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Structural, optical and mechanical properties of amorphous and crystalline alumina thin films

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ABSTRACT

Thin films of amorphous alumina of thickness 350 nm were deposited on fused silica substrates by electron beam evaporation. Amorphous films were annealed at several temperatures in the range: 400–1130 °C and changes in film crystallinity, short-range structure, optical and mechanical properties were studied. X-ray diffraction studies found that crystallization starts at 800 °C and produces γ and δ-alumina, the latter phase grows with heat treatment and the sample was mostly δ and θ-alumina after annealing at 1130 °C. The as-deposited amorphous alumina films have low hardness of 5 to 8 GPa, which increases to 11 to 12 GPa in crystalline sample. ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance was used to study the short-range order of amorphous and crystalline alumina films and it was found that amorphous alumina film contains AlO_5 and AlO_4 structural units in the ratio of 1:2. The concentration of AlO_5 was significantly suppressed in crystalline film, which contains 48% of Al^{3+} ions in AlO_6, 7% in AlO_5 and 45% in AlO_4 units.

1. Introduction

Aluminum oxide exists in several crystallographic polymorphs and its thin and thick films are used in wide range of applications including microelectronics and catalysis, as well as diffusion barrier, thermal barrier and wear resistant coatings for cutting tools [1,2]. Metastable phases like γ-alumina find use in catalysis due to their large surface area [3], while the anodic alumina templates are used for the synthesis of nanowires [4]. α-Alumina films for cutting tool applications are deposited by chemical vapor deposition at high substrate temperature of 1100 °C [5]. Plasma Assisted Chemical Vapor Deposition decreases the deposition temperature for α-alumina to 560 °C [6], while High Power Impulse Magnetron Sputtering forms α-alumina films at ~600 °C [7]. Cr_2O_3 templates have been found to reduce substrate temperature to ~280 °C [8]. Dual hollow cylindrical magnetrons and mid-frequency AC supply (41 kHz) grow crystalline γ-alumina films at a moderate in situ temperature of 350 °C [9]. It is well established that other physical vapor deposition techniques such as electron beam evaporation and pulsed laser deposition (PLD) grow amorphous alumina films up to a substrate temperature of at least 600 °C [10]. PLD grows γ-alumina phase at ~800 °C [11–13]. Significant effort has been devoted during the last three decades towards developing techniques to deposit crystalline alumina films at lower temperatures. Reactive sputtering has several advantages over other techniques that it causes ion bombardment of the growing film and provides high energy that is essential for achieving crystallinity [6,7,14]. Based on theoretical and experimental work, subplantation has been suggested to control the phase formation in alumina thin films [15,16].

It is still not completely understood why aluminum oxide, which is not a glass former and has not been synthesized in the amorphous form in the bulk, produces amorphous phase even at high substrate temperature of 600 °C by thin film deposition. An important insight has recently been provided by the ^{27}Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) studies of amorphous and crystalline alumina films, which revealed that significant fraction of

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Al^{3+} ions are in penta-coordination with oxygen ions in amorphous alumina and it is this structural feature i.e. the presence of AlO_5 (denoted as $^{[5]}Al$) that creates disorder and hinders the growth of crystalline alumina phase [17,18]. High temperature of ~800 °C is required for the transformation of amorphous alumina into γ-phase by the following structural rearrangement reaction:

$$2[AlO_5] \rightarrow [AlO_4] + [AlO_6]. \quad (1)$$

Geometrically speaking, the above reaction mechanism involves the formation of edge-sharing octahedral $^{[6]}Al$ from corner sharing $^{[5]}Al$. Amorphous and molten alumina contain $^{[5]}Al$ and $^{[4]}Al$ in the ratio of 1:2 [17–19], γ-alumina has $^{[6]}Al$ and $^{[4]}Al$ in the ratio of 2:1, θ-alumina has $^{[6]}Al$ and $^{[4]}Al$ in the ratio of 1:1, κ-alumina has $^{[6]}Al$ and $^{[4]}Al$ in the ratio of 1:3, while α-alumina contains only $^{[6]}Al$ [20].

High substrate temperatures that are essential to grow crystalline alumina films by physical vapor deposition techniques are difficult to maintain for long times during deposition since they deteriorate chamber vacuum. Ideally, we need deposition techniques that do not use in situ high substrate heating. Therefore one method that has attracted attention for crystallization of amorphous alumina films is post deposition thermal annealing. This is also important from the fundamental point of view as it provides insights about the thermal stability and phase transformation properties of amorphous and metastable crystalline alumina phases. The thermal stability of amorphous and γ-alumina films has been studied by earlier researchers [21–23] and again in the recent times [14,24,25]. There is some variation in the reported phase transformation properties of alumina films; Eklund et al. found that films containing amorphous or very small amounts of γ-phase show the formation of intermediate θ-phase in the temperature range of 1000 to 1100 °C, while highly crystalline γ-alumina films transform directly into α-phase [24]. Musil et al. have studied the thermal stability of γ-alumina films grown by reactive magnetron sputtering and shown that γ-alumina films are stable on heat treatment at 1000 °C for at least 5 h and that the α-phase grows at ~1050 °C. These authors also found that thin γ-alumina films (thickness ~300 nm) were resistant to transformation to α-phase even after 5 h of heat treatment at 1100 °C, while thicker films (~1200 nm) transformed readily to α-phase on annealing at 1100 °C for 2 h [25]. Edlmayr et al. studied the thermal stability of alumina films deposited on Si(100) substrates and iron foils, by bipolar pulsed magnetron sputtering and reported that amorphous films transform to α-phase at 1150 °C while crystalline γ-alumina films transformed to α-phase at a higher temperature of ~1250 °C [14].

There are few studies on the thermal stability, mechanical and optical properties of alumina films deposited by electron beam evaporation [26], and it is not known whether their structural transformation properties are the same or different from that of reactively sputtered alumina films. The energy of the depositing particles during electron beam evaporation is lower than the energy of particles during reactive magnetron sputtering and because the microstructure and mechanical properties of alumina films depend critically on the incident particle energy [27], the crystallization properties of electron beam and sputter coated alumina may be different.

In this paper we report the effects of heat treatment on the crystal structure, optical and mechanical properties and the short-range structure (i.e. Al–O speciation) in amorphous and crystalline alumina films prepared by electron beam evaporation. Amorphous films of aluminum oxide were grown on the fused silica substrates and subsequently annealed at temperatures between 400 °C and 1130 °C for 6 h in air. Films were characterized by grazing incidence X-ray diffraction, UV–visible absorption spectroscopy, and nanoindentation and ^{27}Al MAS NMR spectroscopy.

2. Experimental

2.1. Thin film deposition

Aluminum oxide thin films were deposited on fused silica substrates by electron beam evaporation of alumina disks (99.5% purity, Carborundum Universal Ltd., Hosur, India). Before deposition, the substrates were ultrasonically cleaned in acetone and ethanol. The growth chamber was equipped with a Varian electron beam gun (maximum power 2 kW) and the target to substrate distance was about 23 cm. The deposition chamber was evacuated with a cryopump to a base vacuum of 4×10^{-6} Pa. The electron beam gun was switched on, and alumina deposition was carried out for 52 min. During deposition the chamber pressure was ~3.3×10^{-5} Pa. The thickness of films was monitored in situ by a quartz crystal monitor. Average deposition rate was 0.11 nm s^{-1} and the final film thickness was 350 nm.

2.2. Post-deposition annealing

One amorphous film on silica substrate (sample code: S1) was sequentially annealed at 400 °C, 600 °C, 800 °C, 950 °C, 1050 °C and 1130 °C. The sample was heat treated at each of these temperatures for 6 h in ambient air, and then slowly cooled to room temperature. Sample heating rate was ~20 °C min^{-1}, and after heat treatment, it was cooled slowly to room temperature at ~200 °C h^{-1}.

2.3. Grazing incidence X-ray diffraction (GIXRD)

XRD measurements were performed on alumina film before and after each annealing treatment on Bruker D8 Focus X-ray diffractometer in the grazing incidence geometry with Cu-K_α radiation (λ = 0.154056 nm). Measurements were done by keeping the incident angle fixed at 2° and by scanning the scintillation counter detector in the 2θ range of 10–70°. The X-ray tube was operated at 40 kV and 35 mA.

2.4. UV–visible spectroscopy

The optical absorption spectra of as deposited film on silica substrate before and after heat treatment were measured on a Cecil UV–visible spectrophotometer (model 3055). The refractive indices of as deposited amorphous and crystallized samples were determined by using the fitting procedure based on Sellmeier's dispersion relations [28].

2.5. Nanoindentation

Nanoindentation testing was performed on two samples on silica substrate (S1 and S1-1130) using a Micro Materials NanoTest system. Hardness and reduced indentation modulus (E_r), were determined from nanoindentation to 0.5–50 mN with a Micro Materials NanoTest system. The reduced indentation modulus, E_r, is defined as:

$$\frac{1}{E_r} = \frac{\left(1-\nu_s^{\,2}\right)}{E_s} + \frac{\left(1-\nu_i^{\,2}\right)}{E_i} \quad (2)$$

where ν_s is the Poisson's ratio for the sample, ν_i, the Poisson's ratio for the diamond indenter (0.07), E_s, the sample elastic modulus and E_i, the diamond elastic modulus.

All indentations were performed with a very sharp Berkovich indenter calibrated against a fused silica reference over a wide depth range. In all indentations the loading time was 20 s loading, 10 s hold at peak load, 20 s unloading and 60 s for thermal drift correction at 90% unloading. All data were corrected for a small (sub-nm) zero point correction prior to analysis.