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The impact of atomic layer deposition technological parameters on optical properties and morphology of Al_2O_3 thin films

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This paper presents some results of investigations on aluminum oxide Al_2O_3 thin films prepared by the atomic layer deposition method on polished monocrystalline silicon. It has been described how the technological parameters of the deposition process, like the number of cycles and substrate temperature, influenced the optical properties and morphology of prepared thin films. Their physical and optical properties like thickness, uniformity and refractive index have been investigated with spectroscopic ellipsometry, atomic force microscopy and UV/vis optical spectroscopy.

Keywords: thin film, aluminum oxide, atomic layer deposition.

1. Introduction

Transparent thin films deposited onto the surface of optoelectronic devices can be used as antireflective coatings. The basic application of this kind of thin films is decreasing of the reflection while the rest of parameters like transmission and emission have controlled values. The optical dependences of optoelectronic devices like transmission or emission should be contained in a 180 to 2000 nm range.

Basing on intensity or/and range of the absorbed, reflected or transmitted light, the described materials are divided into active and passive groups [1–3]. The thin passive films are used as elements of optical filters, reflection and antireflection coatings. The antireflection coatings reduce the intensity of light reflected from the surface. The known and popular materials used as antireflection coatings in photovoltaics are SiO_2, a-SiN_x:H, TiO_2, a-Si:C:H, ZnS, Ta_2O_5, Sn_xO_y, SiN_x, MgF_2 [4–7]. Aluminum trioxide has a good refractive index and excellent transparency in a wide spectral range. In addition Al_2O_3 shows good mechanical properties such as a ratio of resistance to mechanical damage, which has a high value [8].

The deposition methods like chemical vapour deposition (CVD) and physical vapour deposition (PVD) are generally known as methods with high purification and many variable parameters like thermal sources temperature and pressure. The comparison of these methods with atomic layer deposition (ALD) proved that ALD has been the most promising preparation method of Al_2O_3 thin films. The growth of thin films prepared with ALD method can be easily controlled if we note that their thickness depends just on the number of cycles and substrate temperature. Regarding the chemical reaction of precursors used, we see that in the CVD and the PVD methods the reaction occurs already in the flow of reactants used. In the ALD method, the reaction occurs just on the substrate surface. The growth of thin films also does not depend on the uniformity of the flow of precursors, like in case of PVD and CVD [9–11].

2. Materials and methodology

The Al_2O_3 antireflection coatings were prepared with the ALD method. As a precursor we used trimethylaluminum (TMA), water as a reactant and nitrogen as a non-reactive carrier agent. The number of cycles and the temperature of substrate were controlled during the deposition process. Basing on obtained results, we have optimized the deposition process for the controlled growth of thin films and their quality. A different, determined number of cycles was included in every thin films deposition process.

The following steps have been included in one cycle. The TMA used as a precursor was injected into the reaction chamber in one pulse. In the next step, the chamber was flushed with nitrogen gas. Water vapours were injected into the reaction chamber as the second precursor. One monolayer of Al_2O_3 was deposited during one cycle. The reaction between TMA and H_2O occurs in two steps [12]:

$$\text{Al-OH}^* + \text{Al(CH}_3)_3 \rightarrow \text{Al-O-Al(CH}_3)_2^* + \text{CH}_4 \tag{1}$$

$$\text{Al-CH}_3^* + \text{H}_2\text{O} \rightarrow \text{Al-OH}^* + \text{CH}_4 \tag{2}$$

The number of cycles was the parameter which has decided about the thickness of such prepared thin films. As substrates we have used polished silicon wafers. The technological parameters of the deposition process are shown in Tables 1 and 2. The 2D

T a b l e 1. The technological parameters of ALD process.

TMA	The flow rate of the carrier gas N_2	150 sccm
	Pulse time	0.2 s
	Purge time	4.0 s
H_2O	The flow rate of the carrier gas N_2	200 sccm
	Pulse time	0.2 s
	Purge time	5.0 s
	Substrate temperature	200–400°C
	Number of cycles	630–1030

T a b l e 2. The substrate temperatures and number of cycles used for individual layers.

Sample	Deposition temperature [°C]	Number of cycles
A	300	630
B	300	830
C	300	1030
D	200	630
E	400	630

and 3D topographic 2×2 μm images were performed with XE-100 Park Systems atomic force microscope (AFM) and the RMS and R_a coefficient values were determined with XEI Software. The thickness distribution maps and refractive index dispersions were obtained with the use of a spectroscopic elipsometer SENTECH SE 850E and with SpectraRay3 software. The thickness distribution maps were generated in an elipsometer mapping mode, where the theoretical model was a base for determining the thickness values.

3. Results and discussion

The AFM analysis has been performed on Al_2O_3 thin films, deposited onto polished silicon wafers. The topographic and sensor images of thin films obtained with 300°C substrate temperature at a variable number of cycles are shown in Figs. 1–3. The images performed on thin films deposited at 200 and 400°C at a constant number of cycles are shown in Figs. 4 and 5. The values of RMS and R_a coefficients are included in Table 3. The histograms of irregularities are compared in Fig. 6.

It has been found that the value of RMS coefficient is decreasing with the number of cycles at constant temperature. The maximum value is equal to 0.96 nm for a thin film deposited with 630 cycles at 300°C substrate temperature and its lowest value is 0.29 nm at the same number of cycles and at 200°C substrate temperature. The surface

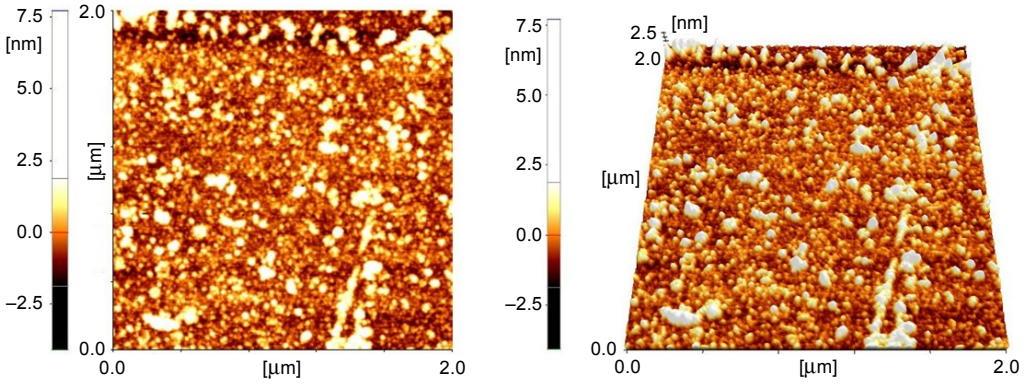

Fig. 1. The 2D and 3D topography of 2×2 μm area of Al_2O_3 thin film obtained with 630 cycles at 300°C substrate temperature (sample A).

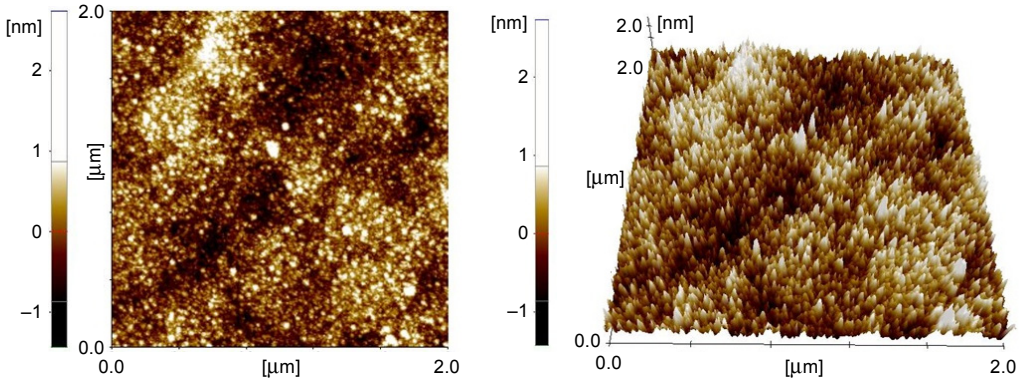

Fig. 2. The 2D and 3D topography of 2×2 µm area of Al_2O_3 thin film obtained with 830 cycles at 300°C substrate temperature (sample B).

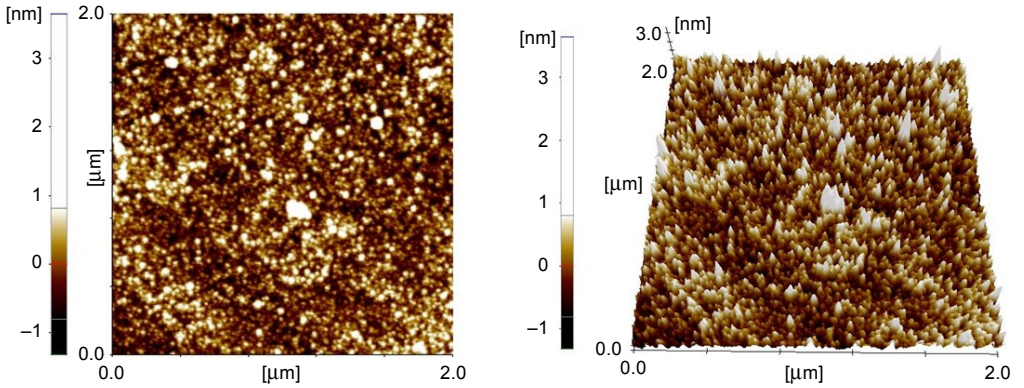

Fig. 3. The 2D and 3D topography of 2×2 µm area of Al_2O_3 thin film obtained with 1030 cycles at 300°C substrate temperature (sample C).

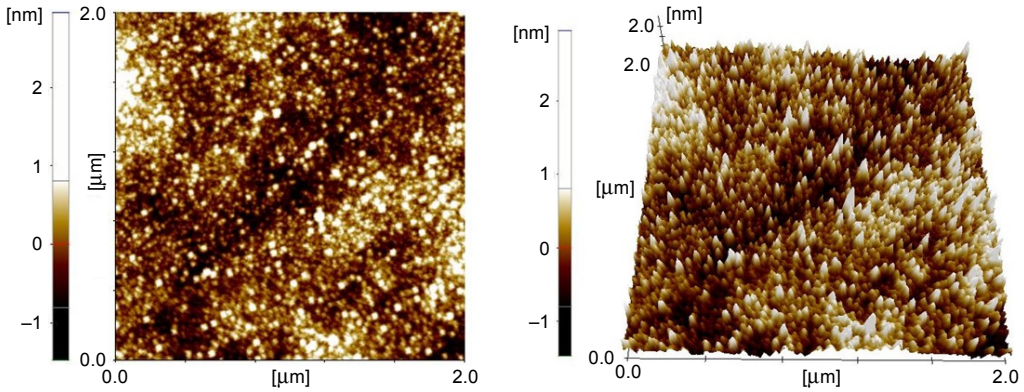

Fig. 4. The 2D and 3D topography of 2×2 µm area of Al_2O_3 thin film obtained with 630 cycles at 200°C substrate temperature (sample D).

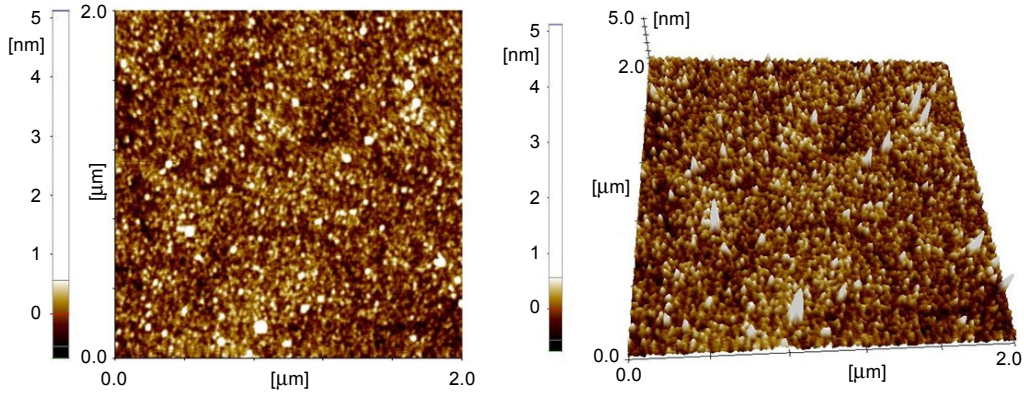

Fig. 5. The 2D and 3D topography of 2×2 µm area of Al_2O_3 thin film obtained with 630 cycles at 400°C substrate temperature (sample E).

roughness does not increase with increasing temperature. It may be connected with the so-called temperature window in the ALD process. For thermal ALD processes there are temperature constraints on the feasibility of successfully carrying out a par-

T a b l e. 3. Values of thickness d, RMS and R_a coefficients for individual films.

Sample	Number of cycles	T [°C]	d [nm]	RMS [nm]	R_a [nm]
A	630	300	66	0.96	0.69
B	830	300	89	0.45	0.35
C	1030	300	109	0.44	0.34
D	630	200	51	0.29	0.19
E	630	400	73	0.47	0.36

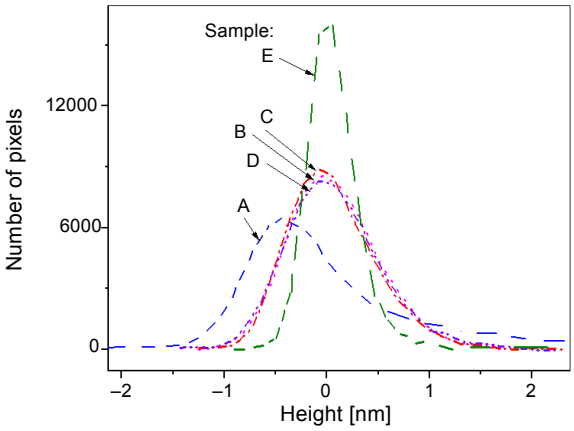

Fig. 6. The histogram of frequencies with the occurred heights for Al_2O_3 thin films deposited after 630 cycles (sample A), 830 cycles (sample B) and 1030 cycles (sample C) at 300°C, and thin films obtained with 630 cycles at 200°C (sample D) and 400°C (sample E).

ticular deposition. If the temperature is very high, then the first chemical reactant may decompose on the surface before having time to react with the second reactant. In this case, the growth rate would be higher than one would expect from an ALD process. Alternately, if the first precursor is stable, it may still desorb from the surface before having a chance to react with the second reactant. Under this circumstance, the growth rate would be less than expected and irregular. On the other hand, if the temperature is too low, we may adsorb more than one monolayer per cycle (or even condense a liquid or solid on the surface), and the deposition rate would be higher than expected. Finally, if the temperature is too low, the reaction rate may be so slow that the reaction time may be too long compared to a practical cycle time. In this case, there may not be enough time for a complete monolayer to be reacted. Determining, contributing and confirmation of this thesis require further research and analysis.

The profile analysis represented by R_a value has confirmed the decreasing tendency of RMS. With higher number of cycles the thickness of films is increasing and the surface of obtained thin films is smoother if we regard the microscopic scale. According to roughness coefficients analysis, the performed images show the surface changes and when the RMS value is higher, the area of small aggregations is visible in topographies. The histograms obtained with AFM microscope software present the number of pixels with different height depending on its value. That corresponds with the area occupied with the highest and lowest points. The obtained histograms are in good coincidence with RMS values.

All samples were scanned with a spectroscopic elipsometer equipped with microspots, where the diameter of the light beam is at about 200 μm. The thickness distribution maps were performed in 25 points on 1.5×1.5 cm area. The maps are presented in Figs. 7–11.

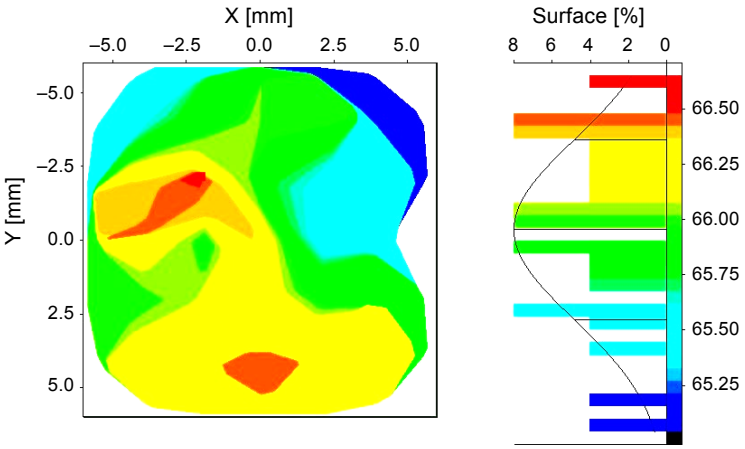

Fig. 7. The thickness distribution map of a sample A deposited with 630 cycles at 300°C substrate temperature.

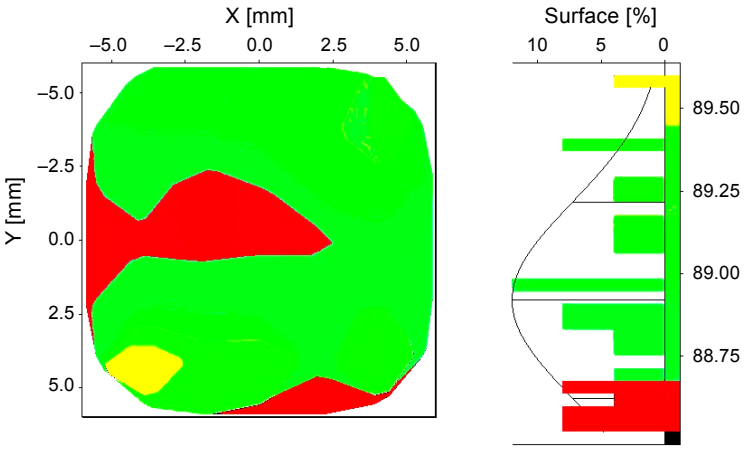

Fig. 8. The thickness distribution map of a sample B deposited with 830 cycles at 300°C substrate temperature.

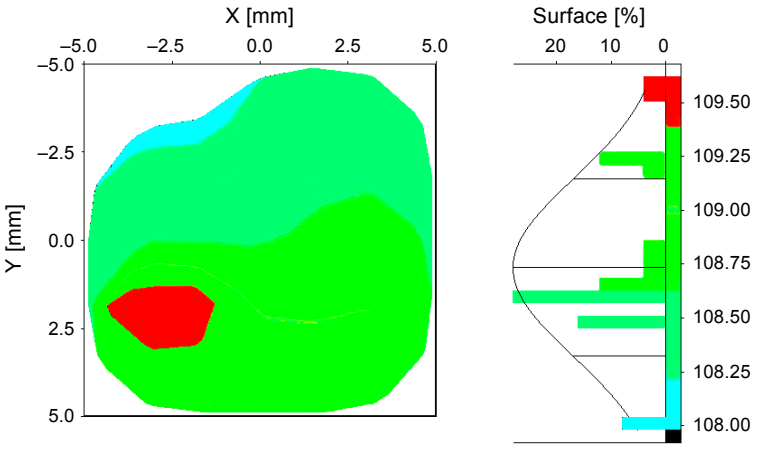

Fig. 9. The thickness distribution map of a sample C deposited with 1030 cycles at 300°C substrate temperature.

The obtained results show very clearly that the quality of obtained thin films was very good even in a macroscopic scale. The thickness value variation was not high. We can see in Fig. 7 that thickness variation (the difference between the lowest and the maximum value of thickness) was 1.25, 0.75 and 1.5 nm in Figs. 8 and 9, respectively. At a bigger number of cycles also the percentage of uniform area with a constant thickness value is higher. The quality of scanned thin films deposited at different temperatures of the substrate (200 and 400°C) showed in Figs. 10 and 11 is comparable with the results presented above. The thickness variations of obtained maps was equal to 0.4 and 0.9 nm.

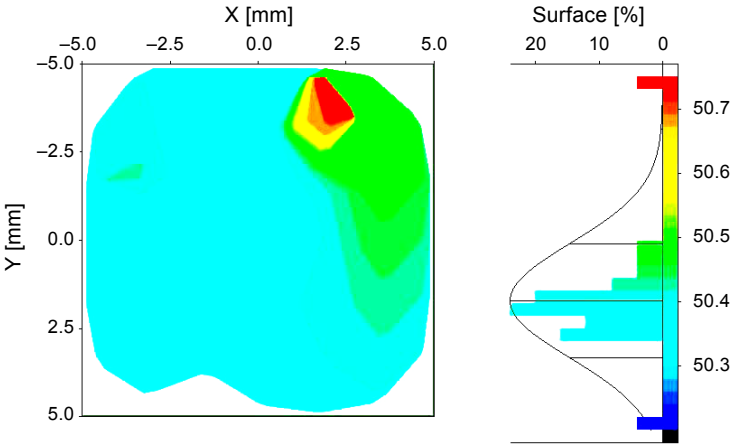

Fig. 10. The thickness distribution map of a sample D deposited with 630 cycles at 200°C substrate temperature.

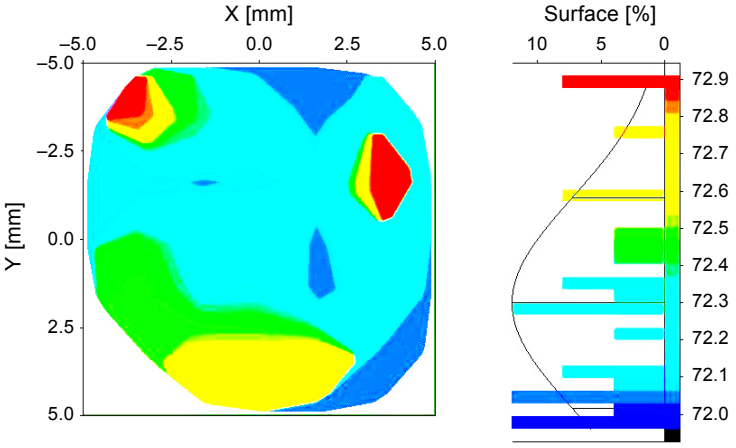

Fig. 11. The thickness distribution map of a sample E deposited with 630 cycles at 400°C substrate temperature.

The dispersions of the refractive index were determined with SpectraRay3 Software basing on a constructed model. Thin films of Al_2O_3 deposited onto silicon wafers were fitted with a simple sandwich model $Si/SiO_2/Al_2O_3$/air. In the case of Al_2O_3 thin films, the Cauchy model was used. This model is most often used for transparent oxide materials. The model includes layers of SiO_2 having a thickness of 1.45 nm found on the surface of silicon. The thickness of the oxide layer was determined based on an analysis of the uncovered silicon substrates. The dependences on wavelength are showed in Fig. 12.

The comparison of refractive index dispersions shows that the value *n* is slightly different in UV-vis range and begins to be constant in the IR, where it is equal to 1.61.

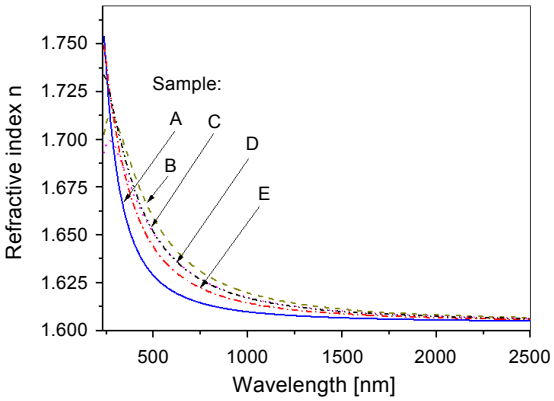

Fig. 12. Dispersion of refractive index of Al_2O_3 thin film.

If we compare the value *n* for 630 nm wavelength, we note that dispersions of samples C and D layers are the same in all ranges. The values of the refractive index noted at about 630 nm are showed in Table 4. The refractive index value depends on a sample structure. Similar values of refractive index suggest that both of these features are comparable in all obtained thin films, however the refractive index value is slightly different than in [12] where the value *n* is increasing with the temperature of the substrate.

The reflectance spectra were performed on Al_2O_3 thin films deposited onto polished monocrystalline silicone wafers. One can see that minima of obtained spectra are shift-

T a b l e 4. Refractive index values of Al_2O_3 thin films.

Sample	A	B	C	D	E
n	1.62	1.64	1.63	1.63	1.63

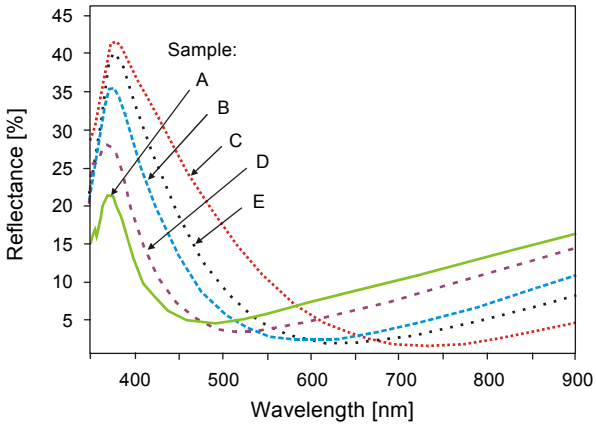

Fig. 13. The spectrum of reflection for the Al_2O_3 thin film deposited with ALD method.

ed into higher wavelength values. The reflectance spectra depend on the thickness and refractive index (which depend on the technical parameters of deposition process). One can see that minima of reflectance spectra of samples A, B and C films are placed at about 475, 600 and 725 nm what agrees with their thickness and with the number of cycles. The minima of samples D and E spectra are placed at about 525 and 630 nm what is also connected with their thickness and temperature of substrate during the deposition process. And it is clearly seen in Fig. 13 that spectra B and E got minimum placed at about 600 and 640 nm, respectively.

4. Conclusions

Thin films of Al_2O_3 were prepared with the ALD deposition method in two ways, where the first one was connected with increasing number of cycles and the second one with different temperature of a substrate during the deposition process. Basing on obtained results, we have found that the best optical and physical properties present layers prepared at 300 and 400°C substrate temperature at 830 and 630 cycles. The mentioned thin films prepared under these conditions have reduced the reflection significantly under 5% over a broad spectral range. Also the uniformity of these samples is very high and the thickness profile across all its volume is not higher than 2 nm.

Basing on obtained results, we can conclude that Al_2O_3 thin films obtained with the ALD deposition method have good antireflection properties and could be applied in photovoltaic industry as an antireflection coating of silicon solar cells.

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