spectrum of In 3d (Fig. 4c) is composed of an asymmetric doublet with In $3d_{5/2}$ appearing at a binding energy of 444.5 eV, characteristic of indium present in ITO as

In_2O_3 . The broad structures at ~ 440 and ~ 450 eV can be contributed to GeO_x auger electrons.²⁰ Elemental indium, if present would appear at a lower binding energy of 443.6 eV.²¹ A chemical shift of 0.9 eV from that expected for elemental indium supports that indium oxides exist at the interface of these materials. This observation, along with the TEM analysis findings that the NWs were identical to those grown on glass suggests strongly that NW growth from the ITO does not proceed *via* a metal seeded mechanism.

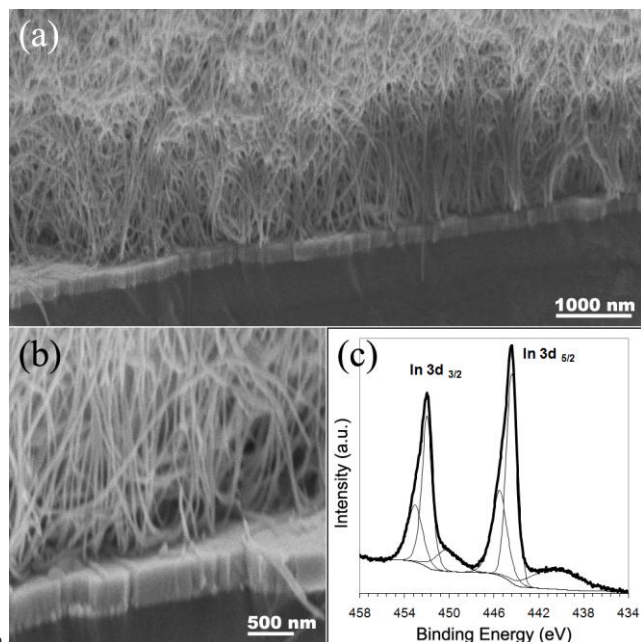


Fig. 4 SEM images (a) and high resolution image (b) highlighting the large-scale perpendicular arrays of Ge NWs, grown from an ITO surface. XPS analysis of the Ge NWs grown on ITO (c).

The key difference between this study and previous metal catalyst-free approaches is that Ge NW growth is uniquely facilitated by the vapor phase of the organic solvent growth medium, with no material formation in solution. The absence of solution born NWs in this study is in good agreement with previous work that observed NW growth in squalene solution only in the presence of metal catalyst seeds of Au or Cu when using DPG as the precursor.¹⁵ We propose that Ge NW nucleation most likely occurs *via* an organic/self-seeded protocol as reported previously by Zaitseva et al.²² In their study, liquid droplets were viewed as sinks for vapor molecules which allowed for accelerated decomposition of the Ge precursor and subsequent 1D growth. In comparison, their work focused on precursors which did not form germane gas upon thermal decomposition. The key difference here is that germane gas is formed in the vapor phase of the system. Through the placement of a substrate in the vapor phase portion of the reactor, precursor gas is allowed to saturate the organic medium allowing the self-seeded growth of NWs, forming extremely high density perpendicular arrays.

In summary, we have presented the vapor phase based, catalyst-free growth of Ge NWs using the thermolytic decomposition of an organometallic precursor. The growth was investigated in both pyrex and quartz reaction flasks and

extended to the perpendicular growth of Ge NWs from ITO coated substrates. We believe that NW nucleation occurs via a self-seeding organic based mechanism and represents a significant step forward in catalyst-free Ge NW synthesis.

Notes and references

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- † Electronic Supplementary Information (ESI) available: Full experimental details, EDX, XPS and EDX analysis. See DOI: 10.1039/b000000x/
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