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Surface morphology and optical properties of Al_2O_3 thin films deposited by ALD method

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ABSTRACT

Purpose: The paper presents the results of investigations on the changes in surface morphology, roughness, and thickness of the prepared aluminium oxide thin films as dependent on conditions of the thin films preparation.

Design/methodology/approach: Thin films have been prepared with use of atomic layer deposition (ALD) method. The changes of surface morphology have been observed in topographic images performed with the atomic force microscope (AFM). Obtained roughness parameters have been calculated with XEI Park Systems software. The thickness distribution have been measured with spectroscopic ellipsometry. The optical transmission spectra have been measured with UV-Vis spectrophotometry.

Findings: Results and their analysis show that the atomic layer deposition method allows the deposition of homogenous thin films of Al_2O_3 with the desired geometric characteristics and good optical properties.

Practical implications: The technology of atomic layer deposition of aluminium oxide thin films causes that mentioned thin films are good potential material for optics, optoelectronics and photovoltaics.

Originality/value: The paper presents results of investigations on aluminum oxide thin films prepared with atomic layer deposition method on glass substrate

Keywords: Thin films; Aluminum oxide; Atomic force microscope; Spectroscopic ellipsometry

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PROPERTIES

1. Introduction

Atomic Layer Deposition (ALD) is a more recent variation of Chemical Vapor Deposition (CVD). Currently, this method is used in branches of industry such as microelectronics, optoelectronics, photovoltaics or medicine [1-9]. In the technique, the injection of the two reactants to the heated surface is separated into two steps. In first step, the substrate is exposed to the precursor after which this reactant is pumped away with an inert gas. During the exposure a monolayer of the reactant adsorbs to the substrate. Then in the second step a reagent is introduced into the chamber, and it reacts with the monolayer of the first reactant. Subsequently one monolayer of the solid thin film of desired material is formed. Finally, the remaining second reactant and any gas phase reaction products are removed from the chamber. The process is repeated as many times as necessary to grow a thin film with the desired thickness [10-13]. The most frequently used ALD method is a thermally activated. Therefore, temperature of the ALD method is the most important technological parameters, which allows to control the growth mechanism of the thin film. The effect of temperature on the course of deposition can be described by introducing the concept of the so-called. "Temperature Window" (Fig. 1) [14-17].

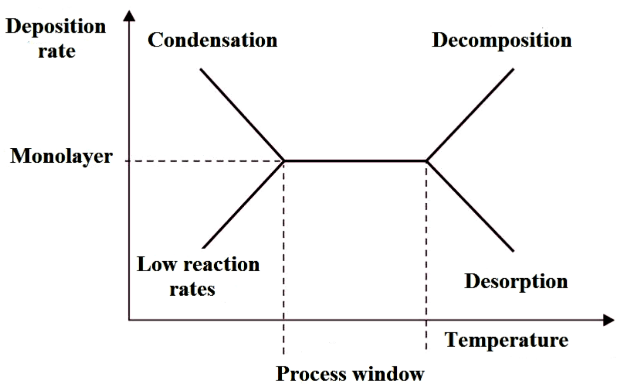

Fig. 1. Temperature window for ALD method

The improper selection of temperature can cause a significant slowdown in the growth of the thin film and its low stability. The temperature in the chamber must be high enough to prevent condensation of the reactants. If the temperature is too low activation energy is not obtained, which could result in incomplete bonds in a monolayer.

The broken reagents can be presented at high temperatures on arolastic products which slows the growth of thin films. The formed monolayer may also be unstable [14-18]. In the early stage of ALD development, the used precursors were the same as those available for the CVD method. However, the specific requirements for strict control of the reactions taking place only on the surface of the coated substrate and connected with the strong reactivity forced the development offered as precursor chemicals used in the ALD method, especially highly reactive organometallic compounds. Examples of precursors used in the ALD method are summarized in Table 1 [19-22]. The use of highly reactive precursors, which immediately reacts with the substrate to form a monolayer and not allowing for further reaction, each cycle results in increase in the thickness of a well-defined value in the range 0.01-0.3 nm.

Table 1.
The selected precursors used in the ALD method

No.	Material	Precursor	Reagent
1	B_2O_3	BBr_3	H_2O
2	Al_2O_3	$AlCl_3$, $AlMe_3$	H_2O, O_3
3	SiO_2	$SiCl_4$, $SiCl_2H_2$	H_2O, O_3
4	TiO_2	$TiCl_4$, $Ti(OMe)_4$	H_2O
5	ZnO	$ZnCl_2$	H_2O
6	Si_3N_4	$SiCl_4$, $SiCl_2H_2$	NH_3
7	TiN	$TiCl_4$, $Ti(NMe_2)_4$	NH_3
8	GaAs	GaCl	AsH_3
9	Lu_2O_3	$Lu[Cp(SiMe_3)]_2Cl$	H_2O
10	$Al_xTi_yO_z$	$AlCl_3$	$Ti(OEt)_4$
11	Pd	$Pd(hfac)_2$	HCOCOOH

With the ALD method very often metal oxides are deposited on the optical devices used in optics, optoelectronics or photovoltaics. Thin films that reduce reflection are widely used wherever maximum use of light energy or to eliminate the effects related with the reflection of light is wanted. The following types of products can be distinguished [23-26]:

- optical devices,
- the monitors, television or mobile phone screens,
- solar cells,
- architectural glass,
- special glass (eg. art).

In the presented work it has been explained how the condition of deposition influence on the surface morphology and optical properties of aluminum oxide thin films prepared by atomic layer method. It has been achieved by analyzing the results obtained by using the atomic force microscope, the scanning electron micro-scope, spectroscopic elipsometry and UV-VIS spectroscopy. The paper presents the results of investigations on the changes in surface morphology, roughness, and thickness of Al_2O_3 thin films obtained by atomic layer deposition method.

2. Materials and methodology

The Al_2O_3 thin films have been deposited by an atomic layer deposition using an R-200 system from Picosun company. As a precursor of Al_2O_3 trimethylaluminum (TMA) has been used, which reacted with water enabling the deposition of the thin films.

The variable technological parameters i.e. temperature of deposition and number of cycles allowed to control the rate of deposition and the thickness of the thin films. On the basis of preliminary tests, the experimentally significant technological conditions which in the part of the experiment remained stable have been chosen (Table 2). Deposition temperature range and the number of cycles has been also established. In Table 3 the process conditions performed experiments are summarized.

Table 2.
Technological conditions of ALD method selected on the basis of preliminary tests

TMA	Carrier gas (N_2) flow rate [sccm]	150
	Pulse time [s]	0.1
	Purge time [s]	3.0
H_2O	Carrier gas (N_2) flow rate [sccm]	200
	Pulse time [s]	0.1
	Purge time [s]	5.0
Substrate temperature [°C]		200-400
Number of cycles		630-1030

Table 3.
Technological conditions of deposition process

No.	Substrate temperature [°C]	Number of cycles
1	300	630
2	300	830
3	300	1030
4	200	630
5	400	630

3. Results and discussion

The films deposited at 300°C by ALD method on a glass substrate have been analyzed based on the number of deposition cycles (Figs 2-4). It has been found out that visible in the images repetitive aggregations of atoms have a similar geometrical features, similar to ellipsoid. With increasing number of cycles of deposition, aggregations of atoms take milder forms, decreasing surface roughness and the surface development. After 630 cycles of deposition, the RMS (root mean square) value is equalled 5.17 nm, while after 1030 cycles, the RMS value decreases to 3.13 nm (Table 4). The R_a value decreases from 4.49 to 2.52 nm with an increasing number of a cycle. The calculated surface development of deposited thin films varies from 4.19 μm^2 (after 630 cycles) to 4.05 μm^2 (after 1030 cycles). In theory, one ALD cycle causes a deposition of a monolayer. However, in real conditions during deposition to reveal structural defects in coated material in the form of discontinuities in the layer. During the next cycle of deposition first of all the gaps are filled. The forces of attraction between atoms in these areas are the most because of the empty atomic bonds. It is therefore concluded that increasing the number of cycles it is possible to fill the defects of construction, which could lead to a reduction in surface roughness (Table 4). Images of the atomic force microscope also allowed to analyse the effect of deposition temperature on the surface morphology of the deposited thin films. The thin film deposited at 200°C on the glass substrate is characterized by small and regular aggregates of atoms (Fig. 5). On the surface of the thin film deposited at 400°C the aggregates are larger and with more elliptical form (Fig. 6). The larger aggregations of atoms have been observed which start to increase with rising temperature deposition. It can be concluded, therefore, that the higher concentrations of atoms appears at a higher temperature deposition, which is consistent with the existence of so-called "temperature window".

Table 4
Summary of roughness parameters for deposited Al_2O_3 thin films

No.	Temperature [°C]	Number of cycles	Surface area [μm^2]	Surface develop. [μm^2]	*RMS*, [nm]	R_a, [nm]
1	300	630	4.00	4.19	5.17	4.49
2	300	830	4.00	4.06	3.54	2.86
3	300	1030	4.00	4.05	3.13	2.52
4	200	630	4.00	4.07	3.28	2.64
5	400	630	4.00	4.09	5.50	3.95

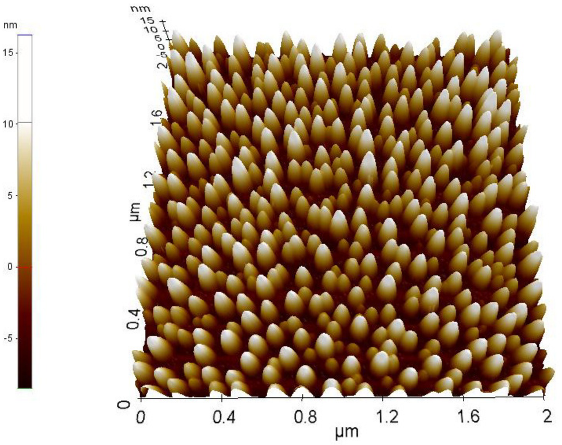

Fig. 2. AFM 3D image of the surface topography of Al_2O_3 thin film deposited on glass substrate at 300°C after 630 cycles

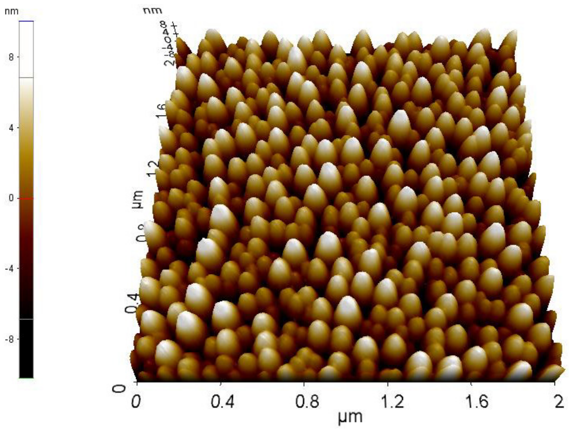

Fig. 3. AFM 3D image of the surface topography of Al_2O_3 thin film deposited on glass substrate at 300°C after 830 cycles

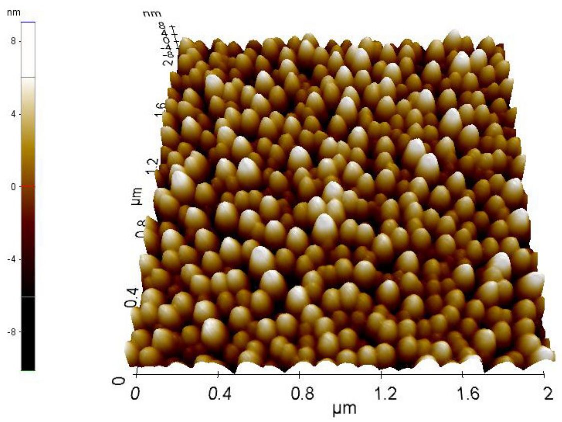

Fig. 4. AFM 3D image of the surface topography of Al_2O_3 thin film deposited on glass substrate at 300°C after 1030 cycles

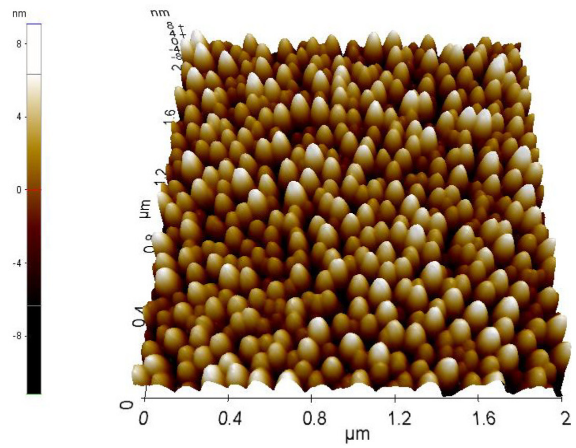

Fig. 5. AFM 3D image of the surface topography of Al_2O_3 thin film deposited on glass substrate at 200°C after 630 cycles

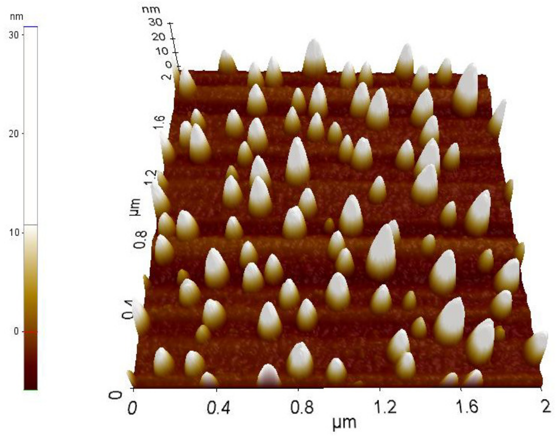

Fig. 6. AFM 3D image of the surface topography of Al_2O_3 thin film deposited on glass substrate at 400°C after 630 cycles

The quality of prepared thin films has been investigated with spectroscopic ellipsometry. The thickness of each film has been measured at 25 points performer SENTECH SE 850 E spectroscopic ellipsometer. The measurements have been carried out at room temperature under angle 70°. The Psi ad Delta measurements have been performed on pure glass substrate as the first step and on substrate with deposited thin film in the second step. The thickness has been determined with Spectra Ray 3 software basing one used model. The thin film of Al_2O_3 has been fitted with Cauchy layer. On the basis of the recorded measurement points the thickness distribution maps of thin films have been obtained using the Origin software (Figs 7-9). It has been noticed that quality of coated thin films is very good. It is also visible that variation of thickness is low and surface of recorded area is very smooth. One can see that surface of thin film deposited with a 300°C after 630 cycles is smooth and uniform and the maximum value of thickness is 65.64 nm and minimum value is 64.03 nm (Fig. 7). The thickness of thin film deposited at 300°C after 830 cycles has been about 88 nm and the deviation from this value is not higher than 1.5 nm (Fig. 8). The thickness of thin film deposited at 300°C after 1030 cycles has been about 107 nm. The maximum value of thickness is 108.56 nm and minimum value is 106.96 nm (Fig. 9).

The optical transmission spectra have been measured with UV-Vis spectrophotometry are presented in Figure 10. The light transmission in all cases is very high and is above 90%. Transmission value decreases with increasing number of deposition cycles. The changes of spectra are connected with thickness value which always will be higher in case of films deposited with a higher number of cycles. The reflectance spectra are the confirmation of ellipsometric measurements. All Al_2O_3 thin films have high transparency which value is over 90%. As required if the material should be useful in optics or optoelectronics its transparency must be above 60%. So the obtained results of optical properties are very good.

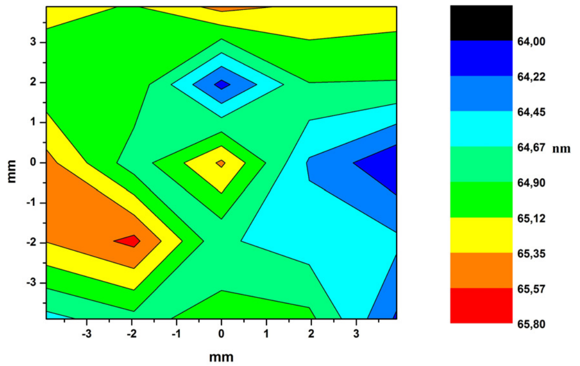

Fig. 7. The thickness distribution map of Al_2O_3 thin film deposited on glass substrate at 300°C after 630 cycles

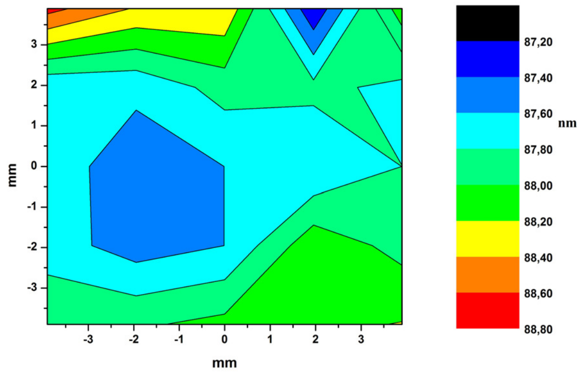

Fig. 8. The thickness distribution map of Al_2O_3 thin film deposited on glass substrate at 300°C after 830 cycles

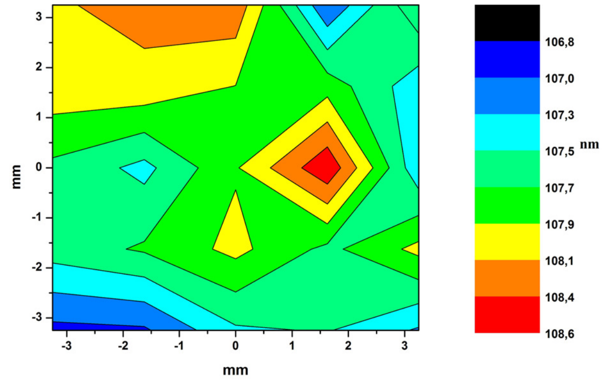

Fig. 9. The thickness distribution map of Al_2O_3 thin film deposited on glass substrate at 300°C after 1030 cycles

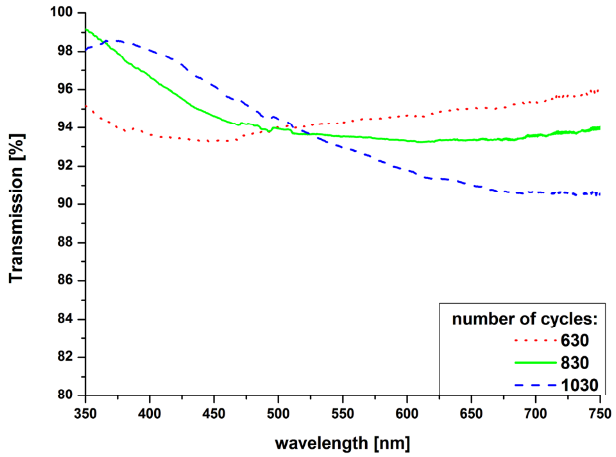

Fig. 10. The spectrum of transmission for the Al_2O_3 thin films deposited by ALD method

4. Conclusions

The Al_2O_3 thin films have been prepared using an atomic layer deposition method. The investigations on Al_2O_3 thin films included analysis of AFM topographic images, thickness distribution maps performed with ellipsometer mapping mode and transmission spectra.

The ALD method allows for the deposition of homogenous thin films with the desired topography, thickness and good optical properties.

By increasing the number of cycles it is possible to fill the defects of construction, which could leads to a reduction in surface roughness. The increase of the size of the aggregate with increasing deposition temperature has been observed. The higher concentrations of atoms appears at a higher temperature deposition, which is consistent with the existence of so-called "temperature window". It can be concluded that the conditions of deposition like temperature and number of cycles influence on the surface morphology of Al_2O_3 thin film, which is confirmed by AFM topographic images, where the molecules aggregations are visible.

Obtained thin films have been very uniform and smooth and the differences between thickness values in different areas of samples were not higher than 3 nm which is confirmed by thickness distribution maps.

The spectroscopic investigations performed on prepared samples shows that thin Al_2O_3 films have high transparency which value is over 90%.

All obtained results have showed that the optical properties and quality of as prepared thin films are very good and could be applied in optoelectronic and photovoltaic industry.

Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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