PROCEEDINGS OF SPIE

SPIEDigitalLibrary.org/conference-proceedings-of-spie

Development of an inorganic photoresist for DUV, EUV, and electron beam imaging

Markos Trikeriotis, Woo Jin Bae, Evan Schwartz, Marie Krysak, Neal Lafferty, et al.

Markos Trikeriotis, Woo Jin Bae, Evan Schwartz, Marie Krysak, Neal Lafferty, Peng Xie, Bruce Smith, Paul A. Zimmerman, Christopher K. Ober, Emmanuel P. Giannelis, "Development of an inorganic photoresist for DUV, EUV, and electron beam imaging," Proc. SPIE 7639, Advances in Resist Materials and Processing Technology XXVII, 76390E (25 March 2010); doi: 10.1117/12.846672

SPIE.

Event: SPIE Advanced Lithography, 2010, San Jose, California, United States

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023 Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

Development of an inorganic photoresist for DUV, EUV, and electron beam imaging

Markos Trikeriotis[a], Woo Jin Bae[a], Evan Schwartz[a], Marie Krysak[a], Neal Lafferty[b], Peng Xie[b], Bruce Smith[b], Paul Zimmerman[c], Christopher K. Ober[a], Emmanuel P. Giannelis[a]

[a]Dept. of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA,
[b]Microsystems Engineering, Rochester Institute of Technology, Rochester, New York 14623, USA,
[c]Intel assignee to SEMATECH, Inc.

ABSTRACT

The trend of ever decreasing feature sizes in subsequent lithography generations is paralleled by the need to reduce resist thickness to prevent pattern collapse. Thinner films limit the ability to transfer the pattern to the substrate during etch steps, obviating the need for a hardmask layer and thus increasing processing costs. For the 22 nm node, the critical aspect ratio will be less than 2:1, meaning 40-45 nm thick resists will be commonplace. To address this problem, we have developed new inorganic nanocomposite photoresists with significantly higher etch resistance than the usual polymer-based photoresists. Hafnium oxide nanoparticles are used as a core to build the inorganic nanocomposite into an imageable photoresist. During the sol-gel processing of nanoparticles, a variety of organic ligands can be used to control the surface chemistry of the final product. The different ligands on the surface of the nanoparticles give them unique properties, allowing these films to act as positive or negative tone photoresists for 193 nm or electron beam lithography. The development of such an inorganic resist can provide several advantages to conventional chemically amplified resist (CAR) systems. Beyond the etch resistance of the material, several other advantages exist, including improved depth of focus (DOF) and reduced line edge roughness (LER). This work will show etch data on a material that is ~3 times more etch-resistant than a PHOST standard. The refractive index of the resist at 193 nm is about 2.0, significantly improving the DOF. Imaging data, including cross-sections, will be shown for 60 nm lines/spaces (l/s) for 193 nm and e-beam lithography. Further, images and physical characteristics of the materials will be provided in both positive and negative tones for 193 nm and e-beam lithography.

Keywords: inorganic photoresist, 193 nm lithography, EUV lithography, electron beam lithography, etch resistance

INTRODUCTION

Optical lithography with deep ultraviolet (DUV) wavelengths has been the standard process for patterning in the semiconductor industry, and extensions to sub-45 nm devices are currently being developed. The common trend for such high resolution is the use of a short wavelength laser of 193 nm (ArF), coupled with liquid immersion technology. The introduction of an immersion liquid between the projection optics and the substrate increases the depth of focus (DOF) and allows operation at a higher numerical aperture (NA), which increases resolution. Using water as an immersion fluid, the NA can reach 1.35, which enables patterning at 45 nm half-pitch, while with second generation immersion fluids and an NA of 1.5 or higher, the half-pitch can be reduced to 32 nm or less.[1] Alternative technologies for higher resolution patterning are also under development such as extreme ultraviolet (EUV) lithography. In either case, one of the

Advances in Resist Materials and Processing Technology XXVII, edited by Robert D. Allen, Mark H. Somervell,
Proc. of SPIE Vol. 7639, 76390E · © 2010 SPIE · CCC code: 0277-786X/10/$18 · doi: 10.1117/12.846672

Lam Research Ex. 1031 - Page 2
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

challenges for patterning at higher resolutions is the requirement that new photoresists with advanced performance characteristics be compatible with the new lithography tools.

New photoresists must meet two important requirements to be applicable to higher NA lithography: First, they should have a higher refractive index (RI) to match the high NA of the optical setup and second, they should show improved etch resistance during pattern transfer. The latter requirement becomes important as the printed features become smaller, because photoresist films need to be thinner to decrease the aspect ratio of the patterned lines and prevent pattern collapse. These very thin photoresist films must then be highly etch-resistant to allow the pattern to transfer to the substrate. Higher etch resistance is also important for electron beam lithography resists, since the patterning resolution can be as low as 15 nm. To meet these requirements, the approach that is presented in this study is to develop a new inorganic photoresist comprised of hafnium oxide (HfO_2) nanoparticles.

Hafnium oxide is the material of choice for the development of a high refractive index inorganic photoresist.[2,3] The refractive index of pure HfO_2 at 193 nm is 2.9.[4] Additionally, a big advantage of an inorganic material like HfO_2 is the higher chemical stability than organic polymers that are commonly used as photoresists. Hafnium oxide cannot be oxidized, it is thermally stable up to very high temperatures, and it does not decompose under exposure to 193 nm light. Moreover, nanoparticles, which are less than 5 nm in diameter, are ideal for the application, since the scattering of light by such small particles is minimized. Additionally, quantum confinement effects result in a blue shift of the absorption peak as the size of the particles gets smaller, resulting in low absorbance of 193 nm light.

The aim of these studies is to develop an inorganic resist made of hafnium oxide nanoparticles that can be used both for optical (DUV or EUV) and electron beam lithography. First, a variety of different synthesis approaches to produce HfO_2 nanoparticles is demonstrated. Second, the characterization of the nanoparticle powders, solutions and thin films is presented. Finally, the photoresist performance is evaluated for both optical and electron beam lithography.

MATERIALS AND METHODS

1.1 Materials

Hafnium oxychloride octahydrate ($HfOCl_2 \cdot 8H_2O$) was purchased from Strem Chemicals. Hafnium isopropoxide monoisopropylate, propylene glycol monomethyl ether acetate (PGMEA), and tert-amyl alcohol were purchased from Sigma-Aldrich. All other solvents and chemicals were reagent grade.

1.2 Nanoparticle synthesis

The building blocks for the inorganic photoresist were hafnium oxide nanoparticles stabilized with various carboxylic acids. Two different methods were used to produce nanoparticles that can form stable suspensions in either water or organic solvents:

A) Controlled hydrolysis of hafnium isopropoxide at 65°C for 21 hours results in the formation of a white precipitate. This precipitate was centrifuged at 8,000 *g* for 10 min and then washed twice with acetone. The final product, a white powder, was obtained after drying at 60°C under vacuum. Photoresist solutions were prepared by adding proper amounts of this powder in PGMEA, followed by stirring and ultrasonication. Any aggregates or dust were removed by filtration using a 0.2 µm filter membrane.

Lam Research Ex. 1031 - Page 3
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

B) A different approach that involves the surface modification of the nanoparticles can be used to synthesize nanoparticles with different properties. The surface ligands are replaced by other carboxylic acids via a direct ligand exchange reaction. In a typical synthesis, 2.0 g of the nanoparticles are dispersed in PGMEA and then the second ligand is added to a small scintillation vial. The solution is then heated at 130°C in an oil bath under stirring until it becomes clear. The product is precipitated by adding water and then is washed repeatedly with acetone to remove any free acid. Finally, the photoresist solutions are prepared by adding proper amounts of the precipitate in PGMEA, followed by stirring and ultrasonication. Any aggregates or dust are removed by filtration using a 0.2 µm filter membrane.

RESULTS AND DISCUSSION

1.3 Nanoparticle powders and suspensions

Hydrolysis and condensation of hafnium isopropoxide lead to the formation of a Hf-O-Hf network similar to hafnium oxide. The yield of the synthesis is about 0.7 g of powder per 1.0 g of hafnium isopropoxide used. The infrared spectrum (Figure 1) shows strong peaks characteristic of a carboxylate group. These are the asymmetric and symmetric stretch of the carboxylate at 1450 cm^{-1} and 1570 cm^{-1} as well as a weak peak at 1710 cm^{-1}, which corresponds to the C = O double bond of a protonated carboxylic acid. The weaker peaks that appear at 1350 cm^{-1} and 1610 cm^{-1} show the existence of mono-dentate acid. These results indicate that both the anionic and the protonated forms of the carboxylic acid are present and that the ligation to Hf ions is either mono- or bi-dentate. Additionally, a broad peak appearing around 3300 cm^{-1} could be attributed either to OH groups that are bridging the Hf atoms or to water that is bound on the nanoparticles. Due to the low synthesis temperature, noncrystalline species with a large number of uncondensed OH groups are expected.

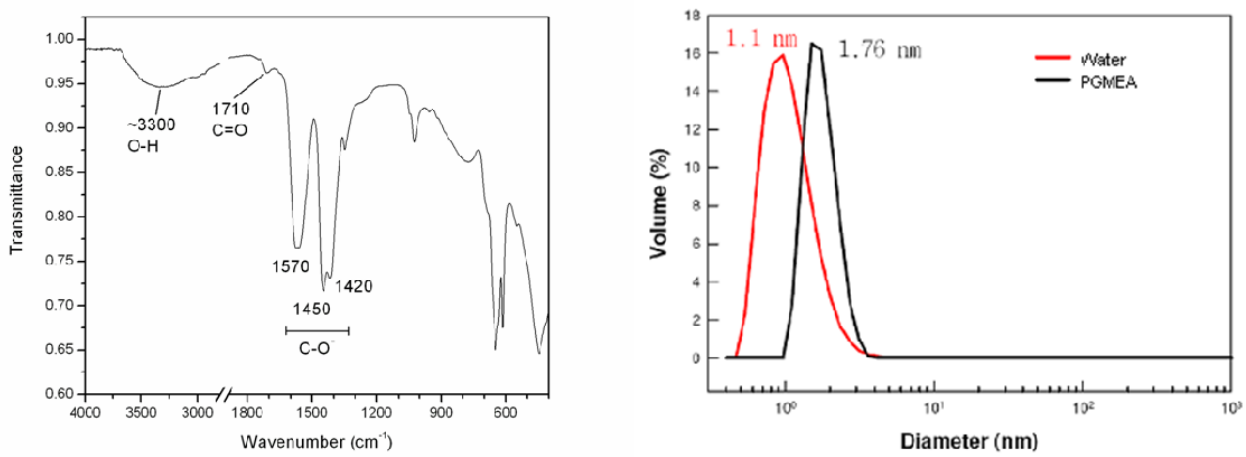

Figure 1. Infrared spectrum of the nanoparticle powder (left) and size distribution of nanoparticle suspensions (right).

The size distribution of the nanoparticles was measured using dynamic light scattering (Figure 1). Depending on the different surface ligands that are used, the nanoparticles can form stable suspensions in either water or organic solvents like PGMEA. In both cases, the size distribution is very narrow with particle diameters ranging from 1–3 nm. Such small sizes are ideal for the application of the nanoparticles as an inorganic photoresist, since the scattering of light by such small particles is minimized and the absorption peak of hafnium oxide is blue shifted due to quantum confinement effects. Additionally, smaller particle sizes are expected to contribute to a lower line edge roughness (LER) value on the relief images of the photoresist.

Lam Research Ex. 1031 - Page 4
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

The composition of the nanoparticle powders was also examined using thermo gravimetric analysis (TGA). As shown in Figure 2, the weight loss occurs in two distinct steps for all the powders that were studied. The first step up to 150°C can be attributed to loss of adsorbed solvent on the nanoparticle surface. The second step, which occurs at 300–450°C, corresponds to the decomposition of the organic acid. The total organic content of the powders varies from 25–35% w/w; this was also confirmed using elemental analysis. The remaining 65–75% is the inorganic core of the nanoparticles. The high inorganic content of the nanoparticles is expected to contribute to the high etch resistance of the photoresist due to the chemical stability of hafnium oxide.

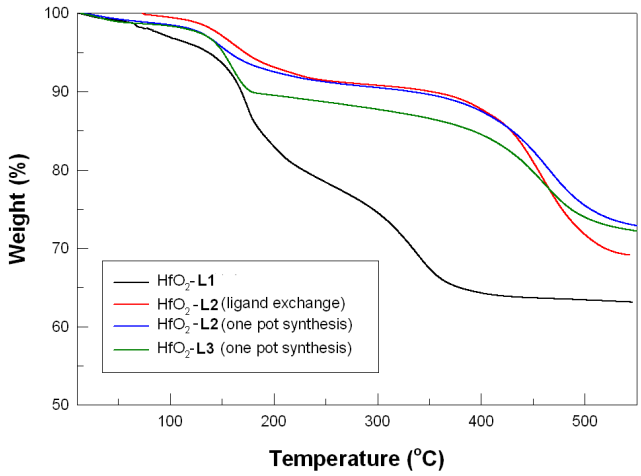

Figure 2. Thermogravimetric analysis of different nanoparticle powders.

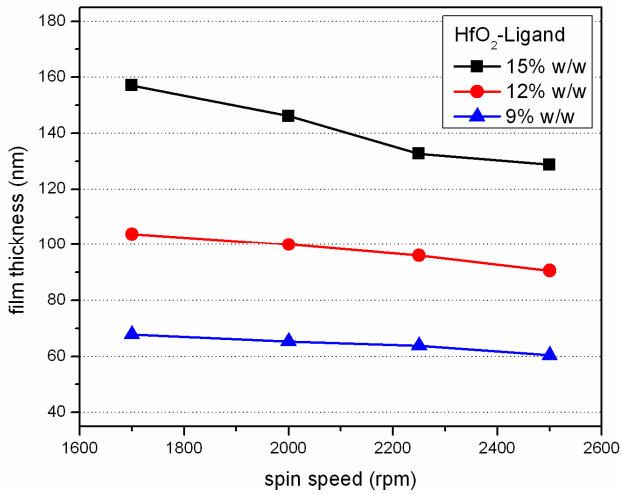

Figure 3. Film thickness versus spin speed at different nanoparticle loadings

1.4 Nanoparticle thin films

Uniform thin films can be spin-coated on Si wafers using either aqueous or PGMEA dispersions of the nanoparticles. Typically, a dispersion containing 5–20% w/w nanoparticles was spin-coated for 60 sec at 1000–3000 rpm. By varying the nanoparticle loading in the dispersion and the spin speed, the film thickness can be controlled. The film thickness was measured with a spectroscopic ellipsometer for different nanoparticle loadings and different spin-coating speeds (Figure 3). In general, film thicknesses ranging from 30 nm to 200 nm can be easily achieved.

The absorbance and the refractive index of the Hf nanoparticle films are important for their application as photoresists. The refractive index of the film, measured using a spectroscopic ellipsometer (Figure 4), was found to be 2.0 at 193 nm. Such a high refractive index can enable patterning up to 1.9 NA. To measure the absorption coefficient of the photoresist, films of a known thickness were spin-coated on quartz slides and their absorbance was measured in the range from 190–400 nm using a spectrophotometer. The absorption coefficient of the films depends on the ligand and the synthesis method that was used. As shown on Figure 4, the absorption coefficient varies from 0.5 to 5.0 μm^{-1}. These measurements show that the absorbance of the nanoparticle films is low enough to allow them to be used as photoresists for optical lithography.

Lam Research Ex. 1031 - Page 5
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

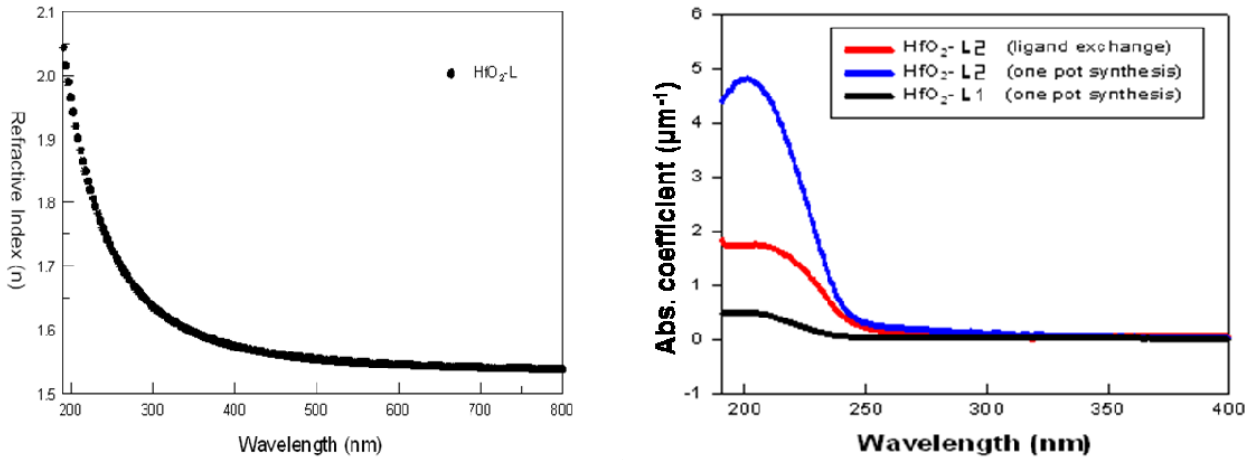

Figure 4. Refractive index (left) and absorption coefficient (right) of the nanoparticle films.

1.5 Optical lithography

The hafnium oxide nanoparticle films are intended for use as inorganic photoresists. To evaluate their potential application in lithography, the Hf nanoparticle films were patterned using DUV light. Various aspects of their performance, such as their patterning resolution capability, their sensitivity, and their etch resistance, were studied.

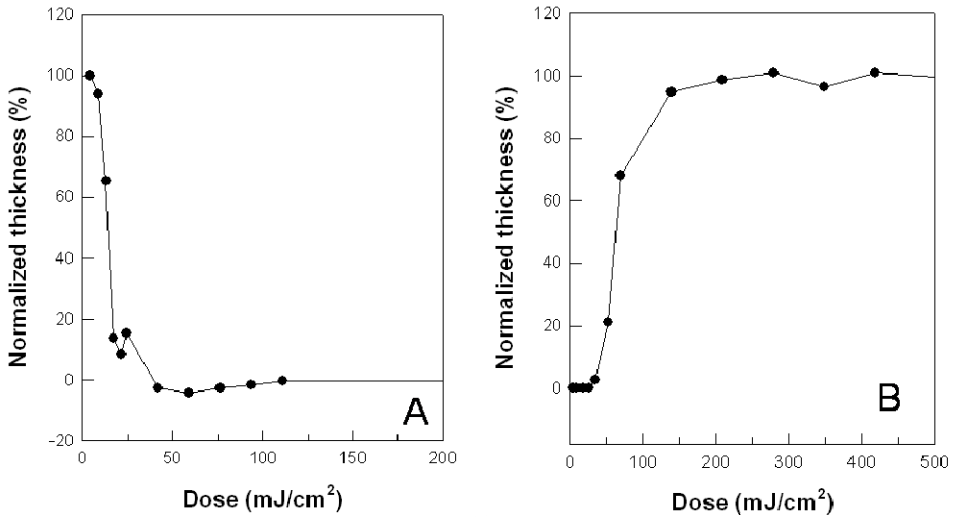

Figure 5. Contrast curves of the nanoparticle films under 254 nm light exposure: positive tone (left) and negative tone (right).

Lam Research Ex. 1031 - Page 6
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

The nanoparticle films with 2,2-dimethoxy-2-phenyl acetophenone (DPAP) as a photoinitiator act both as positive and negative tone photoresists. Films with the desired thickness are prepared and then baked at 130°C for 60 sec on a hot plate. After exposure under DUV light (254 or 193 nm), development in isopropyl alcohol or t-amyl alcohol gives a negative tone image. For the positive tone imaging, the film is baked after exposure (PEB) at 130°C for 3 min and then aqueous tetrametylammonium hydroxide (TMAH) is used for the development.

The contrast curves for the positive and negative tone imaging (Figure 5) were constructed by measuring the thickness of the film after exposure at various doses of 254 nm light and development in 0.26N TMAH for 30 sec (positive tone) or isopropyl alcohol for 2 min (negative tone). Using the same conditions, the films were exposed at 254 nm through a mask to determine the resolution of the positive and negative tone imaging. The optical microscope images of the resulting patterns are presented in Figure 6. For the positive tone image, the resolution is 0.9 µm while for the negative tone it is 0.8 µm.

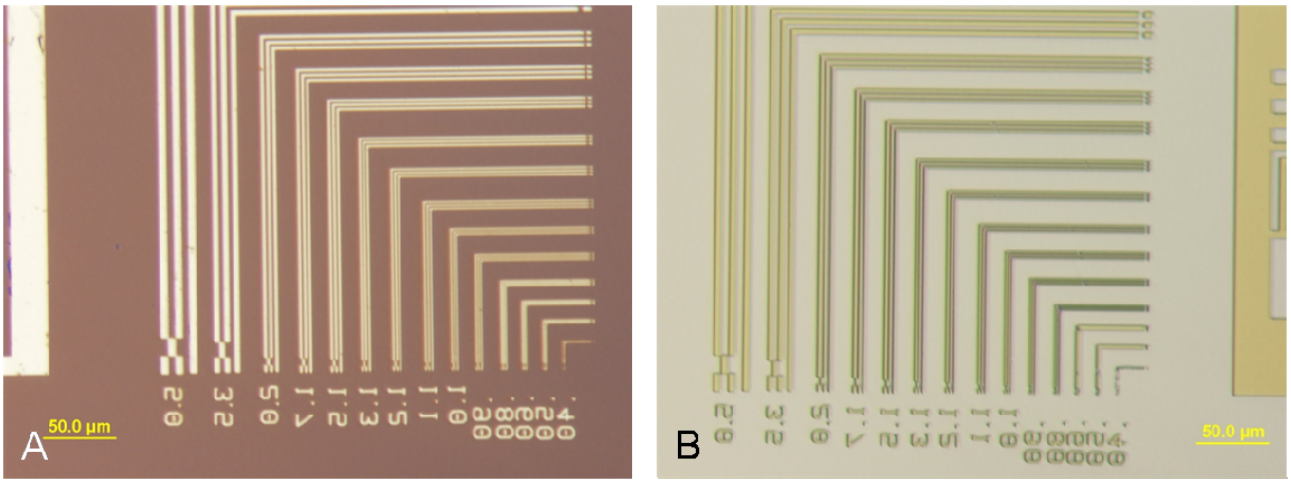

Figure 6. Optical microscope images of patterns printed on the nanoparticle resist using 254 nm light: positive tone (left) and negative tone (right).

Similar films were also exposed at 193 nm light using an Amphibian ArF excimer laser-based interferometric lithography (IL) system. The variable NA system is comprised of a line-narrowed compact excimer laser and projection optics for Talbot interference imaging using a phase grating mask. For the positive tone imaging, a PEB at 130°C for 5 min was applied and the development was done in 0.065N TMAH for 30 sec. For the negative tone, no PEB was required while the images were developed in isopropyl alcohol for 30 sec. Using the IL system with a NA of 0.32, 150 nm lines and spaces were patterned on the Hf nanoparticle films (Figure 7). The scanning electron microscopy (SEM) images show that the negative tone pattern forms well-defined lines and spaces with a square profile. The positive tone image shows a much thinner film than the negative tone, although both films were identical before patterning. This indicates that there is significant dark loss during positive tone imaging.

Lam Research Ex. 1031 - Page 7
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

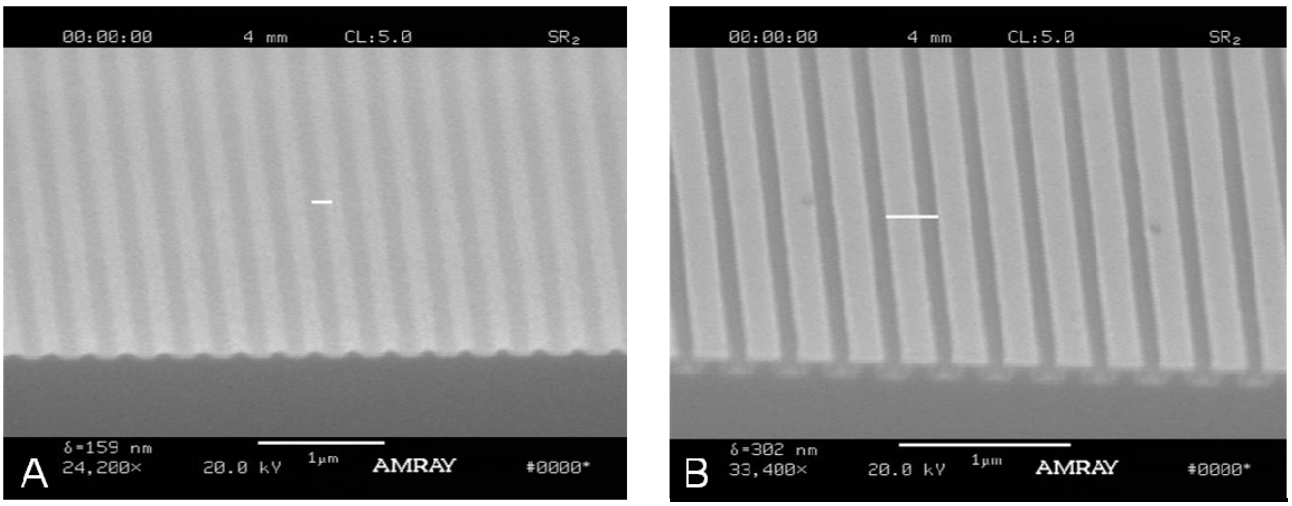

Figure 7. SEM images of patterns printed on the nanoparticle resist using 193 nm light: positive tone (left) and negative tone (right).

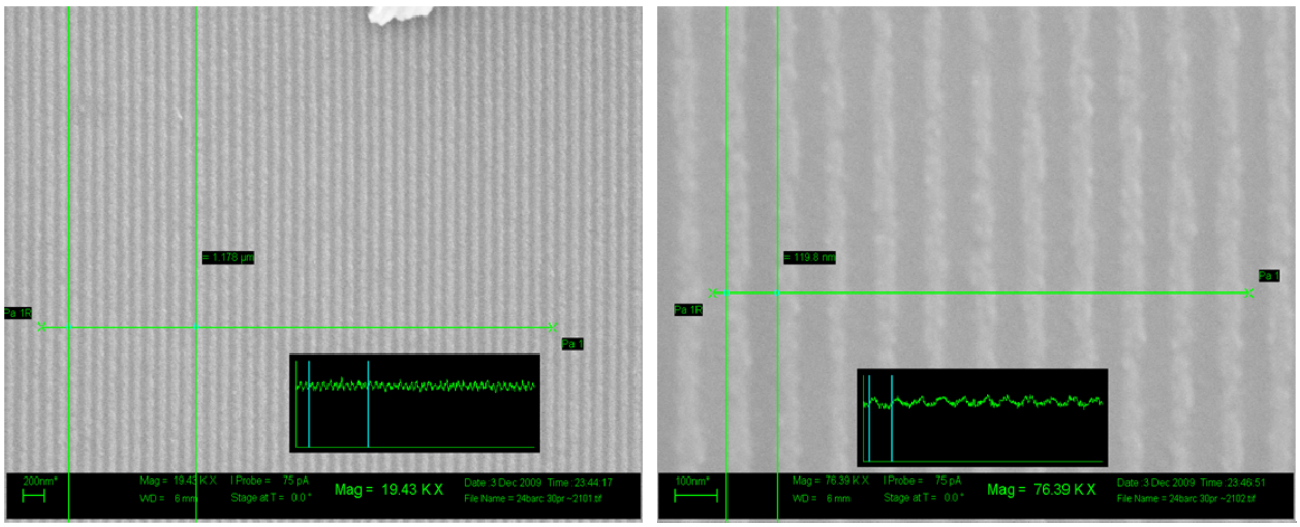

Figure 8. SEM images of 60 nm patterns printed on the nanoparticle resist using 193 nm light.

By changing the optics in the IL system to a NA of 0.80, 60 nm line-space patterns could be imaged to evaluate the negative tone mode of the resist. The films were coated on a bottom anti-reflecting coating (BARC) and tert-amyl alcohol was used as a developer. Figure 8 shows the SEM image of the 60 nm lines and spaces that were printed on the film. The film that was used was only 30 nm thick to minimize the absorbance and reflection of light. Currently, optimization of the photoresist formulation is underway to pattern 60 nm features on thicker films.

Lam Research Ex. 1031 - Page 8
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

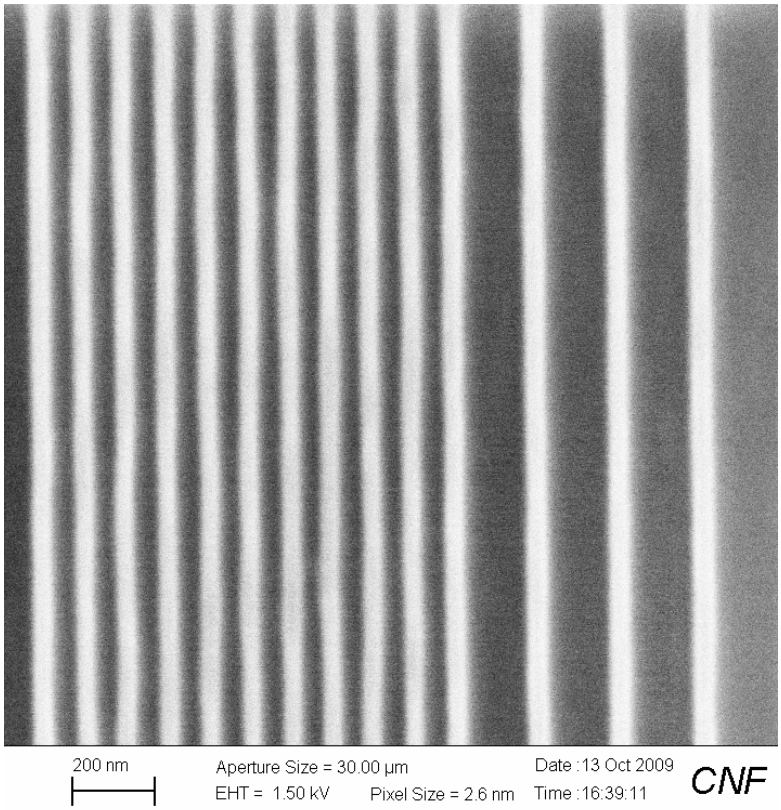

Figure 9. High resolution SEM negative tone images of sub-100 nm patterns.

Etch resistance is an important performance characteristic for photoresist. High resolution patterning in particular requires a very high etch resistance to allow patterns to be transferred from very thin films. The etch resistance of the nanoparticle films was measured and compared to poly-hydroxy styrene (PHOST) films. Both positive and negative tone patterns were etched using SF_6/O_2 plasma for 10s. The results show that the inorganic nanoparticle films are 2–3 times more resistant than PHOST under the same conditions. By reducing the organic content of the Hf nanoparticle films, the etch resistance can be made even higher.

1.6 Electron beam lithography

To determine the ultimate resolution limits of the nanoparticle photoresist, electron beam lithography was used. Just as in optical lithography, both positive tone and negative tone images could be obtained. For the negative tone imaging, the exposed films were developed using either isopropanol for 2 min, or tert-amyl alcohol for 30 sec. The positive tone images required 2 min of baking at 130°C and development in water for 5 min.

The films were exposed using a standard test pattern geometry of regularly repeating lines and spaces of various densities to determine their ability to form well defined high resolution images. An array of these patterns was created with fixed dose increments up to 500 $\mu C/cm^2$. The ideal doses were found to be in the range of 100 to 300 $\mu C/cm^2$ with the use of the radical photoinitiator DPAP. Without the photoinitiator, the resist still images but the required doses were much higher.

Lam Research Ex. 1031 - Page 9
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

Figure 9 shows high resolution SEM images of the negative tone patterns. The required dose was 103 μC/cm^2 and the patterns were developed in isopropanol for 2 min. As seen in Figure 9, both isolated and dense 50 nm lines could be obtained. Even higher resolution is possible for the negative tone photoresist while, in the positive tone case, high resolution imaging was not possible due to the low contrast between the unexposed and exposed areas.

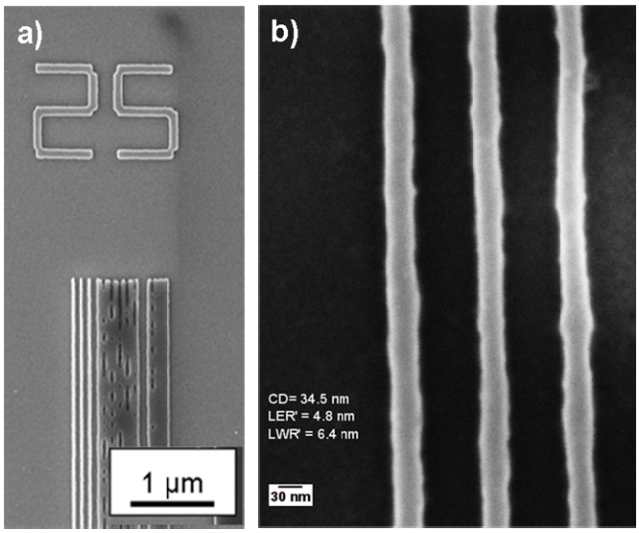

Figure 10. High resolution SEM negative tone images on the nanoparticle film printed at a critical dimension of 35 nm.

Figure 10 shows the highest resolution patterns that were achieved using e-beam lithography on the nanoparticle films. The developer in this case was tert-amyl alcohol, a slightly less polar alcohol than the previously used isopropanol. A less polar solvent was necessary in this case to slow the dissolution of the unexposed film. As shown in Figure 10, SEM analysis of the test patterns at this dose showed 35 nm linewidths without any pattern collapse. The dense lines in this pattern, however, were merged together. Assuming a nanoparticle size of 3 nm (from DLS) and a resist thickness of 60 nm (ellipsometry), a crosslinked stack of about 11 nanoparticles across and 20 nanoparticles high is present. Zooming in on these lines allows a close-up look at the LER and linewidth roughness (LWR). SuMMit software was used for the LER/LWR analysis of these SEM images. The smoothest lines have a 4.8 nm LER and a 6.4 nm LWR. Further optimization of the photoresist formulation could possibly decrease the LER/LWR down to 2.0 nm.

CONCLUSIONS

A new class of photoresist materials, which are mostly inorganic, was developed and tested. The inorganic photoresists are made of hafnium oxide nanoparticles as small as 1.0 nm in diameter. The nanoparticle films have a high refractive index and show low absorbance. Both positive and negative tone imaging is possible using either DUV or e-beam lithography with high resolution. Additionally, the etch resistance of the inorganic photoresists is superior to that of PHOST. Further optimization of the photoresist formulation will lead to higher etch resistance and lower LER/LWR values.

ACKNOWLEDGEMENTS

This work was funded by International SEMATECH. SEMATECH and the SEMATECH logo are registered service marks of SEMATECH, Inc. All other service marks and trademarks are the property of their respective owners.

Lam Research Ex. 1031 - Page 10
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

REFERENCES

[1] Sewell, H., Mulkens, J., McCafferty, D., Markoya, L., Streefkerk, B. and Graeupner, P., "The next phase for immersion lithography," Proc. SPIE 6154, 615406 (2006).

[2] Zimmerman, P., A., Rice, B., Rodriguez, R., Zettel, M., F., Trikeriotis, M., Wang, D., Yi, Y., Bae, W., J., Ober, C., K. and Giannelis, E., P., "The use of nanocomposite materials for high refractive index immersion lithography," J. Photopolym. Sci. Technol. 21(5), 621-629 (2008).

[3] Bae, W. J., Trikeriotis, M., Rodriguez, R., Zettel, M. F., Piscani, E., Ober, C. K., Giannelis, E. P. and Zimmerman, P., "High-index nanocomposite photoresist for 193-nm lithography," Proceedings of SPIE Vol. 7273, 727326 (2009).

[4] Trikeriotis, M., Rodriguez, R., Zettel, M. F., Bakandritsos, A., Bae, W. J., Zimmerman, P. A., Ober, C. K. and Giannelis, E. P., "High refractive index nanoparticle fluids for 193-nm immersion lithography," Proceedings of SPIE Vol. 7273, 72732A (2009).

Lam Research Ex. 1031 - Page 11
Lam Research Corp. v. Inpria Corp.
IPR2024-00033 - U.S. Patent No. 9,823,564

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 11 Oct 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use