Materials Science-Poland, 32(1), 2014, pp. 80-87
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-013-0156-y

VERSITA

Optical properties of the Al_2O_3/SiO_2 and $Al_2O_3/HfO_2/SiO_2$ antireflective coatings

KONSTANTY MARSZAŁEK[1]*, PAWEŁWINKOWSKI[2], JANUSZ JAGLARZ[3]

[1]AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Cracow
[2]PEVIN, ul. Piaskowa 55, 31-341 Cracow
[3]Institute of Physics Cracow University of Technology, ul. Podchorążych 1, 30-084 Cracow

Investigations of bilayer and trilayer Al_2O_3/SiO_2 and $Al_2O_3/HfO_2/SiO_2$ antireflective coatings are presented in this paper. The oxide films were deposited on a heated quartz glass by e-gun evaporation in a vacuum of 5×10^{-3} [Pa] in the presence of oxygen. Depositions were performed at three different temperatures of the substrates: 100 °C, 200 °C and 300 °C. The coatings were deposited onto optical quartz glass (Corning HPFS). The thickness and deposition rate were controlled with Inficon XTC/2 thickness measuring system. Deposition rate was equal to 0.6 nm/s for Al_2O_3, 0.6 nm – 0.8 nm/s for HfO_2 and 0.6 nm/s for SiO_2. Simulations leading to optimization of the thin film thickness and the experimental results of optical measurements, which were carried out during and after the deposition process, have been presented. The optical thickness values, obtained from the measurements performed during the deposition process were as follows: 78 nm/78 nm for Al_2O_3/SiO_2 and 78 nm/156 nm/78 nm for Al_2O_3 /HfO_2/SiO_2. The results were then checked by ellipsometric technique. Reflectance of the films depended on the substrate temperature during the deposition process. Starting from 240 nm to the beginning of visible region, the average reflectance of the trilayer system was below 1 % and for the bilayer, minima of the reflectance were equal to 1.6 %, 1.15 % and 0.8 % for deposition temperatures of 100 °C, 200 °C and 300 °C, respectively.

Keywords: *antireflective coatings; Al_2O_3; HfO_2; SiO_2; optical measurements*

1. Introduction

New standards of the optical technique require special coatings for optical parts. Antireflective coatings (AR) are the basic thin films applied in optics. Nowadays, most of the ophthalmic lenses [1] or lenses in cameras [2, 3], spyglasses, microscopes, etc. are covered with the antireflective coatings. In case of a single lens, which is produced from glass with refractive index $n = 1.5$, transmittance is equal approximately to 92 %, but in case of glass with refractive index $n = 1.8$, it is only 84 %. The rest of light is lost because of reflection. This fact means that the antireflective coating becomes necessary to improve transmittance of the optical systems. Photovoltaic panels are also very important examples of application of the AR coatings [4, 5]. In these devices the larger energy of light generates additional electrical power.

Most of the antireflective coatings are designed for visible range, but some of the applications need the coatings for ultraviolet (UV) or infrared (IR) region [6, 7]. The optical devices designed for ultraviolet region need special glass (for instance made of quartz) and special materials for coatings. Most often, the fluorides and the oxides are used as materials for antireflective coatings [8, 9], but only some of them have properties suitable for the UV region [10]. High transmittance of the UV light and good mechanical features, such as hardness, adhesion to substrate and chemical resistance are needed. In this group, there are materials with different refractive indices. SiO_2 ($n = 1.46$) and MgF_2 ($n = 1.38$) [9] are the most common materials with low refractive index for UV applications. The fluorides LaF_3, NdF_2 (n = 1.60) [11] and the oxide Al_2O_3 (n = 1.63) have

*E-mail: marszale@agh.edu.pl

suitable properties as thef materials with medium refractive indices. The last group is represented by the oxide HfO_2 ($n = 1.90$), which can be used for the applications from IR up to 230 nm of UV [12].

The basic structures of multilayer antireflection coatings are 1M/1L for bilayer coating and 1M/2H/1L for trilayer coating. The L, M and H symbols represent the well known quarter-wavelength optical thickness (QWOT) for materials with low, medium and high refractive indices, respectively. In this paper we present the following materials: SiO_2 ($n = 1.46$ at 500 nm), Al_2O_3 ($n = 1.63$ at 500 nm) and HfO_2 ($n = 1.9$ at 500 nm) as the AR coatings deposited on a quartz glass substrate. The advantage of trilayer coating system is the low reflection in a wide spectral range. However, the cost of production of bilayer antireflection coatings is relatively low and the control of the parameters during evaporation for this type of films is easier.

The bilayer antireflective coating has excellent properties for the optical equipment in the UV range, where high transmission is necessary for only one UV wavelength. These kinds of thin films are recommended for laser technology. The trilayer antireflective coating can be used in numerous UV applications, e.g. UV lasers [13], medical equipment, UV cameras.

2. Reflectance simulations in QWOT coating systems

The optical properties of antireflective coatings depend on refractive indices of the used materials [14]. Moreover, the same material deposited on a heated or unheated substrate may have different refractive indices. The differences in refractive indices of particular films influence then the reflection from the layered system. Therefore, we performed a theoretical analysis of the reflectance of the antireflective coatings with different refractive indices. Thus, we calculated the spectral reflection from bi- and tri- QWOT layer systems on a glass substrate for the different refractive indices of the bottom film in a film stack. The simulations of the spectral reflectance of the QWOT films were performed with the use of the CompleteEASE 5.0 software [15]. The theoretical background describing spectral reflectance and transmittance is presented in many works [16, 17].

We performed the simulations of directional reflectance for bi- (Al_2O_3/SiO_2) and tri- ($Al_2O_3/HfO_2/SiO_2$) layer systems, deposited on the HPFS glass (commercial name for quartz glass from Corning). The calculated reflection spectra for the antireflective coating Al_2O_3 /SiO_2 are shown in Fig. 1. The spectra are presented in wavelength range of 200 nm to 500 nm. We assumed the constant optical thickness of 78 nm for both Al_2O_3 and SiO_2 films. As may be noticed from Fig. 1, all calculated reflection spectra are V-shaped with one minimum at the wavelength $\lambda = 310$ nm. The value of reflectance minima decreases with the increase of Al_2O_3 refractive index.

The optical properties of the films with the optimal thickness, deposited on the substrates at various temperatures, were checked by the simulations. The simulations were performed for a constant refractive index of the SiO_2 film and a dedicated variation of refractive index of the Al_2O_3 film [18].

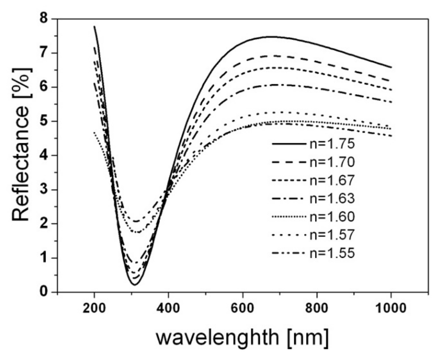


Fig. 1. The simulated reflectance spectra of the Al_2O_3/ SiO_2 deposited on the HPFS glass.

Additionally, we performed a reflectance simulation for the HPFS glass/$Al_2O_3/HfO_2/SiO_2$ system, assuming optical thickness of the respective stack layers as: 78 nm/156 nm/78 nm. The results of the reflectance simulations were obtained for different refractive indices of HfO_2 and are presented in Fig. 2.

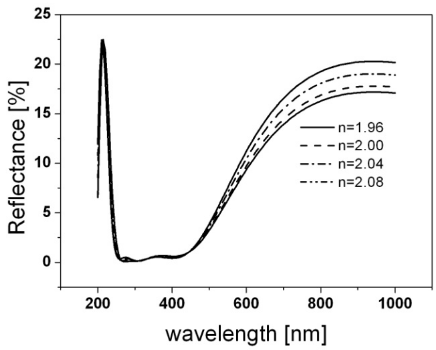


Fig. 2. The simulated reflectance spectra of the $Al_2O_3/HfO_2/SiO_2$ deposited on the HPFS glass.

As shown in Fig. 2, the reflectance spectra of the $Al_2O_3/HfO_2/SiO_2$ system are W-shaped. The reflectance of the layer system is close to zero in the wavelength range of 250 nm to 450 nm and practically does not depend on refractive index of the HfO_2 film.

3. Experimental

3.1. Films deposition

The AR coatings were deposited in a vacuum chamber (model NA501) with a water cooled vacuum bell jar. The base pressure during the processes was kept below 5×10^{-3} [Pa]. The vacuum chamber was equipped with a thermal evaporation source and a multicrucible linear e-gun from Varian–H. The used evaporation setup is shown in Fig. 3.

In the experiment, the evaporation temperature of the materials – Al_2O_3, HfO_2, SiO_2 was above 2000 °C and because of that using of an e-gun as an evaporation source was necessary. Thin films of the Al_2O_3 and the HfO_2 were deposited in the oxygen atmosphere. The film thickness and the deposition rate were measured with the Inficon XTC/2 thickness controller. The quartz glass (Corning HPFS) of 1 mm thickness was used as a substrate. The substrates were fixed to a rotating sample holder and were heated up

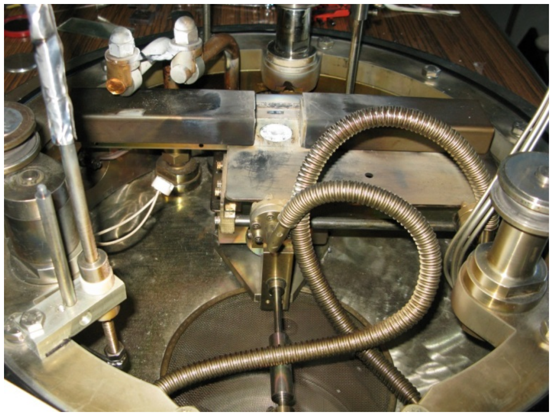


Fig. 3. Multicrucible linear e-gun from Varian and boat type evaporator.

to 100 °C, 200 °C and 300 °C. Additionally, to increase adhesion of the film to the substrate at the temperature of 100 °C, a glow discharge was performed.

3.2. Measurement setups

Transmission and reflection spectra of the coated substrates were measured on a Shimadzu UV1061 spectrophotometer. The ellipsometric measurements were performed for determination of thickness and refractive indices of the films. The ellipsometric technique is well known and widely described in literature [19, 20].

The ellipsometry determines two angles, Psi and Delta, with:

$$\tan(Psi) = |r_p|^2 / |r_s|^2 \tag{1}$$

where Psi is a phase shift between two polarized waves, r_p and r_s are complex Fresnel reflection coefficients for ‘p’ and ‘s’ polarizations, respectively. Both angles enter the equation:

$$r_p/r_s = \exp(iDelta) \cdot \tan(Psi) \tag{2}$$

allowing to determine the thickness of the film d, its refraction index n and extinction coefficient k. Knowing n and k in a wide spectral range one can obtain a lot of interesting information about band structure of materials and their optical and electrical properties.

The ellipsometric measurements were performed for all presented samples, in a spectral range of 190 nm – 1700 nm, with the M-2000 spectroscopic ellipsometer manufactured by J. A. Woollam Co. Inc. The samples were measured at four angles of incidence (60°, 65°, 70°, 75°), the intensity of the reflected light and the depolarization coefficient were measured, simultaneously in the same experiment [21].

To analyze the data, we have combined all angular spectra and fitted all the data simultaneously. For better accuracy, the data have been analyzed using CompleteEASE 5.0 software. The Cauchy model of dispersion for the structure of each film in the wavelength range from 190 nm to 1700 nm has been applied because the studied films were non-absorptive and transparent in the whole wavelength spectrum. The refraction index can be expressed by the following formula:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \qquad (3)$$

where A, B, C are constant terms, λ – wavelength.

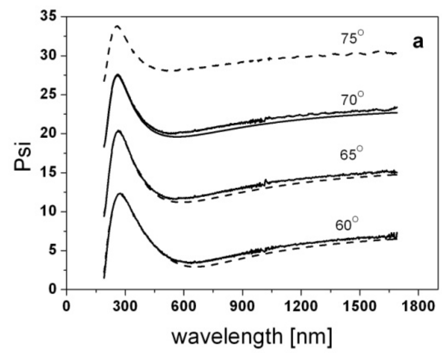
Hardness and adhesion were checked by the eraser test (rubber test) according to MIL-C-48497A standard. All coatings, deposited at different temperatures, were extremely hard.

4. Results and discussion

The surface roughness was determined from the ellipsometric results. In the investigated samples, we assumed the appearance of the surface roughness which can be described using the Bruggeman effective medium approximation (EMA) [22]. This approximation uses a 50:50 mixture of the material and air on the sample surface to get the optical constants corresponding to the effect of the surface roughness [23].

At first, we fitted the theoretical model to HPFS glass substrate alone. We obtained the average values of the refractive index as being equal to 1.465 in visible region and 1.491 for the wavelength of 300 nm. The roughness determined from ellipsometric measurements was 1.6 nm. The ellipsometric investigations of the layers were done step by step starting from a single Al_2O_3 film, then two layers Al_2O_3/HfO_2 and finally three layers in the stack of $Al_2O_3/HfO_2/SiO_2$. The optical model fitted to the ellipsometric data was developed in the same way. The theoretical curves were obtained from simultaneous fitting of ellipsometric parameters for each angle of incidence.

The spectral dependence of the ellipsometric angles Psi and Delta and the fitted theoretical model for Al_2O_3/SiO_2 deposited at the temperature of 300 °C on the HPFS glass are presented in Fig. 4. The ellipsometric parameters Psi and Delta are presented in Fig. 4a and Fig. 4b, respectively. Both parameters were determined for different angles of incidence (i.e. 60°, 65°, 70°, 75°) for Al_2O_3/SiO_2 film systems.



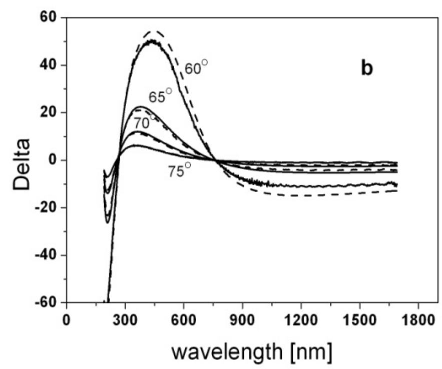


Fig. 4. The spectral dependence of the ellipsometric parameters for Al_2O_3/SiO_2 layered system, deposited at 300 °C on HPFS glass substrate.

Similarly, the ellipsometric results obtained for the trilayer system of $Al_2O_3/HfO_2/SiO_2$ deposited at the temperature of 300 °C on HPFS glass together with fitted curves are shown in Fig. 5. As may be noticed the determined theoretical curves are very well fitted to the experimental data.

The similar ellipsometric study we performed for the $Al_2O_3/HfO_2/SiO_2$ and the Al_2O_3/SiO_2 films deposited on HPFS glass at temperatures of 100 °C and 200 °C.

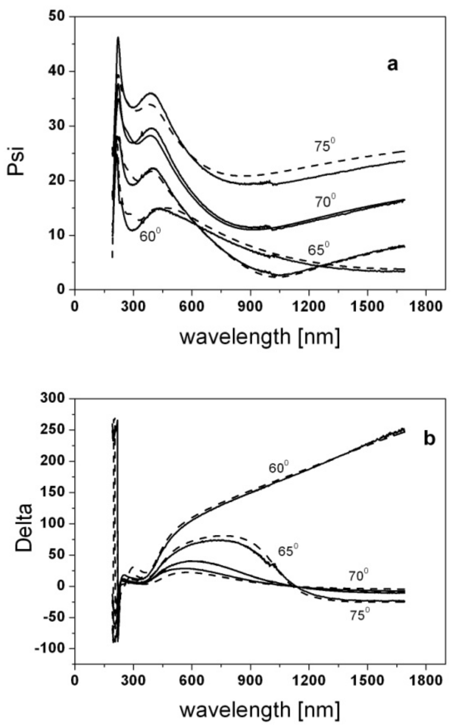


Fig. 5. Spectral dependence of the ellipsometric parameters for $Al_2O_3/HfO_2/SiO_2$ film layered system deposited at 300 °C on HPFS glass substrate.

All layers exhibited very low roughness (less than 2 nm), so the depolarization of the reflected light was close to zero.

The values of the film thicknesses obtained for the deposition temperatures of 100 °C, 200 °C and 300 °C, were determined from ellipsometric investigations and are presented in Table 1. Also the values of the average refractive indices of the layers for visible range of light wavelengths are included in Table 1.

The dispersion of the refractive indices for HfO_2 and SiO_2 layers in the UV-VIS-NIR range was also determined from the ellipsometric study. The spectral dependence of the refractive index n for the Al_2O_3 and the HfO_2 layers obtained for three deposition temperatures are presented in Fig. 6a and Fig. 6b, respectively.

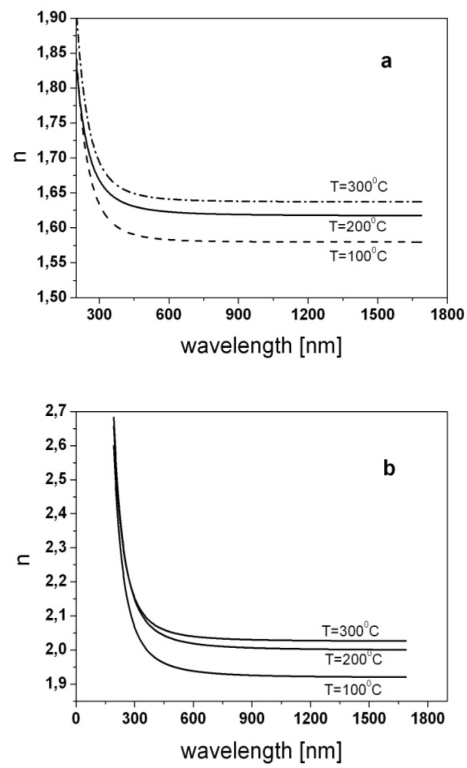


Fig. 6. The spectral dependence of the refractive index of the Al_2O_3 (a) and the HfO_2 (b) obtained at different deposition temperatures.

As may be easily noticed, the refractive indices of the Al_2O_3 and the HfO_2 layers are bigger at higher deposition temperatures.

The calculated total optical thicknesses for the studied film systems are presented in Table 2. To compute the optical thickness, the parameters determined from the ellipsometric measurements were used. The changes in the optical thickness result rather from variation of the refractive indices of the films than their geometrical thicknesses (see Table 2). This is an important conclusion in designing AR coatings for selected wavelength range. In our case the presented AR coatings were optimized for the UV region.

The reflectance and transmittance for normal light incidence were measured by the

Table 1. The thicknesses and the refractive indices of the studied films obtained at different deposition temperatures.

Film	T = 100 °C	T = 200 °C	T = 300 °C
Al_2O_3 refractive index	1.61	1.63	1.65
Al_2O_3-thickness [nm]	51.1	50.9	49.1
HfO_2 refractive index	1.92	2.01	2.05
HfO_2-thickness [nm]	72.1	77.5	75.5
SiO_2 refractive index	51.1	50.9	51.7
SiO_2-thickness [nm]	54.3	53.6	54.1

Table 2. Optical thicknesses (OT) of the studied film systems, deposited at different temperatures.

Film system	Optical thickness (OT)		
	T = 100 °C	T = 200 °C	T = 300 °C
HPFS-Glass/Al_2O_3	79.7	79.7	78.7
HPFS-Glass/Al_2O_3/HfO_2	218.1	234.7	233.5
HPFS-Glass/Al_2O_3/HfO_2/SiO_2	297.9	309.4	309.3
HPFS-Glass/Al_2O_3/SiO_2	159.2	158.2	157.8

spectrophotometer for the QWOT layers on HPFS glass obtained at different temperatures. The reflectance was measured for the deposition temperatures of 100 °C, 200 °C and 300 °C. Fig. 7 and 8 show the experimental results.

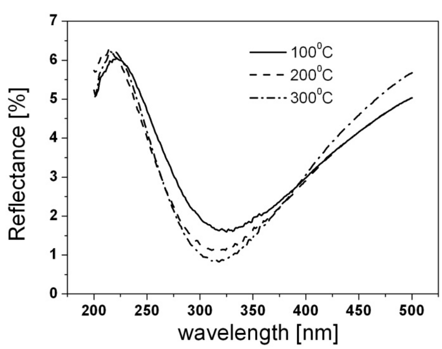


Fig. 7. The reflectance for the Al_2O_3/SiO_2 antireflective coatings on HPFS glass heated to 100 °C, 200 °C and 300 °C.

The Al_2O_3 /SiO_2 coatings have typical for bilayer antireflective coatings "V" shape of the reflection curve (Fig. 7). Minimum of the reflectance is at about 310 nm. The determined reflection coefficients are equal to 1.6 %, 1.15 % and 0.8 % for temperatures 100 °C, 200 °C and 300 °C. Thus higher temperature of the substrate during deposition process allows to obtain better optical properties of the AR coating.

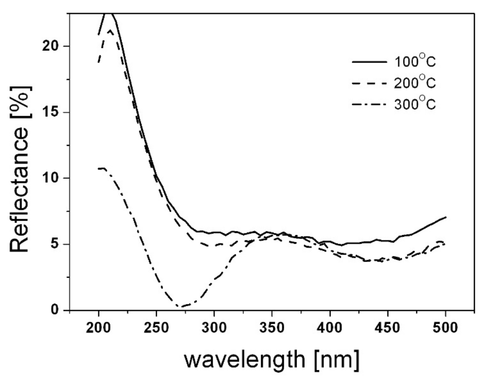


Fig. 8. The reflectance of the $Al_2O_3/HfO_2/SiO_2$ antireflective coatings on HPFS glass heated to 100 °C, 200 °C and 300 °C.

The $Al_2O_3/HfO_2/SiO_2$ coating presented in Fig. 8 has a typical for the trilayer antireflective coatings "W" shape of the reflection curve. The average reflectance in the 240 nm to 400 nm range of the trilayer system is very low – below 1 % for all temperatures of substrates. The reflectances in the spectral range of 240 nm to 450 nm obtained for the deposition temperatures: 100 °C, 200 °C and 300 °C were equal to: 0.75 %, 0.73 % and 0.42 %, respectively. It means that also in this case higher temperature of deposition improves the AR properties of the used QWOT trilayer coatings.

Additionally, for the samples presented in this work we performed transmission measurements with the use from the ellipsometer. The spectral transmission in wavelength region of 200 nm to 550 nm is presented in Fig. 9a for Al_2O_3/SiO_2 and in Fig. 9b for $Al_2O_3/HfO_2/SiO_2$ for the deposition temperatures: 100 °C, 200 °C and 300 °C.

The largest transmission was measured for the lower temperatures of depositions for both bi- and tri- QWOT systems. This may seem to be curious, because in typical AR coatings on transparent substrates smaller reflection corresponds to higher transmission. The peculiar results may be easy to explain if we take into account the losses due to non-directional scattering on the rough interfacial surfaces. Therefore, further measurements of transmittance and reflectance with the use of integrating sphere will be performed to explain these phenomena accurately.

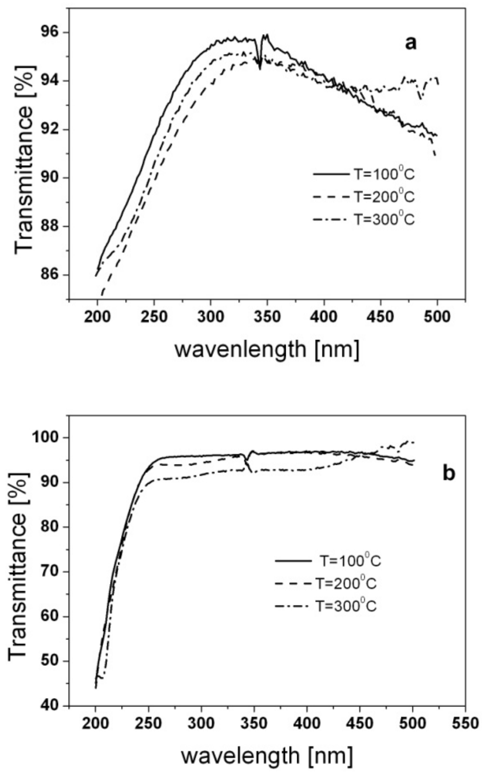


Fig. 9. The transmittance for the HPFS glass with antireflective coatings of Al_2O_3/SiO_2 (a) and $Al_2O_3/HfO_2/SiO_2$ (b) deposited at 100 °C, 200 °C and 300 °C.

5. Summary

The bilayer (Al_2O_3/SiO_2) and the trilayer ($Al_2O_3/HfO_2/SiO_2$) antireflective coatings were deposited by means of e-gun evaporation on quartz glass substrates. The final optical thicknesses of the films were 78 nm/78 nm for the Al_2O_3/SiO_2 and 78 nm/156 nm/78 nm for the $Al_2O_3/HfO_2/SiO_2$ systems. Depositions were performed at different temperatures of the substrates. Both coatings have good optical and mechanical properties.

For improving the transmittance to nearly 99 % in the UV region, double side AR coated HPFS glass should be applied. Our layer systems, deposited on a single surface of a glass have optimal properties for their application in the UV region where high quality wide band antireflective coatings are needed.

Acknowledgements

The paper was financially supported by the project no POIG.01.03.01-30-056/12.

References

[1] CITEK K., *Optometry (DNLM)*, 79 (2008), 143.
[2] YOLDAS B.E., PARTLOW D.P., *Appl. Optics*, 23 (1984), 1418.
[3] BAEUMER S., *Handbook of plastic optics*, Willey-VCH, Berlin, 2005, 139.
[4] STAPIŃSKI T., MARSZAŁEK K., LIPIŃSKI M., PANEK P., SZCZEPANIK W., *Investigations of solar panels with anhanced transmission glass*, in: Z. SUSZYNSKI (Ed.), *Microelectronic materials and technologies*, WUPK, Koszalin, 2012, 285.
[5] STAPIŃSKI T., SWATOWSKA B., *J. Non-Cryst. Solids*, 352 (2006), 1406.
[6] WINKOWSKI P., MARSZAŁEK K., *Proc. SPIE* 8902, (2013), 890228.

[7] ZUKIC M., *Appl. Optics*, 29 (1990), 4284.
[8] SELHOFER H., MUELLER R., *Thin Solid Films*, 351 (1999), 180.
[9] SMITH D, BAUMEISTER P., *Appl. Optics*, 18 (1979), 111.
[10] RAINER F., LOWDERMILK W.H., MILAM D., CARNIGLIA C.K., HART T.T., LICHTENSTEIN T.L., *Appl. Optics*, 24 (1985), 496.
[11] IZAWA T., YAMAMURA N., UCHIMURA R., HASHIMOTO I., YAKUOH T. et al., *Proc. SPIE* 1441, (1990), 339.
[12] ZUBER A., KAISER N., STEHLE L.J., *Thin Solid Films*, 261 (1995), 37.
[13] KAISER N., UHLIG H., SCHALLENBERG U., ANTON B., KAISER U., MANN K., EVA E., *Thin Solid Films*, 260 (1995), 86.
[14] BACH H., KRAUSE D. (Eds.), *Thin Films on Glass*, Springer-Verlag, Berlin/Heidelberg/New York, 1997.
[15] KARASIŃSKI P., JAGLARZ J., REBEN M., SKOCZEK E., MAZUR J., *Opt. Mater.*, 33 (2011), 1989.
[16] CRAWFORD L.J., EDMONDS N.R., *Thin Solid Films*, 515 (2006), 907.
[17] LEE H.M., SAHOO K.C., LI Y.W., WU J.C., CHANG E.Y., *Thin Solid Films*, 518 (2010), 7204.
[18] KUMAR P., WIEDMANN M.K., WINTER C.H., AVRUTSKY I., *Appl. Optics*, 48 (2009), 5407.
[19] FUJIWARA H., *Spectroscopic Ellipsometry: Principles and Applications*, Wiley & Sons, 2007.
[20] AZZAM R.M.A, BASHARA N.M., *Ellipsometry and Polarized Light*, North-Holland, Amsterdam, 1995.
[21] JAGLARZ J., WAGNER T., CISOWSKI J., SANETRA J., *Opt. Mater.*, 29 (2007), 908.
[22] BRUGGEMAN D.A.G., *Ann. Phys.-Berlin*, 416 (1935), 665.
[23] JAGLARZ J., *Thin Solid Films*, 516 (2008), 8077.

Received 2013-09-27
Accepted 2013-12-22