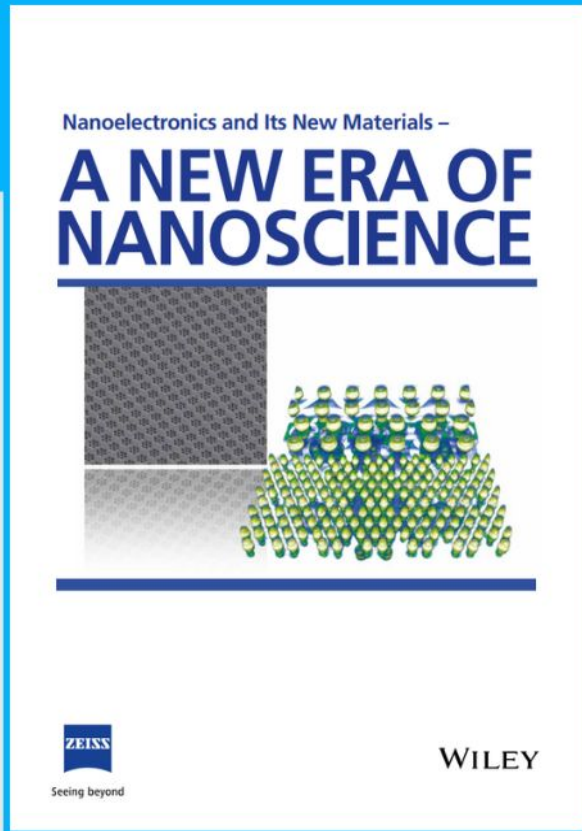




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Solution-Processed HfSO_x and ZrSO_x Inorganic Thin-Film Dielectrics and Nanolaminates**

By Jeremy T. Anderson, Craig L. Munsee, Celia M. Hung, Tran M. Phung, Gregory S. Herman, David C. Johnson, John F. Wager, and Douglas A. Keszler*

New thin-film dielectrics and nanolaminates have been synthesized via aqueous-solution deposition of Hf and Zr sulfates, where facile gelation and vitrification of the precursor solution have been achieved without organic additives. X-ray reflectivity, imaging, and metal-insulator-metal capacitor performance reveal that smooth, atomically dense films are readily produced by spin coating and modest thermal treatment ($T < 325^\circ\text{C}$). Dielectric characteristics include permittivities covering the range of 9–12 with breakdown fields up to 6 MV cm^{-1} . Performance as gate dielectrics is demonstrated in field-effect transistors exhibiting small gate-leakage currents and qualitatively ideal device performance. The low-temperature processing, uniformity, and pore-free nature of the films have also allowed construction of unique, high-resolution nanolaminates exhibiting individual layers as thin as 3 nm.

1. Introduction

Low-temperature, high-speed printing of thin-film devices offers an attractive route to the realization of low-cost electronics. This solution-based processing is readily applicable to many organic and polymeric materials, but the electronic devices derived therefrom generally exhibit quite modest performance characteristics.^[1–3] If similar processing and printing strategies were successfully extended to the deposition of inorganic materials, higher performance could be realized.^[4–6] In this context, we are emphasizing the development of an oxide printing platform for both active and passive components of electronics,^[7–10] providing unique opportunities for application of solution-based additive, environmentally benign, low-temperature, and vacuum-free fabrication in the production of

chemically robust materials and devices. In considering the set of materials—conductors, semiconductors, and insulators—that is necessary for the realization of electronic devices, e.g., thin-film transistors (TFTs) and circuits, the current lack of materials sets for low-temperature, solution-based synthesis of high-quality thin-film insulators represents a major impediment to the realization of useful all-inorganic devices. In a TFT, for example, the insulator (gate dielectric) must not only be smooth, dense, and pinhole-free, but it must also exhibit low leakage current, high breakdown strength, a low interface state density, and preferably a high dielectric constant. Amorphous materials provide these features; they do not have grain boundaries, effectively reducing electronic-defect domains, while enhancing device performance on the basis of their smooth surfaces and associated interfaces. Among amorphous insulators, inorganic oxides with their wide bandgaps, useful polarizabilities, and chemical stabilities dominate practical use. And up to now only vapor methods have been successfully applied to the deposition of these materials. The production of high-quality insulators via solution processing has not previously been demonstrated, as the loss of solvent and other components during drying and annealing typically leads to film crystallization, “mud cracking,” and considerable porosity.^[11] As noted above, these features produce grain boundaries, defects, and charge-conduction pathways that mitigate the desired effectiveness of the insulator.

In this contribution, we describe materials and methods for realizing high-quality, amorphous oxide thin-film dielectrics at relatively low temperatures through development of single-source inks that are applicable in printing. We demonstrate that useful dielectrics can be produced with new hafnium and zirconium oxide sulfates and their derivatives, as exemplified by the parent compositions $\text{HfO}_{2-x}(\text{SO}_4)_x$ and $\text{ZrO}_{2-x}(\text{SO}_4)_x$ ($0.46 \leq x \leq 1$), which we designate HfSO_x and ZrSO_x , respectively. As described below, thin films of these materials are

[*] Prof. D. A. Keszler, J. T. Anderson
Department of Chemistry, Oregon State University
153 Gilbert Hall, Corvallis, OR 97331-4003 (USA)
E-mail: douglas.keszler@oregonstate.edu

C. L. Munsee, C. M. Hung, Prof. J. F. Wager
School of Electrical Engineering and Computer Science
Oregon State University
1148 Kelley Engineering Center, Corvallis, OR 97331-5501 (USA)

Dr. T. M. Phung, Prof. D. C. Johnson
Department of Chemistry and Materials Science Institute
University of Oregon, Eugene, OR 97403-1253 (USA)

Dr. G. S. Herman
Hewlett Packard Company
1000 NE Circle Boulevard, Corvallis, OR 97330 (USA)

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atomically dense, exhibiting relatively high permittivity and exceptional performance in metal-insulator-metal (MIM) capacitors and TFTs. The unique characteristics of the films prompted us to fabricate mixed HafSOx/ZircSOx laminates with nanoscale resolution, demonstrating the versatility of the inks and associated thin films. We first consider the processing chemistry, which inevitably determines all aspects of film fabrication and performance. Subsequently, we describe findings covering the dielectric properties, device function, and laminated structures of the films.

2. Results and Discussion

2.1. Precursor Chemistries and Materials Analyses

Precursor solutions for SOx films are combinations of $\text{HfOCl}_2(\text{aq})$ or $\text{ZrOCl}_2(\text{aq})$ with $\text{H}_2\text{SO}_4(\text{aq})$, and for derivative compositions appropriate metal sulfates or oxides are added. In this section, we describe the chemical processes that enable the conversion of these solution precursors into the solid films. Representative materials HafSOx and HafSOx:La are investigated as both bulk powders and thin films with emphasis on precipitation, dehydration, and crystallization. Comparative analyses reveal that certain bulk and thin-film characteristics are similar, while others (primarily derived from the rapid deposition of the films) are distinct.

A number of phases and crystal structures have been reported from examination of the systems $\text{HfO}_2\text{-SO}_3\text{-H}_2\text{O}$ and $\text{ZrO}_2\text{-SO}_3\text{-H}_2\text{O}$. Several structures have been characterized as simple hydrates, e.g., $\text{Hf}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ or $\text{Zr}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$,^[12] exhibiting variations in the degree of hydration and in the structural dimensionality associated with the condensation of the metal atom, sulfate groups, and water. Materials rich in metal relative to sulfate are known, and they include $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$,^[13] $\text{Hf}(\text{OH})_2\text{SO}_4$, $\text{Zr}(\text{OH})_2\text{SO}_4$, and their hydrates,^[14–18] $\text{Hf}_{18}\text{O}_{10}(\text{OH})_{26}(\text{SO}_4)_{13} \cdot 33\text{H}_2\text{O}$ and $\text{Zr}_{18}\text{O}_4(\text{OH})_{38.8}(\text{SO}_4)_{12.6} \cdot 33\text{H}_2\text{O}$,^[19,20] and $\text{Zr}_3\text{O}_5\text{SO}_4$ and its hydrate.^[21] Additional, largely uncharacterized phases have also been reported.^[22] All of these structures (with the possible exception of $\text{Zr}_3\text{O}_5\text{SO}_4$) are likely unstable when subjected to air at both room and higher temperatures, resulting from spontaneous hydration, dehydration, or changes in hydrogen-bonding frameworks. From our perspective, this has provided the opportunity to use the dehydration and associated condensation processes for the development of amorphous films. Volume changes on dehydration are minimized relative to those associated with metal-organic precursors, and the kinetics of dehydration and condensation can be sufficiently fast to produce dense, amorphous products.

To gain insight and subsequent control of the chemistry in these systems for film deposition, the characteristics of precipitated powders of $\text{HfO}_{2-x}(\text{SO}_4)_x$ have been examined. Starting from aqueous solutions with selected fractions of sulfate relative to Hf (variable x), HafSOx precipitates were formed by heating. As seen from thermogravimetric analysis (TGA) traces in Figure 1, heating a HafSOx precipitate dried at room temperature leads to mass loss in three domains. A large mass

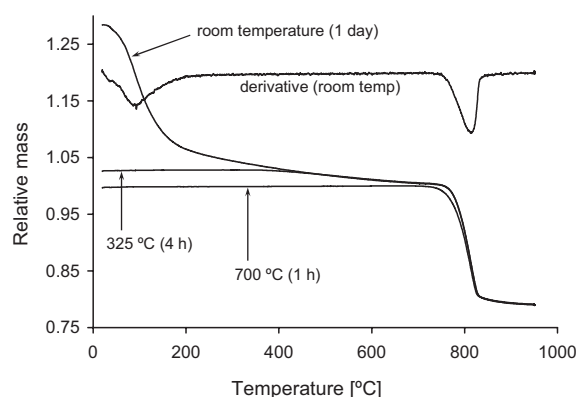


Figure 1. TGA for HafSOx ($x=0.70$) with various pretreatments indicated. Samples heated under flowing $\text{N}_2(\text{g})$ at a rate of $10^\circ\text{C min}^{-1}$.

loss occurs below 200°C , which is attributed to loss of incorporated water, while mass loss in the range $200\text{--}700^\circ\text{C}$ is mainly associated with elimination of more tightly bound hydroxyl species as water. The sharp mass loss, beginning above 700°C , is attributed to sulfate decomposition with production of $\text{SO}_3(\text{g}) \rightarrow \text{SO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$. Similar behavior has been reported in several Hf and Zr oxide sulfate systems,^[23,24] and it extends to the other HafSOx derivative formulations examined here. The results are consistent with findings from heat-treated HafSOx ($x \sim 0.67$ and 0.85) and HafSOx:La films that have been analyzed via transmission Fourier transform infrared (FTIR) spectroscopy. For these films, hydroxyl absorption in the range $3000\text{--}3600\text{ cm}^{-1}$ diminishes with heating between 325 and 600°C . Sulfate vibrations in the range $1000\text{--}1200\text{ cm}^{-1}$ are nearly eliminated between 650 and 700°C for HafSOx films and between 700 and 750°C for the HafSOx:La film.

Assuming dehydrated HafSOx powder is converted completely to HfO_2 between 700 and 950°C , the sulfate fraction can be calculated from the mass loss. In this way, we have found that increasing levels of sulfate in the mother solution correlate to increasing levels of sulfate in (heat induced) precipitates, ranging on the basis of the sulfate-to-Hf ratio from 0.46 to 0.71 for dehydrated formulas of $\text{HfO}_{1.54}(\text{SO}_4)_{0.46}$ and $\text{HfO}_{1.29}(\text{SO}_4)_{0.71}$, respectively. The same maximum sulfate composition precipitated whether $\text{H}_2\text{SO}_4(\text{aq})$ or $(\text{NH}_4)_2\text{SO}_4(\text{aq})$ was used as the sulfate source; products with sulfate levels $x < 0.46$ were not examined. The onset of sulfate loss occurred above 720°C for all samples, though some variations in the TGA profiles were observed. Peak positions, as determined from the derivatives of the heating curves, were used to establish decomposition temperatures between 793 and 817°C with the highest temperatures observed for samples with maximum sulfate content and $\text{H}_2\text{SO}_4(\text{aq})$ as the sulfate source. As additional tests, samples with maximum sulfate content were heated at 325 and 700°C prior to TGA measurements, cf., Figure 1. Mass losses associated with water were reduced, and calculated sulfate contents were similar for preheated samples and those dried at room temperature. This maximum sulfate content $x = 0.70\text{--}0.71$ is similar to values reported by Nekhamkin et al.^[25] for samples prepared under

slightly different conditions, and it also mimics the compositions of the reported crystals $\text{Zr}_{18}\text{O}_4(\text{OH})_{38.8}(\text{SO}_4)_{12.6} \cdot 33\text{H}_2\text{O}$ and $\text{Hf}_{18}\text{O}_{10}(\text{OH})_{26}(\text{SO}_4)_{13} \cdot 33\text{H}_2\text{O}$. From TGA, Ahmed et al.^[23] found that sulfate decomposition for $\text{Hf}_{18}\text{O}_{23}(\text{SO}_4)_{13}$ and $\text{Zr}_{18}\text{O}_{23}(\text{SO}_4)_{13}$ occurs at temperatures higher than those for the Hf and Zr disulfates; the decomposition temperature is also higher than those of the basic sulfates $\text{Hf}(\text{OH})_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Zr}_3\text{O}_5\text{SO}_4$.^[16,21] Given the propensity of its formation from aqueous solution and its enhanced thermal stability, the composition with $x=0.71$ exhibits special stability within this system. As noted below, this behavior extends to thin films, making this formula particularly interesting for applications where enhanced levels of chemical and thermal stability are desired.

Because the sulfate $\text{La}_2\text{O}_2\text{SO}_4$ is known to be thermally stable (decomposition $T > 1300^\circ\text{C}$),^[26,27] La was added to the mother HafSOx solution in an effort to modify dehydration properties and thermal-decomposition temperatures. To explore this mixed-metal system, a solution containing 23 % La (total metal) was prepared, and precipitation was induced by heating; from chemical analysis, however, only 3 % La was found in the product. The sulfate content $x=0.71$ was established from TGA, and the decomposition temperature of 820°C was found to be minimally changed from the undoped sample with the same sulfate content. Coprecipitation was then induced by adding $\text{NH}_3(\text{aq})$ to a solution containing 32 % La. In this case, chemical analysis revealed that the fraction of La in the precipitate matched that in the mother solution. Thermal decomposition of this La-laden precipitate was different from undoped HafSOx. A larger mass loss was observed below 200°C , indicating a more significantly hydrated precipitate. Mass loss attributed to sulfate was apparent above 700°C , though heating features were less abrupt and no constant mass was observed, even with heating to 1000°C at the slow rate of 2°C min^{-1} . For this heating rate, decomposition occurs at approximately 870°C , though this value is strongly dependent on heating rate and gas flow. The sample was completely decomposed to sulfate-free oxides by heating at 1500°C , and from the

measured mass loss, the formula $\text{Hf}_{0.68}\text{La}_{0.32}\text{O}_{1.48}(\text{SO}_4)_{0.36}$ was established for the precipitate that was dried at 650°C for 3 h.

X-ray diffraction (XRD) data were collected for precipitated HafSOx powders to establish temperature ranges for stability of crystalline phases (Fig. 2a). Following room-temperature drying, a complex diffraction pattern was recorded for samples produced with $\text{H}_2\text{SO}_4(\text{aq})$ as the sulfate source and having maximum sulfate content; other samples exhibited no or diffuse diffraction patterns. Samples ($x=0.70$) dried at room temperature and heated for 1 h at temperatures between 100 and 700°C become amorphous. Peaks characteristic of crystalline, monoclinic HfO_2 are observed after heating to 750°C and higher for 1 h; 3 % La samples exhibit similar diffraction profiles. As the onset of sulfate loss occurs at 720°C , cf., Figure 1, crystallization is found to coincide with sulfate loss. Gimblett et al.^[24] noted similar thermal behavior for a zirconium oxide sulfate.

XRD data for HafSOx:32 % La are shown in Figure 2b. Both the precipitated powder and that heated to 700°C are X-ray amorphous. Just as with undoped HafSOx, a detectable crystalline phase forms between 700 and 750°C (1 h heating), which is the temperature interval over which sulfate begins to decompose. Monoclinic HfO_2 , however, is not the observed phase. Rather, the diffraction profile is consistent with cubic (or tetragonal) HfO_2 , the phases of HfO_2 often stabilized by inclusion of lanthanide atoms. At higher temperatures, $\text{Hf}_2\text{La}_2\text{O}_7$ and monoclinic HfO_2 are formed, as predicted from consideration of the applicable phase diagrams.^[28] These results are consistent with the work of Zhang et al.^[29] on the system $\text{ZrO}_2\text{-La}_2\text{O}_3$, where they found stabilization of cubic ZrO_2 with 10–37 % La at 900°C with phase separation into $\text{Zr}_2\text{La}_2\text{O}_7$ and ZrO_2 occurring at 1050°C .

XRD data for thin films of HafSOx ($x \sim 0.67$ and 0.85) and HafSOx:24 % La heated at selected temperatures for 5 min each are summarized in Figure 3. For both HafSOx compositions, films are X-ray amorphous from $325\text{--}650^\circ\text{C}$, and monoclinic HfO_2 is detected as the temperature rises through and

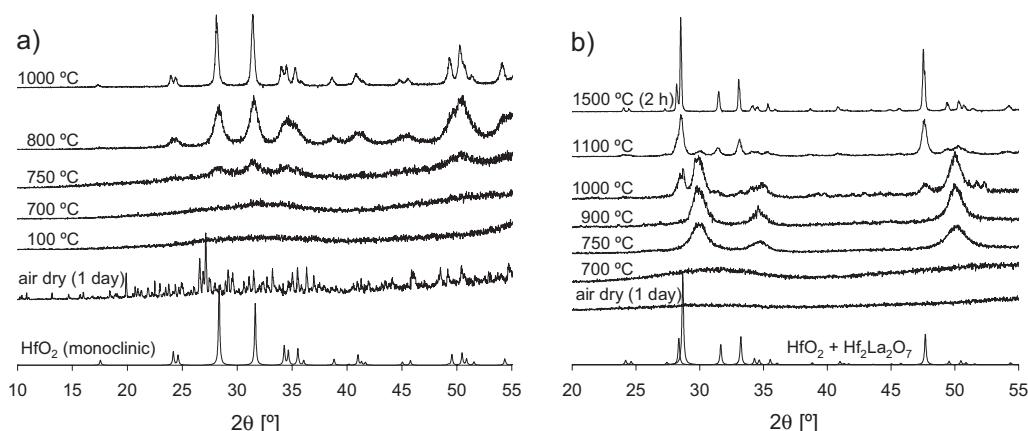


Figure 2. XRD for HafSOx and HafSOx:La powders. a) XRD for HafSOx powders after heating to given temperatures in air for 1 h except as noted; HfO_2 (monoclinic) is a simulated pattern here and in Figure 3. b) XRD for HafSOx:32 % La powders after heating to given temperatures for 1 h except as noted. $\text{HfO}_2 + \text{Hf}_2\text{La}_2\text{O}_7$ is a simulated pattern here and in Figure 3.

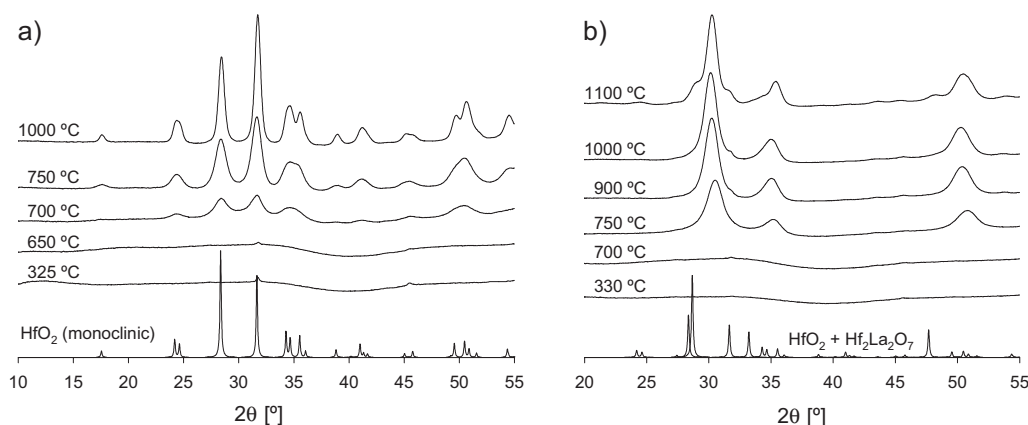


Figure 3. XRD for HafSOx and HafSOx:La thin films. a) XRD for HafSOx films after heating to given temperatures in air for 5 min. Low-intensity features at 31.8° and 45.6° are attributed to the substrate. b) XRD for HafSOx:24% La films after heating to given temperatures in air for 5 min.

above 700 °C. HafSOx:La films are amorphous from 330–700 °C, while a cubic phase is detected from 750–1000 °C. The cubic phase is unstable at 1100 °C and higher temperatures, as separation into monoclinic HfO₂ and Hf₂La₂O₇ phases commences. For films of HafSOx and HafSOx:La, loss of sulfate can be directly correlated with oxide crystallization, which is consistent with the behavior of powders.

Compositions for selected films were established from the relative concentrations of Hf, La, Cl, and S via electron-microprobe analysis (EMPA). Because O concentrations were determined imprecisely, final compositions are expressed as dehydrated formulas with O included for charge balance. Two representative HafSOx films heated at 325 °C (5 min) were determined to be HfO_{0.985}(SO₄)_{0.67}Cl_{0.69} and HfO_{0.915}(SO₄)_{0.85}Cl_{0.47}, representing sulfate compositions of $x = 0.67$ and 0.85 , respectively. The $x = 0.85$ sulfate film was further heated to 650 °C (5 min) and determined to be HfO_{1.275}(SO₄)_{0.71}Cl_{0.03}. Also, a HafSOx:La film heated at 330 °C (5 min) was determined to be Hf_{0.76}La_{0.24}O_{0.73}(SO₄)_{0.96}Cl_{0.38}. A few comments regarding these compositions can be made. The combination of spin-coating, rapid dehydration, and polymerization associated with processing the films results in kinetic trapping of Cl, contrasting with the powder precipitates, which are essentially Cl free. For similar reasons, it is also possible to trap higher concentrations of sulfate in the films than in the powders, although as demonstrated from heating the sulfate-rich, $x = 0.85$ film, the sulfate content was reduced to $x = 0.71$, which matches the composition for precipitated HafSOx powders having maximum sulfate content. For HafSOx:La, the measured fraction of La (24%) agrees well with the 23% La concentration in the precursor solution. Finally, we note that amorphous products are consistently obtained with both powders and films, meaning paths should be available for low-temperature preparation of Cl-free films.

2.2. Thin-Film Dielectric Characterization

For dielectric testing, MIM capacitors were fabricated by spin coating and annealing 150–300 nm of HafSOx, ZircSOx, or derivative compositions on Ta-coated SiO₂/Si substrates. As seen from the micrographs for HafSOx and HafSOx:La in Figure 4, the resulting films are dense and free of cracks and pores. In addition, the relatively rough Ta-SOx interfaces have been effectively planarized, as indicated by the smooth top surfaces of the SOx films. Each of these features is indicative of amorphous films. The MIM electrical test structures were completed by evaporating patterned arrays of 1.2 mm diameter Al dots directly onto the SOx films. The capacitors were tested to determine the relative permittivity and loss tangent at 1 kHz as well as electric-field breakdown strength; we define breakdown as the electric field where current density surpasses 10 $\mu\text{A cm}^{-2}$. Both the parent and doped films were deposited to examine the effects of composition and processing on device properties. Breakdown fields of 4–6 MV cm⁻¹ were demonstrated for films of HafSOx, ZircSOx, and their La- and Ce-doped derivatives; the Ca derivative ZircSOx:Ca exhibited a slightly reduced breakdown of 3.6 MV cm⁻¹. All devices and compositions exhibited leakage current densities < 50 nA cm⁻² at 1 MV cm⁻¹, and densities < 10 nA cm⁻² were commonly measured. Relative permittivities of 9–12 and loss tangents < 1% were measured for all

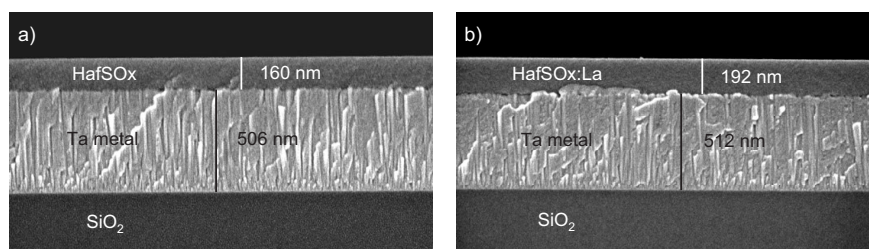


Figure 4. SEM images for HafSOx and HafSOx:La thin-films. a) Image of HafSOx deposited on Ta. b) Image HafSOx:24% La deposited on Ta.

variations. As might be expected for glassy matrices, moderate variations in composition (<25 at % of metal content) did not significantly affect optimum performance characteristics, though many of the derivative compositions provided greater dielectric reliability. Likewise, derivative compositions may have chemical, mechanical, or processing characteristics that benefit other applications.

The SOx dielectric properties are comparable to those observed for other complex oxide films that have been produced via techniques such as atomic layer deposition (ALD),^[30–33] physical vapor deposition (PVD),^[34–36] or other methods^[37–41] in support of conventional silicon-based electronics. In these systems, emphasis has been placed on development of multiple-component materials to inhibit crystallization and produce more robust breakdown characteristics relative to the simple binary oxides. For example, in the aluminates $(\text{MO}_2)_{1-x}(\text{AlO}_{1.5})_x$ and silicates $(\text{MO}_2)_{1-x}(\text{SiO}_2)_x$ ($M = \text{Zr}, \text{Hf}$) with 25–50 mol % $\text{AlO}_{1.5}$ or SiO_2 , permittivities covering the range of 8–16 have been observed.^[31,33,35,41] Like HafSOx and ZircSOx, the Hf and Zr aluminates and silicates are characterized as amorphous films with crystallization occurring at high temperatures (750–1000 °C) in conjunction with phase segregation, producing HfO_2 or ZrO_2 .^[31–33,35,41–43] As we previously described, crystalline HfO_2 forms from HafSOx powders and films at approximately 700 °C in conjunction with sulfate decomposition.

On the basis of performance in MIM capacitors, La derivatives of SOx films were selected for investigation as gate dielectrics in TFTs. These TFTs were fabricated with HafSOx:La or ZircSOx:La as the gate dielectrics and amorphous zinc tin oxide (ZTO)^[8] or zinc indium oxide (ZIO)^[9] as the semiconductor channel layers. Characteristic device performance is depicted in Figure 5. Transistor operation, Figure 5a, is evident from the field-effect current modulation (increased I_D with increasing V_{GS}) and saturation in drain-to-source current at higher values of drain-to-source voltage, resulting in an on-to-off ratio $>10^6$. Most importantly, gate leakage currents I_G , Fig-

ure 5b, are very low—only nA cm^{-2} . Considering the performance in TFTs, the images of Figure 4, and the MIM-test results, it is clear that HafSOx:La and ZircSOx:La, in particular, exhibit the necessary features for a high-quality, thin-film dielectric. The materials are sufficiently robust for device integration, withstanding plasma exposure during sputter deposition of the channel and subsequent thermal processing. The requirements for a high-quality dielectric/channel interface have also clearly been met.

For low-temperature, high-speed printing, our material systems have distinct advantages compared to metal-organic sol-gel precursors that have been extensively used in solution-based deposition of inorganic oxides. The presence of the organic moiety in many cases necessitates a high-temperature burnout step, which leads to significant volume changes and generally to crystallization and the phenomenon of “mud cracking.” These features limit performance in many devices, and they have contributed to the absence of additive solution processing of inorganic materials. Hydrolysis and condensation reactions with metal-organic precursors are also generally quite slow, limiting the applicability of numerous printing techniques. For most oxide systems, such precursors also impart an unnecessary expense, as suitable printing viscosities can readily be achieved through control of pH and species concentrations. We have overcome these limitations and realized amorphous, very high-quality dielectric films through modest thermal processing - without resorting to any type of complex atomic layer-by-layer or surface-mediated process to produce the results. We believe the continued development of the methodology associated with dehydration and condensation of organic-free aqueous solutions similar to that used for HafSOx and ZircSOx deposition represents the optimum route to printed inorganic devices. Already, we have deposited with these methods a number of additional materials as high-quality dielectrics and semiconductors for TFT applications. Such dielectric capability may also logically be extended to hybrid inorganic-organic devices.

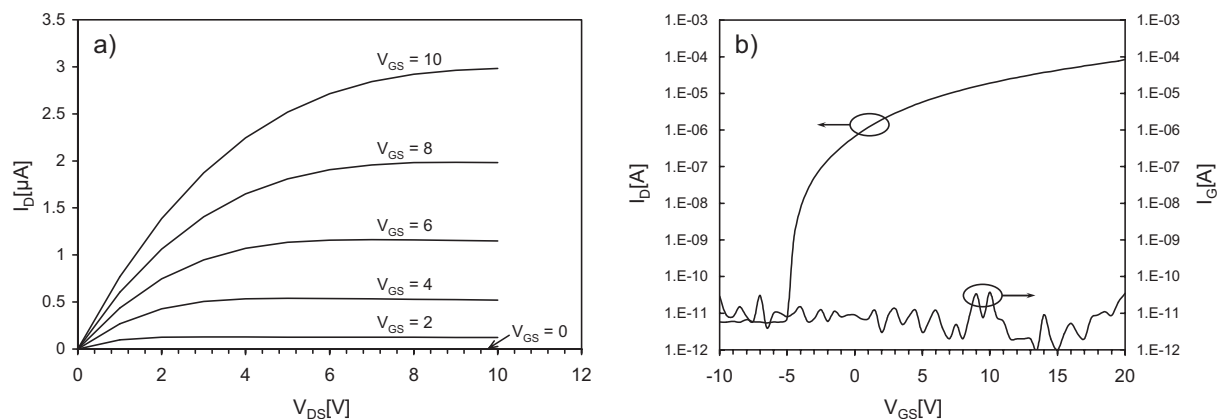


Figure 5. TFT device performance. a) Drain current-drain voltage (I_D – V_{DS}) characteristics of a TFT with HafSOx:La dielectric and ZIO oxide channel layer at selected gate voltages, V_{GS} . b) Representative $\log(I_D)$ – V_{GS} and $\log(I_G)$ – V_{GS} characteristics for TFT with HafSOx:La dielectric and ZIO channel ($V_{DS} = 20$ V). ($\mu \approx 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)

2.3. Nanolaminate Structures

Considering the low processing temperatures, high atomic density, uniformity, and smooth surfaces of the HafSOx and ZircSOx films, it appeared likely that ordered, laminated structures could be produced by alternately depositing the two materials. Because of the difference in scattering factors for Hf and Zr, X-ray reflectivity (XRR) provided a useful means for characterizing such laminates. From initial studies, XRR features were found to extend to high scattering angles, indicating that the HafSOx/ZircSOx bilayers could be deposited with a high degree of precision and regularity. An XRR pattern for a characteristic HafSOx/ZircSOx nanolaminate is displayed in Figure 6a; the more intense diffraction peaks derive from the bilayer thickness, while the smaller oscillations are related to the total laminate stack thickness. By systematically and independently varying the thicknesses of the HafSOx and ZircSOx layers, the thicknesses of single layers were also derived. From this analysis, individual layers of HafSOx and ZircSOx were determined to be 8.6 and 5.3 nm, respectively, with their sum equal to the bilayer measurement of 13.9 nm. The multilayer stacking arrangement and individual layer thicknesses have been corroborated with transmission electron microscopy (TEM) images, cf., Figure 6b. A 16-layer, 8-bilayer sequence is clearly evident from the alternate stacking of dark HafSOx and light ZircSOx layers. These periodic nanolaminates showcase the reproducibility in depositing both materials, and they are also a more stringent measure of precision in film thickness and uniformity than could be demonstrated with a single film.

We have found that layer spacings can be readily controlled over a very broad range by adjusting the concentrations of the precursors. High-order reflections have been observed in all diffraction patterns, indicating bilayers have been consistently deposited with a variability <0.5 nm, including roughness. To date, the thinnest bilayer has measured 6 nm by XRR, which requires single layers ≤ 3 nm. It is noteworthy that both thicker layers (tens of nm) and thinner layers (a few nm) can be deposited with regularity. For solution-processed films, in general, atomic rearrangements during solvent loss and annealing gen-

erate rough surfaces and incomplete coverage, yet SOx films exhibit extremely smooth surfaces with interface displacements over only a few atomic lengths. Production of thin films and laminates of this standard would be expected to require sophisticated vapor deposition systems and atomic-layer mass-transport control, yet we have used straightforward beaker chemistries and inexpensive vacuum-free spin-coating procedures to produce the results.

The laminated structures are also important from the perspective of solution printing; they provide a demonstration of the first step necessary for additive processing and printing of inorganic materials for electronics and electromechanical systems. It is improbable that multiple layers and structures could be realized with highly porous films, as an applied fluid ink is likely to wick into the underlying layer, resulting in interlayer mixing. The absence of pores and voids in the SOx films is a necessary precondition for realizing distinct layers in the laminated stack. The laminates also represent a simple and very low-cost platform for studying and developing a range of other advanced nanoscale technologies.

3. Conclusion

SOx thin-films were deposited in multiple configurations to examine their quality and utility. Rapid condensation kinetics and the amorphous nature of materials allowed a variety of solid phase compositions. Several were found to exhibit exceptional performance as capacitor dielectrics, and HafSOx:La and ZircSOx:La were successfully integrated as gate dielectrics in TFT devices. Their performance characteristics demonstrably exceed those reported for any other solution-processed oxide dielectric material; indeed, they represent the first solution-processed oxide films to be successfully incorporated as a gate dielectric in a functioning inorganic TFT. The extreme smoothness, high atomic density, and low-temperature processing of the individual films have allowed the first demonstration of purely inorganic nanolaminates via solution processing. The

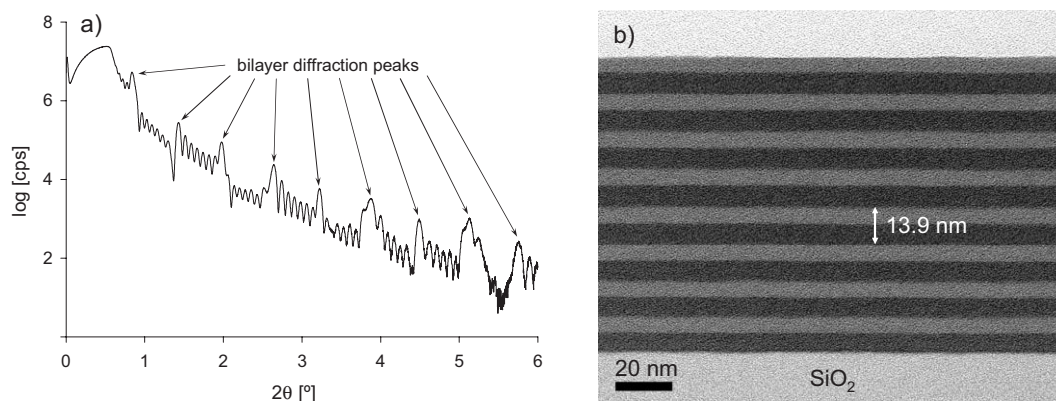


Figure 6. XRR plot and associated bright field TEM for HafSOx/ZircSOx multilayer thin film. a) XRR plot representing periodicity over large areal coverage. b) TEM cross-section image. This configuration consists of 16 alternating layers (8 bilayers), beginning with HafSOx at the SiO₂ interface. HafSOx layers of 8.6 nm and ZircSOx layers of 5.3 nm together compose bilayers of 13.9 nm.

high-resolution laminates exhibit extremely abrupt interfaces, where interdiffusion between adjacent layers extends to a depth of only one or two atoms. Moreover, these films were readily deposited with common chemicals and standard spin-coating techniques.

4. Experimental

Solution Precursors: Aqueous solutions were prepared for bulk precipitation and for use in thin-film deposition. Reagents used were $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ (Alfa Aesar, 99+ % excluding 1.5 % Zr), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Wah Chang spectrographic grade), $\text{La}_2(\text{SO}_4)_3$ (Alfa Aesar, 99.9 %), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Johnson Matthey, 99.9 %), $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (Strem, 99 %), CaO (Alfa Aesar, 99.95 %), $(\text{NH}_4)_2\text{SO}_4$ (Mallinkrodt AR), $\text{H}_2\text{SO}_4(\text{aq})$ (EM Science, GR ACS, 95–98 %) and $\text{NH}_3(\text{aq})$ (EM Science, GR ACS, 28–30 %). All solutions were prepared by combining HfOCl_2 or ZrOCl_2 with $\text{La}_2(\text{SO}_4)_3$, $\text{Ce}_2(\text{SO}_4)_3$, or CaO as necessary for a total metal concentration ~ 0.8 M, followed by addition of sulfate solution, for a total metal concentration of ~ 0.5 M. Additional modifications were made as necessary to serve as precursors for hydroxide precipitation reactions. Precursors for nanolaminate films were prepared by adding $\text{H}_2\text{SO}_4(\text{aq})$ to HfOCl_2 or ZrOCl_2 solutions as 46 % sulfate relative to metal. Solutions were diluted to a metal concentration of 0.03–0.5 M.

Powder Precipitates: Precipitation was induced by immersing tubes of solution in a boiling water bath for 40 min. For the strategy of hydroxide induced precipitation, HfOCl_2 and $\text{La}_2(\text{SO}_4)_3$ were mixed as 23 % La (metal percent), followed by addition of solutions of $\text{La}(\text{NO}_3)_3$ and $(\text{NH}_4)_2\text{SO}_4$ to give $[\text{Hf}] = 0.39$ M, $[\text{La}] = 0.18$ M, and $[\text{SO}_4] = 0.42$ M. 1.9 mol equivalents (relative to total metal) of saturated $\text{NH}_3(\text{aq})$ were added quickly and stirred for 1 min. All precipitates were filtered through paper with suction, followed by several rinses with de-ionized water. The filtrates were dried at room temperature for 1 day. Samples were subsequently heated in alumina crucibles in air at temperatures 100–1500 °C for 1–4 h. XRD data were collected with a Siemens D5000 diffractometer, utilizing Cu K α radiation. Thermogravimetric data were collected with a Shimadzu TGA-50 by heating samples (10–20 mg) in a Pt crucible under flowing $\text{N}_2(\text{g})$, typically at a rate of 10 °C min⁻¹, and holding for 15 min at the highest temperature. Chemical analysis was determined by inductively coupled plasma atomic emission spectroscopy (ICPAES), collected with a Jobin Yvon JY2000 analysis setup. Samples were dissolved in digestion bombs at 200 °C for a few hours and diluted to measurable levels.

Thin Films: Si substrates with a coating of Ta metal or SiO_2 were used. Films were deposited on 500 nm of Ta for capacitor and TFT testing and onto 200 nm of SiO_2 for all other purposes. The surfaces were prepared for deposition by ultrasonic cleaning in Decon Labs, Contrad-70 solution at 45 °C for 45 min, followed by thorough rinsing with deionized water before deposition. Thin films of HafSOx , ZircSOx , and derivatives with added La, Ce, or Ca, were deposited on substrates by spin coating at 3000 rpm for 30 s, followed by immediate hot-plate polymerization at 135 °C for 1.5–2 min; derivatives were additionally heated at 325 °C for 15 s–2 min. This procedure was repeated until desired thicknesses were obtained; 150–300 nm thick films were produced for all purposes with the exception of the nanostructured laminates. Nanolaminates were constructed by alternately depositing HafSOx and ZircSOx layers. This process was repeated until desired thicknesses were obtained. A final oven anneal at 325 °C for 5–10 min completed the process.

MIM capacitor structures were completed by thermally evaporating circular contacts of Al (1.2 mm diameter) via shadowmask on deposited dielectrics. Relative dielectric constant and loss tangent were obtained by using a Hewlett-Packard 4192A impedance analyzer. Leakage currents and breakdown fields were assessed using a Hewlett-Packard 4140B picoammeter with a voltage ramp rate of 1 V s⁻¹. Bottom-gate thin-film transistor structures were fabricated by rf sputtering zinc indium oxide or zinc tin oxide channel materials onto the spin-

coated dielectrics with no intentional substrate heating during sputtering. Zinc tin oxide channel layers were subsequently heated at 300 °C for 1 h. Ti source and drain contacts were thermally evaporated via shadowmask; device width = 1000 μm and length = 200 μm . Electrical characterization of TFTs was performed with a Hewlett-Packard 4156C semiconductor parameter analyzer.

Thin-film XRD data were collected with a Rigaku RAPID diffractometer, employing Cu K α radiation generated from a rotating anode at 50 kV and 270 mA. The incident beam angle was 7.6°, while the diffracted beam was collected with an image plate. XRR data were collected with Cu K α radiation (40 kV, 40 mA) on a Bruker D8 Discover Diffractometer. The incident beam was collimated with a parabolic multilayer mirror and 0.1 mm divergence slit. The exit beam was conditioned with a 0.6 mm anti-scatter slit, a Soller-slit assembly, and a 0.05 mm detector slit. When the intensity reaching the detector exceeded 300k cps, a 0.6 mm Cu attenuator was placed between the beam and the detector. Low-angle reflections up to 10° (2 θ) were collected in 0.005° steps at 0.5 s/step. Transmission FTIR data were collected on a Nicolet 5PC spectrometer with corresponding substrate as reference. EMPA data were collected on a Cameca SX-50. Intensities of O K α , Si K α , Cl K α , Hf M α , La L α , S K α , and Zr L α were collected on wavelength dispersive spectrometers (WDS) using gas flow proportional detectors with P-10 gas. Data were collected at three different accelerating voltages—10, 15, and 20 kV—with experimental intensities determined from the average of ten proximate positions on each sample. LaPO_4 , $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$, CaSO_4 , Hf, Si, Zr, and MgO were used as standards. Raw intensities were corrected by a procedure detailed by Donovan and Tingle [44]. Quantitative elemental analysis was determined by comparing experimental k -ratios to simulated values using StrataGEM thin-film composition analysis software, which employs the PAP formalism developed by Pouchou and Pichoir [45].

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