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Jenn M. Amador, Shawn R. Decker, Stefan E. Lucchini, Rose E. Ruther, Douglas A. Keszler, "Patterning chemistry of HafSOx resist," Proc. SPIE 9051, Advances in Patterning Materials and Processes XXXI, 90511A (27 March 2014); doi: 10.1117/12.2046605

SPIE.

Event: SPIE Advanced Lithography, 2014, San Jose, California, United States

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Lam Research Corp. v. Inpria Corp.

IPR2024-00033 - U.S. Patent No. 9,823,564

Patterning Chemistry of HafSOx photoresist

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ABSTRACT

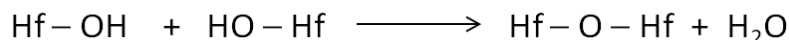
A combination of ICP-OES, titration, and Raman spectroscopy was used to determine the ratio of peroxide to hafnium in the inorganic photoresist HafSOx. By using ICP-OES to determine the hafnium concentration and titration with permanganate to determine peroxide in a solution of dissolved films, the $\text{Hf}:\text{O}_2^{2-}$ ratio was found to be approximately 2:1 in the films. From Raman measurements on precursor solutions, it was determined that that Hf-bound peroxide saturated at this level. Film insolubility is induced through loss of approximately 75% of bound peroxide following exposure to a 30-keV electron beam.

Keywords: HafSOx, inorganic photoresist, EUV, electron beam, ICP-OES, Raman

1. INTRODUCTION

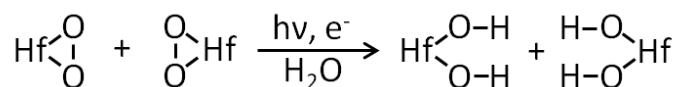
In this contribution, we report results on the determination of the peroxide concentration in thin films of the radiation-sensitive resist $\text{Hf}(\text{OH})_{4-2x-2y}(\text{O}_2)_x(\text{SO}_4)_y \cdot q\text{H}_2\text{O}$ commonly known as HafSOx. This information is needed to develop an understanding of the basic mechanism of lithographic patterning and the intrinsic performance potential of the material. HafSOx free of peroxide was originally investigated as a thin-film high- κ dielectric.¹ The addition of peroxide renders the material sensitive to radiation, yielding a photoresist that can be densely patterned at feature sizes smaller than 10 nm.²⁻⁵

HafSOx films are deposited by spin coating from acidic aqueous solutions. Such solutions are known to contain small nanosized hydroxo clusters containing approximately four Hf atoms. On deposition and heating, these clusters can condense via dehydration (scheme 1) to form rigid gel films. Following



scheme 1

extensive dehydration, the films become insoluble in common resist developers such as TMAH. In HafSOx, this condensation process is inhibited by the binding of peroxide to Hf. As shown in scheme 2,



scheme 2

peroxide decomposition can be induced by high-energy light or electrons. This radiation switch could initiate condensation through dehydroxylation (scheme 1) or a more direct formation of oxo bridges. The presence of $-\text{OH}$ in the films prior to irradiation likely contributes a background level of condensation that must be overcome with radiation exposure to induce solubility changes and contrast in the films.

Hence, the concentrations of hydroxide and peroxide in the films should play a significant role in determining the amount of background condensation.

Because no direct and quantitative method for the determination of peroxide concentration in an inorganic film has been previously reported, we have developed methods involving film stripping to produce solutions for analysis. Hf and peroxide solution concentrations were established through a combination of inductively-coupled-plasma optical-emission spectroscopy (ICP-OES), permanganate titrations, and Raman spectroscopy. The results were then used to examine relationships among peroxide concentration, electron beam exposure dose, and solubility contrast.

2. METHODOLOGY

2.1 ICP-OES

Hafnium concentrations were determined by using a Teledyne Leeman Prodigy ICP-OES in axial mode and monitoring spectral lines at 239.33 and 277.33 nm. A standard solution of 1-M $\text{HfOCl}_2(\text{aq})$ was made from 99.99% $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$, (Alfa Aesar) with 1% v/v nitric acid (ACS Grade, Malinckrodt). The Hf content of $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ was determined from the mass of HfO_2 produced by heating said chloride at 800 °C. Calibration curves were established with solutions diluted to 0.05, 0.5, 5, and 10 ppm with 1% v/v $\text{HNO}_3(\text{aq})$. An additional Hf standard (1000 μg Hf/mL, Inorganic Ventures) was diluted in a similar manner. The 1% v/v $\text{HNO}_3(\text{aq})$ alone was used to establish the baseline for the measurement. Films for analysis were deposited by spinning a 0.4-M HfSOx solution^{2,3,5} onto ten O_2 plasma-treated 6" silicon wafers. Samples for analysis were then stripped from the wafers with 1M $\text{H}_2\text{SO}_4(\text{aq})$. After stripping, the wafers were rinsed with 18.2 M Ω water, then gently blown with Ar(g) to collect the liquid remaining on the wafer. Five samples for ICP-OES analysis were made from 1mL aliquots that were diluted 1:50 with 1% $\text{HNO}_3(\text{aq})$.

2.2 Titration

Peroxide concentrations were determined by permanganate titration⁶ of the samples used for ICP-OES measurements. 0.005-M KMnO_4 (EM Science 99%+), standardized with $\text{Na}_2\text{C}_2\text{O}_4$ (Acros Organics, 99%+), was used as the titrant. Permanganate was added in 10- μL aliquots and allowed to react slowly without heating until the endpoint was visually noted by a change in color from colorless to pale pink. Prior to titration of the film rinses, the measurement was tested by titration of peroxide solutions with known concentration. A measurement error of 1% and a detection limit of 1.25×10^{-7} M peroxide were established.

2.3 Raman Measurements

Raman spectra of HfSOx precursor solutions were collected by using a Nicolet FT-Raman instrument. Data collection and signal averaging were handled with Omnic 8 software. 1-mL samples of 0.5-M $\text{HfOCl}_2(\text{aq})$ were prepared in 20-mL glass scintillation vials. Chilled hydrogen peroxide (Macron, 30% solution) was added in 10- μL aliquots to give ratios of H_2O_2 :Hf up to 3:1. H_2SO_4 (EMD, ACS Grade) was also added concurrently to give a H_2SO_4 :Hf ratio of 0.7:1. Spectra were collected over the range 500 - 3000 cm^{-1} with a total exposure time of 100 s. Measurement of an empty scintillation vial was used to establish background for the experiment.

Films were deposited onto 1 x 1" substrates of 200 nm thermally-deposited Al on SiO₂. Prior to HafSOx deposition, substrates were treated in a Plasma Etch 50 O₂ plasma asher for five min. All films were deposited via spin-coating and then baked at 80 °C for three minutes. The resulting films were analyzed with a Horiba LabRAM Raman instrument equipped with a 100 x objective and 532-nm laser. Spectra were collected over the range 600 – 1300 cm⁻¹ by accumulating three spectra in 15 min. Raman spectra were also measured on films exposed to an electron beam at selected doses. Films were spun on aluminum substrates and then exposed via electron-beam writing to produce a 7 x 3 array of 200 x 200-μm squares with doses ranging from 0 to 800 μC/cm² in increasing increments of 40 μC/cm². A 30-kV beam of an FEI Quanta 3D Dual Beam SEM/FIB was controlled with NPGS software for pattern writing. Following patterning, Raman spectra of the exposed and unexposed regions were obtained.

3. RESULTS AND DISCUSSION

ICP-OES analysis for Hf concentration initially produced inconsistent results. Significant sample-to-sample variation were observed, despite consistent handling and dilution methods. During measurement, the derived concentration of a given sample would decrease with sampling time. In each case, however, the concentration would stabilize at 0.5 mM. We surmised that residual Hf from the standard solution, which was run before each sample, appeared to be the source of the inconsistent results. An acid rinse with H₂SO₄(aq) was then used to clear the delivery lines prior to sample injection. With this procedure, measured concentrations more quickly stabilized at 0.5 mM. To confirm the results, a commercial standard was then used for comparison. The measurements were readily reproduced, again giving a Hf concentration of 0.5 mM with a standard deviation of 2%. Concurrent with the ICP-OES analysis, the concentration of peroxide was determined by peroxide titrations. The equivalent peroxide concentration was found to be 0.27 M, affording a Hf:O₂²⁻ ratio of 1.8:1 in the thin film.

Raman spectra for HafSOx solutions containing increasing concentrations of peroxide are shown in Figure 1. Bands, centered near 1000 cm⁻¹, are attributed to sulfate. The central peak is assigned to sulfate

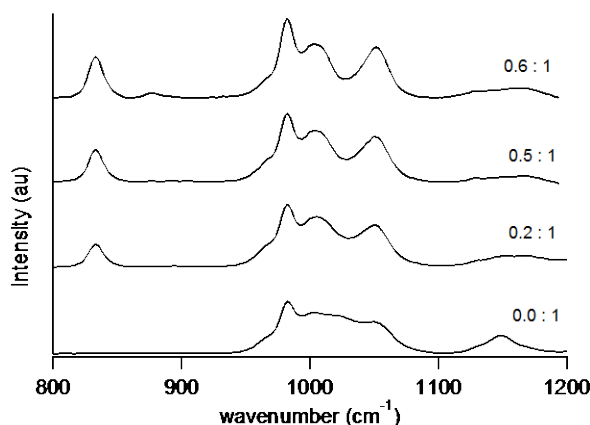


Figure 1. Raman spectra of HafSOx solutions with selected O₂²⁻:Hf ratios.

bound to Hf, and the two remaining shoulders at 970 and 1050 cm^{-1} are assigned to unbound sulfate.⁷ Addition of peroxide to a solution containing only Hf and sulfate results in the appearance of a band near 830 cm^{-1} , *cf.*, bottom two spectra in Figure 1. This signal is assigned to μ_2 binding of peroxide to Hf.⁸ On further addition of peroxide, *cf.*, Figure 2, this signal grows. At a $\text{O}_2^{2-}:\text{Hf}$ ratio of 0.6:1, a new signal appears at 870 cm^{-1} . This peak is also observed in solutions of 1% $\text{H}_2\text{O}_2(\text{aq})$, and it is assigned to the $\nu(\text{O}-\text{O})$ stretch of solvated peroxide.⁹ The unbound peroxide peak only appears beyond a $\text{O}_2^{2-}:\text{Hf}$ ratio of 0.6:1. Hence, this solution result is entirely consistent with the ratio deduced from ICP-OES analysis of thin films. Even with excess peroxide in the precursor solution, the $\text{Hf}:\text{O}_2^{2-}$ ratio saturates near 2:1 in the solution, and it persists in the film.

On the basis of these results and assuming a fully protonated state, the precursor formulation can be approximated as $\text{Hf}(\text{OH})_{1.6}(\text{O}_2)_{0.5}(\text{SO}_4)_{0.7} \cdot q\text{H}_2\text{O}$. During spin coating and the post-application bake a certain amount of $-\text{OH}$ condensation occurs to form a continuous gel-like film. Additional condensation is then initiated through radiation exposure or additional, spontaneous water loss. The peroxide and sulfate Raman signals provide a convenient means for monitoring the effects of radiation exposure. As shown in Figure 2, strong bands at 830 and 1050 cm^{-1} , corresponding to Hf-bound peroxide and sulfate,

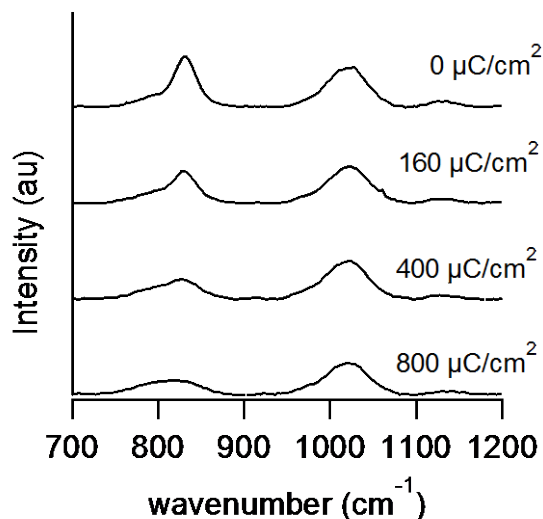


Figure 2. Raman spectra for HafSOx films after exposure with a 30-kV electron beam. The exposure dose associated with each spectrum is noted.

respectively, are readily observed in unexposed films (0 $\mu\text{C}/\text{cm}^2$). The films differ from the solutions in that free peroxide and sulfate are not observed. With increasing exposure (Figure 2) with a 30-kV electron beam, the peroxide signal diminishes relative to the sulfate signal, indicating peroxide is lost. This decreasing signal is correlated to studies of development contrast in Figure 3. Below a dose of approximately 220 $\mu\text{C}/\text{cm}^2$, the development rate of an unexposed film is considerably faster than an exposed film in 25% TMAH(aq). Across the dose range 220-340 $\mu\text{C}/\text{cm}^2$, the film switches from soluble to insoluble. In calibration studies, we have found a linear relationship between the peroxide Raman signal and concentration with a detection limit of 25% peroxide. Hence, a dose of 340 $\mu\text{C}/\text{cm}^2$ corresponds to photodecomposition of nearly 75% of total peroxide content. Through the transition region, no more than 15% of total peroxide is lost as a result of exposure.

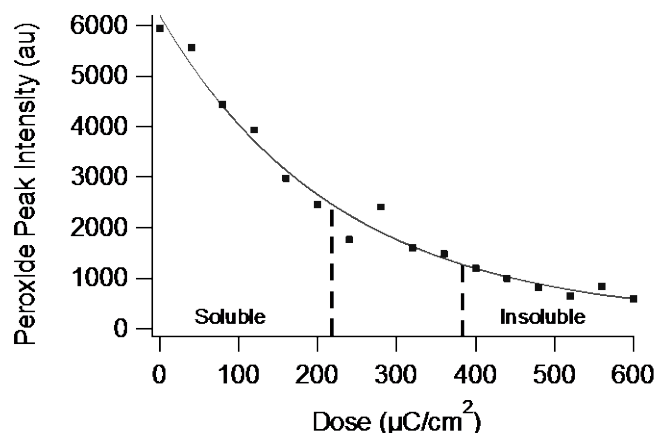


Fig. 3: Raman signal as a function of electron-beam exposure dose and solubility characteristics.

4. CONCLUSIONS

A combination of ICP-OES analysis, chemical titration, and Raman spectroscopy has been used to establish a working formula for a HafSO_x photoresist. The resulting formulation $\text{Hf}(\text{OH})_{1.6}(\text{O}_2)_{0.5}(\text{SO}_4)_{0.7} \cdot q\text{H}_2\text{O}$ represents the upper concentration limit of Hf-bound peroxide both in the solution precursor and the thin film. Under electron-beam exposure, nearly 75% of the bound peroxide must be eliminated to produce an insoluble product. These results represent an initial step toward unraveling the chemical processes that contribute to the production of high-resolution, high-fidelity nanostructures with HafSO_x.

5. ACKNOWLEDGMENTS

This material is based upon work conducted in the Center for Sustainable Materials Chemistry, which is supported by the US National Science Foundation (grant number CHE-1102637). The authors thank Dr. Andy Ungerer for assistance with the ICP-OES measurements and Peter Eschbach and Teresa Sawyer for help with the electron-beam writing experiment.

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