Top Surface Imaging Lithography Processes for I-line Resists using Liquid-Phase Silylation

K. Arshak, M. Mihov, A. Arshak, D. McDonagh

Abstract – In this paper, liquid-phase silylation process for Top Surface Imaging Lithography systems incorporated e-beam exposure has been experimentally investigated using FT-IR spectroscopy, UV spectroscopy, SIM spectrometry and SEM cross-sectionals. The impact of different silylating agents on Shipley SPR505A resist system is presented for both the UV exposed and e-beam crosslinked regions of the resist. Results show that an e-beam dose of 50μC/cm^2 at 30KeV is sufficient to crosslink the resist and prevent silylation. The silylation contrast using HMCTS was found to be the highest (11:1) in comparison with other two agents. It was found that the silicon incorporation in SPR505A resist follows Case II diffusion mechanisms.

I. Introduction

Nowadays optical lithography has been pushed down to 0.13μm technology resolution using shorter exposure wavelengths (248nm, 193nm), advanced chemically amplified resists, sensitive to the above wavelengths, phase shift masks and optical proximity correction techniques [1]. Existing deep UV lithographic technologies and associated optical extensions combined with higher numerical aperture (>0.8) 193nm-based systems are expected to provide sufficient resolution to enable 100nm imaging in the coming couple of years [2]. Several different lithographic technologies are competing to be successor to optical lithography below the 130nm technology node. It is believed that the Extreme Ultraviolet Lithography (157nm) is the most suitable candidate for the nanometer region devices (100nm, 70nm, 50nm) [3].

Although optical lithography has achieved so much in terms of shrinking the device resolution, one of the primary difficulties for 193nm lithography is the higher optical absorbance of the conventional organic materials used in the photoresists. One process alternative to overcome this problem is by using Top Surface Imaging processes (TSI), which have been widely developed in the last 10 years [4]. Processing the top surface layer of the resist will automatically eliminate the higher optical absorbance of I-line (365nm) photoresists under low-wavelength exposures. TSI processes also can greatly improve the optical proximity effects (standing waves and reflection from topography) and the low depth-of-focus (DOF), that is associated with the small feature sizes (considering to be a key limit in optical lithography) [5]. Moreover, surface imaging can be accomplished by selective incorporation of silicon into the resist (silylation process) and consecutive dry etching, resulting in high-anisotropic pattern transfer even in the nanometer region [6].

K. Arshak and M. Mihov are with the Electronic & Computer Engineering Department, University of Limerick, Limerick, Ireland, E-mail: Khalil.Arshak@ul.ie

A. Arshak is with the Physics Department, University of Limerick, Limerick, Ireland.

D. McDonagh is with Integrated Devices Technology Inc., 11555 Medlock Bridge Rd., Suite 170, Duluth, GA30096, USA.

II. Top Surface Imaging Processes

Originally, Top Surface Imaging Processes were developed for improving resolution of I-line (365nm) lithographic systems, as the DESIRE process has been the most extensively studied [7]. In the early stages, the research has been focus on DNQ/novolak resists silylated under vapour-phase using hexamethyldilisazane (HMDS) as a silylating agent. However, selective silicon incorporation via TSI can be applied to both the chemically amplified and e-beam resists, depending on the exposure step carried out. SIMPLE process [8] uses chemically amplified resists exposed under DUV (248nm) or e-beam radiation, while PRIME process [9] uses e-beam exposure with DNQ/novolak based resists.

The silylation process however was also evolving from gas-phase to liquid-phase during the years of TSI processes development. It has been claimed that the liquid-phase has certain advantages over the gas-phase silylation: improved silicon contrast, silylation selectivity and higher silicon incorporation at lower silylation temperatures. Gogolides *et al.* [10] demonstrated a 0.5μm resolution using a commercial novolak resist AZ5214 with HMCTS (Hexamethylcyclotrisilazane) liquid-phase silylation process. Hartney *et al.* [11] has evaluated the performance of poly-vinyl-phenol based resists under 193nm exposure and liquid-phase silylation with HMCTS, achieving a 0.25μm resolution. Ohfuji *et al.* [12] shrink the resolution down to 0.15μm using the same resist under 193nm exposure and Bis[Dimethylamino]dimethylsilane (B[DMA]DMS) liquid-phase silylation agent. Bauch *et al.* [13] has already achieved resolution in the nanometer region using PRIME process with DNQ/novolak based resist. All this indicates that TSI processes incorporated liquid-phase silylation can be extended beyond 0.1μm resolution even with using standard DNQ/novolak based resists under DUV or e-beam exposures.

In this paper, the liquid-phase silylation process of I-line DNQ/novolak resist Shipley SPR505A is investigated,

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as TSI process with this resist has not been reported in the literature except [6]. SPR505A resist, made by m-cresol/p-cresol formaldehyde resins, has superior dry etch properties in comparison with the most novolak based resists and is in the I-line fab production worldwide. The proposed TSI process diagram is shown on Fig.1. Electron beam exposure or excimer laser (248nm, 193nm) radiation are used to crosslink parts of the resist so that to prevent silylation in the exposed areas. The subsequent UV flood exposure (365nm) converts the photoactive compound (PAC) to indene carboxylid acid (ICA) in the non-crosslinked regions. Next, silicon is selectively incorporated in these resist areas during liquid-phase silylation process. The incorporated silicon forms a stable SiO_2 mask during the O_2-RIE dry development process, while all other resist regions are etched away.

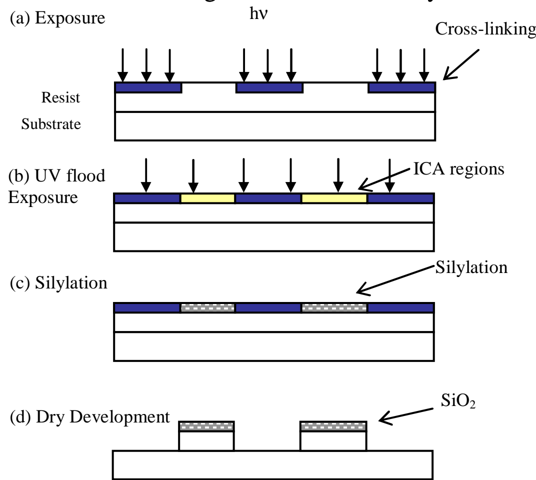

Fig.1: TSI process diagram.

III. EXPERIMENTAL PROCEDURE

Shipley SPR505A resist was spin coated at 4000rpm on Si-wafers and prebaked at 90°C for 60sec on hotplate, giving a nominal film thickness of 0.5μm. The electron-beam exposure of the samples was performed using a modified Jeol JSM-840 SEM at 30 KeV acceleration voltage with exposure doses between 25-100μC/cm^2. The subsequent UV food exposure was carried out on a broadband NUV Karl Suss MJB 21 mask aligner with dose of 250mJ/cm^2. The wafers were postexposure baked at 100°C for 60sec on hotplate.

The liquid-phase silylation was performed at room temperature (19°C) and also at 40°C by immersing the resist-coated wafers in the silylation solution for a given period of time. At the predetermined time, the samples were removed from the silylation bath, submerged in xylene for 10 sec to stop the silylation reaction, rinsed with DI-water and dried with O_2.

Fourier Transform Infrared (FT-IR) spectroscopy analysis of the samples was performed in Reflection mode on Perkin Eimer FTIR Spectrum 2000 Spectrophotometer with an i-series FTIR microscope. Secondary Ion Mass (SIM) depth profile measurements were carried out on Focus Ion Beam FIB-SIM. Ultra Violet (UV) spectroscopy analysis was carried out on Varian DMS 100S UV Visible Spectrophotometer, as for these measurements the resist was spinned on quartz wafers.

Cross-sectional staining of the silylated regions [14] was done by cleaving the wafer across patterned lines followed by partially TMAH based development to decorated the silylated resist layer. The Scanning Electron Microscope (SEM) analysis of the samples was performed using Jeol JSM-840 SEM.

IV. RESULTS AND DISCUSSION

A. Liquid-phase Silylation Mechanisms

The standard silylation solution is consisted of silylating agent, diffusion promoter (resist solvent) and resist non-solvent. The mechanism of liquid-phase silylation is based on an initial softening of the resist with the resist solvent followed by the penetration of the silylating agent and subsequent reaction with the hydroxyl groups in the resin structure of the photoresist. The aim of the resist non-solvent (which also serve as a silylating agent solvent) is to prevent the premature dissolution of the resist.

Bifunctional, rather than monofunctional silylating agents have been examined in this study, as they exhibit the photoresist flow during the subsequent processing by cross-linking the silylated areas [5]. Two cyclic agents, Hexamethylcyclotrisiloxane (HMCTSx) and Hexamethyl cyclotrisilazane (HMCTS) were investigated and compared along with the linear Bis[Dimethylamino]dimethylsilane B[DMA]DMS. Propylene –glycol –methyl –ether -acetate (PGMEA) was used as a diffusion promoter and Xylene as the resist non-solvent. The expected silylation reaction between the phenolic-OH groups of the novolak resin and the silylating agent is shown in Fig.2. The $Si(CH_3)_2$ group of the silylating agent replaces the hydrogen atom in the OH-group to form a resin–bonded silicon.

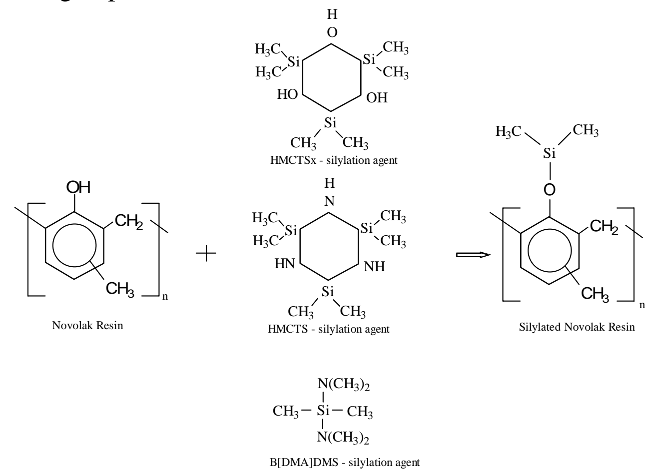

Fig.2: Silylation agents - phenol reaction.

B. Silicon Uptake in SPR505A

The silicon uptake in SPR505A resist was quantified by measuring the integrated IR absorbance of Si-C bond deformation peak ($1280cm^{-1}$-$1240cm^{-1}$).

The liquid-phase silylation of SPR505A resist using HMCTSx agent were firstly characterised. Fig.3 shows the FT-IR difference spectrum, which is before and after a 60 sec silylation with HMCTSx at room temperature (19°C) for the NUV exposed regions of the resist. The presence of the Si-C bond stretching vibration at $1260cm^{-1}$ is clearly noticeable. UV measurements of silylated samples show reduction in the OH sites absorbance at 280nm after silylation (Fig.4). The silylation mixture composition was previously optimised to 20%-5%-75% (HMCTSx-PGMEA-Xylene) [15], showing the highest silicon uptake with changing the concentration of the diffusion promoter from 0% to 20% (Fig.5). It is noticeable that small amount of PGMEA greatly enhances the silylation, while concentration higher than 15% will lead the resist to be dissolved. Also, silylation at 40°C showed the same silicon incorporation as that for the room temperature.

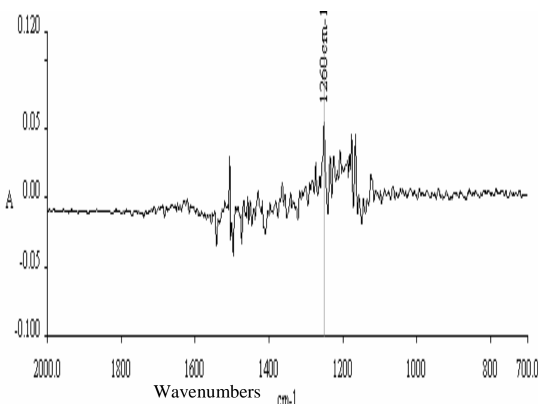

Fig.3: FT-IR difference spectrum for the 60sec HMCTSx silylated resist (after silylation–before silylation).

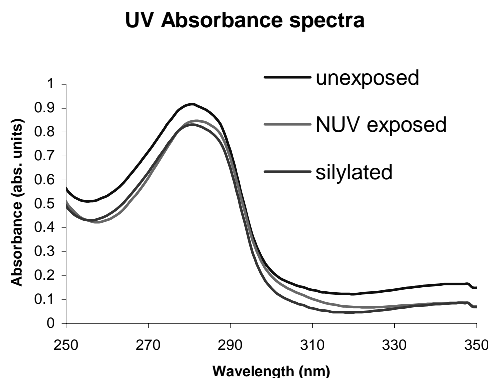

Fig.4: UV absorbance of unexposed, NUV exp, and 60sec HMCTSx silylated resist films on quartz wafers.

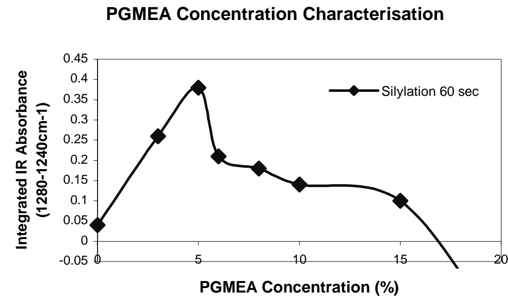

Fig.5: Incorporated silicon content as a function for various PGMEA concentrations.

The Secondary Ion Mass (SIM) depth profile measurements (Fig.6) of 60 sec HMCTSx silylated samples demonstrated silicon incorporation rate of 100nm/min in the NUV exposed parts of the resist. SEM cross-sectionals of the samples also showed approximately 100nm silicon incorporation after 60 sec HMCTSx silylation (Fig.7). These experimental results agreed well with the previously calculated silylation depth in SPR505A resist for the same silylation time [6].

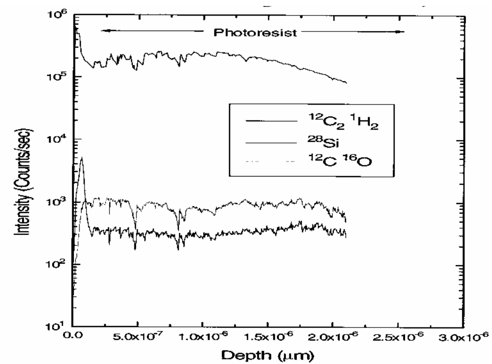

Fig.6: Si-depth profile obtained by SIMS of 60sec HMCTSx silylated resist film.

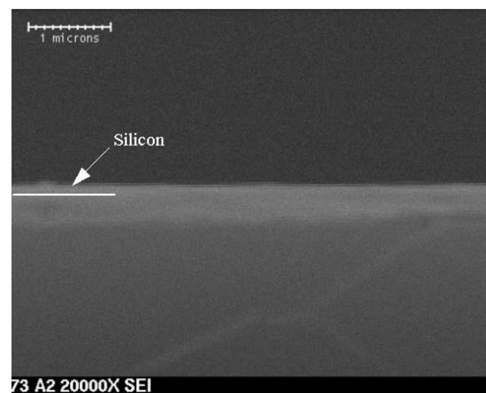

Fig.7: SEM cross-sectional of 60sec. HMCTSx silylated resist.

The effect of crosslinking the SPR505A resist under electron beam exposure was also investigated in order to estimate the required dose so that to prevent silylation in

the e-beam exposed areas (Fig.8). Our results show that an e-beam dose larger than 50μC/cm^2 at 30KeV effectively cross-links the resist, thus decreasing significantly the silicon uptake during silylation.

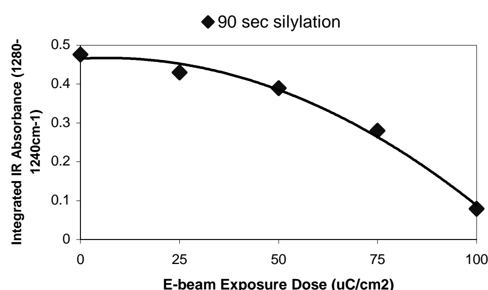

Fig.8: Silicon incorporation in the e-beam crosslinked areas under different exposure doses.

Finally, liquid-phase silylation of SPR505A using HMCTS and B[DMA]DMS agents were characterized in order to improve the silicon uptake in the resist. However, it was found that HMCTS silylation is much more efficient than HMCTSx silylation. The reason for that is possibly due to the more efficient chemical reaction between the silicon groups of HMCTS and resist phenol groups. Such efficient reaction has also been reported by Stewart *et al.* [16], using HMCTS and similar novolak resins. Fig.9 shows IR spectra of SPR505A resist before and after 60sec silylation with 10% HMCTS -5% PGMEA -85% Xylene at 40°C and Fig.10 shows the FT-IR difference spectrum after silylation.

The FT-IR difference spectrum (Fig.10) clearly shows the decrease in OH sites (3500cm^{-1}) absorption and the presence of Si-$(CH_3)_2$ (1265cm^{-1}) bond stretching vibration after silylation. This indicates that the OH sites in SPR505A are replaced with the silylating molecules, as shown in Fig.2. Note that the Si-$(CH_3)_2$ absorption band in Fig.10 increases at much higher level than in the case of HMCTSx silylation (Fig.3), thus validating the higher silicon uptake in SPR505A resist after HMCTS silylation. The changes of the Si-$(CH_3)_2$ absorption at 1265cm^{-1} after 30sec, 60sec, 90sec and after 120sec silylation process with HMCTS are presented in Fig.11, indicating a linear increase with time.

The FT-IR spectrum in Fig.10 also shows an increase in the Si-$(CH_3)_2$ bond deformation at 790cm^{-1}, which is an alternative method for silylation characterization [8,17]. Moreover, the peak at 1076cm^{-1} indicates the presence of silixane structures (Si-O-Si) after HMCTS silylation, which contributes for higher concentration of silicon in the silylated areas. The siloxane structures are products of a polymerization reaction resulting in more than one silylating molecule bonded to each phenolic -OH group [18]. A similar siloxane formation from the reaction of the silylating agent with water impurity in the bath or in the film has been reported earlier [12,16,18], although Hartney *et al.* [11] reported no polymerization has took place after HMCTS silylation.

The liquid-phase silylation of SPR505A resist with B[DMA]DMS were carried out in a mixture containing 10%-5%-85% of the silylating agent, diffusion promoter and resist non-solvent.

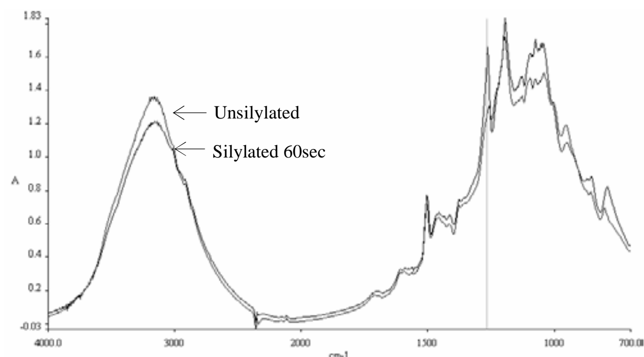

Fig.9: Infrared spectrum of SPR505A before and after 60sec silylation with 10% HMCTS -5% PGMEA -85% Xylene at 40°C.

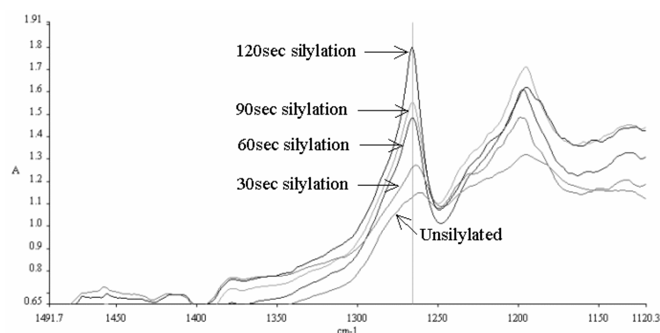

Fig.11: The increase of the Si-$(CH_3)_2$ absorption peak at 1265cm^{-1} after 30sec, 60sec, 90sec and after 120sec silylation with 10% HMCTS -5% PGMEA -85% Xylene at 40°C.

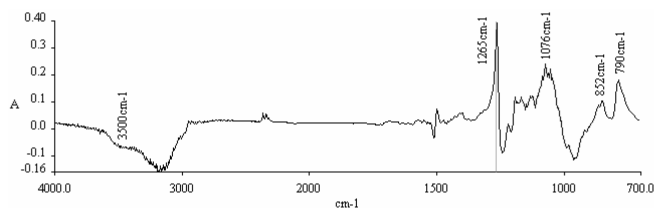

Fig.10: FT-IR difference spectrum for the 60sec HMCTS silylated resist at 40°C (after silylation–before silylation).

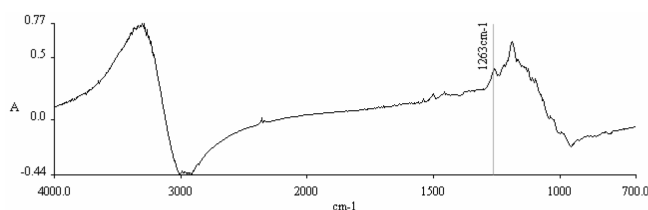

Fig.12: FT-IR difference spectrum for the 60sec B[DMA]DMS silylated resist (after silylation–before silylation).

Samples were silylated at room temperature and at 40°C showing little changes in the silicon incorporation. Fig.12 shows the FT-IR difference spectrum after 60sec B[DMA]DMS silylation, indicating the increase of Si-$(CH_3)_2$ vibration at $1263cm^{-1}$. Again, the silicon uptake with the linear B[DMA]DMS was found to be better than with HMCTSx, although it is not so high as in the case of HMCTS silylation. The siloxane structures are also not observed in the IR difference spectrum after B[DMA]DMS silylation (Fig.12).

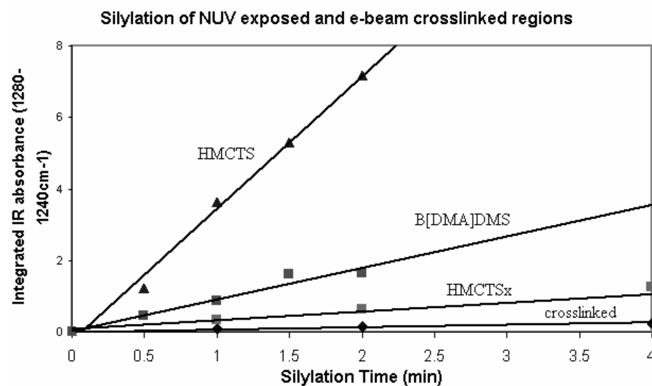

Fig.13: Silicon uptake versus time for the NUV exposed regions and e-beam crosslinked areas ($100\mu C/cm^2$ at 30KeV).

The three silylating agents are compared in Fig.13, showing the silicon uptake for both the crosslinked and NUV exposed resist areas as a function of the silylation time. The crosslinked resist areas are e-beam exposed with a dose of $100\mu C/cm^2$ at 30KeV, resulting in minimum silicon incorporation. The NUV exposed resist areas are silylated with HMCTSx, B[DMA]DMS and HMCTS for different amount of time. The integrated IR peak ($1280cm^{-1}$-$1240cm^{-1}$) increases at much faster rate for HMCTS and B[DMA]DMS silylating agents, indicating better silicon incorporation levels than HMCTSx.

The silylation contrast of the investigated top surface imaging process (Fig.1) as determined by the ratio of integrated IR absorbance of NUV exposed over crosslinked regions, was found to be approximately 11:1 for HMCTS silylation. Hutchinson *et al.* [19] has found a silyation contrast of 6:1 in their TSI process using AZ-5214 novolak resist, HMCTS silylation and excimer laser exposure (213nm) instead of e-beam to crosslink the resist. The results indicate almost twice higher silicon uptake and consecutive silylation contrast in SPR505A resist than in AZ-5214 resist after HMCTS silylation. Also the silicon incorporation over silylation time was found to be linear, indicating a Case II diffusion process for all the HMCTS, B[DMA]DMS and HMCTSx silylation of SPR505A resist. Case II diffusion, rather than Fickian diffusion, denotes that the diffusion of the silylation agent through the polymer and the chemical reaction with the phenolic -OH resin groups occur at comparable time scales. The same behaviour of the liquid-phase silylation process was also observed by Hartney e*t al.* [11], using HMCTS silylation agent and Rutherford backscattering (RBS) analysis.

V. CONCLUSION

In this paper, Top Surface Imaging process for Shipley SPR505A resist has been investigated in order to develop liquid-phase silylation process for e-beam and/or 193nm ArF excimer laser lithography. The effect of SPR505A cross-linking under different e-beam doses was investigated and the liquid-phase silylation with Hexamethylcyclotrisiloxane (HMCTSx), Hexamethyl cyclotrisilazane (HMCTS) and Bis[Dimethylamino] dimethylsilane (B[DMA]DMS) was characterized. It was found that the required e-beam dose for preventing silylation in the e-beam exposed areas should be greater than $50\mu C/cm^2$ at 30KeV. Silylation with HMCTSx results in 100nm/min silicon incorporation in the NUV exposed areas as shown by SIM spectroscopy and SEM cross-sectionals. However, HMCTS silylation and B[DMA]DMS silylation result in higher silicon incorporation in the SPR505A as shown by the FT-IR spectroscopy. The silylation contrast of the process for the HMCTS silylation was found to be the highest one (11:1), showing almost twice higher silicon incorporation in SPR505A resist than in AZ-5214 resist reported earlier [19]. It was also observed that the silicon uptake in SPR505A over time had a linear behaviour for all the investigated silylating agents, indicating a Case II diffusion silylation process.

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