Zinc-Based Nanoparticle Photoresist for Extreme Ultraviolet Lithography

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Affiliation: Departments of Materials Science and Engineering, Cornell University Primary Source of Research Funding: JSR Corporation Contact: cko@cornell.edu, ky373@cornell.edu Primary CNF Tools Used: ABM contact aligner, ASML 300C DUV stepper, Zeiss Ultra SEM

Abstract:

Extreme ultraviolet (EUV) lithography, using 13.5 nm radiation, is considered one of the most prominent candidates for next generation lithography. The main challenge for EUV resists is to simultaneously satisfy resolution, line-width roughness (LWR) and sensitivity requirements. Over the past few years, our main effort has been to focus on ZrO_2 and HfO_2 nanoparticle-based photoresists. However, both Zr and Hf are relatively low EUV absorbing metals [1], and integration of high EUV absorption elements is a more promising route to further improve lithographic performance under EUV radiation. Zinc is a promising metal for higher EUV absorption. In this work, we synthesized a set of zinc-based nanoparticle photoresists with different kinds of toluic acid ligands. These nanoparticles possess small particle size, good solubility in spin-coating solvents, good film-forming abilities and patterning by incorporating a photo-acid generator.

Summary of Research:

HfO₂- and ZrO₂- nanoparticle based photoresists are well-known in the novel inorganic-organic hybrid nanoparticle system [2-6] developed by researchers at Cornell. With significantly higher etch resistance and smaller particle size, these nanoparticle photoresists show promising lithographic performance using DUV, e-beam and EUV exposure. Meanwhile, their superior etch resistance and extremely small constituent size, are clear advantages for ultimate resolution patterning.

However, the Zr and Hf are relatively low EUV absorbing metals [1], and integration of high EUV absorption elements was considered to be one promising route to further improve lithographic performance under EUV radiation. Under this notion, we then developed a series nanoparticle using high EUV absorption element Zn as the metal core. Zinc has shown higher EUV photoabsorption compared to both zirconium and hafnium, thus has a higher potential to achieve the high-sensitivity desired for EUV lithography.

In this work, we synthesized and tested new nanoparticles based on zinc oxide (ZnO). Zinc is a higher EUV absorption metal compared to Zr and Hf. With a similar approach we used for zinc *m*-toluic acid (ZnO*m*TA), zinc *p*-toluic acid (ZnO-*p*TA) and zinc *o*-toluic acid (ZnO-*o*TA) were synthesized to improve patterning ability of zinc-based nanoparticles. The result shows that



Figure 1: Optical microscopic images of zinc-based nanoparticles: (a) ZnO-oTA; (b) ZnO-mTA; (c) ZnO-pTA.

both ZnO-*p*TA and ZnO-*o*TA give good quality patterns after mid-UV exposure and DUV exposure, which indicates these nanoparticles are good candidates for EUV lithography.

Middle-Ultraviolet (mid-UV) Lithography:

Preliminary lithographic evaluations were carried out using the CNF ABM contact aligner (254 nm UV). The resist test formulation contains 5 wt% nanoparticles and PGMEA as solvent. The resist was spin-coated onto a silicon wafer at 2000 rpm for 1 min, then exposed under 254 nm at 150 mJ. Development was conducted immediately after exposure. As shown in Figure 1, clear patterns can be obtained after mid-UV exposure. Pictures were taken by Nikon Microscope Cameras in CNF.

Deep Ultraviolet (DUV) Lithography:

With similar lithographic conditions in mid-UV exposure, the zinc-based nanoparticles are further exposed upon 248 deep-UV radiation using ASML 300C DUV Stepper in CNF. The film is exposed at 150 mJ/cm² as normal condition and developed in acetone. Developing time varies by different nanoparticles. Well-defined 1:1 line-and-space patterns negative tone patterns with feature size from 1000 nm to 250 nm were obtained, as indicated by scanning electron microscope (SEM) images (Figure 2 to Figure 4), taken by CNF Zeiss Ultra SEM.

In summary, we developed new ligands for zinc-based nanoparticles used in extreme ultraviolet lithography. These zinc-oxide based nanoparticles possess good solubility in spin-coating solvents, good film-forming ability and moderate patterning performance under mid-UV and deep-UV radiations. Considering the high EUV photo-absorption of zinc metal, this preliminary work indicates such zinc-based nanoparticles would be promising candidates for EUV lithography. Further structure analysis, patterning mechanism study and lithography tests including EUV lithography patterning tests are ongoing using these zinc-based nanoparticles.

References:

- [1] B. L. Henke et al., X-Ray Interactions: photoabsorption, scattering, transmission, and reflection at $E = 50 \sim 30,000 \text{ eV}, Z = 1-92$. At. Data Nucl. Data Tables, 54, 181-342 (1993).
- [2] M. Trikeriotis, et al., Development of an inorganic photoresist for DUV, EUV, and electron beam imaging. Proc. SPIE 7639, 76390E (2010).
- [3] W. J. Bae, et al., High refractive index and high transparency HfO₂ nanocomposites for next generation lithography. J. Mater. Chem. 20, 5186-5189 (2010).
- [4] M. Krysak, et al., Development of an inorganic nanoparticle photoresist for EUV, E-beam, and 193nm lithography. Proc. SPIE 7972, 79721C (2011).
- [5] M. Trikeriotis, et al., A new inorganic EUV resist with high-etch resistance. Proc. SPIE 8322, 83220U (2012).
- [6] S. Chakrabarty, et al., Increasing sensitivity of oxide nanoparticle photoresists. Proc. SPIE 9048, 90481C (2014).



Figure 2: SEM images of ZnO-oTA nanoparticles: (a) 250 nm; (b) 500 nm; (c) 1000 nm.



Figure 3: SEM images of ZnO-mTA nanoparticles: (a) 250 nm; (b) 500 nm; (c) 1000 nm.



Figure 4: SEM images of ZnO-pTA nanoparticles: (a) 250 nm; (b) 500 nm; (c) 1000 nm.

