THE CHALLENGES OF 157nm NANO-LITHOGRAPHY: SURFACE MORPHOLOGY OF SILICON BASED COPOLYMERS

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Abstract

Lithography at 157 nm using F₂ laser is the next step after 193 nm for ULSI fabrication with dimensions below 50nm. However there are problems related to the development of the 157 nm technology, the most important being the design of photoresists with suitable absorption at 157nm and low outgassing. On the other hand high resolution capabilities of resist depend on the surface roughness and its modification following 157nm illumination of the resist. In this communication, a copolymer of ethyl-polyhedral oligomeric silsesquioxane (ethyl-POSS) and tert-butyl methacrylate (TBMA) was evaluated for surface homogeneity, before and after exposure to 157nm at different concentrations of the homo-polymers. Surface roughness depends on the chemical composition of the resist, and AFM images of exposed areas indicate accumulation of matter at the edge of the boundaries between exposed and non-exposed areas.

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1. Introduction

Fluorine laser lithography at 157nm is the next generation optical of lithography in the international roadmap [1]. It is expected that 157nm lithography will be introduced into production early enough to meet the 70nm node and go possibly below that, before other next generation lithographies take their place in the international arena. Serious research effort has started internationally in this field both in the laser optics systems and resists, aiming in developing an industrial exposure tool and providing a platform for process development. Recent results and earlier studies have shown that the resist challenges to be addressed at 157nm are more serious compared to 193nm [2,3]. Carbon containing resists will not be able to meet the single layer demand without at least partial fluorination. On the other hand silicon containing resists for bilayer applications appear more attractive than ever. However, the out-gassing and the surface roughness issues are both crucial for 157nm lithography, especially if silicon based bilayer resists are to be adopted. Contamination of the lenses by out-gassing products is critical at 157nm [4]. This is more so compared to previous wavelengths such as 193nm, due to the higher photon energy at 157nm and the corresponding higher fragmentation probability. Understanding and limiting out-gassing at 157nm is necessary for further progress.

On the other hand the high value of the absorption coefficient of the polymeric materials in the Vacuum Ultraviolet (VUV), from $10^4$ to $10^6$ cm$^{-1}$, imposes restrictions on the selection of the photoresists for 157nm photolithography demanding high purity materials and defect-free thin films. However the absorbancies of various carbonated polymeric materials at 193nm it might just have the right value of $\sim 0.1-0.4\mu$m$^{-1}$ for lithographic imaging, mainly due to the fact that for all the organic molecules, the dissociative excited electronic states of the small
radicals occupy the energy range above 6.2 eV (200nm). In this case the energy position of the first excited states of the C-C bond and the basic diatomic radicals depends on the chemical structure of the polymeric material, allowing therefore large variations of the absorbance in a narrow frequency range from 180 to 200nm. On the contrary, at 157 nm a different situation occurs. Because for most of the organic materials, the density of the bound or the dissociative excited states around 7.8eV (157nm) is large, the absorption coefficient is high. Hence the absorption of one photon by the organic molecule at 157nm certainly implies complete bond breaking of the organic material. The parent molecule disintegrates to small fragments, atomic, diatomic or triatomic, which are flying apart with supersonic speeds. Therefore the photodissociation process at 157nm could impose serious problems on the optics of the projection system by contaminating it. To solve this problem the complete microscopic description of the photodissociation dynamics involved in the scission of the polymeric chains, and the dynamics of the extraction of the photoproducts is required and basic studies have been carried out for aliphatic and aromatic polymeric materials. This is mainly because the corresponding monomers have the potential to be dissociated into small photofragments in which most of the photoresists to be used for 157nm photolithography are likely to be dissociated. These experimental results suggest that at 157nm there is photochemical bond breaking due to the fact that the density of the dissociative excited electronic states of the small diatomic or triatomic radicals which are correlated with the excited electronic states of the monomer of the different polymeric materials at 7.8 eV is high, therefore photodissociation at this wavelength is taking place. The molecular photofragments are flying apart with supersonic speed, and the presence of steep dissociative excited electronic states is inherent to the molecular structure. This could be a serious
problem for film homogeneity following 157nm illumination, and it depends on the exposure parameters, such as light intensity and total dose.

In this communication one copolymer of ethyl polyhedral oligomeric silsesquioxane (ethyl-POSS) and tert-butyl methacrylate (TBMA), was evaluated for 157nm lithography for different concentrations of homopolymers for surface homogeneity. It was found that surface homogeneity, before exposure to 157nm, depends on the chemical composition of the resist during preparation. Finally AFM images of exposed areas with sharp edges on the boundaries between exposed and non-exposed areas, suggesting photochemical bond breaking of the exposed areas, as it is the case for carbon based aliphatic and aromatic resists. In addition phase separation, with average size of 450nm of different phases was observed for some of the samples.

2. Experimental

The laser source used for this experiment was of the fast discharge type, and it had been described previously [5]. It delivered $1 \pm 0.2 \text{mJ}$ at 157nm per pulse at 10Hz repetition rate, and the pulse duration was $\sim 12\text{ns}$ at FWHM. Thin film homogeneity and phase separation before and after exposure at 157nm was evaluated with an atomic force microscope (AFM). In the contact mode the tip and the sample were in contact and the force between the tip and the sample was kept constant as the tip was scanned over the sample was constant. In this way the topography of the surface was recorded. An effort was made to minimize the force of the tip on the surface to avoid its deformation. A soft AFM tip with an elastic constant of the cantilever of $\sim 0.01 \text{N/m}$ was used. We estimate that the force between the tip and the sample in the contact mode was 1 nN. Thin films of random copolymers comprising of two
monomers (TBMA and ethyl-POSS) while/or ethyl-POSS, Fig.1, were formed on a CaF$_2$ substrate by spinning at different composition (S1: x=40%, y=60%, S2: x=60%, y= 40%).

3. Results and discussion

For the understanding of the mechanisms of the interaction of the laser light with the resists and polymers in general, the complete microscopic description of the photodissociation dynamics involved in the scission of the polymeric chains and the dynamics of the extraction of the photoproducts is required. Up to now, several phenomenological models have been developed describing the interaction of polymers with laser light at different wavelengths, along with the improvement of the experimental methods [6-12]. In the general case of illumination of polymeric material with light, mainly two kind of processes are induced in the monomers: the first being excitation followed by relaxation to the ground state, and the second being excitation followed by molecular disintegration In this former case, the laser energy is expended in breaking the chemical bonds, and forming molecules with smaller number of atoms. The excess energy is converted to translation energy of the photofragments. The energy transfer in this case is considerably faster than vibration relaxation and a molecular dynamics model that attempts to explain the basic ablative processes on a molecular level, should take into consideration besides the two broad categories of the mechanisms involved in the process of vibration excitation and photofragmentation the quantum properties of light. In the case of weak laser fields the photodissociation rate $\Gamma$ is given by the quantum properties of light. In the case of weak laser fields the photodissociation rate $\Gamma$ is given by the expression [13]:

$$\Gamma = \frac{2\pi|d_{12}\sqrt{m\epsilon_0}|}{\nu T |S_1 - S_2|} e^{-\gamma}$$

(1)
where $d_{12}$ is the dipole moment of the transition between the ground and the excited electronic states, $m$ is the monomer mass, $E_0$ is the intensity of the electric field of the laser pulse per unit volume, $S_{1,2}$ are the slopes of the potential energy of the ground and the excited electronic states respectively, $v$ is the average thermal velocity of the molecule, $T$ is the lifetime of the corresponding vibration mode, and $\tau$ is the classical action defined as the time integral of the difference between the kinetic and the potential energy across the path. For the case of a dissociative excited electronic state the classical action takes large positive values and the dissociation rate $\Gamma$ increases rapidly. However, dipole transitions within certain polymeric materials might induce limited dissociation rates when the ground and the excited states fulfill the condition:

$$\left| S_1 - S_2 \right| \rightarrow e^{2\tau}$$  \hspace{1cm} (2)

In the case of dipole transitions between bound excited electronic states, the classical action $\tau$ takes negative values and the exponential term approaches $e^{-2(2m\Sigma D_0)^{1/2}}$, where $\Sigma D_0$ is the sum of the dissociative energies of the ground and the excited electronic states. Furthermore due to the fact that $\Gamma/\tau$ is proportional to the Frank-Condon Factor $\langle x_1 | x_2 \rangle$, it is expected that the absorption coefficient at 157nm, will be a measure of the dissociative rate at this wavelength. At 157nm there is a higher probability for breaking chemical bonds commonly encountered in the organic molecules and causing out-gassing and photochemical ablation in comparison to longer wavelengths [14]. Out-gassing at 157nm cannot be avoided, but it can be reduced, provided that the polymeric materials will have excited dissociative electronic states with the right value of slope at the transition points of their potential energy surfaces in order to fulfil the condition which is described by Eq. 2.
Fig. 2, represents the surface image of the S1 copolymer in the contact mode with the scan size of 30 x 30 µm. The left image represents the real topography (height), while the right one represents the deflection of the cantilever. This is the error signal in the tapping mode and it represents the derivative of the height with respect to lateral position. The surface seems to be flat with a RMS roughness of 0.4 nm.

The surface image of the S2 copolymer is shown in Fig. 3, in contact mode image and with a scan size of 8,92 x 8,92 µm. The surface was flat with a RMS roughness of 0.3 nm. Some irregularities in the scan lines across the image (x direction) can be seen, which is due to the "sticking" of the AFM tip onto the surface. Normally, this is either due to the water capillary force, which could indicate that the coating polymer is hydrophilic with an adsorbed layer of water on it. The second possibility is that the polymer at certain points strongly adsorbs the AFM tip due to local irregularities. The main result of the AFM analysis is that the average dimension of the macromolecules of the silicon based copolymers, and therefore also their surface roughness, depends on the composition of the two polymers.

When the samples were exposed to 157nm light, Figs. 4, the surface of the remaining polymer on the substrate is modified. For low light intensities less than 0.5mJ per pulse, the exposed areas exhibit well defined sharp edges on the boundaries between exposed and non-exposed areas, suggesting photochemical bond breaking of the exposed areas, as it can be seen in Fig. 4 which has been recorded in the tapping mode with a scan size of 80x80µm. The left side of the image represents the unexposed area and the right side the exposed one. At the boundary there is a high and relatively wide rim, 11 microns wide and 1 micrometer high. This rim is due to the
explosive dissociation of the illuminated area and the concentration of photofragments pushed to the edge by the shock wave. The exposed part is rough, and some many "islands" of material can be seen following light illumination with the laser pulse at 157nm with an energy less than 0.5mJ/cm² per pulse. It is expected that with increasing intensity of the radiation, the boundary between the exposed and unexposed areas is less well defined than at lower photon energies. In this case and around the boundaries matter tends to accumulate, as it is pushed away from the shock wave which always follows the photodissociation process.

4. Conclusions

A copolymer of ethyl polyhedral oligomeric silsesquioxane (ethyl-POSS) and tert-butyl methacrylate (TBMA) at different concentrations of the homopolymers was evaluated in terms of surface roughness and homogeneity before and after illumination with laser light at 157nm. Surface homogeneity and phase separation before exposure to 157nm depends on the chemical composition of the resist, and AFM images of exposed areas indicate sharp edges at the boundaries between exposed and non-exposed areas, suggesting photochemical bond breaking of the exposed areas. In addition phase separation, with an average size of 450nm of different phases was observed for some of the samples.

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References


**Figure Captions**

**Fig.1** The random copolymers of this work comprising of two monomers (TBMA:x and ethyl-POSS:y) with different composition.
Fig. 2 Surface image of the S1 copolymer in the contact mode with the scan size of 30 x 30 µm. The left image represents the real topography (height), while the right one represents the deflection of the cantilever. This is the error signal in the tapping mode and it represents the derivative of the height with respect to lateral position. The surface seems to be flat with a RMS roughness of 0.4 nm. This is somewhat lower than the contact mode value, which is expected due to the lower resolution of the AFM in the tapping mode.

Fig. 3 Surface image of the S2 copolymer in contact mode. The image was taken with a scan size of 8,92 x 8,92 µm. The surface RMS roughness was 0.3 nm.

Fig. 4 Surface image of the S1 copolymer taken in the tapping mode after exposure at low light intensities (~ 0.5mJ per pulse). Exposed areas exhibit well defined sharp edges at the boundaries between exposed and non-exposed areas, suggesting photochemical bond breaking at the exposed areas, with a scan size of 80x80µm. The left side of the image represents the unexposed area and the right side the exposed one. At the boundary, there is a high and relatively wide rim, 11 microns wide and approximately 1 micrometer high. This rim is due to the explosive dissociation of the illuminated area and the concentration of photofragments pushed towards the edge by the shock wave. The exposed part is rough, and many "islands" of material can be seen following illumination with the laser pulse at 157nm.
Fig. 1
Fig. 3
Fig. 4