Nanoparticle Photoresists: Synthesis and Characterization of Next-Generation Patterning Materials

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Abstract:

Hybrid metal oxide nanoparticle photoresists are prominent candidates for next-generation photolithography due to their exceptional sensitivity to extreme ultraviolet (EUV) radiation. To improve the resist's resolution, roughness, and sensitivity (RLS) performance, we explored new compositions for this nanoparticle system. In this study, a series of new nanoparticle resist compositions were synthesized and characterized by solubility and radiation dose tests, as well as deep ultraviolet (DUV) and electron-beam patterning.

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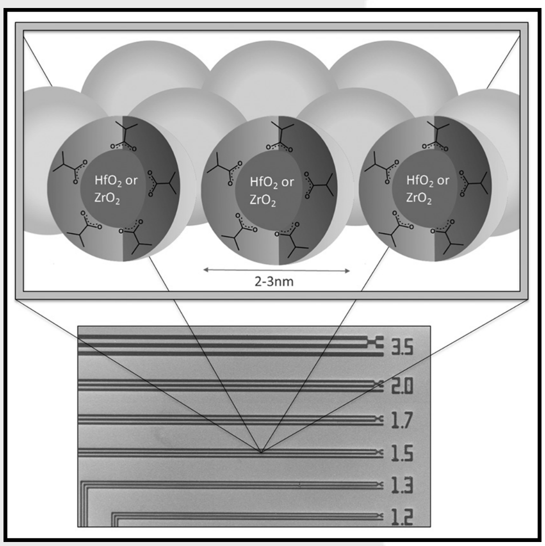

Figure 1: A schematic of the Ober group nanoparticle photoresist.

Introduction:

If the current microelectronics industry is to continue the trend set by Moore's Law, immediate solutions are required for successful next-generation patterning processes. The processes currently in development use EUV radiation at a 13.5-nanometer wavelength. However, the source for this radiation is currently too weak for industrial production throughput. The nanoparticle photoresist developed by Ober and Giannelis, et al. (Figure 1) is one prominent candidate for next-generation photolithography, helping to mitigate the light source issues with its high EUV sensitivity [1]. The inorganic metal oxide core also provides thermal stability and a higher refractive index, increasing the depth of field, while the organic ligand shell defines the nanoparticle's solubility properties. It is believed that the resists' EUV sensitivity relates to the relative binding affinities of the ligand shells; however, this requires further investigation. These properties provide a unique foundation for a patterning material that can be further explored for optimal performance.

Experimental Procedure:

The nanoparticle resist was synthesized by a zirconia precursor and a carboxylic acid. The reaction workup through precipitation, resuspension, and drying yielded a nanoparticle powder. The particles were run through thermogravimetric analysis (TA Instruments) and dynamic light scattering (Zetasizer) to measure organic content and the particle size distribution.

For patterning characterization, a 10 wt% solution of particles with respect to PGMEA, with an 3 wt% addition of photoacid generator (N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate), was prepared and spun onto a silicon wafer at 2000 RPM for 60 seconds. After a 60-second post-apply bake at 110°C, the resist was exposed with 248 or 254 nm UV light on the ASML 300C or ABM contact aligner, respectively. The JEOL 9500 e-beam lithography system was used for higher-resolution exposures.

Developing conditions were found by submerging resist samples in various developing solvents at measured durations. Solvents most commonly tried were o-xylene and 4-methyl-2-pentanol. Several developer mixtures were also attempted to more finely control developer kinetics. The ABM contact aligner was used to flood-expose adjacent regions of the wafer to test a series of doses and overall resist sensitivity. A Tencor P10 profilometer was used for film thickness measurements.

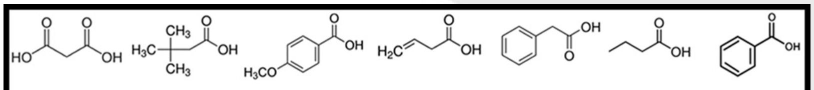

Figure 2: The attempted functional ligands for new compositions, corresponding to the numbering in Figure 3.

	Ligand	pKa	NP size (nm)	Organic content	Patterns?	Developing solvent	Optimal developing time
1	Malonic acid	2.82 5.7	--	--	No	--	--
2	3,3-Dimethylbutyric acid	4.79	4.5	47%	Yes	4-methyl-2-pentanol	30-50 s
3	4-Methoxybenzoic acid	4.47	4.0	60-65%	Yes	5:2 *o*-xylene:butyl acetate	45 s
4	3-Butenoic acid	4.34	--	--	No	--	--
5	Phenylacetic acid	4.31	6.7	59%	Yes	5:1 *o*-xylene:heptane	3-5 s
6	Butyric acid	4.82	--	55%	No	--	--
7	Benzoic acid	4.2	--	~60%	Yes	*o*-xylene	3-5 s

Figure 3: Results of new composition synthesis and developing conditions for each.

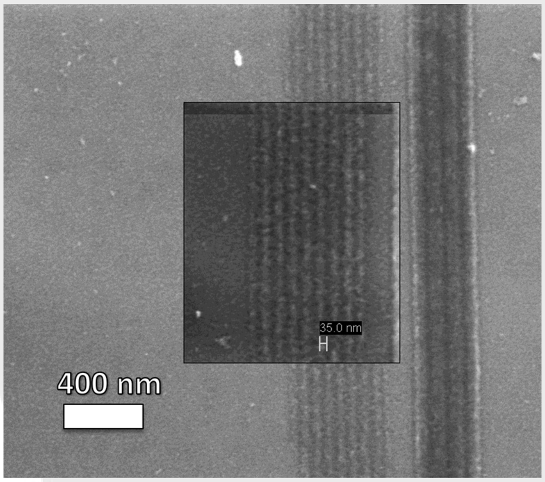

Figure 4: Electron-beam lithography result for the ZrO_2-phenylacetic acid resist.

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Results and Conclusions:

Out of the six studied compositions (compounds 1-6 in Figure 2), two synthesis products agglomerated, and one yielded insoluble particles. The three remaining syntheses were successful; two of which yielded large enough quantities to be studied in greater detail. The two successful ligands were 4-methoxybenzoic acid and phenylacetic acid.

By TGA analysis, it was found that both nanoparticle powders were 60% organic by content, and were approximately 4 to 7 nanometers in diameter. The photoresists patterned effectively under deep ultraviolet light, nearly reaching the 150-nm resolution. Electron beam exposures of 4-methoxybenozic acid resist showed clear 100-nm features and under-developed features at 50 nm. Phenylacetic acid exposures showed clearly defined features at 80 nm, with visible 35-nm features. In order to maximize resist performance, the developing conditions need to be optimized further.

Future Work:

Having established two new patternable compositions and tailored the processing of each, further characterization is necessary for a better assessment of resist performance and optimization. Since our primary goal is to develop resists for EUV patterning, we will study EUV exposures and compare the sensitivity with previous formulations.

We will also characterize the critical dimensions of the patterns, namely the line edge roughness and line width roughness (LER/LWR) through SuMMIT, and performing etch resistance tests for applications involving advanced process integration.

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References:

[1] Chakrabarty, S., Sarma, C., Li, L., Giannelis, E. P., and Ober, C. K. (2014). Increasing sensitivity of oxide nanoparticle photoresists (Vol. 9048, p. 90481C-90481C-5). doi:10.1117/12.2046555.