New Photopatterning Materials for Advanced Lithography

2018 CNF REU Intern: Jordan Phillip Howard-Jennings

2018 CNF REU Intern Affiliation: Engineering, Harvey Mudd College

CNF Project: 2018 Cornell NanoScale Science and Technology Facility Research Experience for Undergraduates Program

CNF REU Principal Investigator: Christopher Kemper Ober, Materials Science and Engineering, Cornell University

CNF REU Mentors: Kazunori Sakai, Materials Science and Engineering, Cornell University; Seok-Heon Jung, Materials Science and Engineering, Cornell University; Christopher Alpha, CNF, Cornell University

Primary Source of CNF REU Funding: National Science Foundation via the National Nanotechnology Coordinated Infrastructure (NNCI) Grant No. ECCS-1542081

Contact: jhowardjennings@g.hmc.edu, ks2288@cornell.edu, sj736@cornell.edu, alpha@cnf.cornell.edu

Website: http://www.cnf.cornell.edu/cnf_2018reu.html

Primary CNF Tools Used: ASML DUV stepper, Au/Pt sputter deposition, Hamatech wafer processor, spin coaters

Abstract:

Photolithography, which is a patterning method used to produce micro/nano-scale features, is currently approaching capabilities of producing sub-10 nm features at EUV wavelengths [1]. We present the findings of material development and characterization of model chemically amplified resists (CARs) to study novel photoacid generators (PAGs), as well as of Zn and Zr metal oxide nanoparticle (MO-NP) resists which offer many advantages over CARs.

Background:

For the past decade, the semiconductor industry has been using immersion lithography to make deep-UV lithography critical dimensions smaller [2]. However, and particularly with CARs which utilize PAGs to “amplify” the photo-reaction that occurs upon exposure, two issues arise: defective patterns resulting from the leaching of resist into the immersion fluid [2], and a sensitivity boost at the expense of line-edge roughness (LER) [3,4]. For EUV lithography to become an industry standard, current materials development of EUV resists must address these issues.

MO-NPs have garnered attention for resist development because they offer many potential and realized advantages to current resist technologies: smaller size relative to polymer photoresists [5], and a ligand-exchange photoreactive mechanism that is more controllable than the deprotection reactions that occur with generated photoacids in conventional resists [6], among other benefits. Currently, metal oxide methacrylate resists produced from hafnium and zirconium have been shown to be potential candidates for EUV resists because of their high resolution and sensitivity [6].

Furthermore, the ligand-exchange mechanism occurring between the acid groups on the metal oxides and the generated photoacids that produces a solubility switch in the exposed area is of interest of further investigation. Since there is a direct correlation between scumming (a phenomena associated with high LER) and the type of PAG used [3], a study of how PAGs alter resist performance is necessary for understanding how newly developed PAGs may provide better compatibility for EUV MO-NP resists.

Materials and Methods; Synthesis

MO-NP Resists. Resist solutions were prepared by combining 91 mg metal oxide, 9.1 mg PAG (N-hydroxynaphthalimide triflate), and 1.9 g PGMEA in a small glass vial. The metal oxide and PAG were dissolved in PGMEA through 12-16 minutes of stirring on a handheld vortex mixer.

Model CARs. Resist solutions were prepared by synthesizing the monomers tert-butyl methacrylate, isobornyl methacrylate, and methacrylic acid with AIBN as an inhibitor. Once this product was formed, it was mixed with a PAG and PGMEA and dissolved by exposure to a heat gun and vigorous hand-mixing for 10-15 minutes.

Materials and Methods; Lithographic Conditions

MO-NP Resists. Resists were spun onto bare silicon wafers at 2000 rpm for 60s and given a 60s soft bake at 40°C (Zr) or 70°C (Zn). The wafers were then exposed using a 248 KrF source ASML DUV stepper at a dose of

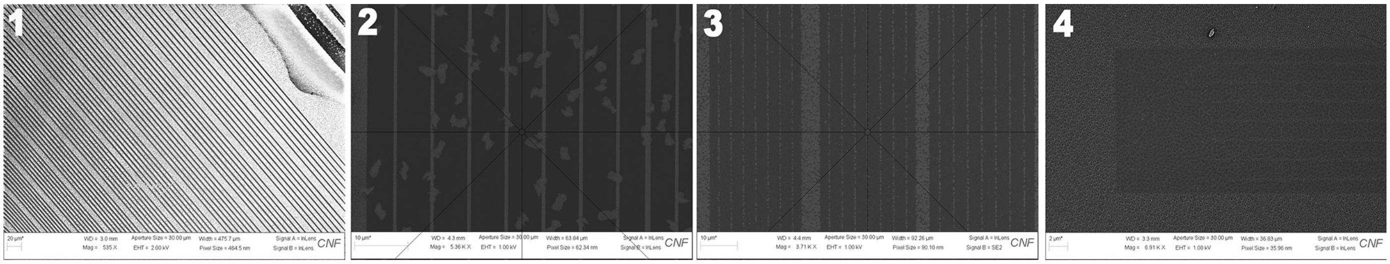

Figure 1: SEM image of various width patterns (largest 1000 nm) of Zn-oxide NP resists. Figure 2: SEM image of a 1000 nm-width pattern from the Zn-oxide NP resist. Figure 3: SEM image of a 500 nm-width pattern (center) from the Zr-oxide NP resist. Figure 4: SEM image of a pattern exposed region from the CARs.

150 mJ/cm^2, and subsequently developed in a range of solvents including o-xylene and m-xylene (Zr) as well as toluene and decaline (Zn).

Model CARs. DUV-42P bottom anti-reflective coating (BARC) was spun onto bare silicon wafers at 4000 rpm and given a 60s soft bake at 200°C. Resists were spun onto these wafers at 3000 rpm for 60s and given a post-annealing bake (PAB) at 100°C. Exposure took place on the ASML DUV stepper using an exposure dose matrix ranging from 10 to 358 mJ/cm^2, and subsequently given a 60s post-exposure bake (PEB) at 100°C before development in diluted TMAH for 60s using the Hamatech wafer processor.

Materials and Methods; Characterization

An assortment of optical microscopes capable of imaging nanometer-grade patterns were used to "check" that patterns had registered among the many pre-final lithographic steps. Once developed, scanning electron microscopy was used to qualitatively evaluate resist performance using the Zeiss Supra and Zeiss Ultra models of their SEMs. For the CARs, a pre-SEM step of sputtering a thin Au/Pt layer on the wafer surface was required to reduce SEM overcharging.

Results and Conclusions:

MO-NP Resists. Current resist development demonstrates that while good feature production is possible (Figure 1), randomly dispersed particle defects (Figure 2) and incomplete pattern registering (Figure 3) significantly distort these features. The cause of these defects is not currently understood. For the Zn-oxide resist evaluated, the gradient-matching between the particle defects and the exposed/non-developed regions (lighter area) suggest that there could be issues in material preparation such as mixing of components.

Model CARs. While the appearance of desired patterns offers confirmation that the lithography happened, the model CARs run into two issues: First, randomly dispersed porous defects dominate both the exposed and non-exposed areas, strongly suggesting that further materials development is needed. Second, the small gradient change between the patterned and non-patterned regions suggests that the height of the patterns is negligible (this observation is confirmed by the optical profilometer), suggesting that lithographic conditions used were not optimal.

Future Work:

Further materials development in conjunction with lithographic parameter optimization is necessary to reduce the preliminary defects observed in both the MO-NP resists and the model CARs. After these defects are eliminated, an expansive design-of-experiments may be implemented to evaluate factor interactions between different material properties (i.e., PAG type/amount, metal oxides, etc.) and lithographic conditions (i.e., spin times, bake times, exposure doses, etc.).

Acknowledgements:

This work was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the NSF (Grant ECCS-1542081).

References:

[1] Li, Li, et al. Chemical Society Reviews. doi: 10.1039/C7CS00080D (2017).

[2] Petrillo, Karen, et al. Advances in Resist Technology and Processing XXII. doi: 10.1117/12.601621(2005).

[3] Kosma, Vasiliki, et al. "Extreme Ultraviolet (EUV) Lithography IX. doi: 10.1117/12.2297383 (2018).

[4] Thiyagarajan, Muthiah, Kim Dean, and Kenneth E. Consalves. Journal of Photopolymer Science and Technology. doi: 10.2494/photopolymer.18.737 (2005).

[5] Krysak, Marie, et al. Advances in Resist Materials and Processing Technology XXVIII. doi: 10.1117/12.879385 (2011).

[6] Jiang, Jing, et al. Journal of Photopolymer Science and Technology. doi: 10.2494/photopolymer.27.663 (2014).