

Photopatternable inorganic hardmask

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The authors present a directly photopatternable inorganic hardmask for 193 nm lithography based on the solution-deposited dielectric metal oxide sulfate (MSOx) system. To demonstrate pattern fidelity, 18 nm half-pitch features were written at a dose near $240 \mu\text{C}/\text{cm}^2$ (30 keV) with line width roughness values between 1.6 and 1.8 nm. Well-resolved and uniform 30 nm contact holes were fabricated via a litho-freeze-litho-etch process employing electron beam exposure and a simple thermal freeze. ZircSOx has a high index of refraction approaching 1.9 at 193 nm, and the extinction coefficient, k , can be varied by an order of magnitude by substituting Zr with Hf. Optical interference lithography at 193 nm was used to realize 60 nm half-pitch lines in MSOx at a dose of $25 \text{ mJ}/\text{cm}^2$. © 2010 American Vacuum Society. [DOI: 10.1116/1.3507889]

I. INTRODUCTION

To meet the needs for continued scaling and fabrication of nanoscale devices, electron beam, 193 nm optical, nanoimprint, and extreme ultraviolet (EUV) lithography technologies need to meet increasingly demanding performance. The progress of lithography is highly dependent on the interplay between innovations in exposure-tool development and breakthroughs in resist chemistry, which together lead to advanced capabilities. Currently, 193 nm immersion (193i) optical lithography is being used in high-volume manufacturing of complementary metal-oxide semiconductor devices. Advanced approaches, e.g., 193i double patterning, and EUV lithography are currently being developed to address feature-size and resolution requirements beyond the 22 nm node. Both technologies share the need for high performance resists that must meet stringent requirements for sensitivity, resolution, line width roughness, and etch resistance.¹ In this article, we describe a new inorganic resist chemistry for optical lithography that is firmly on the path to meeting many of these advanced needs.

Numerous chemically amplified resists (CARs) have been developed to address the sensitivity requirements for all forms of semiconductor lithography. Typically, CARs are polymer-based organic resins with high positive-tone (in some cases, negative-tone) sensitivity that is achieved through the addition of photoacid generators designed for chemical amplification.^{2,3} Amplification occurs in these systems when incident photons stimulate the release of an acid that diffuses through the resist. The acid reacts with the

cross-linked polymer, catalytically breaking many bonds and altering the solubility of the resin. Despite a high sensitivity, progress in CARs is hindered by acid diffusion, which contributes to feature blurring, high line width roughness (LWR), and limited resolution.²⁻⁵

During the past few decades, several inorganic materials have been examined as alternatives to organic resists. Work on these inorganic materials has been stimulated in part by the small, high-quality features that can be written with high-dose electron beam lithography.^{6,7} For example, the interdiffusion chemistry of various layered chalcogenides has been used to produce photoimageable materials.⁸⁻¹⁰ Despite high contrast, the utility of these materials has been limited by vacuum deposition requirements, material toxicity, and deleterious doping of silicon by constituent metals, e.g., silver. Peroxometalates, notably peroxopolytungstates, have also been examined as resists with sensitivity to ultraviolet, x-ray, and electron beams. These materials never garnered much interest because of their tendency to crystallize and their limited sensitivities.¹¹ More recently, sol-gel metal-organic resists have been developed. For these materials, exposure doses can exceed those of CARs by three orders of magnitude; they also suffer from high absorption, only modest feature-size capabilities, and poor LWR.^{12,13} Outgassing of the organic constituents is also likely to be problematic for use in EUV systems, where lens contamination can rapidly occur.

To address many of the past limitations of inorganic resists, we have recently introduced peroxo modified forms of the materials zirconium oxide sulfate (ZircSOx) and hafnium oxide sulfate (HafSOx) as a new family of directly pattern-

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able metal oxide. They provide many advantages with respect to both CARs and all other photopatternable inorganic resists.^{14,15} Because many metal ions other than Hf and Zr can be used in the basic resist chemistry, the family is more generally designated as MSOx.

A sensitive, photopatternable inorganic resist could simultaneously address many issues in advanced semiconductor manufacturing. Current double-patterning techniques, for example, require a vacuum-deposited hardmask, e.g., SiON_x, that must then be patterned with a polymer resist. Additional layers are also often applied to aid in pattern transfer,^{16,17} which can add considerable complexity to the process. Many processing steps—vacuum deposition, polymer processing, and etching—could be eliminated with the introduction of a spin coated, directly imageable hardmask having high sensitivity. Such materials would also enable complete hardmask processing on efficient, low-cost wafer tracks.

Electron beam lithography remains an enabling technology for other forms of lithography. EUV, 193i, and nanoimprint lithography, especially, rely on masks and templates fabricated through the use of electron beam lithography. Therefore, a continuing need exists for a high performance electron beam resist possessing high sensitivity and low LWR.

We describe below the initial results on photopatterning the resists ZircSOx and HafSOx. Before addressing the photoexposure of the MSOx resists, we consider new results on electron beam patterning, demonstrating dense features at 18 nm half-pitch and implementation of a litho-freeze-litho-etch (LFLE) double-patterning methodology.

II. EXPERIMENT

Aqueous MSOx solutions were prepared using an Inpria proprietary formulation technique. Solutions were then spin coated onto silicon substrates at 3000 rpm for 30 s. Following spin coating, a 70 °C postapply bake was conducted for 3 min to partially dehydrate the film. The resulting film thickness from this procedure was typically 30 nm as measured by ellipsometry. A 1 min, 70 °C postexposure bake was conducted on e-beam exposed samples, while 193 nm exposures were baked at 100 °C for 1 min following exposure. The silicon substrates were prepared for spin coating by sonication in Decon Laboratories Contrad-70 solution at 45 °C for 60 min.

Ellipsometry measurements were collected using a J. A. Woollam VASE ellipsometer and modeled with WVASE32 software. The modeling of MSOx resists involved collecting data over the wavelength range from 190 to 600 nm and fitting to a Cauchy–Urbach absorption model.

Electron beam exposures for line and pattern formation were conducted at 30 keV on a Zeiss Ultra-55 scanning electron microscope (SEM) with a Nabity lithography system. Development was conducted by immersion in 25 or 2.38 wt % tetramethylammonium hydroxide for 15 s; this step was followed by thorough rinsing with de-ionized water. The composition of MSOx was tuned for use with each developer. A final hardbake was performed at 220 °C for 5 min.

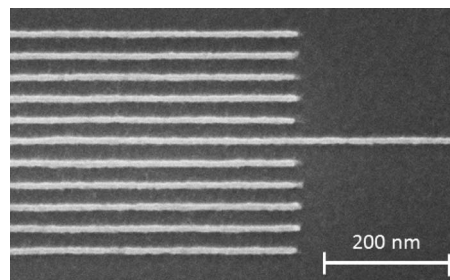


FIG. 1. SEM image showing 18 nm lines and spaces written in MSOx at a dose of 244 $\mu\text{C}/\text{cm}^2$ with a 30 keV electron beam.

Films were exposed at 193 nm by using an interference ArF tool at the Rochester Institute of Technology; exposure methods have been outlined elsewhere.¹⁸ SEM images were collected by using a Zeiss Ultra-55 SEM operating at 5 keV except for 193 nm pattern images, which were collected using a LEO EVO 50 SEM operating at 5 keV. LWR values for electron beam exposures were measured by using Hitachi offline critical dimension measurement software version 4.11 with an inspection length of 500 nm. LWR values for 193 nm exposures were not measured.

III. RESULTS AND DISCUSSION

A. Electron beam results and etch resistance

Electron beam exposures at 30 keV have previously been reported for MSOx,¹⁴ where feature sizes of 28 nm on a 100 nm pitch were demonstrated. A contrast of 5.6 was obtained for MSOx with D_0 and $D_{0.8}$ doses of 200 and 400 $\mu\text{C}/\text{cm}^2$, respectively. A high etch resistance was also demonstrated by reactive ion etching with CHF_3 ; etch rates of 2.2 nm/min were reported, a rate 9 $\times$ slower than thermally grown SiO_2 under the same conditions. Such a high etch resistance for MSOx enables the use of low aspect ratio features for pattern transfer and eases the constraints on resist contrast. As a result, a relatively thin MSOx resist film can effectively be used to pattern transfer features of significantly higher aspect ratios into the substrate. Data and examples of pattern transfer into Si using MSOx resists will be presented in a subsequent publication.

Continued optimization of the MSOx system has resulted in improved resolution and contrast while maintaining similar sensitivity. A SEM image of 18 nm half-pitch lines for an exposure at a dose of 244 $\mu\text{C}/\text{cm}^2$ (30 keV) is shown in Fig. 1. Lines of 21 nm on a 60 nm pitch at a dose of 436 $\mu\text{C}/\text{cm}^2$ can be produced with LWR values in the range from 1.6 to 1.8 nm (Fig. 2), a value significantly lower than was first reported with hydrogen silsesquioxane¹⁹ and superior when compared with organometallic Zr/Hf nanoparticle-based resists.^{12,13}

B. LFLE double patterning

The MSOx chemistry is directly amenable to a negative-tone LFLE process. This process involves two consecutive lithographic steps and two resist coating steps. In the first

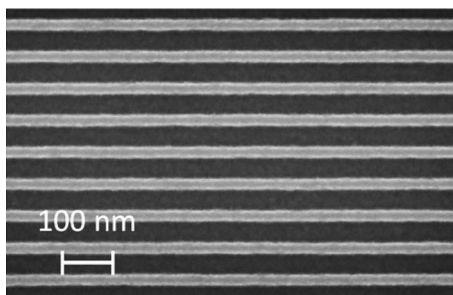


FIG. 2. SEM image of MSOx written with a 30 keV electron beam at a dose of $436 \mu\text{C}/\text{cm}^2$ showing LWR of 1.6–1.8 nm for 21 nm lines on 60 nm pitch.

lithography step, a resist layer is deposited, exposed, baked, and then developed. A freeze step follows, which involves rendering the developed pattern insoluble in the second resist coat. Such freezing is commonly accomplished by exposing the developed pattern to a surfactant or solvent rinse.²⁰ The need for an additional chemical-freeze processing step significantly increases the complexity of the double-patterning process with polymer resists. Alternatively, in a thermal freeze process, the developed resist pattern is simply baked at an appropriate temperature to render the pattern insoluble. In the case of MSOx, a 5 min bake at 220°C is adequate to lock in or “freeze” the pattern. After the 220°C bake, MSOx patterns have been transformed into dense oxides and are no longer soluble in resist or developer. A second lithography process can then be performed on top of the existing pattern. Finally, an etch step can be performed to transfer the doubly exposed pattern. The LFLE process is a commonly proposed method to realize pitch doubling and patterning of contact holes.^{20,21}

By implementing a negative-tone LFLE process with a thermal freeze, contact-hole patterns were generated in ZircSOx by electron beam lithography at a dose near $500 \mu\text{C}/\text{cm}^2$. SEM images of the crosshatched patterns (Fig. 3) clearly reveal resolved 30 nm square holes. The features are uniform and exhibit sharp angles—structures that are very difficult to obtain with positive-tone chemically amplified resists.

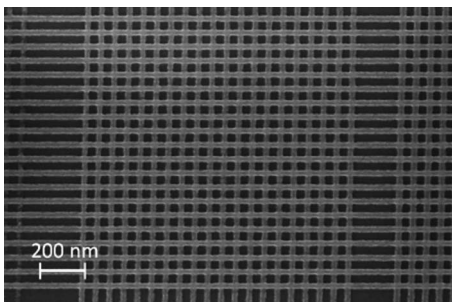


FIG. 3. Well-resolved 30 nm contact holes achieved using LFLE double-patterning process with a 30 keV electron beam at $500 \mu\text{C}/\text{cm}^2$.

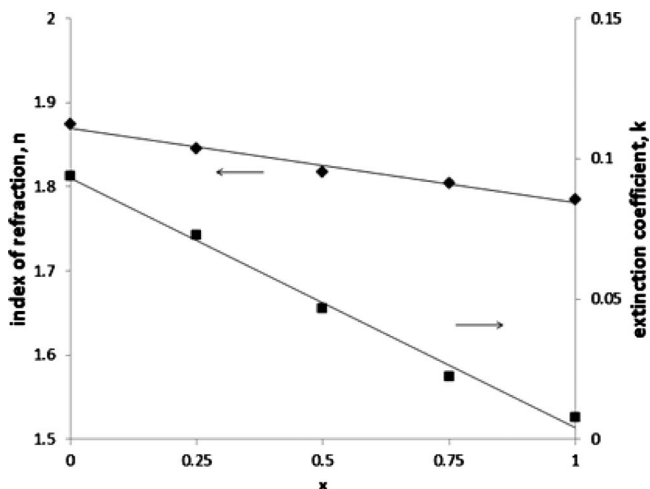


FIG. 4. Index of refraction and extinction coefficient as a function of x in $\text{Zr}_{1-x}\text{Hf}_x\text{SOx}$ resist.

C. Application to 193 nm lithography

Tunability of the optical properties of the MSOx resist platform is a unique capability for optimizing 193 nm lithography. As with typical resist design, the primary objective was to optimize absorbance to balance efficient coupling of the incident radiation with a uniform light distribution through the film. To take advantage of the high etch resistance and to mitigate pattern collapse, the films are targeted for a thickness of approximately 30 nm. This implies a target absorbance of $3 \mu\text{m}^{-1}$ and an extinction coefficient (k) of approximately 0.1.

To tune the optical properties, Zr, for example, can be readily replaced by Hf without affecting the chemical or mechanical properties of the film. In the $\text{Zr}_{1-x}\text{Hf}_x\text{SOx}$ system, the entire range of compositions, from $x=0$ to $x=1$, can be accessed. Variable angle spectroscopic ellipsometry has been used to measure the optical constants across this entire range, see Fig. 4. Indeed the extinction coefficient can be modulated by nearly an order of magnitude across the series. As the fraction of Hf in ZircSOx increases, both the refractive index (n) and the extinction coefficient (k) decrease. These results demonstrated that while HafSOx is too transparent ($k \sim 0.01$), ZircSOx is a good candidate with $k \sim 0.1$.

Interference exposures at 193 nm were performed on a range of HafSOx/ZircSOx formulations. For each condition, 60 nm half-pitch lines were written. As expected, dose improved with the more absorptive Zr-rich formulations. For HafSOx, $E_{1:1}=90 \text{ mJ}/\text{cm}^2$; for $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{SOx}$, $E_{1:1}=60 \text{ mJ}/\text{cm}^2$; and for ZircSOx, $E_{1:1}=25 \text{ mJ}/\text{cm}^2$. Representative SEM images of 60 nm lines on a 60 nm half-pitch in ZircSOx exposed at a dose of $25 \text{ mJ}/\text{cm}^2$ are shown in Fig. 5.

An additional benefit of the MSOx family is the ability to access indices of refraction above 1.8, as such, a resist provides additional process latitude stemming from increased depth of focus.^{22,23} Typically, achieving an index of refraction above 1.8 with an organic resist forces an unacceptably high absorbance. ZircSOx has the appropriate absorbance

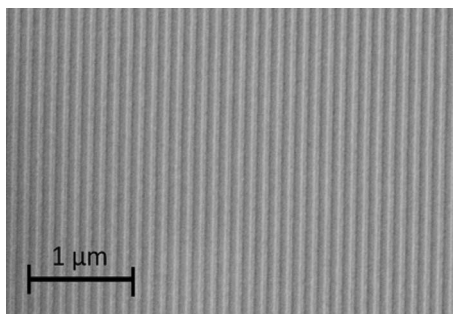


FIG. 5. 60 nm lines on a 60 nm half-pitch written in ZircSOx using 193 nm optical interference lithography at a dose of 25 mJ/cm².

and an index of approximately 1.9. The magnitude of the improvement in process latitude has not yet been quantified.

Not only can Hf and Zr be substituted within the resist, but so too can other metals. A unique aspect of the MSOx systems is that their chemistries allow for inclusion of a variety of both transition and *p*-block metals in varying amounts. Substitution of additional metals into organometallic systems is often difficult, if not impossible, because of differing rates of ligand exchange, hydrolysis, and solubility. An advantage to compositional variability is a larger potential range of optical properties than the ZircSOx-HafSOx system alone. Therefore, MSOx represents a unique platform that allows the tuning of optical and etch properties appropriate for a variety of processes including electron beam, 193 nm, and EUV lithography. For example, sub-20-nm EUV patterning using this platform has been described elsewhere.²⁴

The MSOx materials are aqueous systems, so extension to 193 nm immersion lithography requires a water impermeable topcoat. In addition, a hydrophobic surface appropriate for scanning, i.e., contact angle >70°, is required. To test immersion capabilities and to avoid the need for a topcoat, initial experiments were performed with cyclohexane as the immersion fluid. However, as no bottom antireflective coating was used, a significant intensity drop at the bottom of the resist became evident as partial delamination was observed. Evidence for 40 nm half-pitch lines was observed in spite of this issue. Given the high-resolution patterning shown by electron beam lithography, there is a path to features <40 nm with 193 nm immersion lithography with appropriate topcoat and reflection management.

IV. CONCLUSION

The solution-deposited MSOx platform has been developed as high performance electron beam and 193 nm resists.

With electron beam exposures, 18 nm half-pitch lines and spaces with LWR values <2 nm at 30 keV have been realized at a modest dose of 244 μC/cm². The materials also function as sensitive, high-resolution, negative-tone photopatternable hardmasks. At 193 nm, 60 nm half-pitch features were readily written at a dose of 25 mJ/cm². A negative-tone LFLE double-patterning process was demonstrated, showing extendibility to 30 nm and below. A method to tailor the optical and chemical properties of the MSOx platform was shown by alloying ZircSOx and HafSOx. Extending such capabilities to other metals provides a new route to effectively manage the interactions among resist optical properties, exposure chemistries, and development processes. Altogether, the MSOx platform presents an unprecedented approach to resist performance optimization.

ACKNOWLEDGMENT

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