## INTRODUCTION

Inorganic coatings are ubiquitous in modern technology. While the majority of inorganic coatings are made via high-vacuum processes (e.g., sputtering, evaporation, and atomic-layer deposition), there has long been an interest in preparing dense, smooth inorganic coatings using a solution route. Perhaps the most widely studied solution route to thin films is the sol–gel method, which generally employs non-aqueous solvents.\(^1\) This method has been used to prepare films with varying degrees of porosity and a wide range of pore sizes. Sol–gel-derived monoliths and films can generally be described as porous rigid oxide networks in which the pores are filled with liquid or gas.\(^1,2\) More recently, Keszler and co-workers have developed a “prompt inorganic condensation” (PIC) aqueous route to prepare ultrasmooth amorphous inorganic films with a variety of cations by controlling the condensation process.\(^3\)–\(^10\) This method allows the preparation of dense oxide films with near-atomic surface smoothness, presumably due to the surface tension of the water-based solution during spin coating.\(^3\)–\(^10\) Film thicknesses can easily be controlled via the concentration of the solution and the physical parameters used to spin the films. Thin films made via PIC have been incorporated into thin-film transistor components using spin coating and low-temperature annealing to obtain devices that meet or exceed the performance of conventional vapor-deposited devices.\(^5\)\(^,\)\(^11\)–\(^15\)

PIC films prepared from solutions of hafnium oxychloride dissolved in sulfuric acid (HafSO\(_x\)) with added peroxide have been shown to function as ultrahigh-resolution resists, patternable with electron beam or extreme ultraviolet radiation.\(^16\)\(^,\)\(^17\) These resists enable patterning with minimum line widths and edge roughnesses superior to those obtainable using organic resist materials using conventional lithography techniques. These advantages are expected to become even more important for extreme ultraviolet (EUV) lithography in next generation semiconductor manufacturing.\(^18\)

For solution-processed films, developing a fundamental understanding of the chemistry occurring in each processing step is critical for improving film morphology and performance.\(^19\)–\(^23\) In the case of inorganic metal oxide films (using sol–gel or PIC), processing steps include the following: film deposition (via spin coating or dip coating), a “soft bake” to drive off excess solvent, and higher temperature annealing to

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**ABSTRACT:** A variety of metal oxide films (InGaO\(_x\), AlO\(_x\), “HafSO\(_x\)” prepared from aqueous solutions were found to have non-uniform electron density profiles using X-ray reflectivity. The inhomogeneity in HafSO\(_x\) films (Hf-(OH)\(_{6-2x}\)O\(_x\))\(\cdot\)(SO\(_4\))\(_2\)\(\cdot\)zH\(_2\)O), which are currently under investigation as inorganic resists, were studied in more detail by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and medium-energy ion scattering (MEIS). The HAADF-STEM images show a greater concentration of heavy atoms near the surface of a single-layer film. MEIS data confirm the aggregation of Hf at the film surface. The denser “crust” layer in HafSO\(_x\) films may directly impact patterning resolution. More generally, the phenomenon of surface-layer inhomogeneity in solution-deposited films likely influences film properties and may have consequences in other thin-film systems under investigation as resists, dielectrics, and thin-film transistor components.

**KEYWORDS:** metal oxide thin film, HafSO\(_x\), aqueous solution, crust, inhomogeneity, XRR, MEIS, HAADF-STEM
facilitate counterion removal and condensation. In the sol–gel process, evaporation of organic solvent molecules and simultaneous hydrolysis reactions at relatively low temperatures lead to a stiff inorganic network, and subsequent drying occurs via evaporation from pores.24 By contrast, in the aqueous PIC route, evaporation of solvent (water) involves considerably more energy due to hydrogen bonding and increased solvent/solute interaction strength. The loss of water leads to condensation reactions that directly link the inorganic species as their concentration increases.25

Although fundamentally different chemistries occur in the various methods used to prepare inorganic films, drying and densification models generally assume the resulting films are homogeneous.24 However, there are a few previous studies that show inhomogeneities in sol–gel-derived multilayer films observable by TEM26 or X-ray reflectivity (XRR).26,27 Denser surface “crusts” in single-layer films have also been observed via ellipsometry in sol–gel silica coatings28 and by XRR in PIC aluminum oxide phosphate films.29 The nature of these inhomogeneities, whether due to density variations or compositional inhomogeneity, has not been determined. This prompted us to undertake a systematic study of density and compositional inhomogeneity in PIC-prepared films using multiple techniques.

In this work we present XRR data on a diverse set of films made using PIC with different metal precursor solutions. The three material systems investigated were selected based on their ability to form dense, smooth, amorphous thin films. Films comprised of multiple layers yielded XRR patterns inconsistent with those expected for homogeneous films, suggesting a general phenomenon of density or composition gradients in the individual layers of PIC-derived films. Using HafSOx as a model system, single-layer and multilayer films annealed at different temperatures were examined using XRR, cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and medium-energy ion scattering (MEIS). These techniques reveal the evolution of density and compositional inhomogeneity in the films during processing. They suggest a thin, dense surface crust forms during spin coating, presumably because the reactants near the surface dehydrate faster than in the interior of the film. This surface crust persists during subsequent low-temperature annealing, but surprisingly does not increase in thickness. Because the performance of photoresists has been shown to be very sensitive to processing conditions, controlling the inhomogeneity in HafSOx films may be an important avenue toward improving performance in ultrahigh-resolution resist applications. More generally, the presence of a dense surface layer may affect the kinetics of film formation, as well as the final properties of metal oxide films derived using PIC. Therefore, understanding and controlling the formation of the surface layer is important for tailoring the evolution and properties of films made using this method.

**Experimental Section**

**InGaOx and AlOx Precursor Solution Preparation.** A 2.00 M total metal concentration (6:7 In:Ga) solution of In(NO3)3·H2O (Sigma-Aldrich, 99.99% In) and Ga(NO3)3·xH2O (Alfa Aesar, 99.999% Ga) and a 1.70 M metal concentration solution of Al(NO3)3·9H2O (Alfa Aesar, 98% Al) were electrochemically treated to reduce nitrate counterion concentrations according to previously reported methods.30,31 Water contents of the indium and gallium nitrate hydrate salts were determined through calcination of the salts to form the oxide and back calculation of the hydrate content (≈5 and 8 H2O for the indium and gallium nitrate hydrate salts, respectively). Both solutions were diluted to 0.25 M (total metal concentration) with 18 MΩ nanopure water and filtered through 0.45 μm PTFE filters.

**HafSOx Precursor Solution Preparation.** A 1.00 M stock solution of HfOCl2·8H2O (Alfa Aesar, 98% Hf) was prepared by dissolution and dilution with 18 MΩ nanopure water. Solutions for spin coating were prepared by mixing 2.000 N H2SO4(aq) (VWR) and 30 wt % H2O2(aq) (EMD Millipore) followed by the addition of HfOCl2(aq).32 The final solution was diluted using 18 MΩ water to a concentration of 0.105 M sulfuric acid, 0.45 M hydrogen peroxide, and 0.15 M Hf. The four-coat multilayer was synthesized from a solution without peroxide to decrease the solubility of the film, allowing for a lower annealing temperature to prevent subsequent layers from dissolving the previous.33

**InGaOx, AlOx, and HafSOx Film Preparation.** N-type, 5b-doped silicon substrates (0.008–0.02 Ω-cm) received surface treatments using a MDRA CH CS-1701 plasma cleaner running on O2 plasma at 30% O2 in N2 using 150 W for 60 s immediately before spin coating. Films were prepared by filtering the solutions through a 0.45 μm filter and spin coating at 3000 rpm for 30 s. The HafSOx thin films were subjected to a 1 min anneal at either 80 °C for a single layer or 180 °C for the multilayer samples. The InGaOx and AlOx multilayer films were annealed at 450 °C for 20 min per coat followed by a final 60 min anneal at 450 °C. All films were annealed on a preheated, calibrated hot plate.

XRR patterns were obtained on a Bruker D8 Discover instrument (Cu Kα radiation). Sample alignment was checked to ensure that the incident and exit angles were equal and that the sample was in the center of the goniometer. Alignment procedures involved iteratively performing rocking curves and z (height) scans to ensure the aforementioned criteria were met.34

Fits of the XRR data were performed using the BEDE ref. software package, which creates a population of solutions based on an initial model and uses a genetic algorithm to minimize residuals.35 Once the best fit was achieved, the models were perturbed to confirm that the model was not a local minimum. Films were initially fit as a single film, to determine the average density and total film thickness. For single-coat films, the model was then split in half, with each half being allowed to vary thickness and density independently to improve the fit. A gradient was also added to the fit, as the abruptness of the interface was unknown. Comparison of the difference between the simulated and experimental data (i.e., residuals) over a constant range allows for the quantitative comparison of the fits for a single data set.

Comparison of residuals between different data sets requires a more detailed analysis, as the noise inherent in the experimental data contributes differently to the residuals for each data set. Multilayer films were modeled similarly; each coat was split into a two-layer unit, and each layer was allowed to vary independently in thickness and density (all coats assumed to be identical). For scanning transmission electron microscopy (STEM) investigations, a thin cross-section sample was prepared from a section of the film using an in situ lift-out process on a FEI Helios 600 equipped with a Sidewinder ion column and a Quorum cryo stage.36 Steps were taken to avoid exposure of the beam-sensitive film while imaging with the SEM and sputtering with the focused ion beam (FIB). Prior to loading the sample in the FIB–SEM, the sample was coated with a 30 nm protecting layer of evaporated carbon. A second 1.5 μm thick protecting layer of FIB-induced carbon was deposited over the area of interest using a 2 keV accelerating voltage (<5 nm stopping range in evaporated carbon). The lift-out and thinning process was carried out using a 500 eV accelerating voltage on the electron beam to minimize the interaction volume of the beam (<9 nm interaction depth). After completing the lift-out, the sample remained 1.5 μm thick to ensure no beam interaction had taken place. The sample was then cooled to −170 °C throughout the thinning process. The FIB accelerating voltages used were lowered as the thickness decreased, 30 keV (1.5 to 0.5 μm), 5 keV (500 to 100 nm), and 2 keV (100 to 40 nm). During thinning the sample was monitored using low dose electron beam conditions to reduce risk of exposure and excessive heat (periodic single frames using 500 eV, 90 pA, 500 ns dwell per pixel, 50 um

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RESULTS AND DISCUSSION
Four-coat samples of InGaO$_x$, Al$_{2}$O$_3$, and HafSOx were prepared using PIC as described earlier and examined by XRR (Figure 1). For all samples, the XRR patterns consist of regular Kiessig fringes with a pattern of varying intensity. Figure 2a contains a schematic of two potential structures of these films, one that is homogeneous and one that contains a repeating structure of four layers (coats) where each layer has an identical non-uniform electron density gradient. Figure 2b contains the simulated XRR patterns for these two films. Since XRR is very sensitive to variations in electron density, small (1%) differences in electron density can be detected. The simulated XRR pattern for a homogeneous single-coat film shows a characteristic systematic decay in the Kiessig fringe intensity with increasing diffraction angle. The simulated XRR pattern of the film with a repeating structure of 4 identical layers with nonuniform electron density contains a characteristic modulation of the Kiessig fringe decay, with more intense diffraction maxima corresponding to the thickness of the individual layers resulting from the coherent scattering of the electron density profiles in each layer. Between these more intense maxima are $n - 2$ smaller maxima, where $n$ is the number of coats, resulting from incomplete destructive interference. All of the multilayer films prepared via PIC have XRR patterns (Figure 1) characteristic of films consisting of repeating layers of non-uniform electron density profiles, inconsistent with those expected for homogeneous films. This suggests that this inhomogeneity is a general characteristic of PIC solution-deposited thin films. We elected to study the effects of this phenomenon in more detail for the HafSOx system.

In Figure 3, we model the XRR data of the four-coat HafSOx film assuming that each deposited coat consists of a bilayer: a “bulk” layer and a surface layer. The density and thickness of the bulk and surface layers were allowed to freely vary in order to obtain the best possible fit. It was also assumed that all four coats were identical as a simple, first approximation. This model is not quantitative, as the actual structure is more complex due to the different thermal treatment for each layer. Within these constraints, the best fits were obtained with a thin surface layer (or crust) in each coat with a higher electron density than the underlying bulk layer. Attempts to perturb the models to give a bulk layer of higher density than the surface layer resulted in low-quality fits. Although this model is an oversimplification, it indicates that the films have a higher density surface region within each deposited layer.

A single-coat film was also investigated to determine if the crust is inherent in each coat or whether it is induced by the processing conditions used to make the four-coat multilayer. To match the processing of the four-coat multilayer, the film was annealed at 180 °C for 1 min. XRR data for the single-coat film was modeled both as a homogeneous single-layer film and as a bilayer separated by a gradient. For the latter model, the surface and bulk layer were allowed to freely vary in thickness and electron density (Figure 4).

Between the two models, the two-layer model with a thin, denser crust has a 20% reduction in the residuals as compared to the single-layer model when both models are allowed to search for the minimum using the genetic algorithm and modeling procedure described previously. Perturbing the models from the fits to find better solutions was unsuccessful, indicating the refined fits represent global minima. In XRR, the density values are derived from the critical angle, which is directly related to electron density. In order to obtain density in g cm$^{-3}$, the composition of the film must be assumed. Therefore, the density values of the layers should be viewed as being approximate, as they depend on the model used. The modeling suggests the best description of the film within the applied modeling constraints is that of a less electron-dense
layer topped by a thin, higher electron density crust. These are probably separated by a thin gradient region between the surface and bulk layers, which was included in the model of the single-coat films. This two-layer model with a thin, dense crust therefore qualitatively agrees well with the modeling of the individual coats in the four-coat films, which was previously discussed. Not surprisingly, the simple model assuming four identical bilayers does not quantitatively match the model used for the single-coat films, where the addition of a gradient layer increases the density of the surface layer. In both models, a denser surface crust and less dense bulk layer are required to obtain good fits.

Since it has previously been reported that peroxide-containing HafSOx films used for lithography were homogeneous, a new films containing peroxide were prepared to test whether the crusts observed previously also occur when peroxide is added. These peroxide-containing films were also used to examine the effect of annealing temperature. In order to replicate HafSOx films used for patterning, a single-coat film containing peroxide was annealed to the soft-bake temperature of 80 °C for XRR studies. As seen in Figure 5, not only does the bilayer model give a better fit to the data but also the residuals are reduced by 50% when the model is allowed to create two layers separated by a gradient. This supports the formation of a crust in films containing peroxide, even at the low soft-bake temperatures used for lithography.

XRR studies reveal electron density gradients and periodicity (in multilayers), but do not reveal the source of the density gradients (i.e., whether they are due to density variations of a single chemical composition or a chemical gradient). Additional information on the HafSOx films was obtained using HAADF-STEM. Cross-sections of a single-coat film containing peroxide were prepared with care to maintain its condition prior to exposure, and a representative cryo-HAADF STEM image is shown in Figure 6a. The image reveals a bright thin band at the top of the sample indicating an increased density of heavy atoms at the surface. Integration of the average HAADF signal intensity over the highlighted area in Figure 6a provides a two-dimensional plot of the heavy atom density profile across the film (Figure 6b). This indicates that, in addition to the concentration of heavy atoms at the surface of the film, there is also a slight increase of heavy atom density near the bottom of the film. These data provide direct evidence that there is electron density inhomogeneity within the films and supports the two-layer XRR model used earlier.

In order to obtain information about chemical inhomogeneity, MEIS data were collected as a function of annealing temperature and time. MEIS, a low-energy, high-resolution version of RBS, is a quantitative technique. The experiment directly measures the number of backscattered ions of each mass. Using calibrated instrumental parameters and well-established cross-sections, these can be converted into areal densities. Further, the ions lose energy as they travel through the film, with the amount of energy loss being a measure of the distance traveled. The width of a peak in an MEIS spectrum is therefore a measure of the thickness of the corresponding layer, and its integrated area yields a direct quantitative areal density (atoms/cm²). The highest energy peak results from protons backscattered from the heaviest atom (i.e., Hf) in the film. The areal density can be converted into a thickness if the bulk density is known (e.g., from XRD), and, conversely, the density can be determined if one has an alternative measure of
thickness (e.g., from TEM). Because there is some uncertainty in the water content of the HafSOx films (which depends on processing conditions, film history, temperature, and gas-phase partial pressures during characterization), precise comparisons between different samples is challenging. Nevertheless, the relative density changes from MEIS in the film as a function of depth are quite meaningful.

Hafnium segregation to, or densification at, the surface is readily apparent from the raw MEIS data (Figure 7). If Hf were distributed uniformly throughout the film, the highest energy peak (corresponding to Hf) would have a "flat" plateau. However, the intensity of the Hf MEIS peaks is greatest at the highest detected energy (at the surface) and is decreased at lower energies (further below the surface). This is consistent with the increased intensity in the HAADF-STEM image at the surface due to an increased concentration of heavy atoms (i.e., Hf). It is also readily apparent in the MEIS spectra that the film thickness decreases (with corresponding increase in density) as the annealing temperature is increased (Figure 7b). Qualitatively, the MEIS data are consistent with the results obtained from XRR and STEM investigations. All three techniques indicate the presence of a Hf-enriched denser surface crust in all HafSOx films reported in this work (annealed from 80 to 300 °C, with or without peroxide).

**SUMMARY**

The data presented suggest that films prepared from aqueous solutions via the PIC process are inhomogeneous in composition and density throughout their thickness. For HafSOx films, a dense region forms at the surface after a low-temperature anneal. This may result from enhanced evaporation of solvent at the surface of the film, increasing concentration and resulting in condensation reactions between the Hf-containing moieties to yield a dense surface layer on the film. Presumably this acts as a diffusion barrier, leading to the lower density observed in the bulk of the film. We postulate that the slow rate of water diffusion through the crust relative to the rate of diffusion within the bulk layer of the film prevents the formation of density gradients in the bulk of the film during subsequent annealing. In the case of HafSOx, the denser surface layer may influence the patterning resolution and contrast obtainable with this system. It may be possible to control the density and/or thickness of the surface crust by adjusting annealing conditions (e.g., temperature, atmosphere, and ramp rate) and to correlate changes with patterning metrics. We also show that crust formation is quite general for PIC-processed films and that the density inhomogeneities in single coats result in periodic density gradients in multilayer films, which may affect film properties such as electrical conductivity or breakdown voltage. In the case of multi-metal-component oxides deposited from solutions of mixed metal cations, the chemical composition profiles are expected to be more complicated and dependent on a number of factors (e.g., metal solubility and diffusion rate differences). Determining chemical composition gradients at the nanoscale would enable the development of a mechanistic picture of the chemistry occurring during film formation and provide avenues to design chemical inhomogeneities to obtain enhanced properties. The determination of chemical composition gradients at the nanoscale, however, remains a major analytical challenge. Ultimately, understanding and controlling film inhomogeneities will provide an additional tool to modify the physical and chemical properties of films prepared using the PIC approach.

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**Notes**

The authors declare no competing financial interest.

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