

## Rapid communication

# Formation of crystalline aluminum silicate hydroxide layer during deposition of amorphous alumina coatings by electron beam evaporation

Priyanka Nayar, Atul Khanna\*

Department of Physics, Guru Nanak Dev University, Amritsar, Punjab 143005, India

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## ABSTRACT

Aluminum oxide films were deposited on fused silica and borosilicate glass substrates by electron beam evaporation, without any substrate heating. Grazing incidence X-ray diffraction measurements found that a layer of crystalline aluminum silicate hydroxide was formed at the interface of the substrate and the amorphous alumina film, the latter transformed to  $\gamma$ -alumina phase on heat treatment at 800 °C. The aluminum silicate hydroxide layer was produced by the chemical reaction between condensing Al and Al–O species, OH<sup>−</sup> from the residual water vapors in the chamber and Si atoms from the underlying silica and borosilicate glass substrates.

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The preparation and characterization of ceramic coatings of corundum ( $\alpha$ -alumina), magnesia (MgO), mullite (aluminum silicate) etc. is technologically an important area of research as these materials find applications in hard coatings industry due to their chemical and thermal durability and in microelectronics due to their high dielectric constant and electrical resistivity [1]. The growth of  $\alpha$ -alumina films is challenging because it requires high *in situ* substrate temperature of 560 °C–750 °C by techniques such as plasma assisted chemical vapor deposition [2,3], high power impulse magnetron sputtering [4] and pulsed DC magnetron sputtering [5]. Chemical vapor deposition which is commercially used for depositing  $\alpha$ -alumina coatings on cutting tools requires even higher temperature of ~1100 °C [6]. Such high temperatures damage the substrates and semiconductor devices and therefore significant efforts have been made during the last three decades to develop techniques for the preparation of ceramic thin films at low temperatures [7]. Aluminum silicate is an important ceramic, which finds application as a refractory and wear resistant coating and as a dielectric layer in semiconductor devices [8]. The growth of

amorphous aluminum silicate thin films has been reported by metal organic chemical vapor deposition (MOCVD) [9], sol–gel process [10], pyrolytic decomposition of polymers containing aluminum and silicon [11], pulsed laser deposition [12] and sputtering [13]. Earlier Klein et al. had reported the formation of interfacial aluminum silicate layer during CVD of amorphous alumina on Si(100) wafers at 400 °C [14]. It was found by nuclear reaction resonance and X-ray photoelectron spectroscopy studies, that during CVD of amorphous alumina coating on silicon wafer, a thin intermediate layer of amorphous aluminum silicate (thickness ~ a few nm) grows on the substrate [14].

In this letter it is shown that crystalline aluminum silicate hydroxide layer is formed spontaneously at the interface of silica and borosilicate glass substrates during deposition of amorphous alumina films by electron beam evaporation without any deliberate substrate heating.

Aluminum oxide films were deposited on fused silica (SiO<sub>2</sub>) and borosilicate float glass substrates by electron beam evaporation of alumina disks (99.8% purity, Carborundum Universal Ltd., Hosur, India) in five repetitive deposition runs. Prior to each deposition, substrates were ultrasonically cleaned in acetone and ethanol. The deposition chamber was equipped with a Varian electron beam gun (maximum power 2 kW) and the target to substrate distance was

\* Corresponding author. Tel.: +91 183 225 8802x3168; fax: +91 183 225 8820.  
E-mail address: [ak.ap@gndu.ac.in](mailto:ak.ap@gndu.ac.in) (A. Khanna).

**Table 1**  
Conditions used for alumina deposition in five runs.

PARAMETER	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5
Base vacuum [mPa]	0.067	0.13	0.11	0.027	0.027
Pressure during deposition [mPa]	3–7	3–7	3–7	0.13–0.26	0.13–0.26
Average deposition rate [ $\text{nm s}^{-1}$ ]	0.33	0.16	0.32	0.21	0.14
Deposition time [s]	1380	2940	1560	2160	3180
Film thickness [nm]	460	460	503	456	456

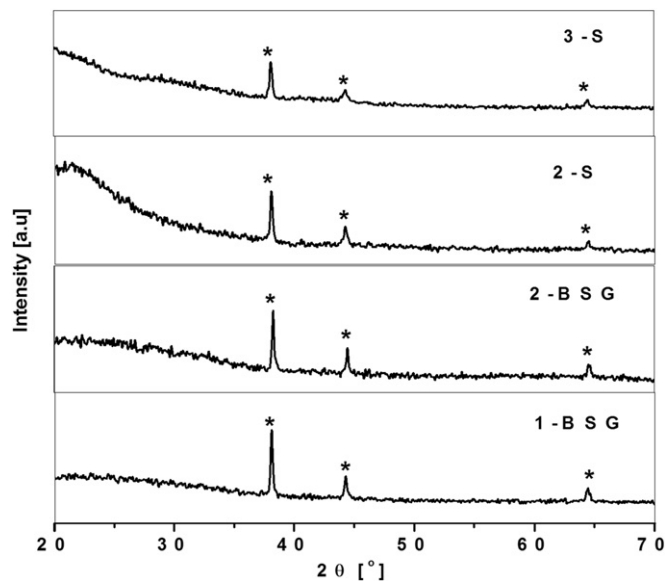
15 cm. The chamber was evacuated to a base vacuum of 0.13 to 0.027 mPa with a diffusion pump and a liquid nitrogen trap. No deliberate substrate heating was provided during evaporation. The thickness of films was monitored *insitu* by a gold-coated quartz crystal oscillator. The average deposition rate was 0.1–0.3  $\text{nm s}^{-1}$  and final coating thickness was in the range: 456–503 nm in five separate runs, which were repeated to verify the reproducibility of thin films' structure and properties, the deposition time during 5 runs varied from 1380 to 3180 s. The deposition parameters of five runs are given in Table 1. Samples from five runs were numbered as 1-BSG, 2-BSG, 2-S, 3-S, 4-S and 5-S where "BSG" denotes the borosilicate glass substrates and "S" fused silica substrates.

Two samples (2-S and 4-S) were annealed in air at temperatures of 400 °C, 600 °C, 800 °C and 950 °C for 6 h each to study the effects of heat treatment on the thermal stability of the coatings. One sample (5-S) was annealed in air at 400 °C for 6 h. After each annealing treatment the samples were cooled to room temperature and analysed by X-ray diffraction. Table 2 gives the post deposition heat treatment given to the three samples.

X-ray diffraction measurements were carried out on all samples on Bruker D8 Focus X-ray diffractometer in the grazing incidence geometry with Cu- $K_{\alpha}$  radiation ( $\lambda = 0.154056$  nm) by keeping the incident angle fixed at 2° and scanning the scintillation detector in the  $2\theta$  range of 10°–70°. The XRD patterns of four alumina samples prepared during the first three runs are shown in Fig. 1. All four samples gave the remarkable result of three sharp peaks at 38.1°, 44.4° and 64.5°. The XRD patterns of the four samples from the first three runs were identical, indicating that same crystalline phase was formed. It is known that electron beam evaporation grows amorphous alumina coatings upto a substrate temperature of at least 600 °C [15]. Crystalline  $\gamma$ -alumina films can be grown by pulsed DC magnetron sputtering at *insitu* substrate temperatures of ~500 °C [16], while pulsed laser deposition requires even higher temperatures of ~800 °C [17], moreover  $\gamma$ -alumina films usually exhibit two broad XRD peaks of equal intensity at 45.9° and 67.1° [16–18], on the contrary crystalline phase formed during deposition showed three sharp peaks at 38.1°, 44.4° and 64.5°. These peaks match closely with the powder diffraction file of aluminum silicate hydroxide ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) phase [19] and were not due to metallic aluminum or any of the transient or thermodynamically stable crystalline phases of aluminum oxide.

**Table 2**  
Post-deposition annealing treatment of samples.

Sample no.	Heat treatment
2-S-H-400	Sample 2-S annealed at 400 °C for 6 h
2-S-H-600	Sample 2-S-H-400 annealed at 600 °C for 6 h
2-S-H-800	Sample 2-S-H-600 annealed at 800 °C for 6 h
2-S-H-950	Sample 2-S-H-800 annealed at 950 °C for 6 h
4-S-H-400	Sample 4-S annealed at 400 °C for 6 h
4-S-H-600	Sample 4-S-H-400 annealed at 600 °C for 6 h
4-S-H-800	Sample 4-S-H-600 annealed at 800 °C for 6 h
4-S-H-950	Sample 4-S-H-800 annealed at 950 °C for 6 h
5-S-H-400	Sample 5-S annealed at 400 °C for 6 h



**Fig. 1.** XRD patterns of films on silica and borosilicate glass substrates prepared during the first three deposition runs. Peaks labeled as \* are due to the intermediate layer of aluminum silicate hydroxide.

During the deposition run 4 and 5, the as-deposited samples (4-S and 5-S) were found to be amorphous and the crystalline peaks detected in four samples from runs 1–3 were absent, however after annealing the samples at 400 °C for 6 h, X-ray diffraction measurements detected three peaks at 38.1°, 44.4° and 64.5° (Fig. 2a–b), which again confirmed the formation of crystalline  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  after heat treatment. Further annealing of the sample 4-S at 600 °C increased the intensity of the peak at 38.1°. After annealing at 800 °C, the XRD patterns displayed two additional, broad peaks at 45.9° and 67.1° which were due to the growth of crystalline  $\gamma$ -alumina phase in the upper layers of the coating [20]. Heat treatment at 950 °C increased the size of  $\gamma$ -alumina crystallites, however aluminum silicate phase was thermally stable and its XRD peaks sharpened and the relative intensity of the peak at 38.1° also increased (Fig. 2a).

The formation of  $\gamma$ -alumina at 800 °C demonstrated that the entire thin film structure was not aluminum silicate hydroxide but the latter existed at the bottom, near the substrate and that the top layers were amorphous alumina, which crystallized on heat treatment at 800 °C. It is known from the thermal stability studies of amorphous aluminum oxide coatings that crystallization of  $\gamma$ -phase is initiated at 800 °C [18,21,22].

One coating sample from run 2 that showed crystalline peaks due to aluminum silicate hydroxide (sample: 2-S) was subjected to post deposition heat treatment upto 950 °C (Table 2). This sample like the sample 4-S, showed the formation of  $\gamma$ -alumina at 800 °C, which grows with further annealing at 950 °C, interestingly the crystalline peaks due to aluminum silicate hydroxide disappeared after its annealing at 950 °C, this was probably due to the masking of the underlying crystalline aluminum silicate hydroxide layer by the top layers of crystalline  $\gamma$ -alumina layer, formed at 800 °C (XRD patterns of sample 2-S after annealing are not shown). The aluminum silicate compound is thermally stable upto at least 950 °C, as indicated by annealing studies on sample 4-S (Fig. 2a). The thickness of intermediate layer of aluminum silicate hydroxide in sample 2-S must be less than the thickness of the layer in sample 4-S, and therefore the XRD peaks due to silicate layer in sample 2-S were masked by the growth of top layer of  $\gamma$ -alumina at 800 °C.

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