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Spectrometric and ellipsometric studies of $(1-x)TiO_2 \cdot xLn_2O_3$ (Ln = Nd, Sm, Gd, Er, Yb) thin films

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Abstract

Spectrometric and ellipsometric studies of $(1-x)TiO_2 \cdot xLn_2O_3$ (Ln = Nd, Sm, Gd, Er, Yb; $x = 0.33, 0.5$) thin films at room temperature were performed. The obtained dispersion dependences of refractive indices are successfully described by the optical-refractometric relation. The dependence of optical pseudogap and refractive indices on composition and molar mass of the films is investigated. The influence of compositional disordering on the energy width of the exponential absorption edge is studied.

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Keywords: Films and coatings; Ellipsometry; Optical spectroscopy

1. Introduction

Titanium dioxide (TiO_2) thin films have many interesting applications in microelectronics, optics and medicine due to their excellent visible and near-IR transmittance, large energy gap, relatively high refractive index and dielectric constant [1–5]. They are effectively employed as functional elements for electrochromic devices, protective antireflecting coatings, solar cells, gas sensors etc [6–10]. Besides, 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 [11–13]. Rare-earth elements introduced into Hf-, Zr- and Ti oxide-based materials result in modification of the host structure and new physical properties. It should be noted that $HfO_2(ZrO_2)$–Ln_2O_3 (Ln = Nd, Sm, Gd, Er, Yb) compounds exhibit different contributions to electrical conductivity from ionic and electronic components and attract great interest as promising materials for solid state ionic devices [14].

The variety of applications of titanium dioxide-based films requires knowledge of their optical parameters. Thus, the present paper is aimed at ellipsometric and spectrometric studies of refractive indices, their dispersion curves and an investigation of the behaviour of the refractive indices, optical pseudogap and the energy width of the exponential absorption edge in $(1-x)TiO_2 \cdot xLn_2O_3$ (Ln = Nd, Sm, Gd, Er, Yb; $x = 0.33, 0.5$) thin films versus their composition and molar mass.

2. Experimental section

$(1-x)TiO_2 \cdot xLn_2O_3$ (Ln = Nd, Sm, Gd, Er, Yb; $x = 0.33, 0.5$) thin films were deposited onto a silica glass substrate by electron-beam evaporation, their thickness being 0.4–0.5 μm. The structure of the deposited films was analyzed by X-ray diffraction; the diffraction patterns have

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shown the films to be amorphous. The substrate temperature was 200–300 °C, 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-2M laser ellipsometer ($\lambda = 632.8$ nm). The ellipsometric software enables one to calculate refractive indices and extinction coefficients of the substrate and the film as well as the film thickness by subsequent numeric solution of the main ellipsometric equation [15]. The refractive indices and extinction coefficients were determined within the error of $\pm 5 \times 10^{-5}$, and the film thicknesses – within $\pm 5 \times 10^{-4}$ μm. The transmission spectra of the films at room temperature were studied by a LOMO MDR-3 grating monochromator (spectral resolution 5×10^{-4} eV). Transmission coefficients were determined within $\pm 5 \times 10^{-3}$. The computer processing of the interferential transmission spectra enabled the dispersive dependences of the refractive index $n(\lambda)$ of the investigated films to be obtained. In addition, the experimental transmission spectrum was used 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 $k(\lambda)$ [16].

3. Results

The ellipsometric studies and subsequent computations enabled us to obtain the values of refractive indices n_L, extinction coefficients k_L at the wavelength $\lambda = 632.8$ nm and film thicknesses d (the refractive index and film thicknesses values are listed in Table 1). The spectrometric studies resulted in interferential transmission spectra which were used for (i) 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; (ii) for calculation of spectral dependences of extinction and absorption coefficients and (iii) for obtaining the calculated transmission spectra using optical-refractometric (OR) synthesis method [17,18].

In order to determine the optical pseudogap value, optical absorption edge spectra obtained from the OR synthesis of transmission spectra [17,18] were used. Note that the OR synthesis differs from conventional inverse synthesis [16] by the fact that (i) for the description of dispersion $n(\lambda)$ the above OR relation is used and (ii) an algorithm for separation of the edge $k_{\mathrm{edge}}(h\nu)$ and background $k_{\mathrm{back}}(h\nu)$ absorption is employed:

Table 1
Film thicknesses d; optical pseudogap E_g^*; refractive index n_L at $\lambda = 632.8$ nm; energy of plasma vibrations of valence electrons E_{pv} and adjustment parameters E_2, E_3, η_2, η_3 in (3) for $(1-x)TiO_2 \cdot xLn_2O_3$ (Ln = Nd, Sm, Gd, Er, Yb; $x = 0.33, 0.5$) thin films

Film	d (μm)	E_g^* (eV)	n_L	E_{pv} (eV)	E_2 (eV)	E_3 (eV)	η_2	η_3
$0.5TiO_2 \cdot 0.5Nd_2O_3$	0.404	4.960	1.914	18.41	10.4	8.2	1.365	1.413
$0.5TiO_2 \cdot 0.5Sm_2O_3$	0.415	3.932	1.893	18.36	7.4	6.2	1.468	1.497
$0.5TiO_2 \cdot 0.5Gd_2O_3$	0.442	3.338	1.957	19.25	6.7	5.7	1.503	1.534
$0.5TiO_2 \cdot 0.5Er_2O_3$	0.406	3.224	2.137	20.95	9.5	7.1	1.406	1.489
$0.67TiO_2 \cdot 0.33Nd_2O_3$	0.508	3.703	2.081	20.66	9.8	7.5	1.397	1.470
$0.67TiO_2 \cdot 0.33Sm_2O_3$	0.408	3.454	2.076	21.62	9.1	7.2	1.429	1.498
$0.67TiO_2 \cdot 0.33Gd_2O_3$	0.484	3.301	2.091	21.75	8.9	7.0	1.436	1.505
$0.67TiO_2 \cdot 0.33Yb_2O_3$	0.468	3.007	2.110	21.95	8.2	6.7	1.457	1.523
TiO_2	0.422	3.250	2.281	25.13	16.0	9.4	1.356	1.477

The film thickness was determined within the error of $\pm 5 \times 10^{-4}$ μm, optical pseudogap – within $\pm 5 \times 10^{-4}$ eV, refractive indices – within $\pm 5 \times 10^{-5}$.

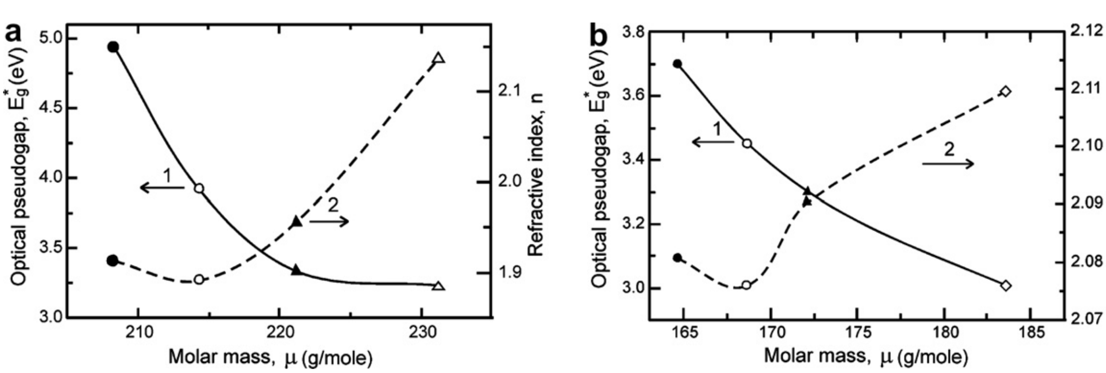

Fig. 1. Dependences of optical pseudogap E_g^* (1) and refractive index n_L (2) (at $\lambda = 632.8$ nm) at room temperature for $0.5TiO_2 \cdot 0.5Ln_2O_3$ (a) and $0.67TiO_2 \cdot 0.33Ln_2O_3$ (b) thin films on the film molar mass. Ln symbol stands for Nd (dark circles), Sm (open circles), Gd (dark triangles), Er (open triangles), and Yb (open diamonds). The solid and dashed lines are drawn to guide the eye. The size of the experimental point symbols exceeds the error bars which are $\pm 5 \times 10^{-4}$ eV for E_g^* and $\pm 5 \times 10^{-5}$ for n.