

Characterization of high-resolution HafSOx inorganic resists

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ABSTRACT

Inorganic resists are of considerable interest for advanced lithography at the nanoscale due to the potential for high resolution, low line width roughness (LWR), and high sensitivity. Historically inorganic resists suffered from low sensitivity, however approaches have been identified to increase sensitivity while maintaining high contrast. An aqueous precursor of $\text{Hf}(\text{OH})_{4-2x-2y}(\text{O}_2)_x(\text{SO}_4)_y \cdot q\text{H}_2\text{O}$ (HafSOx) has been demonstrated with excellent sensitivity to EUV and electrons, while still obtaining high resolution and low LWR. In this work, we characterize both HafSOx precursor solutions and spin-coated thin films using high-resolution transmission electron microscopy (HR-TEM) with energy-dispersive X-ray spectroscopy (EDS) elemental analysis. HR-TEM of precursor solutions drop cast onto TEM grids confirmed the presence of nanoscale particles. HR-TEM cross sectional images showed that spin-coated HafSOx films are initially uniform in appearance and composition for thin (12 nm) films, however thicker (30 nm) films display segregation of species leading to multilayer structures. Regardless of film thickness, extended exposure to the high energy TEM electron beam induces significant migration of oxygen species to the Si interface. These species result in the formation of SiOx layers that increase in thickness with an increase in TEM electron beam dose. Sulfate is also very mobile in the films and likely assists in the significant condensation exhibited in completely processed films.

Keywords: Inorganic resist, electron beam lithography, solution film deposition, hafnium oxide, thin film, cross-sectional TEM

1. INTRODUCTION

The ability to pattern structures on the nanoscale is crucial for advances in many materials and device related fields. For example, as the feature size of integrated circuits continues to decrease, the search for materials capable of high resolution patterning under conditions suitable for large-scale integration becomes increasingly important. Among the potential candidate technologies for generating suitable nanopatterns, two of the most promising are extreme UV lithography and electron beam lithography (EBL).^{1,2} EBL is particularly regarded as one of the most promising direct write methods due to the small wavelength and spot size of the electron beam (e-beam).² Organic resists such as polymethyl methacrylate (PMMA) are the current leading technology for EBL.^{3,4,5} Resists based on these materials have shown great success due to the relatively high resolution that can be obtained, but suffer from low sensitivity and low etch resistance. Chemically amplified resists (CARs) offer higher sensitivity and etch resistance, but at the expense of decreased resolution.⁶ As the desired patterned feature size falls below 10 nm the aforementioned organic resists become limited by their relatively large thicknesses and large molecular size, leading to pattern instability and large line edge roughness, respectively. To address this challenge, a number of inorganic materials have been investigated due to their small molecular size and inherently high etch resistance such as metal oxides⁷, metal fluorides⁸ and hydrogen silsesquioxane (HSQ)^{9,2}. For sub-10 nm lithography the use of inorganic materials allows extremely thin layers to be used for pattern generation primarily due to their high etch selectivity, which minimizes resolution limitations due to electron scattering and pattern instability.¹⁰ However, inorganic materials can suffer from low e-beam sensitivities and require long write times thereby limiting their widespread adoption for high throughput manufacturing.

Metal peroxide sulfates (MSOx) such as HafSOx have recently emerged as a class of inorganic materials which are promising as negative tone resists with high sensitivity.^{11,12,13} These materials form dense, atomically smooth thin films via spin coating from an aqueous solution.¹⁴ It has been proposed that exposure to electron or photon irradiation causes decomposition of peroxide species in the film leading to metal oxide network formation, which acts as the solubility

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contrast mechanism for patterning.¹¹ Patterned lines have been demonstrated in MSOx based resists below 10 nm half pitch.¹⁵ Other Hf-based resists have been previously investigated but exhibited lower resolutions¹⁶ and lower sensitivities¹⁷ than that of the HafSOx system. Despite the promising patterning capabilities, there has been relatively little detailed characterization of HafSOx precursors and spin-coated films to gain insight into key factors governing the patterning process.

In this contribution we employ TEM techniques to investigate the HafSOx system, including solution precursors and spin-coated films. We demonstrate that HR-TEM imaging provides unique information about solution precursors and, combined with spatially resolved energy dispersive X-ray spectroscopy (EDS), this capability allows for the direct visual and elemental inspection of ultra-thin films. Furthermore, due to the nature of the technique this allows for *in-situ* inspection of films subjected to e-beam radiation and thus insight into the chemical and structural transformations occurring during patterning of the material via e-beam lithography.

2. EXPERIMENTAL

1.0 M stock solutions were prepared by dissolution and dilution of $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ (Alfa Aesar) and $\text{H}_2\text{SO}_4(\text{aq})$ (Mallinckrodt) with 18.2 M Ω purified water. Solutions for spin coating were prepared by adding 30 wt% $\text{H}_2\text{O}_2(\text{aq})$ (Macron) to the $\text{HfOCl}_2(\text{aq})$ solution followed by sequential addition of $\text{H}_2\text{SO}_4(\text{aq})$ and 18.2 M Ω purified water. Final solutions contained a molar ratio of 1 : 0.7 : 3 hafnium : sulfate : peroxide and were 0.15 M or 0.5 M in concentration on the basis of hafnium. Film thicknesses were approximately 12 nm (0.15 M) and 30 nm (0.5 M). A J. A. Woollam V-VASE Ellipsometer was used for film thickness measurements. Data was collected for 400-1100 nm (10 nm step size) at angles of incidence of 65-75° (5° step size) and a Cauchy model was used to extract film thickness. Prior to spin coating the substrates were treated with an O_2 plasma to improve wetting of the substrate. Films were deposited by dispensing solutions through a 0.45 μm filter and spin coating at 3000 rpm for 30 sec. The films were then baked on a hot plate at 300 °C for 5 min. An FEI Titan G2 80-200 TEM operating at 200 kV and an FEI Titan G2 80-300 TEM operating at 300 kV were used for imaging HafSOx clusters. An FEI Titan G2 80-200 TEM with ChemiSTEM operating at 200 kV was used for imaging and elemental analysis of HafSOx film cross-sections. Cluster samples were prepared by drop casting the 0.15 M precursor solution described above onto an ultra-thin holey carbon grid or a surface functionalized Si_3N_4 grid. Cross-sections were prepared via the focused ion beam lift-out method using an FEI Quanta 3D Dual Beam scanning electron microscope. Approximately 30 nm of amorphous carbon was thermally evaporated on the sample to serve as a protective layer during the lift-out process. EDS line scans were taken in STEM mode, and the areas were correlated to the bright field TEM images that were acquired on nearby locations of the sample to avoid significant damage during STEM operation. The scans were analyzed with Bruker Esprit 1.9 software by using an automatic background subtraction and quantification without standards.

3. RESULTS AND DISCUSSION

It has been reported that zirconium sulfates form clusters on the order of 1 nm or smaller in aqueous solutions and it is assumed that hafnium analogues behave similarly.¹⁸ Similar structures may exist in HafSOx solutions and films as fundamental units and their small size may be key to patterning, however no direct evidence of these nano-clusters has been reported. Figure 1 shows TEM images of a 0.15 M HafSOx solution drop-cast onto a TEM grid. Figure 1a shows a monolayer of clusters with near spherical structure ranging from 2-4 nm in diameter. These sizes are larger than the species expected to exist in solution and have likely experienced some degree of polymerization or agglomeration upon evaporation of the precursor solution. Nevertheless, this points to the existence of a near monodisperse sub-5 nm species in HafSOx solutions. HR-TEM images of similar samples are shown in Figures 1b and 1c. Though it is difficult to say conclusively due to the ultra thin nature of these species, it appears clusters as small as sub-1 nm can be resolved in the HR-TEM image in Figure 1b. A degree of atomic structural ordering is observed in the clusters for these high resolution images. This suggests that despite the spin-coated films exhibiting an amorphous structure via X-ray diffraction, they are likely composed of similarly small building blocks with some degree of short-range order. Figure 1c shows the beginning of what appears to be a polymerization process resulting in a chain-like structure and may be representative of what exists in spin-coated HafSOx films upon deposition and drying.

A TEM cross-section of a 0.15 M HafSOx film annealed to 300 °C is shown in Figure 2. Despite the 300 °C anneal, the films are seen to be very reactive under the high energy TEM e-beam. Figure 1a shows an image of the HafSOx film after 10 sec e-beam exposure for a total areal dose of 16 C/cm². The film initially appears uniform with a thickness of

approximately 12 nm and a native oxide SiO_x thickness of approximately 3 nm, in good agreement with ellipsometry measurements. With extended exposure to the e-beam the film is seen to change dramatically¹⁹ as shown in Figure 2b for a 600 sec exposure with a total areal dose of 960 C/cm². The SiO_x layer and total (HafSO_x + SiO_x) film thickness are seen to increase with increasing electron dose with a corresponding decrease in HafSO_x thickness as depicted in Figure 2c. Although it is difficult to make direct comparisons between HafSO_x film cross-sections exposed to the TEM e-beam and those exposed top-down during patterning due to difference in orientation, sample volume and electron energy, the highly reactive nature of the films points to their promising patterning capabilities via electron exposure. In particular, it is possible that the electron-assisted migration of one or more oxygen species to the film interface, as depicted in Figure 2, plays an important role in initiating the solubility transition exhibited in HafSO_x films exposed to electron and EUV radiation.

TEM cross-sections of HafSO_x films annealed to 300 °C with the corresponding EDS line scans are shown in Figure 3. A TEM image of a 0.15 M (12 nm) HafSO_x film in Figure 3a shows the SiO_x layer had increased in thickness relative to the unexposed sample (Figure 2a) in the time required to collect the EDS scan. As seen in Figure 3b, the HafSO_x layer retains both the Hf and S species, which confirms that O migration is responsible for the onset of the interfacial layer discussed in Figure 2. Despite the high mobility of O, both Hf and S are seen to remain relatively uniform throughout the 12 nm film thickness.¹⁹ A TEM image of a 0.5 M (30 nm) HafSO_x film is shown in Figure 3c. As with its 12 nm counterpart (Figure 3a), the SiO_x layer increases significantly with e-beam exposure relative to its initial 3 nm native oxide thickness. However, unlike the 12 nm film, this thicker 30 nm film displays significant species segregation as depicted by the EDS line scan in Figure 3d. In particular, Hf and S are seen to segregate into two distinct regions throughout the film. These composition variations are in good agreement with the contrast exhibited in the bright field TEM image in Figure 3c. That is, darker regions (higher electron density) of the film correlate well to Hf-rich compositions while lighter regions are Hf-poor. This multi-layer structure was observed immediately upon imaging and thus is thought to occur upon film deposition and/or annealing to 300 °C rather than via e-beam exposure.

The presence of sulfate in HafSO_x is necessary for patternability since films containing no sulfate are not soluble in basic solutions. It has also been found that less reliable patterning occurs for thicker films and thus 0.15 M solutions (corresponding to the 12 nm films shown here) are typically used. The problems encountered with patterning thicker films could be related to a number of factors. For example, the elemental inhomogeneity through the films as seen in Figure 3d likely plays a critical role. In particular it is expected that sulfate plays an integral part in the condensation pathway following radiation exposure which allows for the solubility transition demonstrated for this system. Regions with sulfate will inhibit metal oxide network formation and will require an increased dose to induce a solubility transition whereas regions devoid of sulfate will insolubilize readily. This would lead to a lower achievable contrast and an associated decrease in patterning performance. In addition to the elemental inhomogeneity, problems likely exist for thicker films due to the competing ion exchange and dissolution processes occurring during the development step in basic solutions. That is, HafSO_x films exchange sulfate for hydroxyl during development in base, leaving an insoluble hafnium oxide hydroxide product.¹⁹ For thinner films the dissolution process is dominant and thus unexposed regions are washed away readily. As the film thickness increases the ion exchange is no longer negligible and some unexposed regions will lose sulfate before the entire thickness is washed away, leaving behind some insoluble hafnium oxide hydroxide product. Although thicker films are less suitable for patterning purposes, these results suggest HafSO_x and similar metal sulfate systems may be interesting materials to study from a self-assembly perspective for applications benefiting from such multi-layered structures.

Convergent beam electron diffraction (CBED) patterns taken on the same location of a 0.15 M HafSO_x film cross-section annealed to 300 °C as a function of TEM e-beam exposure are shown in Figure 4. Initially, the films are amorphous or contain limited short-range order as seen in Figure 4a. However, with relatively little exposure to the TEM e-beam (2.7 C/cm²) the film is seen to undergo distinct crystallization as depicted by the onset of diffraction spots in Figure 4b. These spots increase in number and intensity for increasing e-beam exposure as seen in Figures 4c and 4d indicating an increasing degree of crystallization with increased e-beam exposure. It is prudent to note that the film cross-section shown in Figure 3a has undergone little change in appearance despite receiving approximately six times the dose necessary to induce significant crystallization as seen in Figure 4b. Furthermore, the total dose corresponding to Figure 4b (2.7 C/cm²) is relatively close to that required for patterning in the HafSO_x system for the solution composition used herein (approximately 0.8 C/cm²). Thus, a similar crystallization process likely occurs with top-down e-beam exposure during film patterning. This is in agreement with the proposed condensation pathway¹¹ where cleaving of hafnium peroxide bonds result in a hafnium oxide network formation insoluble in basic solutions.

4. CONCLUSIONS

TEM has been used to investigate the aqueous based peroxo hafnium sulfate system. It was confirmed that nm-sized clusters are the predominant species in precursor solutions. By combining high resolution imaging, elemental mapping and electron diffraction as a function of electron exposure dose on spin coated HafSO_x films we have gained insight into key processes involved in patterning of this material. It is expected that this work will help develop this class of materials as promising next generation inorganic resists.

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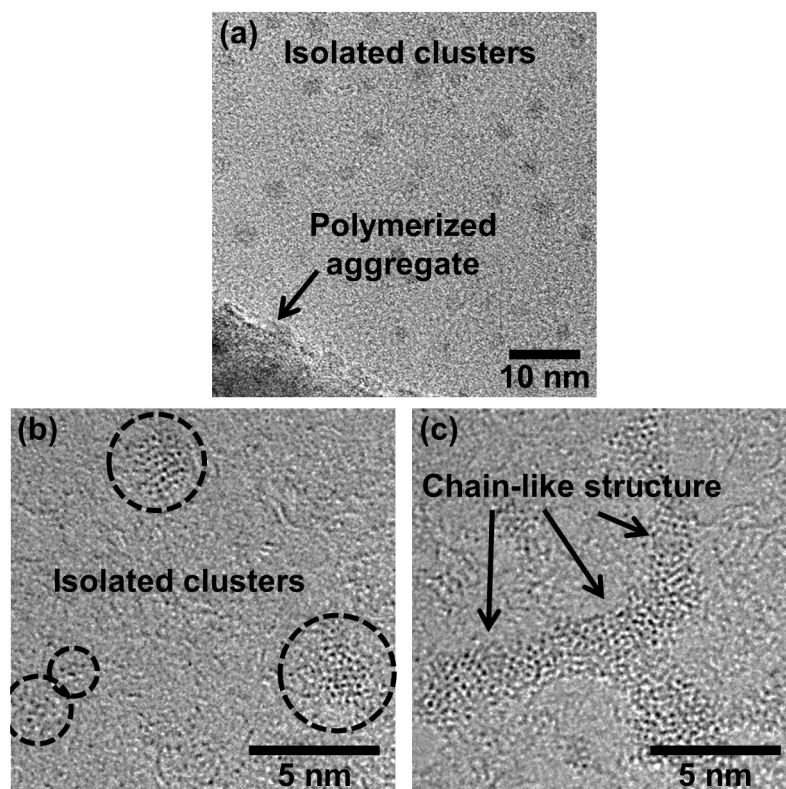


Figure 1. TEM images of HafSO_x clusters drop-cast from aqueous solution. TEM image of isolated clusters (a), HR-TEM images of isolated clusters (clusters circled for clarity) (b) and slightly polymerized clusters (c).

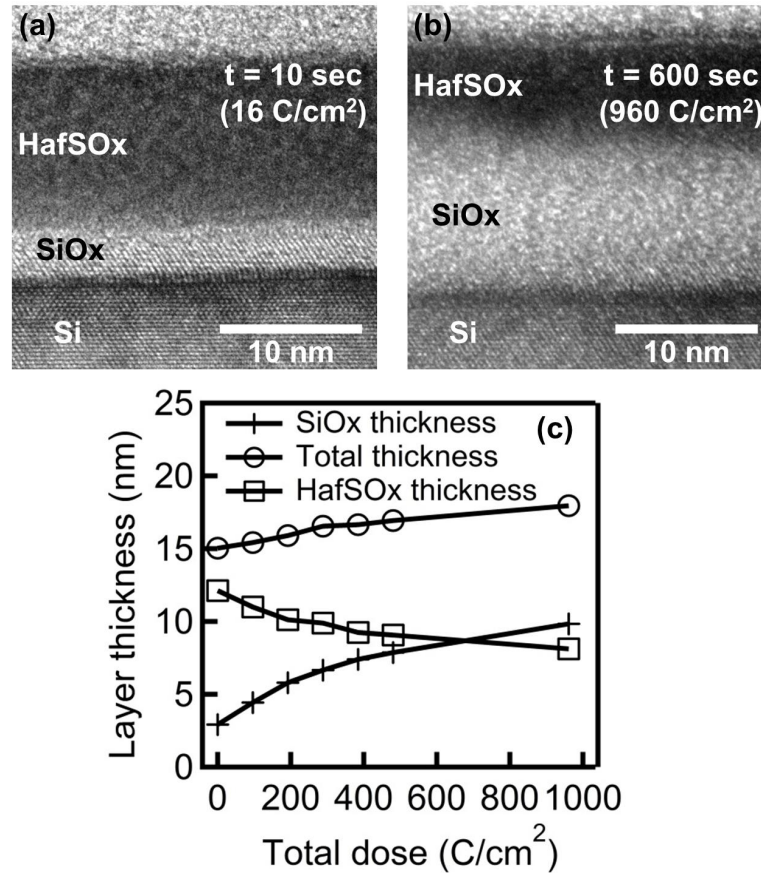


Figure 2. TEM images of 12 nm HafSOx film after 10 sec (a) and 600 sec (b) exposure to the TEM e-beam (total exposure dose shown in parentheses) and a plot of the thickness variation of the HafSOx, SiOx, and total film thickness as a function of total exposure dose (c).

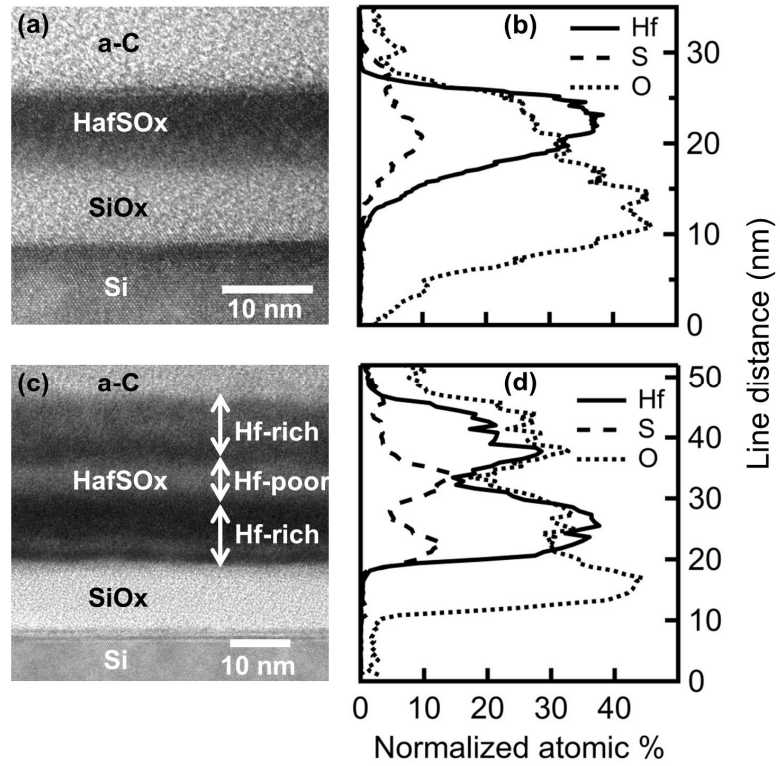


Figure 3. TEM images of 12 nm (a) and 30 nm (c) HafSOx films and EDS line scans corresponding to the 12 nm film (b) and 30 nm film (d) showing relative concentrations of Hf, S and O across the film cross-section.

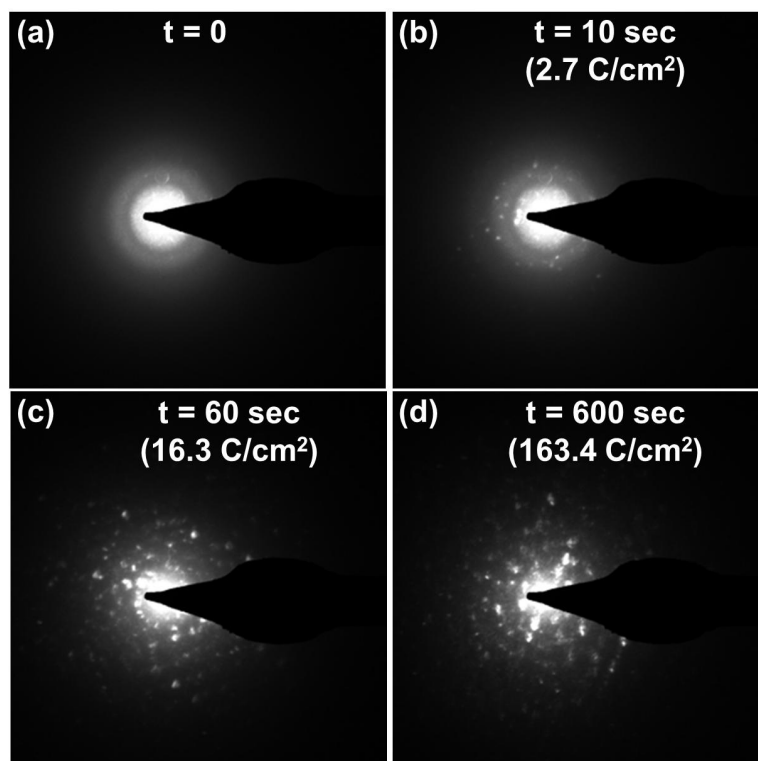


Figure 4. CBED patterns of 12 nm HafSOx film cross-section annealed to 300 °C. Patterns shown are for same area on the film initially (a) and after 10 sec (b), 60 sec (c) and 600 sec (d) exposure to the TEM e-beam (total dose indicated in parentheses).