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Compositional dependences of optical parameters of $Ti_{1-x}Zr_xO_2$ thin films

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Ellipsometric and spectroscopic investigations of $Ti_{1-x}Zr_xO_2$ thin films were performed. Dispersion dependences of refractive indices and extinction coefficients in the wavelength interval 0.2–0.7 μm were obtained by optical-refractometric synthesis of transmission spectra; optical-refractometric relation was applied to describe the dispersion of the refractive indices. A nonlinear increase of optical pseudogap and a nonlinear decrease of refractive indices with substitution of Ti by Zr was revealed.

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1. Introduction

Titanium dioxide (TiO_2) and zirconium dioxide (ZrO_2) are materials which have been extensively studied because of their hardness, high chemical stability, excellent dielectric properties, large transparency range from UV to IR and relatively high refractive indices [1-5]. Besides, TiO_2 thin films are effectively employed as functional elements for electrochromic devices, protective antireflecting coatings, solar cells, gas sensors etc [6-9]. Today TiO_2 thin films belong to the most important photocatalytic materials due to the low operation temperature, low cost and rather low energy consumption [10-12].

It should be noted that ZrO_2 films are used as buffer layers for superconductors [13], as biomedical and prosthetic coatings [13, 14], as gas sensors [15] and as components of solid oxide fuel cells [16]. Moreover, Y_2O_3-stabilized ZrO_2 (YSZ) is one of the most important solid electrolyte materials [17]. Through the recent years ZrO_2 have been intensely used as gate dielectrics in metal-oxide-semiconductor field effect transistors and as storage capacitors in dynamic random-access memory devices [18, 19]. ZrO_2 are considered as potential substitutes for SiO_2 due to their high dielectric constant, large band gap, high breakdown field, low leakage current level and superior thermal stability.

Optical properties (transmission spectra, refractive index and extinction coefficient) of TiO_2 and ZrO_2 thin films obtained by different evaporation techniques have been studied in [10, 20-22]. TiO_2-ZrO_2 oxide system exhibit higher photocatalytic activity than pure TiO_2 [23]. The structure and photoluminescence properties of $x TiO_2(1-x)ZrO_2$ ($0 \le x \le 0.7$) nanocrystals prepared by sol-gel method are investigated in [24].

The present paper is aimed at ellipsometric and spectroscopic studies of refractive indices and their dispersion curves, investigation of compositional behaviour of the refractive indices and optical pseudogap of $Ti_{1-x}Zr_xO_2$ thin films, because they are promising materials for various optoelectronic devices, in particular for creation of multilayer dielectric coatings for optical elements of laser engineering. For their elaboration the values of optical and refractometric parameters of the films are of special importance.

2. Experimental

The films were deposited onto a silica glass substrate by electron-beam evaporation, their thickness being 0.4–0.6 μm. The structure of the deposited films was analyzed by X-ray diffraction; the diffraction patterns have shown the films to be amorphous. The substrate temperature was 200-300 °C and standard evaporation rates (~1-2 nm/s) were applied. High-purity initial materials were used, the film composition was controlled by chemical analysis.

Ellipsometric parameters were measured at room temperature by a LOMO LEF-3M-1 laser ellipsometer (λ=632.8 nm). The elaborated ellipsometric software enables one to calculate refractive indices and extinction coefficients of the substrate and the film as well as the film thickness by numeric solution of the main ellipsometric equation [25]. Transmission spectra of the films at room temperature were studied by a LOMO MDR-3 grating monochromator. Computer processing of the interferential transmission spectra enabled the dispersive dependences of the refractive index $n(\lambda)$ of the investigated films to be obtained. Besides, the experimental transmission spectrum is used in order to obtain the spectral dependence of the extinction

coefficient $k(\lambda)$ and to perform the reversed synthesis of the transmission spectrum on the basis of the calculated $n(\lambda)$ and $k(\lambda)$ [26].

3. Results and discussion

The performed ellipsometric studies and subsequent computations enabled us to obtain the values of refractive indices n_L, extinction coefficients k_L at the wavelength λ=632.8 nm and film thicknesses d (the refractive index values are listed in Table 1). The spectrometric studies resulted in interferential transmission spectra, an example of which for TiO_2 thin film is presented in Fig. 1. The transmission spectra were used (i) for calculation of dispersion dependences of refractive indices using thickness values known from the ellipsometric studies and the known numbers of all interferential maxima and minima (insert to Fig. 1); (ii) for calculation of spectral dependences of extinction and absorption coefficients (an insert in Fig. 1) and (iii) for obtaining the calculated transmission spectra using optical-refractometric (OR) synthesis method [27, 28].

The dispersion dependences $n(\lambda)$ of $Ti_{1-x}Zr_xO_2$ thin films, obtained using the above method, are shown in Fig. 2. They can be described by the known OR relation [29]:

$$\frac{1}{3}\frac{n^2(h\nu)+2}{n^2(h\nu)-1}=\left(\frac{\eta_s}{2}\right)^s\left(1+\frac{E_g^*}{E_{p\upsilon}}\right)^s-\left(\frac{h\nu}{E_s}\right)^s, \quad (1)$$

where s=2 for the medium part of the transparency range and s=3 for its high-energy part; E_g^* is the optical pseudogap (E_g^* value corresponds to the energy position of the exponential absorption edge at the coefficient value $\alpha=10^3$ cm^{-1} [30]); η_s and E_s are fitting parameters. The energy of the valence electron plasma vibrations $E_{p\upsilon}$ is determined as [29]

$$E_{p\upsilon}=28.82\sqrt{\frac{n_\upsilon \rho}{\mu}} \text{ (eV)}, \quad (2)$$

where n_υ is the number of valence electrons per formula unit, ρ is density, μ is molar mass. Note that the choice of the OR relation is determined by its advantages with respect to other empirical formulae by Sellmeier, Moss, Ravindra, Wemple-DiDomenico etc. [31-33], namely, based on relating such important parameters as refractive index n, optical pseudogap E_g^* and energy of plasma vibrations of valence electrons $E_{p\upsilon}$, it enables the dispersion of the refractive index to be successfully described. The values of the parameters that provided the best fit between the calculated and experimental $n(\lambda)$ dependences of $Ti_{1-x}Zr_xO_2$ thin films are listed in Table 1.

Table 1. Optical and refractometric parameters of $Ti_{1-x}Zr_xO_2$ thin films.

Film	E_g^* (eV)	n_L (λ=632.8 nm)	$E_{p\upsilon}$ (eV)	E_2 (eV)	E_3 (eV)	η_2	η_3
TiO_2	3.25	2.281	25.13	16.0	9.4	1.3560	1.4770
$Ti_{0.83}Zr_{0.17}O_2$	3.26	2.273	24.90	16.3	9.7	1.3613	1.4750
$Ti_{0.5}Zr_{0.5}O_2$	3.51	2.217	24.45	17.0	10.3	1.3717	1.4712
$Ti_{0.17}Zr_{0.83}O_2$	4.08	2.103	23.99	17.6	10.8	1.3821	1.4673
ZrO_2	4.55	2.016	23.76	17.9	11.1	1.3874	1.4653

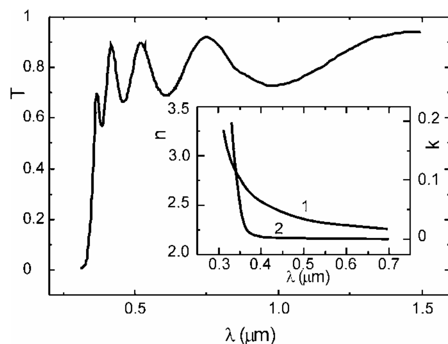

Fig. 1. Spectral dependence of transmission coefficient for TiO_2 thin film at room temperature. The insert shows the dispersion curves of refractive index n (1) and extinction coefficient k (2).

In order to determine the optical pseudogap value E_g^*, optical absorption edge spectra, obtained from the OR synthesis of transmission spectra [27, 28], were used. The performed studies have enabled the character of the dependence of E_g^* and n on the film composition to be elucidated (Fig. 3). With substitution of Ti atoms by Zr the optical pseudogap E_g^* is shown to increase nonlinearly (with downward bowing) from 3.25 eV for TiO_2 to 4.55 eV for ZrO_2. Contrary, the refractive index n (at λ=632.8 nm) of the films decreases nonlinearly (with upward bowing) with the increase of Zr content from n=2.281 for TiO_2 to n=2.016 for ZrO_2.

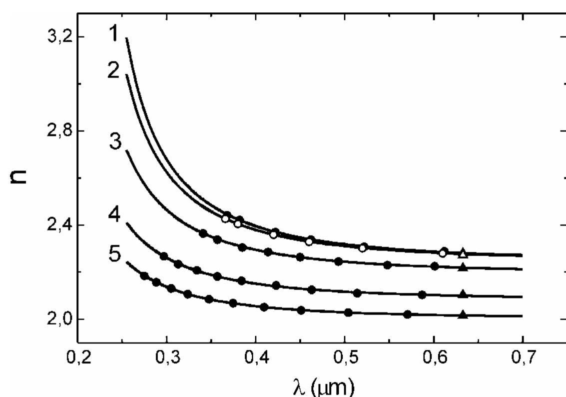

Fig. 2. Dispersion curves of the refractive indices at room temperature for thin films of TiO_2 (1), $Ti_{0.83}Zr_{0.17}O_2$ (2), $Ti_{0.5}Zr_{0.5}O_2$ (3), $Ti_{0.17}Zr_{0.83}O_2$ (4) and ZrO_2 (5). Experimental values of refractive indices, obtained from interferential transmission spectra, are shown by dark (1,3-5) and open (2) circles, the OR-based calculations are indicated by solid lines; triangles denote the n_L values obtained from ellipsometric studies at λ=632.8 nm.

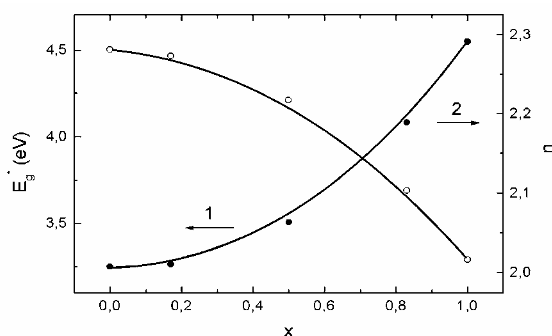

Fig. 3. Compositional dependences of optical pseudogap E^*_g (1) and refractive index n (2) (at λ=632.8 nm) at room temperature for $Ti_{1-x}Zr_xO_2$ thin films. The size of the experimental point symbols exceeds the error bars which are $\pm5\times10^{-4}$ eV for E^*_g and $\pm5\times10^{-5}$ for n.

It should be noted that compositional dependence of the optical pseudogap of mixed solid state systems is with high accuracy described by the expression [34]

$$E^*_g(x) = E^*_g(0) + [E^*_g(1) - E^*_g(0)]x - c_1 x(1-x) \quad (3)$$

where $E^*_g(x=0) \equiv E^*_g(0)$, $E^*_g(x=1) \equiv E^*_g(1)$, c_1 is a so-called bowing parameter being a measure of deviation of $E^*_g(x)$ function from linearity. It is worth mentioning that the description of the experimental dependences $E^*_g(x)$ by Eq. (3) for $Ti_{1-x}Zr_xO_2$ films has led to a positive value c_1=1.59 eV which means downward bowing. It was shown in Refs. [34, 35] that bowing of the $E^*_g(x)$ plot can result from such factors: (i) energy band deformation due to the change of lattice parameters in solid solutions; (ii) change of electronegativity; (iii) structural changes due to the anion bond length variation. The compositional dependence of the refractive indices $n(x)$ of $Ti_{1-x}Zr_xO_2$ thin films is well descibed by a relation similar to Eq. (3):

$$n(x) = n(0) + [n(1) - n(0)]x - c_2 x(1-x) \quad (4)$$

where $n(x=0) \equiv n(0)$, $n(x=1) \equiv n(1)$, c_2 is the bowing parameter, its negative value c_2=–0.276, being the evidence for the upward bowing.

4. Conclusions

Experimental ellipsometric and spectrometric studies of $Ti_{1-x}Zr_xO_2$ thin films have resulted in dispersion dependences of refractive indices which are well described by optical-refractometric relation, relating the refractive index, optical pseudogap and the energy of plasma vibrations of valence electrons. The compositional studies have shown that optical pseudogap nonlinearly increases and the refractive index nonlinearly decreases with Zr content increase. The knowledge of the compositional dependence of main optical-refractometric parameters of $Ti_{1-x}Zr_xO_2$ thin films can be used for construction of optical coatings for laser devices based on the films under investigation.

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