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In situ study of the crystallization kinetics of Al_2O_3 coatings deposited from aluminum isopropoxide during thermal annealing

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Aluminum oxide exists in several polymorphic modifications, each of which determines a specific set of properties important for protective, thermal barrier, and dielectric coatings. The temperature evolution of the phase composition and microstructure of CVD-deposited Al_2O_3 coatings obtained from aluminum isopropoxide was investigated during annealing up to 1200 °C. X-ray diffraction and electron microscopy data were correlated to reveal the mechanisms of crystallization and the formation of various polymorphic modifications of Al_2O_3.

Keywords: chemical vapor deposition, thin films, aluminum oxide, corundum, thermal stability.

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Aluminum oxide (Al_2O_3) is a polymorphic material that includes a number of metastable modifications (γ, δ, θ, κ, etc.) and a stable α-phase. Each modification has its own crystallographic parameters and physical and mechanical properties (density, hardness, permittivity, etc.), which is why materials based on Al_2O_3 have a wide use range of uses spanning from wear-resistant and protective coatings to thermal barrier and electrical applications [1,2]. Phase composition control is of fundamental importance, since it largely determines the performance characteristics of the material.

Classical methods of chemical deposition of Al_2O_3 coatings rely on the use of precursors, such as aluminum chloride and trimethylaluminum. The high reactivity of these precursors, which is coupled with toxicity and pyrophoricity, is a barrier to their practical application and necessitates enhanced safety measures [3]. In view of this, alternative technological approaches utilizing safer precursors are of interest [4,5].

In the present study, aluminum isopropoxide ($Al(OC_3H_7)_3$) was chosen as a precursor for CVD (chemical vapor deposition) synthesis of Al_2O_3 coatings, since it provides a number of technological and practical advantages. Aluminum isopropoxide is highly volatile at a relatively low evaporation temperature (~ 150 °C). This distinguishes it from heavier alcoxides (e.g., aluminum butoxide), which require higher evaporation temperatures or deeper vacuum [6]. In addition, the products of thermal decomposition of isopropoxide (propylene and isopropanol) are easily removed from the reaction zone, minimizing the risk of carbon inclusions in the coating, which is especially important for synthesis of pure oxide films with high dielectric and chemical resistance. Moreover, isopropoxide is relatively safe to handle: it is not pyrophoric or toxic and does not require special transportation and storage conditions (unlike, e.g., trimethylaluminum and aluminum chloride, which are widely used in ALD processes [3,5]). Another commonly used organic precursor is aluminum acetylacetonate ($Al(C_5H_7O_2)_3$), which is distinguished by a high thermal activity in an oxidizing environment at low temperatures (~ 250 °C) [4]. However, the decomposition of acetylacetonate requires an oxidizing environment, since its thermal dissociation in an inert atmosphere is impeded and leads to synthesis of coatings with carbon residues [7]. In contrast, aluminum isopropoxide decomposes readily in both oxidizing and inert environments at temperatures starting approximately from 300 °C. The final important factor is the high coating growth rate, which reaches $\sim 0.9\,\mu$m/min [8]. This exceeds significantly the typical values attainable in most CVD processes for Al_2O_3 and is indicative of a high efficiency of isopropoxide used as a precursor.

The present study is aimed at examining the mechanisms of phase transformations in Al_2O_3 coatings deposited by CVD from aluminum isopropoxide. The study is fundamental in nature and reveals the potential of this approach in obtaining both the stable α-phase and metastable modifications (γ, δ, θ). X-ray diffraction spectra and morphology data recorded during thermal annealing from room temperature to 1200 °C were analyzed, and a comparison of phase transformations with the observed microstructural transformations was made. The obtained results reveal the possibility of controlling the phase composition of coatings through temperature regimes of annealing.

Al_2O_3 coatings were synthesized by CVD in a specialized reactor (its diagram and operating principle were detailed earlier in [8]). Aluminum isopropoxide was used as a precursor. The precursor and the substrate holder heating temperature was 170 ± 10 °C and 600 ± 20 °C, respectively. The pressure in the chamber was maintained at a level of $(1.5 \pm 0.2) \cdot 10^{-1}$ Torr. Polycrystalline sintered silicon carbide SiC wafers (for scanning electron microscopy (SEM)) and single-crystal strontium titanate

$SrTiO_3$ (110) wafers (for X-ray diffraction analysis) were used as substrates. Their preliminary preparation included mechanical hydroabrasive machining, which was performed to achieve surface roughness $R_a = 250 \pm 30$ nm, and subsequent cleaning in isopropyl alcohol in an ultrasonic bath for 10 min. The coating deposition rate was $0.85 \pm 0.1\,\mu$m/min, and the thickness of synthesized coatings was $1.8 \pm 0.2\,\mu$m.

X-ray diffraction spectra were recorded *in situ* in the process of sample heating using an XRD-7000S (Shimadzu) diffractometer and CuK_α radiation. The recording range was $2\Theta = 25-42°$, since it covers the characteristic peaks of Al_2O_3 modifications, but the $SrTiO_3$ substrate reflections are excluded. The samples were heated from room temperature to 1200 °C. The heating rate was 25 °C/min and 10 °C/min within the ranges of 30–1000 °C and 1000–1200 °C, respectively. The samples for SEM examination were prepared by annealing in a muffle furnace (PM-2PTR, Plavka.Pro) in air for 60 min at the same heating rate as in the X-ray diffraction study. SEM studies were carried out using an Apreo 2S (Thermo Fisher Scientific) microscope fitted with an Octane Elect (EDAX) energy-dispersive spectroscopy (EDS) platform.

Figure 1 shows the X-ray diffraction maps of the coating heated from 30 to 1200 °C. SEM images of the as-deposited samples and the samples subjected to annealing in a furnace for 60 min at control temperatures of 600, 800, 1000, and 1200 °C are presented in Fig. 2. The as-deposited coating is characterized by a pronounced columnar microstructure. The material is predominantly amorphous, which is confirmed by X-ray diffraction analysis data. The as-deposited sample has only a weak peak of the γ-phase of aluminum oxide at angle $2\Theta = 37.5°$.

With subsequent heating, the coating crystallizes, which is evidenced by an increase in intensity of the corresponding diffraction peak at temperatures up to ~ 525 °C. Additional reflections of the δ- and θ-phases of aluminum oxide emerge at $2\Theta = 37.7$ and 38.3°, respectively, at a temperature of 500–600 °C. The SEM image of the sample annealed at 600 °C reveals sintering of the coating material and densification of its structure, but its fine-grained nature is retained.

An enhancement of crystallinity of the coating, which is manifested in narrowing of the reflection of the γ-phase of Al_2O_3, is seen upon reaching ~ 800 °C. At the same time, the intensity of this reflection decreases due to $\gamma \rightarrow \delta \rightarrow \theta$ phase transformations, and the reflection of the θ-phase becomes dominant as a result. This is coupled with the emergence of a new reflection of the θ-phase at $2\Theta = 38.75°$ at ~ 775 °C. The SEM image of the sample annealed at 800 ° reveals an increase in grain size of the coating without any noticeable increase in porosity.

Further heating to a temperature of 1000 °C is accompanied by continued $\gamma \rightarrow \delta \rightarrow \theta$ phase transitions. This is evidenced by an increase in intensity of (111) and (401) θ-Al_2O_3 reflections and the formation of a new diffraction peak of the θ-phase at $2\Theta = 39.2°$ at ~ 1000 °C. The formation of the θ-phase is indicative of an increase in

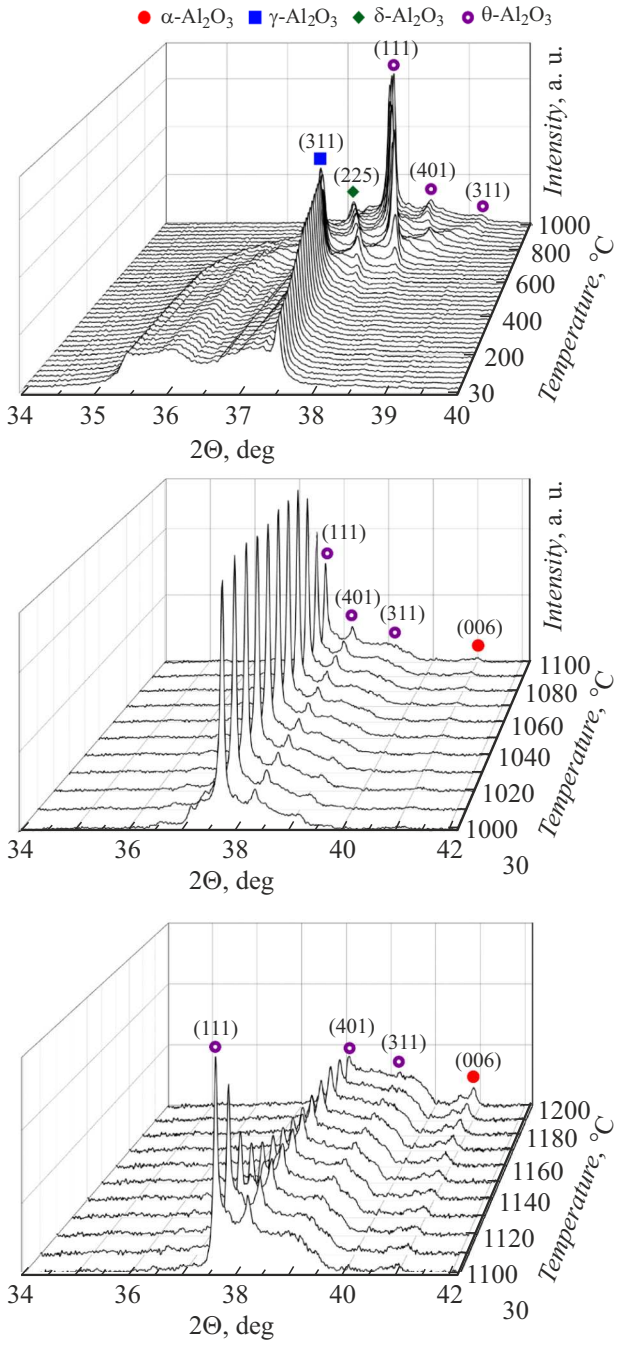

Figure 1. X-ray diffraction maps of the sample heated from 30 to 1200 °C.

size of crystals and partial densification of the coating. The peaks of γ and δ-phases vanish at ~ 900 °C and ~ 925 °, respectively. When the sample is heated to temperatures above 1000 °C, a new reflection at $2\Theta = 41.08°$ identified as α-Al_2O_3 arises. Its emergence at temperatures this high verifies the validity of identification and provides evidence of the onset of formation of a stable α-phase in the coating. The SEM image of the sample annealed at 1000 °C demonstrates pronounced changes in the microstructure: the coating becomes denser, shrinkage occurs, and individual

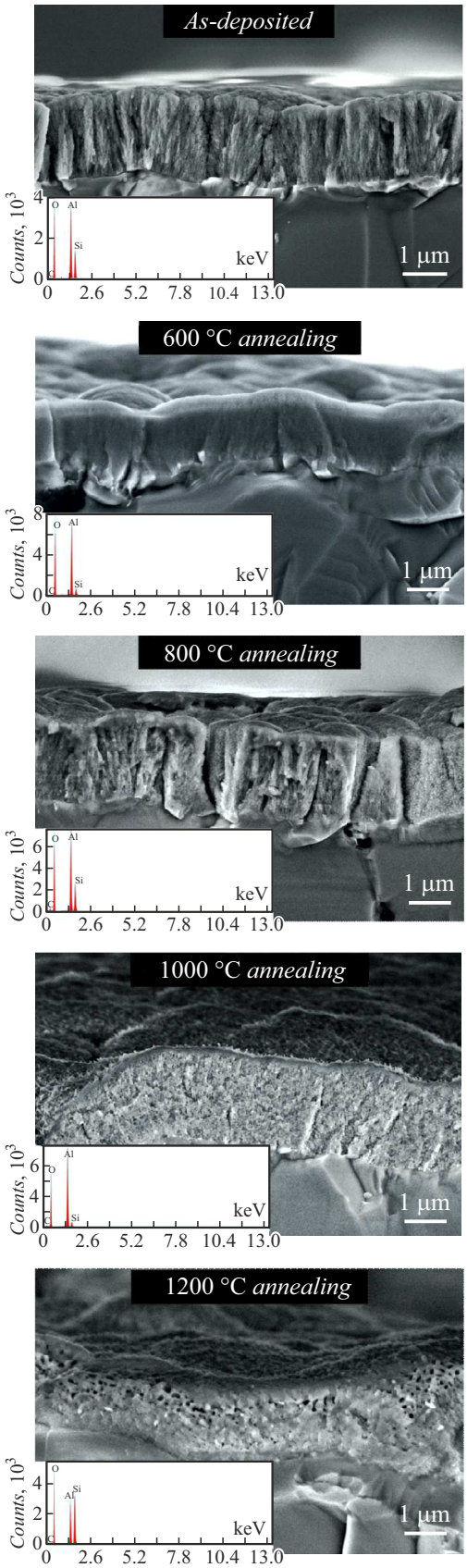

Figure 2. SEM images and EDS spectra of the as-deposited coating and samples after annealing at temperatures of 600, 800, 1000, and 1200 °C.

grains become visible. It is known that the transformation of metastable phases of Al_2O_3 into the α modification is accompanied by a reduction of crystal lattice parameters, which induces tensile stresses and local formation of microcracks [9].

With further heating to 1200 °C, the X-ray diffraction pattern changes: the intensity of reflections of the transition modifications decreases, while the intensity of the α-phase increases, and the peak assumes a distinct shape. The presence of κ modification [8] alongside with the identified aluminum oxide phases cannot be excluded. The formation of pores in the coating during high-temperature annealing is likely to be attributable in part to the chosen heating rate. It was demonstrated in [10] that a lower heating rate leads to a more complete densification of the structure.

EDS analysis of the coatings was performed in order to evaluate their elemental composition at different stages of thermal annealing. Signals of aluminum and oxygen in the coating composition were recorded in all the examined samples, while the presence of silicon and carbon is attributable to the contribution of the silicon carbide substrate in the analysis zone. The Al:O atomic ratio in the coating varied with annealing temperature: 0.5 ± 0.1 for the as-deposited amorphous coating, 0.6 ± 0.1 at 600 °C, 0.5 ± 0.1 at 800 °C, 0.7 ± 0.1 at 1000 °C, and 0.2 ± 0.1 at 1200 °C. Near-stoichiometric values ([Al]:[O] ≈ 0.66 for Al_2O_3) are typical of all samples except for the one annealed at 1200 °C. This deviation observed at 1200 °C is apparently associated with the onset of intense oxidation of the substrate surface at high temperatures, which results in an increase in oxygen content in the examined volume due to the contribution from formed SiO_2.

The results of *in situ* X-ray diffraction analysis revealed the temperature ranges of phase transformations of Al_2O_3 that reflect the kinetic features of thermal evolution of the material. The $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ phase sequence is observed with gradual heating and is accompanied by a change in intensity and width of the corresponding diffraction reflections. Specifically, the γ-phase is identified in the as-deposited sample, forms at annealing temperatures up to ~ 525 °C, and vanishes by ~ 900 °C; the δ-phase is observed within the 600–925 °C interval; and the θ-phase is stabilized at temperatures from ~ 775 to 1100 °C, which is followed by the formation of the stable α-phase. These temperature ranges characterize the sequence and nature of phase transformations, suggesting that this sequence may be regarded as a manifestation of thermokinetics of transformations in thin-film Al_2O_3. Thus, a comprehensive study of phase and morphological changes in coatings deposited by CVD from aluminum isopropoxide was carried out. The identified sequence of phase transformations is consistent with literature data (specifically, the pattern observed in thermal annealing of boehmite [10]). A relation between phase transformations and morphological changes in coatings was established: densification of the structure and grain growth at the early stages are followed by the formation of a coarse-crystalline α-phase during

high-temperature annealing. These data are of practical importance for control over heat processing and formation of the phase composition of Al_2O_3 coatings tailored to deliver specific performance characteristics.

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Conflict of interest

The authors declare that they have no conflict of interest.

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