Nanoparticle Photoresists: Ligand Exchange as a New and Sensitive EUV Patterning Mechanism

Marie Kryask, Markos Trikeriotis, Christine Ouyang,
Souvik Chakrabarty, Emmanuel P. Giannelis and Christopher K. Ober*

Dept. of Materials Science and Engineering, Cornell University, Ithaca, NY 14853

Hybrid nanoparticle photoresists and their patterning using DUV, EUV, 193 nm lithography and e-beam lithography has been investigated and reported earlier. The nanoparticles have demonstrated very high EUV sensitivity and significant etch resistance compared to other standard photoresists. The current study aims at investigating and establishing the underlying mechanism for dual tone patterning of these nanoparticle photoresist systems. Infrared spectroscopy and UV absorbance studies supported by mass loss and dissolution studies support the current model.

Keywords: Nanoparticle photoresist, dual tone patterning, ligand exchange, lithography.

1. Introduction

For several years EUV lithography has been considered one of the leading technologies for achieving the patterning goals for next generation lithography [1]. Recent studies of hybrid nanoparticle systems developed by researchers at Cornell University has shown remarkable patterning capabilities using DUV, EUV and e-beam techniques, with remarkably high EUV sensitivity [2-4]. Figure 1 shows SEM images of patterns generated by DUV (A), EUV (B) and e-beam (C) lithography, demonstrating good resolution capabilities of the resist. The nanoparticle resists, synthesized by sol-gel technique, consists of an inorganic metal oxide core, which in this case is a hafnium or zirconium oxide and an organic shell composed of methacrylic acid moieties. The presence of the organic shell drives miscibility in organic solvents, facilitating processability while the inorganic metal oxide core provides excellent thermal and chemical stability, along with superior etch resistance to various etch gases compared to other organic photoresists [5].

The present study aims at understanding the mechanism that is responsible for the dual tone patterning of these nanoparticle photoresists.

Figure 1. SEM images of DUV (A), EUV (B) and e-beam (C) patterns obtained using ZrMAA nanoparticles as a photoresist.

2. Experimental

2.1. Materials.

All chemicals were purchased from Sigma Aldrich unless indicated otherwise and used without further purification. Solvents were reagent grade and obtained from Sigma Aldrich, unless noted otherwise. Syringe filters used in the resist processing was obtained from Fisher. Test silicon wafers (N type, 10-20 Ω) were obtained from WRS materials.

2.2. Formulation of the resist film.

Nanoparticles were synthesized according to a standard protocol as reported earlier [4]. A typical resist film involves a formulation comprising 10 wt%

nanoparticles well dispersed in an organic solvent that is suitable for spin coating. This resist dispersion also contains minute quantity of a photoactive compound, typically forming 1 wt% to 5 wt% of the nanoparticle. In the present study, PGMEA is used as the spin coating solvent. Large particulates present in the resist dispersion are removed by filtering the solution through a 0.2 μm syringe filter. The photoresist was spin coated on pre-cleaned silicon wafers at 2000 rpm for 60 second (@ 400 rpm/sec) to obtain a thin, uniform film. The spin coated film was then baked at 110 $^{\circ}\text{C}$ for 60 seconds to remove any excess solvent.

2.3. Characterization.

Particle size was measured using the Malvern Zetasizer NanoZS. ATR-IR spectra on the photoresist films at different stages of resist processing were obtained using a Nicolet 400 spectrometer and analyzed using the Omnic software. UV absorbance spectrum was taken using the Molecular Devices 384 spectrophotometer. Thermogravimetric analysis (TGA) was performed using a Q500 thermogravimetric analyzer, TA instruments. Dissolution study was done using a Quartz Crystal Microbalance.

3. Results and Discussion

Studies were undertaken to understand the methods of pattern formation, already shown not to be chemical amplification. This study therefore aims at understanding the underlying mechanism for patterning of the nanoparticle photoresists. Spectroscopic analysis coupled with mass loss and dissolution studies have been undertaken to provide a rationale. The two possible routes for patterning of the photoresist films are:

- i. Photochemical crosslinking at the carbon double bonds present in the methacrylic acid ligands.
- ii. Exchange of ligands at the surface of the nanoparticles with the photoactive compound, leading to a switch in solubility during development.

3.1. Photochemical Crosslinking.

Crosslinking of the double bond present in the methacrylic acid moiety mediated by UV exposure leads to formation of a network. Such a network of organic ligands would make the exposed regions insoluble in the developer and hence a negative tone pattern would be generated. To investigate the

formation of crosslinks initiated by UV exposure, infrared spectroscopy and UV absorbance studies were performed on exposed resist films.

Figure 2. UV absorbance spectrum (A) and IR spectrum (B) of ZrMAA resist film exposed to 500 mJ/cm^2 of DUV radiation (254 nm)

Figure 2A shows the UV absorbance spectrum of a resist film subjected to 500 mJ/cm^2 of DUV radiation at 254 nm wavelength. A peak absorbance at 210 nm is observed which corresponds to the carbon double bond in the methacrylic acid ligand. Similarly, Figure 2B shows an IR spectrum of a resist film subjected to the same amount of DUV exposure. The peak observed at 1640 cm^{-1} is characteristic to the carbon double bond in the methacrylic acid. These results show that the site of unsaturation remains intact even after exposing the film to a relatively high dose of UV. Hence, from the above results, a possibility of photochemical crosslinking at the site of unsaturation in the organic ligand is unlikely.

3.2. Concept of Ligand Exchange

Resist solutions were prepared by the standard protocol as noted earlier. Photoresist films were spin cast on unprimed silicon wafers and subjected to a post application bake. The resist was then subjected to a flood exposure (UV) at 150 mJ/cm^2 and finally a post exposure bake step at 130 $^{\circ}\text{C}$ for 2 mins. The films were designated as the unexposed, exposed and the PEB films respectively. A systematic IR study was performed on these resist films to spectroscopically investigate the chemical changes occurring in the photoresist as a function of processing conditions in order to study the patterning mechanism.

The resist composition has a very small amount of a photoactive compound, which is a nonionic photoacid generator or a photoradical initiator. The

Scheme 1. Schematic representation of the ligand exchange mechanism.

basic concept of ligand exchange has been outlined in Scheme 1, where the photoacid generated on UV exposure, most likely a sulphonic acid or benzoic acid, would displace the weaker ligand from the nanoparticle and bind to the core. This phenomenon would bring about a solubility change between the exposed and unexposed regions of the resist, leading to generation of the desired pattern.

3.3. Spectroscopic Analysis.

The hybrid nanoparticles that have been discussed in this section have *core-shell* architecture, that is, they have an inorganic metal oxide core surrounded by a shell comprised of organic ligands. Methacrylic acid, the ligand in this study, is bound to the core of the nanoparticles in the form of methacrylate ions. Based on our proposed mechanism, sulphonate ions generated as a photoacid from UV exposure of the photoactive compound has a stronger affinity for the nanoparticle core. The liberated sulphonate ions could displace the weakly bound methacrylate ions from the nanoparticle and bind to the inorganic core.

A qualitative estimate of ligand exchange and binding can be obtained from infrared spectroscopic studies since methacrylate and sulphonate ions have different characteristic peaks in the IR spectrum. A carboxylate ion gives a characteristic IR peak at 1540 cm^{-1} whereas, a sulphonate ion has a characteristic peak at 1361 cm^{-1} , while the peak shifts to 1372 cm^{-1} for bound sulphonate ions.

Figure 3 shows the IR spectra for a ZrMAA photoresist at different stages of resist development.

The portion of the spectra ranging from 1325 to 1400 cm^{-1} has been magnified in order to detect the subtle

Figure 3. IR spectra of ZrMAA resist film at different stages of resist processing

transitions in the nanoparticle ligand functionality. It is observed that the spectrum for the unexposed resist shows a peak at 1361 cm^{-1} , characteristic of the sulphonate ions present in sulphonic acid. The next three spectra correspond to different DUV exposure times of 1, 2 and 3 min respectively. It can be observed that the spectrum at 1 min of exposure shows two convoluted peaks, one at 1361 cm^{-1} and the other one at 1372 cm^{-1} . This observation provides evidence of the fact that at 1 min of exposure, a certain fraction of the photoacid moieties generated by UV undergoes an exchange with the methacrylate ions and binds to the nanoparticles. The subsequent spectrum for 2 min exposure shows the peak completely shifted to a higher wavenumber of 1372 cm^{-1} , indicating that the sulphonate ions are present in the bound state in the photoresist. The final spectrum of the resist after post exposure bake (PEB) shows that the peak for bound sulphonate ions at 1372 cm^{-1} remains unchanged.

Now, the peak areas corresponding to the carboxylate ions, bound sulphonate ions and the carbon double bonds were calculated and normalized with respect to a peak in the fingerprint region of the spectrum. Considering the peak areas obtained at 2 min exposure time as a basis, the change in the respective areas was plotted as a function of

Figure 4. Normalized IR peak intensities of methacrylate ions, sulphonate ions and the carbon double bond as a function of exposure time.

exposure time in Figure 4. From the graph it can be observed that with increase in exposure time, the amount of sulphonate ions bound to the nanoparticle core increases, whereas, the percent of bound methacrylate ions decrease. Peak area for the carbon double bond remains unchanged with exposure. This signifies that with increasing exposure time, there is an increasing number of bound methacrylate ions that are being displaced by sulphonate groups from the nanoparticle shell and hence the observation. On the other hand the displaced methacrylic acid moieties still remain in the vicinity of the photoresist and hence the peak area for the carbon double bond remains undiminished.

Sulphonate, carbonate and the carbon double bond IR peak intensities were measured with respect to a signature peak in the fingerprint region in order to study the changes as a function of PEB time. It was observed that the intensities for bound methacrylate and sulphonate ions remain the same whereas; there is a subsequent reduction in the peak intensity for the carbon double bond. This observation indicates that during PEB, some fractions of the free methacrylic acid produced during ligand exchange (exposure) are baked off from the photoresist, resulting in a reduction in the double bond peak area.

3.4. Thermogravimetric Analysis.

Mass loss study was performed using a TGA in order to quantify the amount of free, bound and total organic content in the nanoparticles. Resist films were removed from silicon wafers at different stages

of resist treatment and analyzed in the TGA for organic content. The respective values for free, bound and total organic content have been plotted in Figure 5 as a function of the respective stages of resist treatment for ZrMAA resist films.

Figure 5. Percent organic content for the unexposed, exposed and PEB resist films

It can be observed that the total organic content in the unexposed and exposed films are comparable at 44% and 45.2% respectively. The free or 'unbound' organic content in the exposed film is higher than the unexposed film by 2.5% due to generation of free methacrylic acid moieties from ligand exchange. For the PEB film, the bound organic content is comparable with that of the exposed resist film, which shows that the bake step does not affect the bound organic moieties. On the other hand there is a significant decrease in the free organic content by 9% suggesting that a PEB step bakes off the free methacrylic acid moieties that are produced as a result of ligand exchange with the photoacid. This phenomenon translates to an overall low total organic content at 36% for the PEB film.

3.5. Dissolution Study.

Prior studies have shown that photoactive compounds generate sulphonic and benzoic acid moieties on UV exposure. It has been observed in this investigation that due to a stronger affinity of these liberated photoacid to the metal oxide core, upon exposure, they displace the weakly bound carboxylate ligand and attach to the core of the nanoparticle. Hence, for the methacrylate bound hafnium/zirconium oxides, an exposed region would have a high concentration of sulphonate/benzoate

moiety (depending on the liberated photoacid), whereas, the unexposed region would still retain the carboxylate ligand on the nanoparticle surface.

Figure 6. Dissolution behavior of ZrMAA and ZrBA resist in 4-methyl-2-pentanol developer.

This aspect of the study aims at mimicking the exposed region of the HfMAA/ZrMAA photoresists by synthesizing nanoparticles having benzoic acid ligands. Dissolution behavior of these nanoparticle photoresists in a negative tone developer, which in this case is 4-methyl, 2-pentanol, was investigated using a quartz crystal microbalance. Resist solutions of ZrMAA and ZrBA nanoparticles were spin coated on quartz crystals followed by a post applied bake. Figure 6 shows that the ZrMAA resists undergo a rapid dissolution in 4M2P, such that a 90% reduction in film thickness is observed in the first 4 seconds, which stabilizes within the next 10 seconds. On the contrary, ZrBA resist films have very poor dissolution in the developer, wherein, only 5% of the film dissolves in the first 25 seconds and finally after a minute of immersion, there is only a reduction of 7% in the film thickness of the resist. This striking contrast in the dissolution behavior brought about by a change in ligands further supports the concept that the presence of a more strongly binding acid ligand in the exposed regions would induce a solubility change between the exposed and unexposed parts, leading to formation of patterns upon development.

4. Conclusion

The present study investigates and offers a plausible explanation for the underlying mechanism involved in patterning of the nanoparticle photoresists. For a negative tone pattern, the exposed regions undergo a ligand exchange with the stronger

binding photoacid that is generated from the photoactive compound. This phenomenon makes the exposed regions less soluble in the negative tone developer, which in this case is 4-methyl, 2-pentanol, whereas, the unexposed regions still have the methacrylate ligands on the nanoparticle surface, making them more soluble.

For a positive tone pattern, the unexposed regions become less soluble in the developer. A plausible reason for this phenomenon is that the PEB step contributes to two changes in the composition of the unexposed region. Infrared spectra and mass loss studies have shown that there is a loss of carboxylic acid moieties from the resist after a PEB step. A reduction in the organic content of the nanoparticles reduces the solubility of the unexposed region in the solvent. Moreover, UV absorbance study has shown the formation of acid anhydrides in the unexposed region, which also contributes to a diminished solubility of those regions in the aqueous base developer.

Based on the ligand exchange mechanism, nanoparticles with organic ligands having a lower binding affinity than that of the generated photoacid would be suitable candidates for photolithographic patterning.

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