Metal Oxide Films Produced by Polymer-Assisted Deposition (PAD) for Nuclear Science Applications

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Abstract

The Polymer-Assisted Deposition (PAD) method was used to create crack-free homogenous metal oxide films for use as targets in nuclear science applications. Metal oxide films of europium, thulium, and hafnium were prepared as models for actinide oxides. Films produced by a single application of PAD were homogenous and uniform and ranged in thickness from 30 to 320 nm. The reapplication of the PAD method (six-times) with a ten percent by weight hafnium(IV) solution resulted in an equally homogeneous and uniform film with a total thickness of 600 nm.

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Introduction

The preparation of homogenous metal oxide films (100 to 750 nm) is of interest to nuclear science for use as targets in nuclear reactions. Metal oxide targets, prepared for nuclear science applications, are conventionally made by molecular plating [1, 2]. However, the method suffers from poor adhesion to the backing material and lacks homogeneity at target thicknesses less than about 300 nm [3]. Jia *et al.* [4, 5] recently reported an alternative method, polymer-assisted deposition (PAD), for producing crack-free homogenous metal oxide films with uniform thicknesses between 20 and 400 nm [6, 7]. In the PAD method, a water-soluble multidentate polymer binds to metal precursors resulting in a homogenous distribution of the metal in solution. The solution is spin coated and then annealed to yield a high-quality metal oxide film. In this paper, metal oxide films prepared by PAD were created as an alternative method of target production.

Targets composed of actinide oxides are necessary to synthesize the relatively long-lived and neutron-rich isotopes of transactinides ($Z > 103$). The PAD method was used to study the oxide films of europium (Eu) and thulium (Tm) as models for actinides with an oxidation state of +3 (*e.g.*, americium and curium). Hafnium (Hf) was used as a model of +4 actinides (*e.g.*, uranium and plutonium). The metal oxide film thickness was determined as a function of the weight percent of the metal in solution. The reapplication of the PAD technique on an existing metal oxide layer to build thicker high-quality films was also investigated.

Methods

Solution Preparation

All solutions were composed of 15% polyethylenimine (PEI) by weight, with varying weight percentages of metal chlorides. PEI (10 kDa, Aldrich) was dissolved in water and adjusted to a pH between 6 and 6.5 using 37% HCl and a pH meter with attached electrode (Model 231, Orion Research). Solutions were mixed using a vortex mixer followed by stirring on a magnetic stir plate. An appropriate amount of europium(III) chloride hexahydrate (99.99%, Aldrich), thulium(III) chloride hexahydrate (99.999+%, MV Laboratories), or hafnium(IV) chloride hexahydrate (98%, Aldrich) was added to the dissolved polymer. All solutions were prepared in a non-clean room environment and were stirred for at least one hour before use.

Caution

Hafnium(IV) chloride (CAS# 013499053) is highly volatile and a strong irritant. Handling should be limited to ventilated environments.

Single Layered Metal-Organic Films

Silicon [100] wafers (WaferNet) were cut into rectangles (2.00 cm by 0.85 cm). These cut wafers were placed individually into a spin-coater, and 100 µL of the appropriate solution was evenly distributed onto the surface by pipette. The wafers accelerated for 11 s to a maximum angular velocity of 1500 rpm and spun for 3.0 minutes in air to form a layer of metal-organic polymer. The angular acceleration was the same between trials. The surface of each sample was scratched three times down to the silicon with sharp tweezers to determine film height. Samples were placed in a muffle oven. The temperature increased by 50º C every 15 minutes from 50º C to 900º C. After 15 minutes

at 900º C the oven was turned off and allowed to cool at room temperature for several hours.

Reapplication

Three circular silicon [100] wafers (WaferNet) with diameters of 10 cm were used to test the viability of forming thicker hafnium(IV) oxide films by reapplication of the PAD method. One aliquot of 3.0 mL from a solution composed of 10% Hf and 15% PEI was evenly distributed onto each wafer surface. The wafers were accelerated to a maximum angular velocity of 2500 rpm and spun for 3.0 minutes in air to form a layer of metal-organic polymer. The metal-organic coated wafers were annealed in the same manner as described above, and the entire process was repeated six times.

Film Thickness and Visual Assessment

The height of a single layered metal oxide film was determined by using a profilometer (Dektak 150, Veeco) to scan perpendicular to a scratch. Average film thicknesses were measured from three samples spun identically with the same solution. Each sample had three scratches and each scratch was scanned three times at different locations. A plain silicon wafer was scratched similarly to the samples described above, and the tweezers left no measurable indentation into the silicon surface. Outliers were Q-tested out of the data set at 90% confidence. The thickness of the multiple layered metal oxide films were determined by weight, because scratching and scanning by profilometry would have introduced an inhomogeneous surface for the spin coating of consecutive layers.

A scanning electron microscope (SEM) (Ultra 55VP Fesem, Zeiss) was used to determine surface homogeneity on the 200 nm to 200 μm scale by imaging the surface

and the cross-section. An atomic force microscope (AFM) (MFP 3D, Asylum Research) was used to obtain a high resolution image of a 1μm x 1μm representative section of the surface. The AFM used cantilevers with a spring constant of 3 N/m (Multi75, Budget Sensors) for imaging in the attractive regime in AC mode. The crystal structure of the film created from reapplication of PAD was determined with an X-ray Diffraction machine (Diffraktometer D500/501, Siemens). The wafer was scanned using 2θ values of 20 to 66 degrees in 0.05 degree increments at one second per step.

Results and Discussion

Single Layer Films

The thickness of the metal oxide film produced by the polymer-assisted deposition method is a function of several variables: angular acceleration of the spin coater, viscosity of the solution, metal ion concentration, maximum velocity of the spin coater, total time spun, and the annealing temperature profile [4]. To determine the optimum conditions for the PAD method, a systematic study was performed studying the effect that varying metal ion concentration has on film thickness for Eu(III), Tm(III), and Hf(IV).

The a-priori expectation of a linear relationship between film thickness and metal ion concentration was not observed, as seen in Figure 1. Spin coating yields film heights having an $\eta^{1/3}$ dependence [8], where η is the viscosity. It is hypothesized that the deviation from linearity is due to the increase in viscosity from increasing metal ion weight percent in solution while fixing the polymer weight percent at 15%, thus decreasing the total amount of water available for solvation. Attempts at preparing

solutions above 8% Eu, 10% Tm, and 12.9% Hf, all in 15% PEI, were unsuccessful due to a precipitation that could not be re-dissolved. For hafnium, the highest quality film was produced with the 10% by weight (b.w.) Hf solution. Likewise, 6% (b.w.) Eu and 8% (b.w.) Tm yielded the best results for those elements. The standard deviation for each sample was found to be less than 13% of its film height except for those derived from the 8% (b.w.) Eu solution, and the 2% (b.w.) metal ion solutions. The 8%-Eu film appeared inhomogeneous by SEM analysis, and consisted of micro-scale amorphous structures of Eu_2O_3. The 2%-metal ion solutions yielded films with a standard deviation of about 10 nm, which are similar to those produced by the more concentrated metal ion solutions.

Surface SEM and cross-section SEM images of europium, thulium, and hafnium are shown in Figures 2a-c. The surface of 6% Eu and 8% Tm were homogenous with an even distribution of metal oxide grains. However, there was a random distribution of surface aggregates of 2-5 μm in length in the 8%-Tm films, likely caused by being near the saturation point of Tm/PEI in water. The 10% Hf had the most homogenous surface of all the metals, although some minor surface aggregates are apparent as shown in Figure 2c. The cross sections for all metals, Figures 2a-c, show highly uniform films. AFM images of the metal oxide films show that the surfaces are composed of grains. The largest grains occur in the Eu_2O_3 films (30-40 nm in diameter) and the smallest in the HfO_2 films (10-15 nm in diameter). The AFM images confirm the surface homogeneity and uniformity of all the films as shown in Figure 3. AFM and profilometry data verify that hafnium forms the most highly uniform and homogenous metal oxide film when SiO_2/Si is used as the backing material. The roughness, as measured by AFM, had a root

mean square, rms, of 7.46 nm, 1.87 nm, and 1.45 nm for europium, thulium, and hafnium films, respectively, over 1 μm^2.

Multi-layered Films

The PAD method was applied to an already formed metal oxide layer to create thicker targets than were possible by spinning a concentrated metal ion solution once. Due to the large size of the wafers, it was necessary to spin at an angular velocity of 2500 rpm to minimize comets and to form a uniform layer over the entire surface. The process resulted in multilayered films of HfO_2 with an average final height of 598 nm. Uniform film thickness across the width of the wafer was confirmed by imaging several locations by cross-section SEM. The change in height of hafnium(IV) oxide after each interval is summarized in Figure 4. Film thickness increased by 99 nm (±2 nm) after each interval step. The upper limit of the method toward reapplication was not determined. Surprisingly, no striations were seen from a cross-section SEM (Figure 5) of the final wafer, indicating uniform growth. An AFM image (Figure 6) of the film shows that the surface is composed of grains between 15 and 20nm in diameter with a roughness rms of 2.35 nm over 1 μm^2.

X-ray Diffraction (XRD) analysis was conducted on the multilayered HfO_2 film and compared with HfO_2 powder produced from baking several milliliters of a 9% (b.w.) Hf solution in a glass vial at 900 ºC until a white powder formed. Figure 7 shows the close correlation between the HfO_2 film XRD pattern and the HfO_2 powder XRD pattern for polycrystalline HfO_2. The most intense peaks from the HfO_2 film are at 28.4º, 31.7º, 34.4º, 35.6º, and 55.8º. This agrees well with the library XRD pattern of simple monoclinic HfO_2 (PDF# 34-0104). The sharp peak at 33.1° is likely caused by the silicon

backing. The relative intensities of the powder HfO_2 XRD pattern and the HfO_2 library XRD pattern were similar as seen in Figure 7a. However, differences in relative intensities in the HfO_2 film XRD pattern versus the HfO_2 powder XRD pattern were observed. This is likely due to the HfO_2 powder having a random distribution of lattice planes while the HfO_2 film has preferred orientations which skew the peaks. The broad widths of the peaks imply small grain sizes [9] in agreement with AFM and SEM analysis.

Method Advantages

Molecular plating has been used by Trautmann *et al.* [1] and Mullen *et al.* [2] to create uranium, plutonium and curium oxide films. Their films ranged from 150 to 550 nm in thickness, which are typical for nuclear science applications. We have independently shown that the PAD method can produce films in a wider range of thicknesses than molecular plating. In addition, an advantage of using PAD is that it produces highly uniform and homogenous metal oxide films below 300 nm, while molecular plating method suffers in this region. A second advantage of the PAD method is that it can be reapplied to create thicker films without losing uniformity. A disadvantage of the PAD method is that the coating efficiency for a single application is ~33%. However, the solution that did not adhere to the surface can be collected and reused resulting in minimal loss of a precious metal, with the overall deposition efficiency approaching 100%. Molecular plating has ~90% efficiency for the deposition of metal out of solution [1, 2] comparable to PAD. Thus, the PAD method is likely a robust route to create metal oxide films suitable for nuclear science applications which require film uniformity and controlled film thickness.

It should be noted that the potential for silicon diffusion into the metal oxide films was not investigated, because this would not affect the overall energy loss of a high-energy beam passing through a metal oxide film and substrate. Future work will study the mechanical properties of metal oxide films of uranium, plutonium and curium created by the PAD method, before and after high intensity heavy-ion irradiation.

Conclusion

Europium, thulium and hafnium oxide films were annealed onto silicon substrates using polymer-assisted deposition. The films were characterized by SEM, AFM and profilometery. The characterizations showed that the films were crack free, uniform, and homogenous. Advantages of PAD over molecular plating include that it produces high-quality thin films below 300 nm in thickness and that reapplication of the method creates thicker metal oxide films of equal quality.

Acknowledgements

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Captions

Figure 1. Film thickness as a function of metal ion concentration: (a) europium(III) oxide, (b) hafnium(IV) oxide, (c) thulium(III) oxide. Error bars correspond to one standard deviation. The trend lines are meant to guide the eye. Error for all solutions are negligible (<.05%).

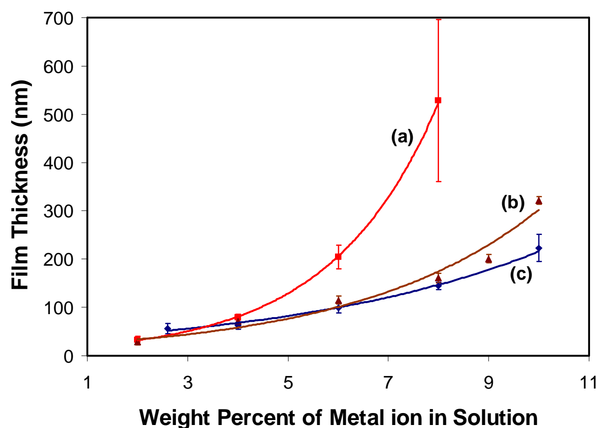

Figure 2. (a) europium(III) oxide film (produced from a 6% by weight europium solution); (b) thulium(III) oxide film (produced from a 8% by weight thulium solution); (c) hafnium(IV) oxide film (produced from a 10% by weight hafnium solution.).

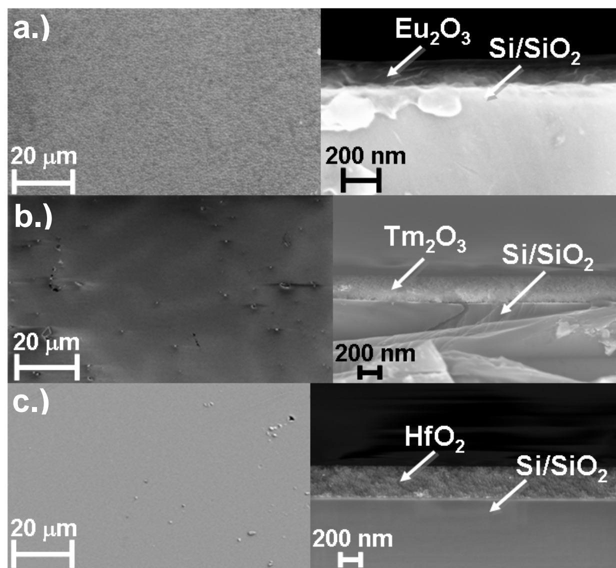

Figure 3. AFM images of metal oxide films after single application of the PAD method: (a) europium(III) oxide film produced from a 6% by weight europium solution, (b) thulium(III) oxide film produced by an 8% by weight thulium solution, and (c) hafnium(IV) oxide film produced from a 10% by weight hafnium solution.

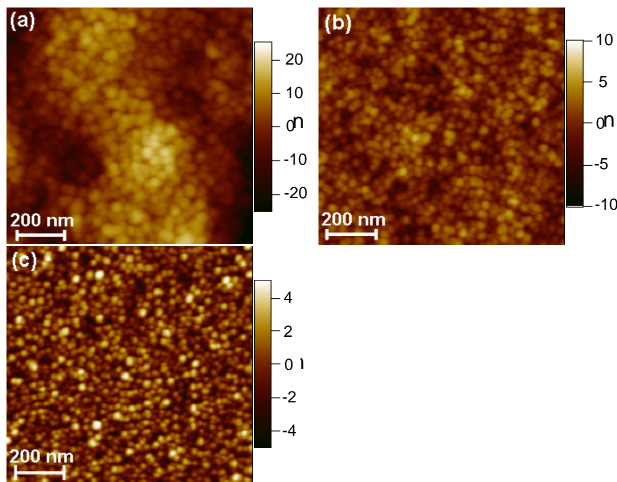

Figure 4. The graph shows the cumulative height of hafnium(IV) oxide after reapplication of the PAD method. The experiment was done in triplicate and the results averaged, except layer 6 which was done in duplicate. Uncertainty from the analytical balance translates to ±2 nm.

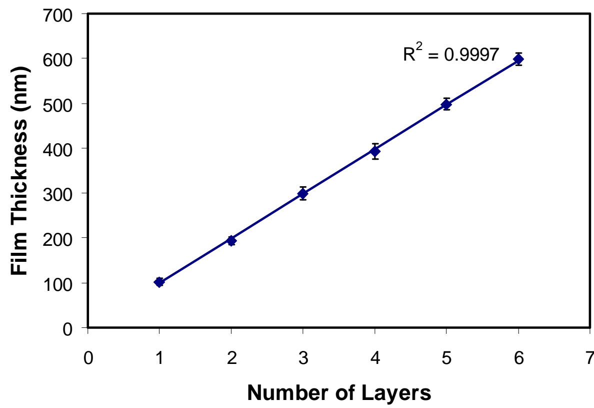

Figure 5. Left: Representative surface SEM of a hafnium oxide film produced from reapplication of the PAD method using a 10% by weight hafnium solution. Right: Representative cross-section SEM of the same hafnium(IV) oxide film.

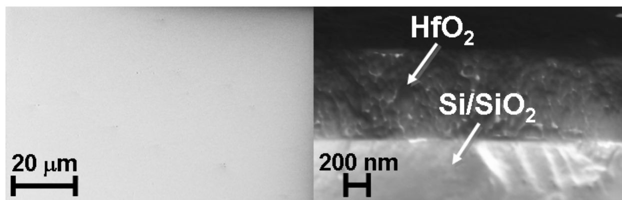

Figure 6. AFM image of a hafnium oxide film produced from reapplication of the PAD method using a 10% by weight hafnium solution.

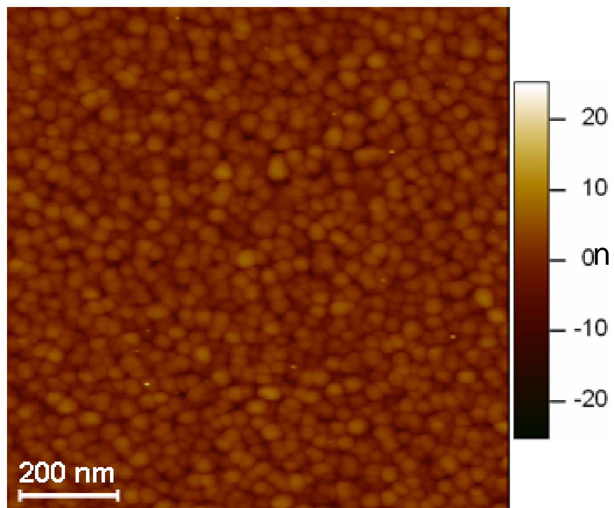

Figure 7. a.) X-ray Diffraction pattern of HfO_2 powder. b.) X-ray Diffraction pattern of a multi-layered film of HfO_2 on Si [100]. The vertical bars show the reference XRD pattern's relative intensities.