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DEPOSITION OF ZIRCONIUM DIOXIDE THIN FILMS BY ELECTRON BEAM EVAPORATION AND REACTIVE MAGNETRON SPUTTERING

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Absract. Zirconium dioxide thin films deposited by electron beam evaporation (EBE) and reactive magnetron sputtering (RMS) on glass and potassium chloride single crystal substrates have been investigated. EBE ZrO_2 thin films packing density and index of refraction increase in the ranges 0.6—0.9 and 1.83—2.08 respectively when the substrate temperature increases from 30° C to 400° C. The films grow in a crystalline defined columnar structure at above 150° C. RMS ZrO_2 thin films have a packing density near unity and an index of refraction of about 2.20. Films with very good optical quality can be deposited with oxygen partial pressure P_{O_2} from region of the maximum of $U - P_{O_2}$ curve, where U is the discharge voltage during the sputtering.

Резюме. Нанесены тонкие пленки из ZrO_2 методами электронно-лучевого испарения и реактивного магнетронного распыления на подложках из стекла и из монокристаллов хлорида калия. Проведено исследование их оптических свойств и относительной плотности в зависимости от температуры подложки в диапазоне 30÷400° C.

Тонкие пленки из Zr_2O, полученные методом электронно-лучевого испарения, показали нарастание показателя преломления на длине волны 550 nm и относительной плотности в диапазоне 1.83—2.08 и 0.6—0.9 соответственно при изменении температуры подложки от 30° C до 400° C. При температурах подложки выше 150° C пленки имеют колоновидную структуру, определяемую кристаллитами. При температурах ниже 150° C имеются некоторые отклонения в сторону аморфной структуры с пустотами.

Тонкие пленки из ZrO_2, полученные методом реактивного магнетронного распыления, имеют относительную плотность, близкую к единице, и показатель преломления на длине волны 550 nm около 2.20. Пленки с хорошими оптическими свойствами получаются в диапазоне парциального давления кислорода, соответствующего максимуму кривой $U = P_{O_2}$, где U — напряжение разряда во время распыления.

1. Introduction

Zirconium dioxide thin films are well-known dielectric films. They are transparent in a wide wavelength region (0.24—12 μm) and show very good mechanical stability [1]. ZrO_2 thin films have successfully been used as protective and antireflective coatings in optical systems for the visible and infrared wavelength ranges [2].

Generally, ZrO_2 thin films are deposited using electron beam evaporation. During the deposition by this technique the films grow in a columnar structure with many voids perpendicular to the substrate surface resulting in a packing density that is lower than unity. Therefore, the index of refraction of the evaporated films is lower than that of the bulk material. Some of the voids are filled with water changing in this way the refractive index of the film [3]. The voids in ZrO_2 thin films decrease the film's mechanical stability and deteriorate their water protective properties. Hence, technologies for the deposition of ZrO_2 with the highest packing density must be developed.

In this paper we present the results from the investigation of the optical properties and the packing density of thin ZrO_2 films deposited by electron beam evaporation (EBE) and reactive magnetron sputtering (RMS) on glass or KCl single crystal substrates.

2. Experimental technique

Zirconium dioxide thin films were deposited in a vacuum vessel evacuated to a background pressure of 4.5×10^{-3} Pa. A rectangular planar magnetron and an electron gun were used to deposit the film by RMS and EBE, respectively.

Thin film was deposited by EBE under pressure of 6×10^{-3} Pa and at constant power of the electron gun of 580 W. For the evaporation "Merck" ZrO_2 powder with optical purity was used.

The films obtained by RMS were deposited by sputtering of a Zr target in $Ar+O_2$ atmosphere at total pressure of 0.3 Pa. The partial pressure of the oxygen was varied in the range $0.2-15\times10^{-2}$ Pa. During the deposition at different oxygen partial pressures the average discharge current density was maintained constant at 425 A/m^2. The distance between the target (or the evaporator in the case of EBE) and the substrate was 12 cm.

Glass or KCl single crystal plates were used as substrates. In the case of KCl plates, ⟨100⟩ planes were covering surface. Before the deposition the substrates were cleaned in argon discharge at pressure 0.15 Pa for 5 min. During the deposition the substrate temperature was maintained constant in the 30—400° C range. It was measured with a chromel-allumel thermocouple mounted on the substrate holder very near to the centre of the substrate plate.

The reflectance and transmittance in the 0.33—25 μm wavelength range were measured with dual-beam-spectrophotometer "Specord UV/VIS" and "Specord 71 IR". The index of refraction, the absorption coefficient and the thickness of the films were determined from the transmission scans by the envelope method described by S w a n e p o e l [4].

The stability of ZrO_2 films in water was controlled by annealing the samples in supersaturated vapours of KCl solution in water saturated at 75° C. Periodically the reflectance and transmittance were measured and the film has been observed by optical microscope.

The packing density of the deposited films was obtained using the absorption of water at 2.97 μm.

The infrared (IR) transmission spectra of thin films with water filled pores show an absorption band at 2.97 μm due to the vibration of the water molecules. Measuring the absorption coefficient α at the maximum of this band one can determine the film packing density P using the relation:

$$P = 1 - \frac{\alpha}{\alpha_w}$$

where α_w is the water absorption coefficient at 2.97 μm ($\alpha_w = 12700$ cm^{-1} [5]).

3. Experimental results

3.1. General considerations

The crystalline and morphological microstructure of evaporated thin films are related to the material's properties and deposition conditions in a complex manner. Empirical structure-zone-models for evaporated or sputtered films have shown [6, 7] that in the case of low substrate temperatures T_s($T_s < 0.5$ T_M, T_M — melting temperature of the material), the films consist of columnar or needle-like grains and a large quantity of differently shaped voids and pores. For most optical materials, particularly metal oxides, the conditions $T_s < 0.5\,T_M$ are usually realized. Because of the voids the density of a deposited film ρ_f is lower than the density of the bulk material ρ_B. The ratio $\rho_f/\rho_B = P$ is called packing density. It gives the volume concentration of the material within the whole layer volume.

Optical properties, mainly the refractive index and its dispersion, are strongly influenced by the microstructure of the film. Materials like TiO_2 [8], which may exist in several crystalline phases with large differences in the refractive index, can show optical properties which depend on the film's crystal phase composition. Generally the refractive index of a coating is determined by the grain structure and by the quantity and shape of the voids and pores.

In contact with moist air, most of the voids and pores fill up with water by adsorption and capillar action, changing in this way the average film's refractive index and special characteristics (transmission and reflection spectra).

Therefore, each film which nominally consists of a single material only, has to be considered as a mixture of bulk material and empty or water-filled voids.

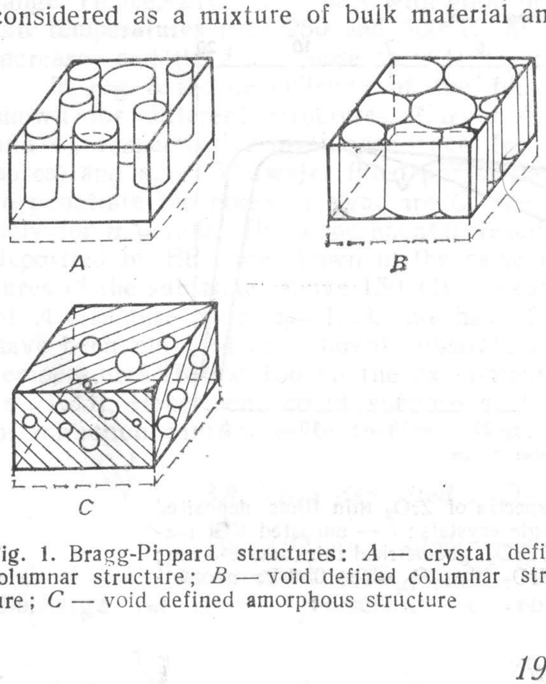

Fig. 1. Bragg-Pippard structures: *A* — crystal defined columnar structure; *B* — void defined columnar structure; *C* — void defined amorphous structure

The interpretation of the dependence of refractive index on packing density *P* can be done on the basis of well-known mixing models [9—11], taking into account information on the microstructure of the film.

Figure 1 shows three types of idealized microstructures: structure *A* — isolated, columnar grains are embedded into voids; structure *B* — isolated, elongated pores are embedded into the film material; structure *C* — isolated holes are distributed in the film.

Structures *A* and *B* are typical for columnar growth mode of the film, but in different ranges of packing density, i. e. structure *A* for low packing density and so-called "crystal defined behaviour" and structure *B* for a packing density higher than 0.9 and "void-defined behaviour". Structure *C* may describe an amorphous state, which is void-defined [12].

As reported elsewhere [13], the use of the Bragg-Pippard model leads to different relations between the refractive index n of the film and its packing density P for these three structures:

$$n^2=\frac{(1-P)n_p^4+(1+P)n_p^2\,n_B^2}{(1+P)n_p^2+(1+P)n_B^2} \qquad (2)$$

for structure *A*,

$$n^2=\frac{Pn_B^2+(2-P)n_B^2\,n_p^2}{(2-P)n_B^2+Pn_p^2} \qquad (3)$$

for structure *B*, and

$$n^2=\frac{2Pn_B^4+(3-2P)n_B^2\,n_p^2}{(3-P)n_B^2+Pn_p^2} \qquad (4)$$

for structure *C*, where n_B is the index of refraction of the bulk material and n_p is the refractive index of the pores ($n_p=1.00$ in vacuum and $n_p=1.33$ in air when all pores are filled with water).

3.2. *Thin ZrO_2 films deposited by EBE*

EBE deposited thin films generally show lower packing density and lower index of refraction than the bulk material. Curve *2* in Fig. 2 shows the IR transmission spectrum of ZrO_2 thin film deposited by EBE on the ⟨100⟩ plane of KCl single-crystal plate at room temperature (RT). One can see the strong water band

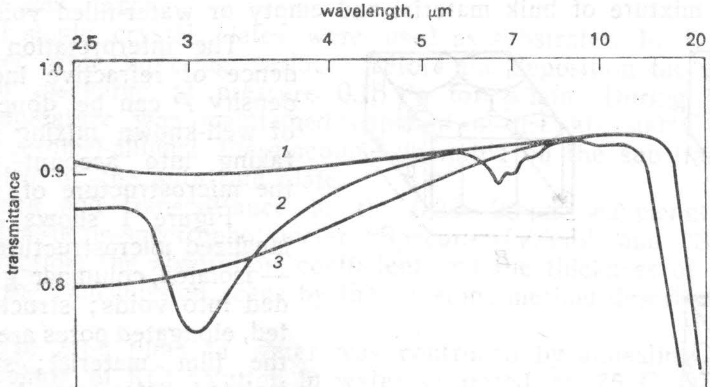

Fig. 2. Infrared (IR) transmission spectra of ZrO_2 thin films deposited at RT on ⟨100⟩ surface of KCl single crystals: *1* — uncoated KCl plate; *2* — KCl plate coated with EBE ZrO_2, geometrical thickness 243 nm; *3* — KCl plate coated with RMS ZrO_2 film, $P_{O_2}=7\times10^{-2}$ Pa, geometrical thickness 174 nm

located at 2.97 μm. Curve *1* in the same Figure is the spectrum of an uncoated KCl plate.

In Fig. 3 two relative transmission spectra ($T_r = T_f/T_s$ where T_f is transmittance of the film-substrate, T_s is transmittance of the substrate, T_r is the relative transmittance) of EBE deposited ZrO_2 films are shown: spectrum 1 was measured immediately after deposition and spectrum 2 was obtained after 5 hours annealing in the way described previously. The geometrical thickness of the film is 177 nm. The comparison of curve *1* with curve *2* in Fig. 3 shows the change of the transmittance because of the increased index of refraction of the film during the annealing. The reason is that during the annealing additional voids or pores are filled with water. The annealing was prolonged for 65 hours but there are no additional changes in the spectra because of the saturation.

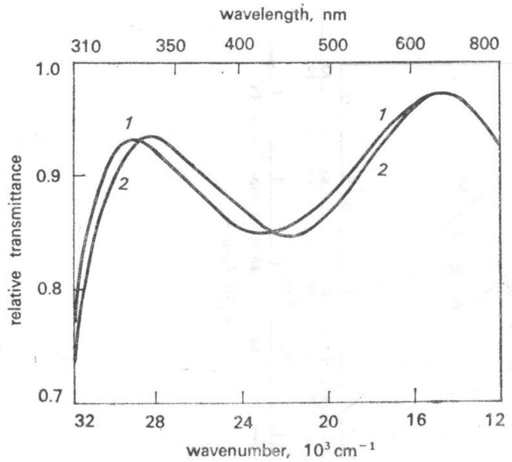

Fig 3. Relative transmission spectra of ZrO_2 thin films deposited by EBE at 160° C on glass substrate: *1* — immediately after the deposition; *2* — after 5 hours annealing in the saturated vapours of a saturated KCl solution in water at 75° C. The geometrical thickness of the film is 177 nm

The substrate temperature is a parameter which essentially determines the film structure and packing density, and the index of refraction, respectively. Figure 4 shows the packing density, index of refraction and absorption coefficient ZrO_2 thin films deposited by EBE at different substrate temperatures. The packing density and index of refraction increase with increasing substrate temperature but the absorption coefficient is minimal in the 250—300° C range. Hence, ZrO_2 thin films with good optical properties could be deposited at substrate temperatures near 250 and 300° C. At higher substrate temperatures the absorption increases and the films loose their transparency.

In Fig. 5 the dependence of the film refraction index on the packing density is shown for different structures. Curves *A*, *B* and *C* were obtained by relations (2, 3 and 4), respectively. *n-P* dependence for *A* structure is plotted for $n_p = 1.00$ (empty pores) and $n_p = 1.33$ (water filled pores). Because of the difficulties for water molecules to penetrate the pores of structure *C*, the calculations in this case have been made only for $n_p = 1.00$. The experimental results for *n-P* dependence of ZrO_2 thin films deposited by EBE are shown in the same Figure with full circles. At higher temperatures of the substrate (above 150° C), the experimental points are very close to the curve of *A* structure with $n_p = 1.33$. We have to note here that coatings with different *P* have been obtained at different substrate temperatures (see Fig. 4). At lower substrate temperatures (below 150° C) the experimental points are situated higher than curve *A* ($n = 1.33$). Hence, one could suppose that some other structure with a higher index of refraction contributes to this case. That could be the amorphous structure *C*.

3.3. RMS deposited ZrO_2 thin films

The ZrO_2 thin films were deposited by RMS on unheated substrates and at constant current (425 A/m²). The dependence of the discharge voltage discharge (at constant discharge current) on the oxygen partial pressure is shown in Fig. 6 by curve *1*. Curves *2* and *3* in the same Figure show the P_{O_2}-dependences of the index of refraction and the packing density. In this case the packing density P was calculated by relation (4) for structure C (at room tempe-

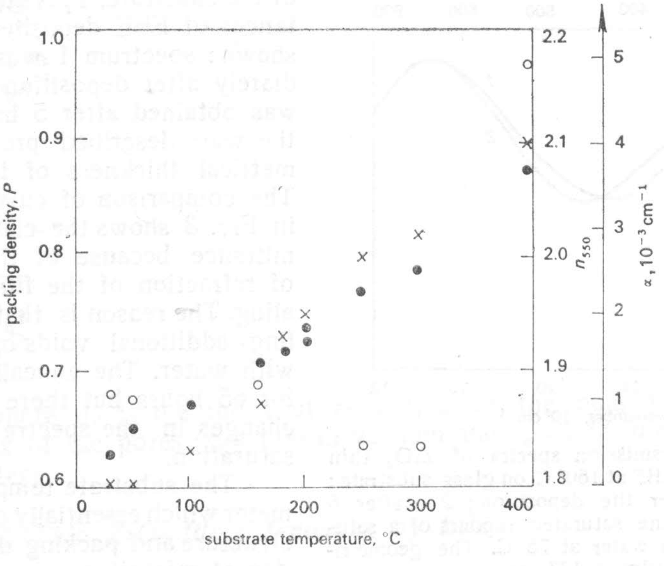

Fig. 4. Substrate temperature dependence of the packing density P (— × —), index of refraction n (— ● —) and absorption coefficient α of ZrO_2 thin films (— ○ —) for films deposited on glass substrates. The index of refraction n and the absorption coefficient α are defined at wavelength 550 nm

rature the sputtered films are generally amorphous). At oxygen partial pressure P_{O_2} below 5×10^{-2} Pa the films show very high absorption in the visible region because of the free Zr which they contain, so n could not been calculated for this P_{O_2}-region using the method described in [4]. At pressure above 5×10^{-2} Pa the films are transparent in the visible region and have a highest index of refraction (about 2.20). The optimum oxygen partial pressure for the RMS-deposited ZrO_2 thin films at RT is that in the region of the maximum of the U-P_{O_2} curve. That is so because at higher P_{O_2} (regardless of the good film quality), the deposition rate drops because of the target oxidation.

Reactive magnetron sputtering of Zr in $Ar+O_2$ atmosphere leads to the deposition of thin films with packing density near unity. The transmission spectra of these films in IR region do not show any absorption of water at 2.97 μm (Fig. 2, curve *3*). It can be seen (Fig. 5) that it is difficult to draw conclusions for the film structure by measuring the index of refraction. It is not possible to distinguish B and C structures. A detail structure investigation is necessary to separate these structures.

4. Conclusions

Zirconium dioxide thin films have been deposited on glass or KCl single crystal substrates by electron beam evaporation or reactive magnetron sputtering.

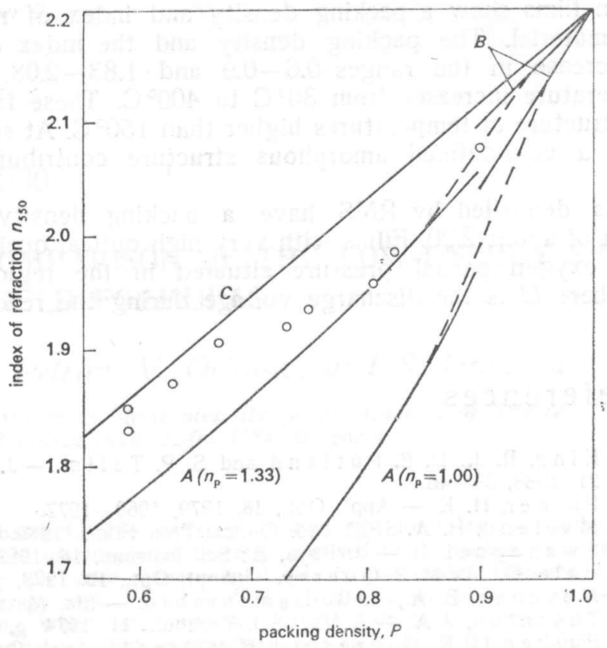

Fig. 5. Dependence of the index of refraction n on the packing density P of ZrO_2 thin films. Curves A, B, C correspond to the structures shown in Fig. 1. n_p is the refractive index of the substance in the pores. Calculation of n for these curves was made, using the relations (2—4) for the corresponding structures. The experimental n-P dependence is shown by full circles

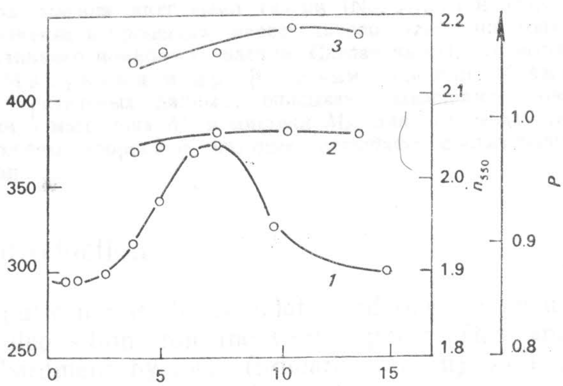

Fig. 6. RMS sputtering of Zr in $Ar+O_2$ atmosphere: *1* — dependence of the discharge voltage U (at constant discharge current density 425 A/m²) on the oxygen partial pressure P_{O_2}; *2*— P_{O_2}-dependence of the index of refraction of ZrO_2 thin films deposited by RMS on glass substrates: *3* — P_{O_2}-dependence of the packing density P

EBE ZrO_2 thin films show a packing density and index of refraction lower than those of the bulk material. The packing density and the index of refraction of EBE ZrO_2 thin films increase in the ranges 0.6—0.9 and 1.83—2.08, respectively, where the substrate temperature increases from 30° C to 400° C. These films grow in crystal-defined columnar structure at temperatures higher than 150° C. At substrate temperatures lower than 150° C a void-defined amorphous structure contributes to the index of refraction.

ZrO_2 thin films deposited by RMS have a packing density near unity and an index of refraction of about 2.20. Films with very high optical quality can be deposited in the range of oxygen partial pressure situated in the region of the maximum of $U\text{-}P_{O_2}$ curve, where U is the discharge voltage during the reactive sputtering.

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