

Chemical Vapor Deposition of Aluminum Oxide Thin Films Using Aluminum Isopropoxide as a Precursor

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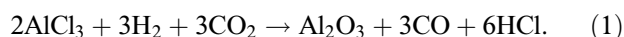
The chemical vapor deposition process of aluminum oxide thin films using aluminum isopropoxide as a precursor was investigated. Deposition parameters enabling a high growth rate of up to $\sim 0.94 \mu\text{m}/\text{min}$ were identified. The resulting coatings were found to have an amorphous structure, with subsequent annealing at 1200°C inducing crystallization and the formation of $\alpha\text{-Al}_2\text{O}_3$, $\kappa\text{-Al}_2\text{O}_3$, and $\gamma\text{-Al}_2\text{O}_3$ phases. It was demonstrated that aluminum isopropoxide allows the synthesis of high-purity coatings at relatively low deposition temperatures.

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

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Functional coatings based on aluminum oxide are used for various purposes: as protective coatings to increase the wear resistance of products or protect against corrosion, as thermal barrier and dielectric coatings, etc. [1]. A number of approaches to application of thin-film coatings based on aluminum oxide, including both physical (PVD) and chemical (CVD) vapor deposition methods [1,2], have already been developed. Chemical deposition techniques are used most often, since they allow one to achieve high growth rates and form coatings with controlled structures and phase compositions.

The classical methods of synthesis involve the use of aluminum chloride and trimethylaluminum as precursors [3,4]. In the former case, deposition is carried out by pyrolysis of aluminum chloride with water vapor produced in the water–gas shift reaction from a gas mixture of hydrogen and carbon dioxide. The overall reaction formula is as follows:



In the case of trimethylaluminum, the coating is deposited by hydrolysis of trimethylaluminum with water:



Both methods have a number of limitations. In the case of AlCl_3 , the release of corrosive HCl in the course of the reaction leads to degradation of the reactor equipment, forcing one to use costly materials, such as quartz or ceramics. The hygroscopicity of AlCl_3 and its hydrolysis with the release of toxic vapors also create risks for personnel and require complex safety systems. The most critical restriction is the high process temperature (above 800°C), which limits the range of suitable substrates and contributes to an enhancement of internal thermal stresses in the coating, which may exert a negative influence on its adhesion properties

and durability. The use of trimethylaluminum allows one to reduce the process temperature, since its decomposition temperature is 332°C [5], and the use of plasma activation methods provides an opportunity to lower the reaction temperature further to $< 200^\circ\text{C}$, preventing the degradation of heat-sensitive substrates [6]. However, $\text{Al}(\text{CH}_3)_3$ itself is a pyrophoric substance and ignites spontaneously in air; therefore, it must be stored under strict conditions and handled in an inert atmosphere. The accumulation of carbon impurities due to insufficient purification of the gas phase and the high cost of the precursor complicate the scaling of this method further.

Thus, the development of methods utilizing alternative safe precursors and enabling the deposition of aluminum oxide at relatively low temperatures appears to be a relevant scientific challenge. One of the promising candidates here is aluminum isopropoxide $\text{Al}(\text{OC}_3\text{H}_7)_3$, which combines the advantages of organometallic precursors, such as low decomposition temperatures and high purity of coatings, and is devoid of certain disadvantages typical of aluminum chloride and trimethylaluminum (i.e., is more stable and significantly less toxic and dangerous in storage and handling). The aim of the present study is to test experimentally the approach to CVD synthesis of thin-film coatings based on aluminum oxide with aluminum isopropoxide used as a precursor and to perform structural characterization of these coatings.

Coatings were synthesized in a specialized CVD reactor that is shown schematically in Fig. 1. The reactor chamber was fitted with a vacuum system; the pressure in the chamber was maintained at a level of $1\text{--}1.5 \cdot 10^{-1}$ Torr. To prevent overheating, the chamber was constructed with jacketed walls and cooled with circulating water. Aluminum isopropoxide powder was used as a precursor. The precursor was evaporated by heating a tungsten wire. The wire heating temperature varied within the range of $130\text{--}200^\circ\text{C}$ (the melting point of aluminum

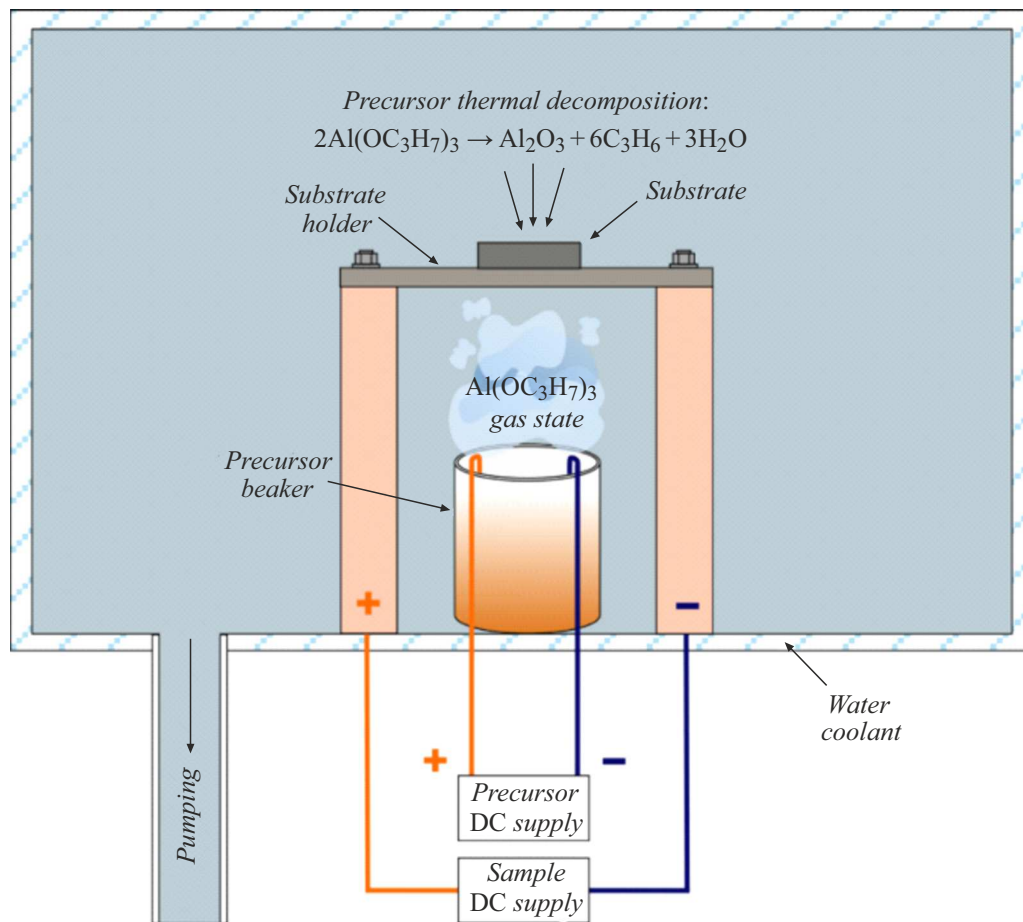
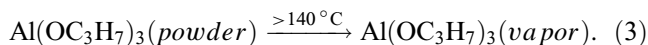


Figure 1. Schematic diagram of the experimental setup for coating deposition.

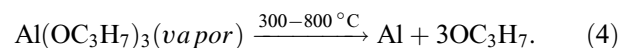
isopropoxide is 112°C , and its boiling point is 140°C . The substrate was heated by a tantalum substrate holder; in the course of experiments, the substrate temperature varied within the range of $300\text{--}800^\circ\text{C}$. The substrates used were single-crystal silicon wafers with the $\langle 100 \rangle$ orientation (for infrared Fourier spectroscopy) and sapphire wafers with the $\langle 0001 \rangle$ orientation. Prior to the application of coatings, the surface of these substrates was subjected to hydroabrasive treatment, which ensured a roughness value of $R_a = 250 \pm 30 \text{ nm}$.

An aluminum oxide film forms in the proposed procedure due to the thermochemical decomposition of the aluminum isopropoxide precursor. An important factor here is the interaction of decomposition products on the substrate surface (in the region of the heated substrate holder), which enhances the efficiency of material deposition. The precursor is first heated to the boiling point, which leads to its transition to the gaseous phase:

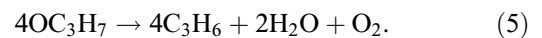


Following vaporization, the precursor interacts with the hot substrate. Aluminum isopropoxide decomposes on the substrate surface, breaking the covalent bonds between

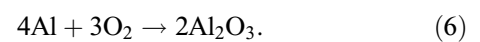
aluminum atoms and isopropyl groups (OC_3H_7):



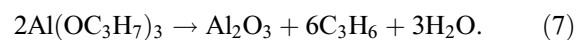
Isopropyl groups dehydrate to form propylene (C_3H_6) and water (H_2O) in the gas phase:



Aluminum atoms remaining on the surface react with oxygen to form aluminum oxide (Al_2O_3), which is deposited on the substrate as a coating:



The overall formula of the process is as follows:



The following analytical methods were used in the study: optical microscopy (Axio Imager.A2m, ZEISS), transmission electron microscopy (TEM) (JEM-2100F, JEOL), infrared Fourier spectroscopy (Nicolet 5700, Thermo Electron), and X-ray diffraction analysis in the grazing beam mode with CuK_α -radiation (XRD 6000, Shimadzu). A muffle furnace (PM-2PTR, Plavka.Pro) was used to anneal the samples.

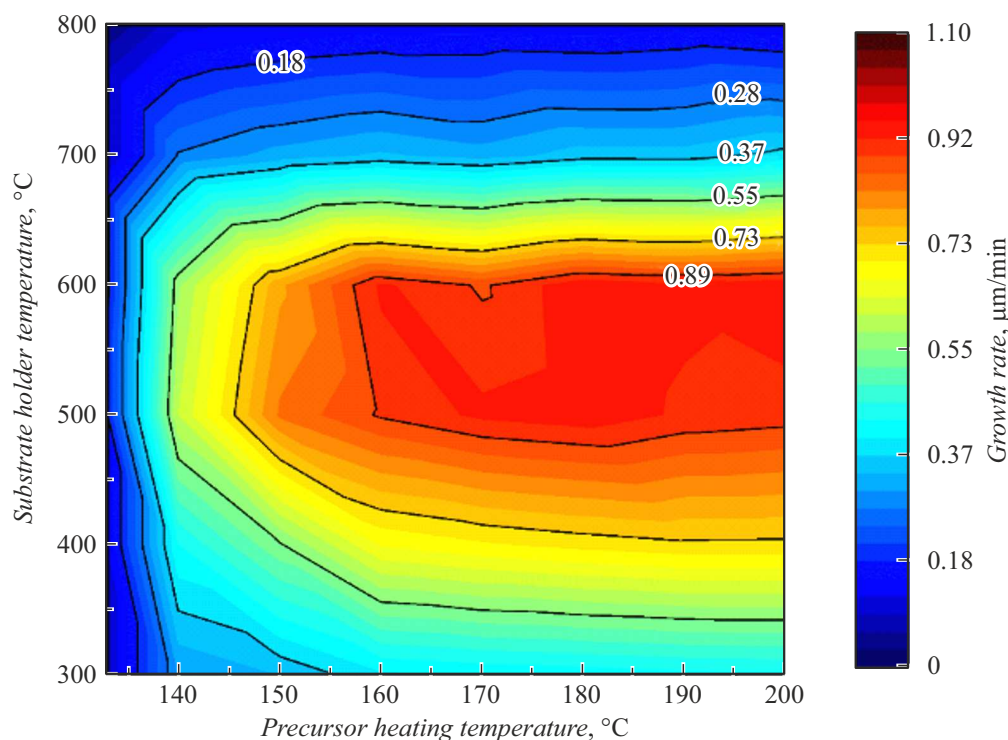


Figure 2. Map of coating growth rates plotted as functions of temperature of the precursor and the substrate holder.

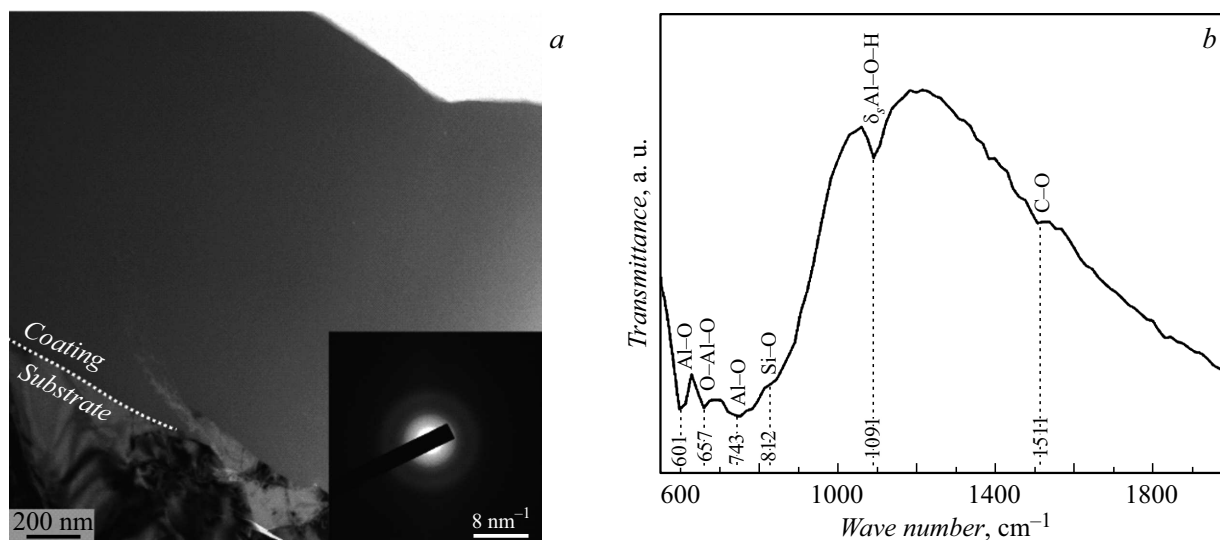


Figure 3. *a* — TEM image of the cross section of the coating and its electron microdiffraction pattern (inset); *b* — IR transmittance spectrum of the coating.

Figure 2 shows the diagram of coating growth rate as a function of the deposition parameters.

The coating synthesis process was initiated when the temperature of the precursor electric heater reached $\sim 140^\circ\text{C}$. The deposition rate increased significantly (by 43% on the average) as the heater temperature grew from 140 to 160°C . Specifically, at a substrate temperature of 500°C , the deposition rate increased from ~ 0.61 to $\sim 0.89\ \mu\text{m}/\text{min}$. This is attributable to a more active replenishment of active precursor radicals in the reaction

zone. However, with a further temperature rise, the deposition rate reached a plateau, and an increase in temperature to 200° led only to an increase in precursor consumption without any significant enhancement of the deposition rate (6% on the average). Thus, the optimum precursor temperature is 160°C , which provides a balance between deposition efficiency and process economy.

The substrate temperature is crucial to deposition kinetics. At temperatures below 400°C , the growth rate remained low, since the energy was insufficient for efficient

decomposition of the precursor molecules. The maximum deposition rate (up to $\sim 0.94 \mu\text{m}/\text{min}$) was observed within the $450\text{--}650^\circ\text{C}$ range, where the process of precursor decomposition on the substrate surface was the most intense. However, when the level of 650°C was exceeded, the growth rate decreased due to desorption of active components and the fact that the precursor decomposed partially in the gas phase before reaching the surface.

Thus, the optimum conditions for coating deposition include a precursor heating temperature of 160°C and a substrate heating temperature of $450\text{--}650^\circ\text{C}$. These parameters ensure a high coating growth rate with minimum precursor consumption and process stability.

The examination of synthesized coatings revealed that all the obtained films had an amorphous structure. The TEM image (Fig. 3, *a*) shows a uniform film without any signs of crystalline inclusions or grain boundaries. The lack of a crystalline structure was confirmed by selected area electron diffraction (SAED): the diffraction patterns did not feature well-defined rings or point reflections characteristic of crystalline phases.

Figure 3, *b* shows the infrared absorption spectrum of coatings deposited on substrates made of monocrystalline silicon. Bands corresponding to the stretching vibrations of Al–O bonds at wave numbers of 601 and 743 cm^{-1} , which is typical of aluminum oxide [7], were identified in the „fingerprint“ region ($< 1500\text{ cm}^{-1}$). The band at 657 cm^{-1} is associated with the O–Al–O deformation vibrations [8]. The band at 1091 cm^{-1} is indicative of the $\delta_s\text{Al–O–H}$ mode, which suggests partial hydroxylation of the surface [9]. The band at 812 cm^{-1} corresponds to the deformation vibrations of Si–O [10], revealing the interaction of the silicon substrate with the precursor and the formation of a thin surface layer of silicon oxide. The additional band in the region of 1511 cm^{-1} may be associated with the adsorption of carbon-containing compounds on the sample surface and the formation of a surface layer of silicon oxide. Thus, the results of FTIR analysis confirmed that the deposited coating consisted of aluminum oxide.

The results of X-ray structural analysis confirmed that the synthesized coatings were amorphous (Fig. 4). Thermal annealing at 1200°C was performed in air for an hour in order to assess their crystallization capacity and the possibility of controlling the phase composition. This led to the formation of several aluminum oxide phases, including $\alpha\text{-Al}_2\text{O}_3$ (corundum), $\kappa\text{-Al}_2\text{O}_3$, and $\gamma\text{-Al}_2\text{O}_3$ [11]. These results are consistent with the known data on phase transformations of Al_2O_3 at high temperatures, which suggest that the formation of pure corundum ($\alpha\text{-Al}_2\text{O}_3$) requires long-term annealing. The obtained data confirm that the coatings have the capacity to crystallize in the process of high-temperature annealing. However, precision control of the phase composition and crystallinity of coatings remains a challenge to be addressed in further comprehensive research.

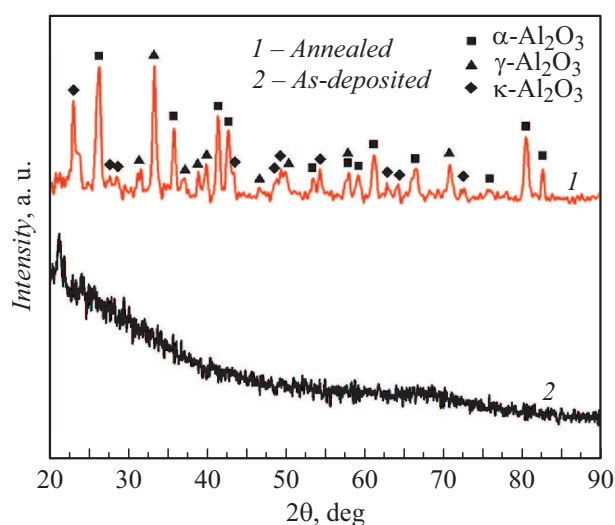


Figure 4. X-ray spectra of the as-deposited and annealed coatings.

Thus, an approach to application of thin-film aluminum oxide coatings by the CVD method with the use of aluminum isopropoxide was tested successfully. It was demonstrated that the proposed method provides a high deposition rate (up to $0.94 \mu\text{m}/\text{min}$) and the resulting coatings have a dense and uniform structure. The examination of coatings revealed their amorphous nature, and thermal annealing at 1200°C resulted in phase transformations and the formation of α -, κ -, and $\gamma\text{-Al}_2\text{O}_3$. In addition, the method is relatively easy to implement, which makes it promising for further study and scaling.

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Conflict of interest

The authors declare that they have no conflict of interest.

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