Metal Oxide Nanoparticle Photoresists for EUV Patterning

Jing Jiang, Souvik Chakrabarty, Mufei Yu and Christopher K. Ober*

Department of Material Science and Engineering, Cornell University, Ithaca, NY 14853

Previous studies of methacrylate based nanoparticle have demonstrated the excellent pattern forming capability of these hybrid materials when used as photoresists under 13.5 nm EUV exposure. HfO₂ and ZrO₂ methacrylate resists have achieved high resolution (~22 nm) at a very high EUV sensitivity (4.2 mJ/cm²). Further investigations into the patterning process suggests a ligand displacement mechanism, wherein, any combination of a metal oxide with the correct ligand could generate patterns in the presence of the suitable photoactive compound. The current investigation extends this study by developing new nanoparticle compositions with trans-dimethylacrylic acid and o-toluic acid ligands. This study describes their synthesis and patterning performance under 248 nm KrF laser (DUV) and also under 13.5 nm EUV exposures (dimethylacrylate nanoparticles) for the new resist compositions.

Keywords: nanoparticle, EUV, photoresist, metal oxide

1. Introduction

The progression of Moore’s law demands shrinkage in dimension of the technology nodes to sub 25 nm features. Currently, the industry has been relying on 193 nm immersion lithography with double patterning to print finer features on resist materials. Demands for further reduction in pattern dimension would require multiple patterning steps at the given 193 nm wavelength, leading to a manifold increase in processing expenditure. Recent developments in patterning has shown that EUV radiation at 13.5 nm wavelength holds promise in printing smaller features in a single exposure step. A major drawback of EUV sources is its low power output, which would lead to a decreased throughput in high volume manufacturing. To address this issue, significant studies are being performed aiming at intensifying the EUV power source. Similarly, another approach mitigate the issue of low throughput is to enhance sensitivity of photoresist materials to EUV radiation while still maintaining a high resolution and pattern LER.

An initial study on methacrylate based nanoparticle resists have demonstrated enhanced EUV sensitivity with high resolution patterns.¹ ² ³ Gaining insights from prior observations, the present study describes new nanoparticle compositions, using ligands of different strengths which led to resists with extremely high EUV sensitivity. Extending the study further, nanoparticles with o-toluic acid (strong ligand, figure 1b) was successfully synthesized and evaluated for patterning under 248 nm KrF laser (DUV).

2. Materials and Methods

2.1. Materials

The respective isopropoxide of hafnium and zirconium were obtained from Sigma Aldrich. Dimethylacrylic acid, o-toluic acid, photoactive compounds and reagent grade solvents were purchased from Sigma-Aldrich and used as received, without further purification. Silicon wafers were purchased from WRS materials.

Nanoparticles were synthesized by sol-gel technique as described previously. Photoresist formulation and film formation has been reported

Figure 1. trans-dimethylacrylic acid (a) and ortho-toluic acid (b)
in earlier studies, where for DUV applications a film thickness of ~ 80-100 nm is typically used and for EUV applications a thinner film (~40 nm) is preferred.

2.2. Characterization

Particle size was measured by dynamic light scattering (DLS) using a Malvern Zetasizer. Organic content was measured by Thermogravimetric Analysis (TGA, TA instruments). Ultraviolet exposure and patterning studies were performed using the ASML 300C DUV stepper and the Berkeley Micro Exposure Tool (BMET) at LBNL.

3. Results and Discussion

3.1. Lithographic Patterning of Dimethylacrylate based resists

3.1.1. 248 nm DUV lithography

Initial pattern formation in the sub-micron scale regime was investigated by exposing HfO2-DMA and ZrO2-DMA resists under a 248 nm KrF laser. Photoresist compositions were formulated containing 1 wt% of a nonionic photoacid generator (PAG) as per protocols mentioned in earlier studies. The resist formulation was spin coated on silicon wafers at 2000 rpm for 60 seconds at 400 rpm/sec forming uniform films. The resist films were exposed to 248 nm DUV radiation at a dose of 50 mJ/cm². The dose is comparatively lower than the previous methacrylate resists, which patterned at 150 mJ/cm² dose of DUV. Figure 2 shows high resolution line-space (150 nm) and contact (300 nm) patterns obtained with good contrast between the exposed and unexposed regions. The pattern resolutions were limited by the mask resolution. Enhanced sensitivity for these resists with the weaker dimethylacrylate ligands prompted further study at extreme ultraviolet wavelengths of 13.5 nm to investigate their ultimate resolution, sensitivity and pattern roughness.

3.1.2. EUV lithography.

Our prior investigations on methacrylate based resists have showed that the resist sensitivity increases progressively at lower wavelengths. For EUV exposures, HfO2-DMA and ZrO2-DMA resist films were spin coated on bare silicon wafers to a thickness of ~ 40 nm and were investigated for pattern formation. Figure 3 shows line-space patterns for HfO2-DMA and ZrO2-DMA resist films in the presence of 3 wt % nonionic PAG. Extremely high EUV sensitivity of the resists is observed from Figure 3, with HfO2-DMA forming 30 nm and 20 nm line-space patterns at a dose of 2.4 mJ/cm², whereas, ZrO2-DMA has a dose to pattern of 1.6 mJ/cm². The EUV sensitivities observed for this resist system is superior to the industrial standard of 10 mJ/cm². Attainment of such sensitivity and resolution does have a trade-off with the pattern roughness, with LER values ranging from 5-7 nm for these resists at the given resolution. The difference in sensitivity observed for the HfO2 and ZrO2 resists could be explained in terms of difference in binding affinity between the ligand and the respective metal oxide core.

3.2. Ortho-toluic acid ligand – synthesis and characterization

Figure 2. DUV (248 nm) lithography on ZrO2-DMA resists demonstrating the feasibility for pattern formation.

Figure 3. EUV lithography demonstrating 20 nm and 30 nm line-space patterns on HfO2-DMA and ZrO2-DMA resists films with very high EUV sensitivity.
Ortho-toluic acid, an acid that is comparatively stronger than dimethylacrylic acid, was chosen as a second organic ligand for the present study. A sol-gel synthetic route was adopted with the corresponding metal isopropoxide and o-toluic acid as the reactants and THF as solvent. The reaction was performed at 65 °C for 18 hours in the presence of trace amounts of water, to produce a slightly yellowish dispersion. Keeping in mind the water solubility of o-toluic acid, precipitation and washing was performed with three different solvent systems, namely, water, acetone-water and THF-water. Nanoparticles isolated from this step were dried for 24 hours in a vacuum oven. Particle size measurement by DLS, ligand incorporation via IR spectroscopy and organic content evaluation by TGA was performed to select the nanoparticle out of the three different precipitation and washing techniques performed earlier, for further lithographic evaluation.

### 3.2.1. Lithographic evaluation (248 nm DUV)

Nanoparticles obtained from the acetone-water solvent system, having ~ 2.4 nm particle size and 55% organic content, was selected for further lithographic investigation. Photoresist formulations containing 7.5 wt% of HfO$_2$-TA and ZrO$_2$-TA, in the presence of 3 wt% nonionic PAG were spin coated on silicon wafers as mentioned previously, to form thin, uniform films. From preliminary patterning results, 150 ml/cm$^2$ was chosen as the optimum dose for performing exposures at 248 nm DUV. Figure 4 shows line-space patterns for HfO$_2$-TA and trench patterns for ZrO$_2$-TA resists. The toluic acid based resists form sharp patterns with very high contrast between the unexposed and exposed regions. An ultimate resolution of 150 nm is achieved for these resists, which is yet again limited by the resolution of the mask used at this wavelength.

### 4. Conclusion

The present study on the dimethylacrylate based resists, HfO$_2$-DMA and ZrO$_2$-DMA, has demonstrated high EUV sensitivity (~ 1.6-2.4 mJ/cm$^2$), producing high resolution line-space patterns (20 nm) with a compromise in pattern roughness. To compare other ligands, nanoparticles with o-toluic acid ligand were successfully synthesized in order to enhance the binding affinity with the metal oxide core. Characterization results show successful incorporation of toluic acid in the particle, with the particle size and organic content conforming to prior standards. Patterning results under 248 nm KrF laser (DUV) demonstrates high resolution patterning ability of these resists reaching the resolution limit of the mask at 150 nm. Although at the given wavelength of 248 nm, the toluic acid based resists have a lower sensitivity as compared to the dimethylacrylate resists, from our prior investigations we have observed these nanoparticle resists to demonstrate enhanced sensitivity at lower (13.5 nm) wavelengths. Further studies entail EUV exposures on the o-toluic acid based resists in order to investigate the RLS characteristics at lower wavelengths of radiation.

### Acknowledgements

The authors gratefully acknowledge SEMATECH for funding, as well as the Cornell Nanoscale Science and Technology Facility (CNF), Cornell Center of Materials Research (CCMR), the Nanobiotechnology Center (NBTC) and the KAUST-Cornell Center of Energy and Sustainability (KAUST_CU) and Lawrence Berkeley National Lab (LBNL) for use of their facilities.

### References

