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Transmission electron microscopy investigation of the effect of Si alloying on the thermal stability of amorphous alumina thin films deposited by filtered cathodic arc deposition

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ABSTRACT

The effect of thermal annealing treatments on the morphology and structure of amorphous unalloyed and amorphous Si alloyed alumina thin films has been investigated. All amorphous thin films were deposited by filtered cathodic arc deposition at room temperature onto Si_3N_4 coated Si substrates and subsequently annealed in argon atmosphere at temperatures in the range of 610 °C–1100 °C with a heating rate of 20 °C/min. After each heating sequence the thin film samples were investigated by means of transmission electron microscopy. Upon alloying 2 at.% of Si to alumina, the amorphous to crystalline transition is shifted by ≥290 °C to higher temperatures. For the unalloyed thin film crystallization of γ-Al_2O_3 in an amorphous matrix is observed at 630 °C. Fully crystalline γ-Al_2O_3 is formed at 750 °C. Evidence for the transition of γ-Al_2O_3 to α-Al_2O_3 is obtained after annealing at 900 °C concomitant with substantial crack formation and coating-failure. In contrast, the Si alloyed alumina thin film remains amorphous until 900 °C. At 950 °C first traces of γ-Al_2O_3 in an amorphous matrix are observed and further annealing at 1100 °C results in the formation of a mullite phase in addition to the γ-Al_2O_3-phase. The thermal stability range of amorphous alumina thin films is hence significantly enhanced by alloying with 2 at.% of Si.

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1. Introduction

Alumina (Al_2O_3) is a polymorphic ceramic material and has many technological applications in widely differing areas due to its abundance and the diverse physical properties of its stable and metastable phases. The thermodynamically stable α-Al_2O_3-phase is for example used as a protective coating material because of its high hot hardness and high wear resistance [1,2]. Low temperature crystalline alumina thin films are formed when ionized film forming species are employed during deposition [3], by using template layers [4,5] or by suitable alloying [6–9]. Among the metastable alumina phases, the γ-Al_2O_3-phase exhibits mechanical properties which are comparable to the α-Al_2O_3-phase [10]. The advantage of the γ-Al_2O_3-phase over the stable α-Al_2O_3-phase is that it can be deposited by magnetron sputtering at about 500 °C [11] and by cathodic arc deposition at 200 °C [12] and thus at much lower temperatures than the α-Al_2O_3-phase, which is usually synthesized by chemical vapor deposition (CVD) at 1000 °C [13,14], by pulsed sputtering at about 700 °C [15], by high power impulse magnetron sputtering at 650 °C [16] and by cathodic arc at 720 °C [17]. Music et al. suggested that energetic Al-ions are subplanted and thereby enable the formation of the α-Al_2O_3-phase [18].

However, the phase transformation of the metastable γ-Al_2O_3-phase into the stable α-Al_2O_3-phase at temperatures in the range of 1000 °C leads to a volume shrinkage of about 14% and hence may induce adhesive and/or cohesive failure and limit coating lifetime [19]. Therefore enhancing the thermal stability of γ-Al_2O_3 thin films and coatings is of particular interest in many fields of application. One possibility to improve the thermal stability of γ-Al_2O_3 is to alloy it with a suitable alloying element. A broad range of possible alloying elements, such as As, B, Ba, Ce, Co, Cr, Cu, La, Mo, N, S, Sc, Si, Th, Ti, Y or Zr and their effect on the thermal stability of the metastable γ-/θ-Al_2O_3-phases have been discussed in literature [20–24]. Si additions to amorphous alumina thin films are not reported in the literature. However, based on the ab initio results of Jiang et al. [20] and Nahif et al. [25], in which Si was positioned at different substitutional sites in the γ-/α-Al_2O_3-phases, Si is attributed to stabilize the γ-Al_2O_3-phase with respect to the unalloyed α-Al_2O_3-phase. Experimental results based on annealing experiments of unalloyed and Si alloyed alumina thin films deposited by the filtered cathodic arc technique at 650 °C [26] exhibited an alloy element induced increase in α-Al_2O_3-formation temperature of more than 200 °C. According to the observed temperature induced changes in phase evolution, chemical states and crystallite sizes it was proposed that the observed stabilization upon Si addition

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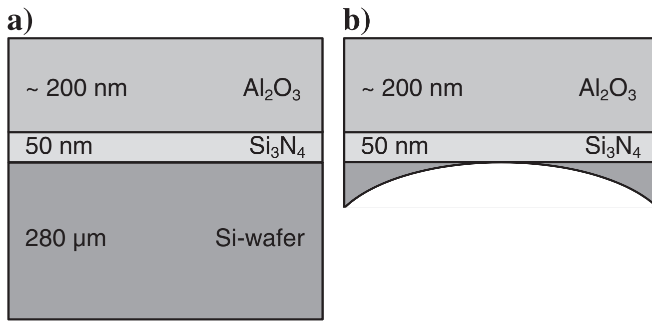

Fig. 1. Layer structure of the unalloyed/Si alloyed FCA alumina thin film samples a) before TEM sample preparation and b) after TEM sample preparation.

is due to the presence of SiO_2 at the grain boundaries limiting mass transport and hence crystal growth. At this point it is unclear if amorphous alumina thin films can be stabilized by Si additions as the stabilizing mechanism proposed in [26] is based on the presence of SiO_2 in grain boundaries.

In the present study the effect of Si alloying on the thermal stability of amorphous alumina thin films grown by filtered cathodic arc (FCA) deposition at room temperature is investigated by TEM analysis of as-deposited and annealed samples. The thermal stability range of amorphous alumina thin films alloyed with 2 at.% of Si is significantly enhanced compared to the unalloyed films.

2. Material and method

Amorphous unalloyed and amorphous Si alloyed alumina thin films were deposited at room temperature by using an industrial filtered cathodic arc source described in detail elsewhere [27]. One Al cathode (99.5% purity) and one Si alloyed Al cathode with 10 at.% of Si were used and the deposition process [27] was performed in an $Ar–O_2$ atmosphere at a working pressure of 1 Pa. The depositions were performed without intentional heating. In order to facilitate the preparation of electron transparent membranes for transmission electron microscopy (TEM) analysis, Si(100) wafers with a 50 nm amorphous Si_3N_4-interlayer were used as substrate materials. The substrate was kept in stationary mode on a floating potential of −8 V for all depositions. Furthermore, all depositions were performed with a monoenergetic Al^+-plasma beam having an average ion energy of 1 eV, as described elsewhere [27]. The Si content within the Si alloyed thin film is 2 at.% as determined by energy dispersive X-ray analysis with an EDAX genesis 2000 analyzer at an acceleration voltage of 6 kV. It is evident that the Si/Al ratio in the target is up to 50% larger than in the as-deposited film. This reduction may be related to scattering phenomena in the gas phase during transport through the magnetic filter [27] and/or to formation of volatile SiO_x species [28]. The Si_3N_4-interlayer served as an etching barrier between the Si-wafer and the alumina thin film in the TEM sample preparation conducted after deposition. TEM specimens were prepared by the following sample preparation steps: In first step, disks with a diameter of 3 mm were drilled out of the as-deposited $Al_2O_3/Si_3N_4/Si$ wafers with the unalloyed and Si alloyed alumina thin films. Then these disks with an initial thickness of 280 μm were grinded on the Si-wafer side to a final thickness of about 100 μm. Furthermore, the silicon in the center of the disks was thinned to a thickness under 40 μm by dimple grinding. In a final step, the remaining silicon in the center of the disk was removed by etching with 30% potassium hydroxide (KOH), resulting in a TEM sample with an electron transparent window consisting of the alumina- plus Si_3N_4-layers and a 100 μm thick outer area, supported by the Si wafer, which can be mounted in a conventional TEM sample holder (Fig. 1b).

The as-prepared TEM samples were annealed in a differential scanning calorimeter (DSC) in an Ar-atmosphere. The unalloyed and Si alloyed samples were annealed at the following maximum temperatures: 610 °C, 620 °C, 630 °C, 640 °C, 750 °C, 850 °C and 900 °C with a heating and cooling rate of 20 °C/min and without holding time. The Si alloyed sample was annealed in addition to the aforementioned temperature also at 950 °C and 1100 °C. We chose a temperature profile with no holding time because of the almost instantaneous occurrence of the phase transformations at the highest temperatures. Of course, this will result in the fact that the samples will not reach thermal equilibrium at the peak temperatures in the lower temperature regime and the transitions will rather depend on the whole time (t) and – temperature (T) – profile. However, the present work focuses on the comparison between unalloyed and Si-alloyed alumina thin films, which were annealed in the same manner. Thus the relative changes observed in the different films are meaningful and the chosen procedure was proven to be a good compromise between the different kinetic speeds at different temperatures.

After each annealing step, subsequent TEM analyses of the unalloyed and Si alloyed alumina-samples were performed by using a FEI Tecnai F20 microscope operated at 200 kV. Hence, the annealed samples were investigated in the TEM, then further annealed at higher temperatures, then investigated in the TEM again and so on. For the TEM investigations conventional TEM methods, such as TEM bright field imaging (TEM BF) and selected area diffraction (SAD), as well as scanning TEM (STEM) techniques were applied to characterize the as-deposited and annealed samples, particularly with regard to their morphology and microstructure. TEM methods were chosen as primary experimental tools in this phase formation study because of the excellent spatial resolution and sensitivity with respect to phase formation.

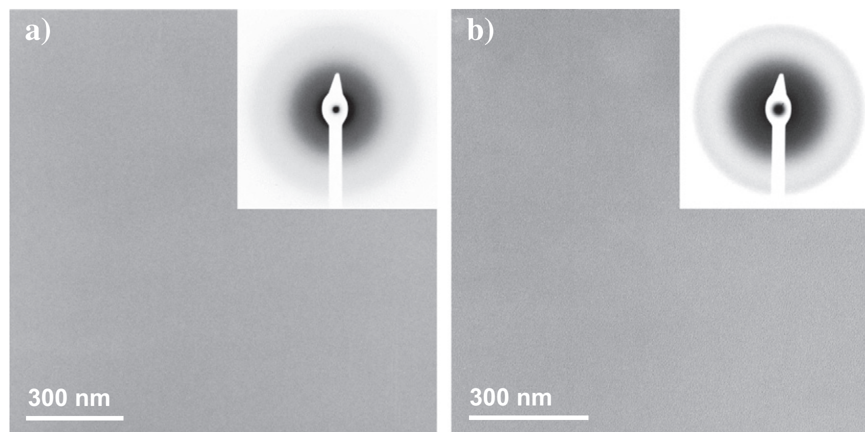

Fig. 2. TEM BF images and SAD pattern of the as-deposited (a) unalloyed alumina thin film and (b) Si alloyed alumina thin film (SAD aperture size 200 nm).

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