



The effect of Si alloying on the thermal stability of Al₂O₃ films deposited by filtered cathodic arc

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ABSTRACT

The effect of Si alloying on the phase transformation sequence and phase formation temperatures of Al₂O₃ thin films deposited by filtered cathodic arc was investigated by annealing experiments in air. By addition of Si the transformation of γ - to δ - and θ -Al₂O₃ is restrained by 100 °C. The thermal stability range of the δ - and θ -phase is also increased by ≥ 200 °C with respect to the unalloyed Al₂O₃ thin film and the formation of α -Al₂O₃ is restrained by 200 °C upon addition of Si. Based on the observed Si addition induced changes in phase formation, crystallite size and bonding it appears reasonable that the presence of SiO₂ at the grain boundaries impeding mass transport governs the Si induced stability enhancement of the metastable γ -/ δ - and θ -Al₂O₃ phases and the restrained α -Al₂O₃ formation. The competing proposal assuming a random substitution of Al by Si on the lattice sites is not consistent with the XPS data.

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1. Introduction

Al₂O₃ thin films synthesized by physical or chemical methods have been used for a variety of applications because of their outstanding properties such as good chemical and thermal stability, high electrical resistivity and wear resistance. Amorphous Al₂O₃ thin films are discussed as a potential alternative for SiO₂ as complementary metal-oxide-semiconductor transistor gate dielectric, which demands a high thermodynamic stability and interface quality [1]. Furthermore amorphous alumina coatings are employed as heat and electrical insulating coatings for W-Ta-thin thermocouples [2] and magnetohydrodynamic generators [3].

The transition aluminas γ -, δ -, and θ -Al₂O₃ are widely used as catalyst in chemical processes because of their catalytic activity and high surface area [4–6]. However, due to their metastable nature these phases transform to α -Al₂O₃ at elevated temperatures which limits the application range of the transition alumina phases to only low temperature chemical processes.

While α -Al₂O₃ coatings have been applied in surface protection of cutting tools for many years, most of the commercial products are chemical vapor deposited [7,8] on Cemented Carbide substrates. Although the thermodynamically stable α -Al₂O₃ phase (space group $R\bar{3}c$, corundum) is often used for applications at high thermal and mechanical load, the required deposition temperature in excess of 1000 °C [9] limits the use of available substrate materials. During the mid 90s synthesis pathways for low temperature crystalline alumina were investigated by [10,11]. Most published alumina growth data suggest that ionized [10]

and energetic [12–15] film forming species are prerequisites for crystalline growth at low temperatures. Ramm et al. [16] reported the synthesis of a corundum type α -(Al_{1-x}Cr_x)₂O₃ solid solutions by pulsed arc evaporation at 500–600 °C at non-equilibrium conditions as the corresponding phase diagram [17] shows the formation of α -(Al_{1-x}Cr_x)₂O₃ solid solutions at temperatures larger than 1200 °C over the whole composition range.

Besides the thermodynamically stable α -Al₂O₃ phase also the metastable γ -Al₂O₃ (space group $Fd\bar{3}m$) has been investigated as a potential alternative for wear resistant applications [18]. However, due to its metastable nature, physical vapor deposited [18] γ -Al₂O₃ transforms to the α -Al₂O₃ phase. According to high temperature XRD data reported by Trinh et al. the transformation occurs in the range of 950–975 °C [19], which restricts the applicability of γ -Al₂O₃ coatings to temperatures lower than 950 °C. Musil et al. [20] reported the transition of γ - to α -Al₂O₃ at 1050 °C for magnetron sputtered alumina thin films. The formation of the θ -Al₂O₃ was also observed at this temperature, however, only in mixture with the evolving α -Al₂O₃ phase. Furthermore, Edlymayr et al. [21] observed the formation of the intermediate δ -Al₂O₃ phase at 900 °C in addition to γ -Al₂O₃. The intermediate γ -/ δ -Al₂O₃ phases then transformed to α -Al₂O₃ at 1100 °C. Thus, identifying strategies to restrain phase transformations is a key challenge to be addressed for extending the application temperature range of metastable alumina polymorphs.

In this context the addition of alloying elements such as Er [22], La [23], Sr [24] and Y [22] on the thermal stability of alumina polymorphs has been investigated. The effect of Si additions on the stability of alumina polymorphs was experimentally investigated in the past [25]. However, the underlying mechanisms driving the observed retardation of phase transitions are not fully understood.

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In this paper the effect of the Si concentration on the thermal stability of silicon alloyed alumina thin films deposited by filtered cathodic arc is investigated systematically. The aim of this work is to identify the underlying mechanism responsible for the enhanced thermal stability of silicon alloyed alumina. It is shown that Si additions expand the stability window of metastable γ -/ δ - and θ - Al_2O_3 phases and restrain the α - Al_2O_3 phase formation. Based on our phase formation and bonding data we suggest that the presence of intergranular SiO_2 impeding mobility is responsible for the Si addition induced changes in stability. The random distribution of Si in the alumina lattice appears to be in conflict with XPS data.

2. State of the art

The following section reviews the different mechanisms responsible for the thermal stabilization of the metastable alumina phases upon Si alloying proposed in literature.

Iler et al. [26] reported the thermal stabilization of γ - Al_2O_3 by 150 °C by addition of silicic acid to fibrillar colloidal $\text{AlO}(\text{OH})$ (boehmite). The authors postulated the formation of a glassy and viscous phase upon the reaction of silica with alumina. Thereby silica wets the alumina surface and restrains the migration of alumina. However, no experimental evidence was given in support of this notion. Gani and McPherson [27] studied the structure of Al_2O_3 - SiO_2 sub-micron powders which were prepared by oxidation of aluminum-silicon halides in an oxygen-argon high frequency plasma flame. The authors reported that the addition of SiO_2 restrained the formation of α - Al_2O_3 from 1230 °C to temperatures ≥ 1500 °C. The restrained transformation of the metastable γ -/ δ - and θ - Al_2O_3 phases to α - Al_2O_3 was suggested to be due an increase of the activation energy of the γ -/ δ - and θ - Al_2O_3 to α - Al_2O_3 transformation process. The authors suggested that the incorporation of Si ions at tetrahedral sites of the initial γ - Al_2O_3 structure may increase the activation energy of the α - Al_2O_3 phase formation. This was based on the high energy which is required to break Si-O bonds in the distorted face centered cubic packing of oxygen ions of the γ - Al_2O_3 phase and rearrange oxygen ions to the close packed hexagonal packing of the α - Al_2O_3 phase.

Mekasuwandumrong et al. [25] investigated the thermal stability of χ -alumina solutions synthesized by solvothermal methods and reported a retardation of 100 °C of the α - Al_2O_3 formation. They [25] inferred a homogeneous incorporation of silicon atoms in the alumina matrix based on the crystallization of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) which according to the authors requires atomic-scale mixing of alumina and silica. The increased thermal stability of χ -alumina was argued to be due to the reduction of hydroxyls in the Si alloyed alumina. Yoldas et al. [28] investigated the effect of silicon addition on monolithic active alumina prepared by sol-gel method. They reported a retardation of the α - Al_2O_3 formation from 1200 °C to 1380 °C upon 6% alloying. The authors speculate that silicon occupies certain sites in the alumina structure without specifying the substitutional sites. These substitutions were assumed to cause disturbance in the lattice and restrain phase transition by increasing the structural stability of the alumina structure.

On the basis of the research discussed above it can be learned that the addition of Si to alumina appears to retard the alumina transformation sequences and stabilize the metastable γ -/ δ -/ θ -phases. However, different mechanisms leading to this retardation effect are proposed in the literature. Iler et al. [26] suggest that the formation of a glassy silica phase decreases mobility as schematically depicted in Fig. 1a. Other studies [25,27,29] suggest on the other hand that the enhanced stability of metastable phases is due to incorporation of Si into the alumina lattice. This is usually referred to as Si incorporated intermediate Al_2O_3 or Al-Si spinel phase, as schematically shown in Fig. 1b. This Si incorporation notion has been a point of controversy in many studies [29–35]. The Al-Si spinel phase exhibits poorly defined X-ray diffraction peaks similar to those of γ - Al_2O_3 . To clearly distinguish the diffraction peaks originating from γ - Al_2O_3 and from an Al-Si spinel phase based on XRD data is hence challenging.

Chakraborty et al. [34,35] suggested based on transmission electron microscopy (TEM) analysis of leached samples that the spinel type transition phase which is observed during the kaolinite-mullite transition sequence reveals a Al-Si spinel with compositions similar to mullite ($\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of 3/2). A similar suggestion was made by Okada et al. [32] by using analytical TEM. In contrast to these findings Brown et al. [36] deduced by Si nuclear magnetic resonance (NMR) spectroscopy pure γ - Al_2O_3 as intermediate phase of the kaolinite-mullite reaction sequence. Similar results were reported by Hoffmann et al. [33] and Wei et al. [37] by using TEM analysis and Si NMR spectroscopy. The authors concluded that the spinel phase was Si-free γ - Al_2O_3 and no evidence for an Al-Si spinel was found.

Gerardin et al. [29] investigated the effect of mixing homogeneity of three stoichiometric sol-gel precursors prepared in three different ways on the phase formation sequence of mullite by NMR, X-ray diffraction and drop solution calorimetry. The results obtained by Gerardin et al. suggest that the degree of intermixing of alumina and silica in the amorphous state is determining the crystallization path and, therefore, the possibility and temperature of Al-Si spinel formation, silica segregation and mullitization.

The question whether Si is incorporated into physical vapor deposited γ - Al_2O_3 grains (Fig. 1b) or is segregated at the grain boundaries (Fig. 1a and c) remains unanswered. From this review it is also evident that the underlying mechanisms responsible for the experimentally reported enhanced thermal stability of the metastable alumina phases upon Si alloying are controversially debated for other synthesis pathways than PVD.

All theoretical efforts in describing the phase stability of alumina polymorphs on the atomistic level assume that the alloying element is incorporated into the metastable alumina phases: comparative density functional theory (DFT) studies on θ - and α - Al_2O_3 by Wallin et al. [38] revealed that addition of Mo, W, Sc, Si, B, Cu, Cr and Co influence the stability of the θ - Al_2O_3 phase. It was reported that Cu stabilizes α - Al_2O_3 while the other additives shift the relative stability toward θ - Al_2O_3 . Jiang et al. [39] investigated the effect of Si, Cr, Ti, Sc and Y additives on the relative stability of γ - Al_2O_3 with respect to α - Al_2O_3 . By using ab initio calculations, the authors proposed that addition of Si with

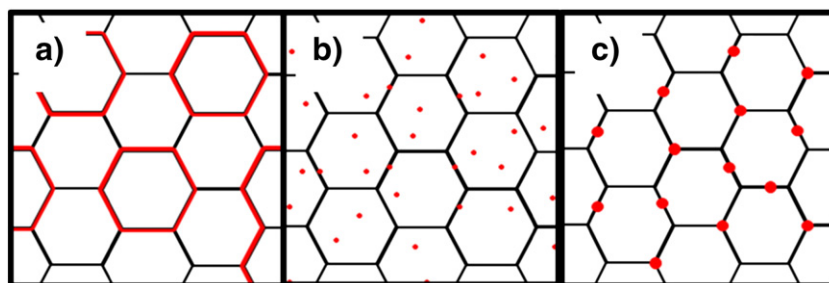


Fig. 1. Schematics of a) SiO_2 wetting of Al_2O_3 grains/grain boundaries, b) Si incorporation into the Al_2O_3 matrix and c) segregation of SiO_2 regions between Al_2O_3 grains. Hexagons indicate Al_2O_3 grains and red areas symbolize the presence of SiO_2 .

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