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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 10% by weight hafnium(IV) solution resulted in an equally homogeneous and uniform film with a total thickness of 600 nm.

Keywords: Metal oxide; Target preparation; Transactinide; Polymer-assisted deposition; Atomic force microscopy

1. 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.

2. Methods

2.1. 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

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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 1 h before use.

2.2. Caution

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

2.3. 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 min 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 50 °C every 15 min from 50 °C to 900 °C. After 15 min at 900 °C the oven was turned off and allowed to cool at room temperature for several hours.

2.4. 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 min 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.

2.5. 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 1 μm × 1 μm 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 the 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° in 0.05 degree increments at one second per step.

3. Results and discussion

3.1. 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 Fig. 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,

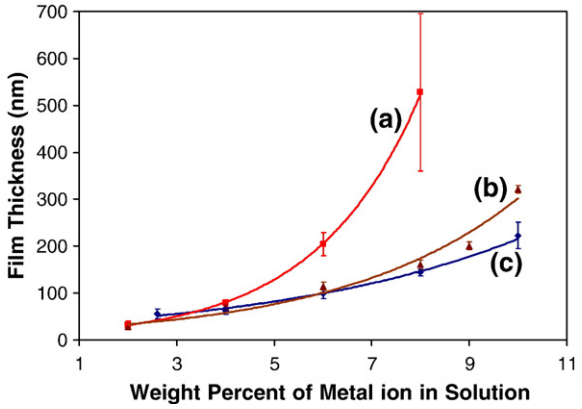

Fig. 1. Film thickness as a function of metal ion concentration: (a) europium(III) oxide, (b) hafnium(IV) oxide, (c) thulium(III) oxide. Error bars correspond to one standard deviation. The trend lines are meant to guide the eye. Error for all solutions is negligible (<0.05%).