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Impact of Relative Humidity during Spin-Deposition of Metal Oxide Thin Films from Aqueous Solution

Paul N. Plassmeyer, Gavin Mitchson, Keenan N. Woods, David C. Johnson, Catherine J. Page*

Department of Chemistry and Biochemistry and Material Science Institute, University of Oregon, Eugene, Oregon, 97403, United States

ABSTRACT: Relative humidity during the spin-processing of thin-film solution precursors is often not controlled or measured, and its effect on film thickness is generally unappreciated. Herein we report that the relative humidity during spin-processing has a marked impact on film thickness of amorphous metal oxide (aluminum oxide, "AlOx," and lanthanum zirconium oxide, "LZO") and hafnium oxide-sulfate (HafSOx) thin films deposited from aqueous precursors. In the humidity range studied (20% to 95% relative humidity, RH) film thicknesses varied by a factor of nearly three, and this effect is independent of the metal precursor identity. Our data suggest that film thickness depends linearly on evaporation rate (100-RH%) for all systems studied, suggesting this effect is predominantly due to the unique characteristics of water as solvent. In-situ X-ray reflectivity (XRR) studies on HafSOx films deposited under different humidities reveal that, while the thickness varies significantly with humidity, the density of the as-deposited films is similar, suggesting that humidity primarily affects the relative amount of material deposited. Because reproducible film thickness is critical for many applications, our data highlight the importance of controlling humidity during spin-processing.

INTRODUCTION

The proliferation of mass-produced display media, such as smart phones and tablets, has accelerated research into new processes for deposition of thin-film components. Typically these are deposited via vapor-phase deposition (VPD), which produces high-quality films but requires expensive equipment and precursors, and has low atom efficiencies. Furthermore, VPD is not amenable to producing materials with variable composition or more than one metal component.[1,2] Solution deposition routes to metal oxide thin films provide an attractive alternative to traditional VPD techniques. For example, high performance amorphous $In_xZn_yO_z$ transistors have been fabricated by annealing sol-gel precursors,[3] and $La_2Hf_2O_7$ thin films deposited from acetic acid solution show excellent performance as gate dielectrics in thin film transistors (TFTs).[4] Aqueous solution deposition routes are also known, employing either water-soluble complexes with organic ligands,[5] all-inorganic clusters,[6–9] or salts.[10–12] The latter two systems can lead to high-quality films without the use of toxic precursors and generation of volatile organic byproducts.[6–12]

Due to its ubiquitous nature, water has the potential to play important roles in many of the film formation processes that occur as precursors are converted to metal oxides. For example, water plays an integral role in sol-gel processes (e.g., hydrolysis), water vapor can dramatically increase thermal oxide growth rates on Si (due to hydroxide diffusion through the surface oxide),[13,14] and water vapor decreases the temperatures at which $Zn(CH_3COO)_2$ and $Zn(acac)_2$ thermally decompose (by changing the decomposition pathway).[15–17] Additionally, some thin film metal oxides absorb atmospheric H_2O after fabrication, often adversely affecting film properties and electrical performance.[18,19] These examples highlight the importance of monitoring and controlling atmospheric H_2O during thin film fabrication and analysis.

While the importance of water in the context of chemical processes during *synthesis* and *analysis* has been previously reported, the effect of water vapor during *spin-processing* of aqueous solutions is virtually unreported. To our knowledge, there have been no reports on the effects of humidity on deposition of films from aqueous solutions of inorganic salts or clusters, although one prior report demonstrates an inverse relationship between thickness and humidity for films of bone gelatin, a water-soluble biopolymer.[20] While the effects of spin-processing parameters on the thickness of polymer films from *non-aqueous* solvents are well documented,[21–23] many of the phenomena which have been shown to be unimportant for organic polymer films (such as evaporative cooling)[21] may be important for aqueous-deposited films. Water has dramatically different properties than most organic solvents. For example, viscosity changes with concentration are different for a salt in water than for a polymer in organic solvent.[24,25] Strong hydrogen bonding in water leads to a significantly larger ΔH_{vap} relative to organic solvents, resulting in significantly larger evaporative cooling effects. Because humidity is directly related to the partial pressure of solvent (water) in aqueous spin-coating, it will directly affect the rate of solvent evaporation. This is distinctly different than the role humidity plays in spin-processing from organic solvents, where immiscibility can lead to the formation of 'breath pattern figures'.[26]

In this study we compare the effects of relative humidity (RH) during the spin-deposition of three different aqueous precursors used to prepare amorphous metal oxide and metal oxide-sulfate thin films. We focus initially on $HfO_{1.3}(SO_4)_{0.7}$ ("HafSOx"), a material of interest as an ultrahigh-resolution resist[27,28], but also expand this study to include aluminum oxide ("AlOx") and lanthanum zirconium oxide ("LZO"), which are of interest as gate dielectrics for thin-film transistor applications.[29–31] These systems were chosen because aqueous deposition routes have been previously developed to produce high quality films, and because collectively they span a broad range of aqueous precursor compositions. For all systems studied, we show that the relative humidity (RH) during the spin-coating process has a dramatic effect on as-deposited film thickness (up to a factor of nearly three). Surprisingly, this effect is essentially independent of the identity of the metal precursor and is therefore independent of any chemical reactions occurring during spin-coating. Instead, it appears to be directly related to the solvent (water) evaporation rate, and we are able to fit the data using a simple model based on this phenomenon.

EXPERIMENTAL METHODS

Precursor Preparation. A modified method of the version used by Fairley et. al. was used for the preparation of 1.0 M HafSOx precursors.[32] 1.0 M H_2SO_4(aq) (VWR), 30 wt% H_2O_2(aq) (EMD Millipore), $HfOCl_2 \cdot 8H_2O$ (98+%, Zr < 1.5% Alfa Aesar) in 18.2 MΩ·cm H_2O were used to prepare a solution with a Hf^{4+}:SO_4^{2-}:H_2O_2 ratio of 1.0 : 0.7 : 3.0. The solution was diluted so that $[Hf^{4+}] + [SO_4^{2-}] = 1.0$ M.

AlOx precursors were prepared by using an electrochemical method described elsewhere.[30] Briefly, a reductive current was passed through a ~1.2 M $Al(NO_3)_3$(aq) (99.9% Alfa Aesar) solution until a pH of ~3 was achieved. Exact concentration was determined by slowly heating a 5 ml portion of the reduced solution to 800 °C and obtaining the mass of the remaining AlOx. The reduced AlOx precursor solution was diluted to 1.0 M $[Al^{3+}]$ for deposition.

LZO precursors were prepared by dissolving $La(NO_3)_3 \cdot 6H_2O$ (99.9% Alfa Aesar) and $ZrO(NO_3)_2 \cdot 8H_2O$ (99.9% Sigma Aldrich) in 18.2 MΩ·cm H_2O to achieve a 1:1 La:Zr ratio and a total metal concentration of 1.0 M.

Thin Film Deposition. N-type, P-doped Si substrates (0.008-0.02 Ω·cm) were cut to approximately 1" x 1", sonicated for 10 min in a 5% Decon Labs Contrad 70 solution, and plasma cleaned for 5 min in a Plasma Etch, Inc. PE-50 Benchtop Plasma Cleaner using 30% O_2/70% N_2 and maximum power. Thin films were prepared by depositing 7-8 drops of precursor through a 0.2 µm PTFE syringe filter onto a freshly cleaned Si substrate. Precursors were allowed to rest on the substrate for 5-6 s before spin-coating at 3000 RPM for 30 s in a Laurell Model WS-650MZ-23NPP spin-coater. All films were deposited between 20 and 25 °C (RT). To maintain low relative humidities during spin-deposition, N_2 was gently blown through the spin-coater chamber while taking care not to alter the airflow around the sample during spinning. High relative humidities were achieved by filling the spin-coater trough with warm water. Relative humidity and temperatures in the spin-coater were measured using a RH511 multimeter (Omega) immediately prior to solution deposition. After spinning, films were transferred to a hot plate set to 50 °C then ramped at a rate of 12.5 °C·min^{-1} to 500 °C for 1 h.

XRR. Films for in-situ X-ray Reflectivity (XRR) measurements were spin-cast as described above, then transferred to a preheated, temperature programmable XRR stage set to 25 °C. In-situ XRR measurements were obtained using a Bruker 8D-Discover diffractometer with Cu Kα radiation. Data were collected from 0 to 6 ° 2θ with 0.016 ° increments and 1 s/step. The first data set was collected at 25 °C. Immediately following data collection, the temperature was ramped to the next temperature, held for 1 h before repeating data collection. Data was collected at 25, 100, 200, 300, 400, and 500 °C. Film density, thickness, and roughness were extracted from the XRR data using the Bede REFS modeling software.[33]

HAADF-STEM. Specimens for cross-sectional high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging were prepared using a Ga^+ FIB lift out and thinning procedure similar to the Wedge Pre-milling method described by Schaffer et al.[34] The HAADF-STEM images were collected using an aberration-corrected FEI Titan 80-300 S/TEM at Pacific Northwest National Laboratory, operated at 300 keV.

RESULTS AND DISCUSSION

The impact of relative humidity (RH) on the thickness of spin-cast films can be easily seen by eye, as shown in Fig. 1 for two as-deposited (not annealed) films prepared using 1.0 M aqueous HafSOx precursors deposited under two different RH values (~22% and ~71%) while keeping temperature, spin speed, spin acceleration, and solution composition constant. XRR was used to determine the quantitative thicknesses for these films, and an almost two-fold thickness difference was observed (78 nm and 42 nm for ~22% and ~71% RH, respectively).

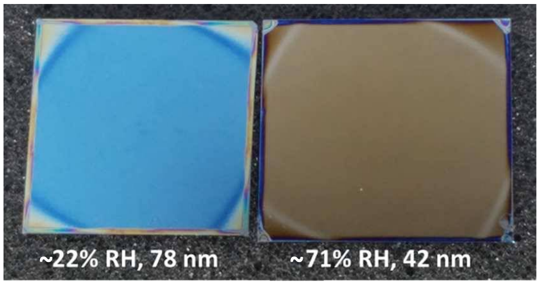

Figure 1. Pictures of as-deposited HafSOx thin films deposited at ~22% and ~71% RH. The film thicknesses (determined using XRR) are 78 and 42 nm, respectively.

To investigate whether the marked thickness differences in as-deposited HafSOx films persist with thermal processing, film thicknesses were measured at selected annealing temperatures via in-situ XRR. The XRR data indicates that the films differ in thickness by a factor of almost two and are extremely smooth at all temperatures

(< 1 nm RMS roughness), as evidenced by the persistence of Kiessig fringes to relatively high angles (> 6 ° 2θ). The Kiessig fringe spacing increases for films as they are heated, indicating a monotonic decrease in thickness with annealing temperature for both films. XRR also provides information about film density, which is related to the critical angle. As can be seen in Figure 2, the critical angles (and hence the densities) of the as-deposited films under both humidities are essentially identical, and trend to higher values similarly as the films are heated.

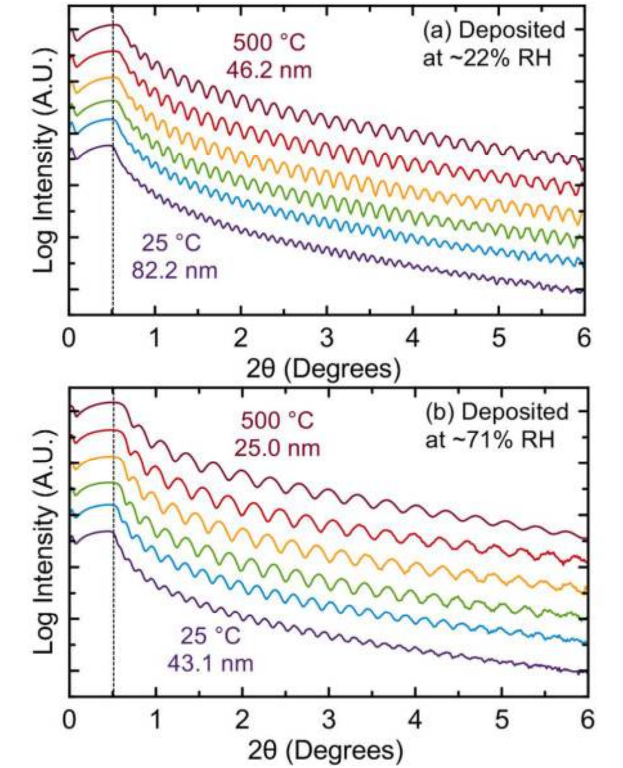

Figure 2. XRR of HafSOx films deposited at (a) ~22% and (b) ~71% RH as a function of processing temperature (RT, 100, 200, 300, 400, and 500 °C). Dashed lines show the critical angle for the as-deposited films, and serve as a reference to track changes as films are heated.

While both films become thinner with increasing temperature, the ratio of their thicknesses remains essentially constant (Fig. 3). This is consistent with the critical angle data and implies that humidity primarily influences the quantity of material deposited on the substrate, but has little effect on initial film density or subsequent film densification. Fig. 3 explicitly shows that the dramatic difference in film thickness observed in as-deposited films spun under different RH persists with thermal treatment, and is therefore a critical parameter for controlling *final* film thickness.

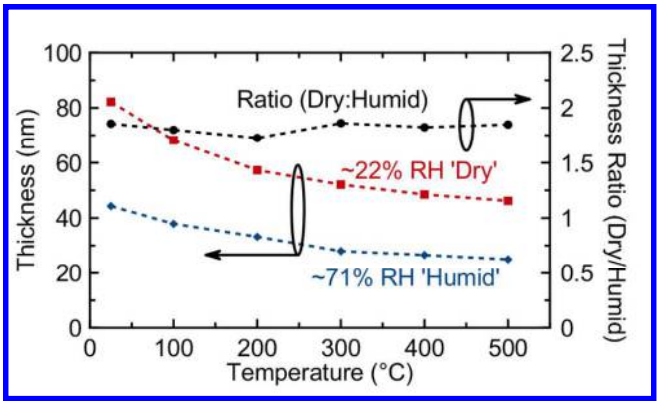

Figure 3. Thickness comparison of HafSOx films deposited at ~22% (red) and ~71% RH (blue). A ratio of film thickness (dry:humid) is plotted in black.

A recent report on aqueous-deposited HafSOx films demonstrates that spin-processing produces films that have inhomogeneous chemical and density profiles, including a denser, Hf-rich surface layer.[32] This previous study did not measure or control humidity. To determine whether humidity would affect the density profile of these films, we used HAADF-STEM to examine films deposited under ~22% and ~71% RH and subsequently annealed to 500 °C (Fig. 4). The HAADF-STEM images give a striking visual assessment of the film thickness difference. Variation in heavy atom concentration (corresponding to brightness in the images) can be better visualized by integrating the image intensity to give heavy-atom density profiles (Fig. 4c). These integrations have been normalized to the intensity at the film-SiO_2 interface and depend on both the sample thickness and the heavy atom concentration. The FIB lift out produces lamella that can vary in thickness from top to bottom, leading to a systematic slope in the intensity data that will vary from sample to sample. However, the higher intensity at the surface seen in both samples cannot be explained as a FIB artifact and is consistent with the previous study.[32] We can conclude that humidity does not prevent the formation of a Hf-rich capping layer, although there may be subtle differences in the composition of the capping layer for films deposited under different humidities.

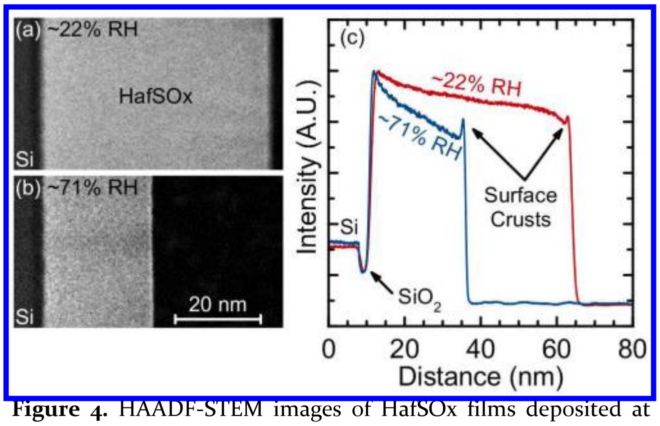

Figure 4. HAADF-STEM images of HafSOx films deposited at ~22% RH (a) and ~71% RH (b). Heavy-atom density profiles derived from HAADF-STEM images (c).

To determine the generality of the effect of spin-deposition humidity on thickness, we also examined two other aqueous-deposited metal oxide systems (AlOx and LZO). Films of AlOx, LZO, and HafSOx were prepared at four relative humidities between 20% and 95%, followed by annealing at 500 °C. The 500 °C processing temperature was chosen because AlOx and LZO films are difficult to study as-deposited (water absorption and de-wetting are issues), and all systems investigated are fully densified at this temperature.[31,35] Since we show in Fig. 3 that the thickness of thermally processed films track those of as-deposited films, comparing films heated to the same temperature should allow a valid comparison of film thicknesses for films deposited under different RH.

The films deposited from these three aqueous precursor solutions display similar thicknesses and dependence on deposition RH (Fig. 5, XRD data shown in Fig. S1). Because all precursor solutions were 1.0 M in total metals (or in Hf^{4+} + SO_4^{2-} in the case of HafSOx), this suggests that, to a first approximation, the total concentration determines the resulting film thickness for a given humidity and thermal treatment.

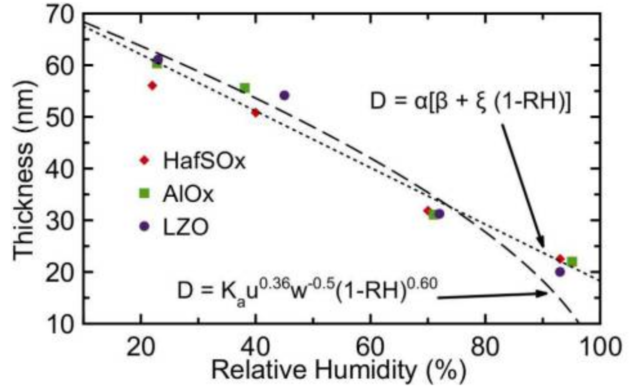

Figure 5. Thickness vs spin RH for HafSOx, AlOx, and LZO derived from aqueous precursors. Empirically-derived trend of thickness vs RH from ref. 20 represented by dashed line. Dotted line is a linear fit to the data discussed below. Here, RH is the fractional relative humidity (%RH/100%).

Spin-deposition can be described by two partially overlapping processes. The first process (spin-off) involves physical 'thinning' of the solution adhered to the substrate as centrifugal force removes excess solution.[22,36] The second process is evaporation, in which the precursor is concentrated to a viscous gel state.[22] The amount of precursor solution (or gel) retained on the substrate is determined by the viscosity of the solution and surface-solution interactions. In the second process, evaporation serves to both concentrate and to cool the precursor film, both of which will result in an increase in the viscosity, yielding a thicker film. Because evaporation rates are proportional to (100-RH%) the evaporation rate is high at low RH, resulting in higher viscosity (from increased concentration and lower temperature). At high RH, evaporation rates are slower, so the viscosity remains lower, resulting in a thinner film.

In the previous study on bone gelatin,[20] the authors derived an empirical relationship between humidity and film thickness (shown as dashed line in Fig. 5):

$$D = K_a \mu^{0.36} \omega^{-0.5} (1\text{-}RH)^{0.6} \qquad (1)$$

where D is thickness in nm, K_a is the concentration, ω is the angular velocity during deposition, and RH is the fractional relative humidity. The numerical values for the exponents were adjustable parameters used to fit the effect of humidity on thickness of polymeric bone-gelatin films.[20] Equation (1) predicts the unphysical result that film thickness is zero at 100% humidity and is a strictly empirical relationship.

While many processing parameters (solution concentration, spin speed, temperature) affect film thickness, we held all of these constant while varying only relative humidity in collecting the film thickness data shown in Figure 5. Our data is consistent with a linear relationship (shown as a dotted line in Fig. 5):

$$D = \alpha[\beta + \xi\,(1\text{-}RH)] \qquad (2)$$

where α is proportional to the concentration of the initial solution and inversely proportional to the square root of the spin speed (fixed in our fit for value of 1.0 M and a spin speed of 3000 rpm).[37] The strength of the substrate-solution interaction (wetting) and the surface tension of the solution probably also affect the value of α, although the dependence of the thickness on these parameters has not been well documented in the literature. β is the viscosity of the initial solution at ambient temperature (approximated in our fit as the viscosity of pure water). The temperature of the solution on the substrate during spin-coating will be the ambient temperature at 100% RH since the evaporation rate would be zero. ξ is a term that describes the change in the viscosity of the solution as a function of (1-RH), which is proportional to the evaporation rate.[38] The fit in Fig. 5 to Eq. 2 yields a value of $\xi = 3.0 \times 10^3$ Pa·s. Evaporative cooling during spin-deposition can account for substantial change in the viscosity, as the viscosity of pure water increases significantly with cooling (it increases by a factor of ~two as temperature is decreased from 25 to 5 °C).[39] Concentration increases due to evaporation will increase the viscosity further. Qualitatively, at low deposition RH, cooling and the increase in concentration of the solution from rapid evaporation rates increases the viscosity of the remaining solution on the substrate significantly leading to thicker films. Conversely, deposition at high RH (corresponding to low evaporation rates, and thus lower viscosity) will yield thinner films.

Eq. 2 is an oversimplification, since the magnitude of the temperature change with evaporation rate will depend on the thermal conductivity of the various components (solution, substrate, spin-coater chuck, and the thermal impedance of the interfaces between them), and the temperature dependence of the viscosity of H_2O is not linear.[39] Within the uncertainty of our data, however, this expression fits the thickness trend seen in Fig. 5 better than the previous empirical relationship, and provides some insights to parameters that influence ξ. Parameters for the line fit in Fig. 5 to the data are given in the SI. The dramatic changes in thickness as a function of humidity highlight that this must be controlled during processing to obtain reproducible thicknesses.

CONCLUSION

This is the first report focused on the impact of relative humidity during spin-deposition of aqueous-derived metal oxide thin films. While it is generally understood that parameters such as concentration and spin speed affect the thickness of films prepared via aqueous deposition,[40] the effect of deposition humidity has not been widely appreciated. We show that relative humidity during spin-deposition of all-inorganic aqueous precursors has a dramatic effect on film thickness. Specifically, decreasing RH from 95% to 20% RH results in a ~three-fold increase in film thickness (all other conditions kept constant). The observed thickness change with relative humidity can be fit to an equation linear in (1-RH), which is proportional to the evaporation rate. In addition, we show that when concentration and humidity are held constant, film thickness does not depend (at least to a first approximation) on the nature of dissolved species. This study highlights the importance of controlling spin-deposition humidity for preparing films with reproducible thicknesses using aqueous spin-deposition.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

XRR patterns for HafSOx, AlOx, and LZO films deposited at various relative humidities; values for parameters used for the line derived from Eq. 2 in Fig. 5.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cpage@uoregon.edu (C.J.P.)

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no conflicting financial interest.

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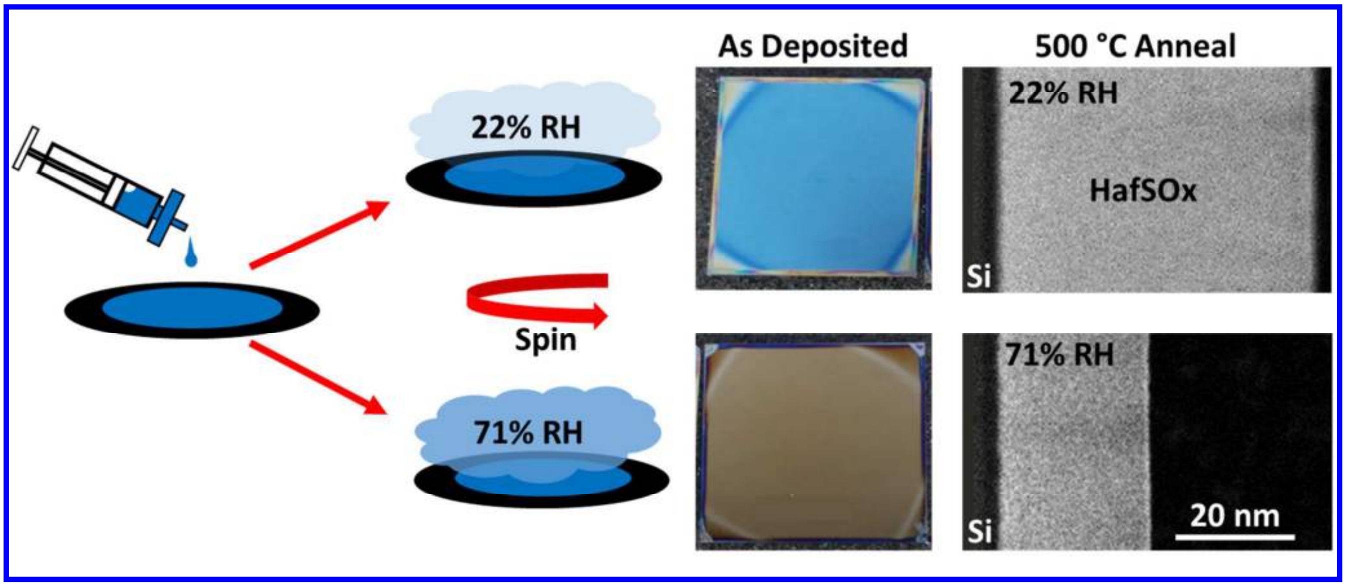

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