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Optical Studies of Nanocrystalline and Amorphous TiO_2 Thin Films Deposited by HiTUS Technique

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Abstract. TiO_2 thin films were deposited on glass substrates by HiTUS (high target utilization sputtering) technique. Structural studies of TiO_2 thin films of different thickness were performed by X-ray diffraction. Refractive index and extinction coefficient were measured by spectroscopic ellipsometer. Transmission spectra of TiO_2 thin films were investigated in the temperature interval 77–300 K. The temperature behaviour of Urbach absorption edge for TiO_2 thin film was studied. The effect of temperature on the optical parameters and order-disorder processes in TiO_2 thin films was analysed.

Keywords. thin film; optical absorption; refractive index; Urbach behaviour; structural disorder

I. INTRODUCTION

Titanium dioxide (TiO_2) thin films are interesting for practical applications in microelectronics, optics and medicine due to their visible and near-IR transmittance, optical and dielectric constants [1-5]. They are effectively used as multifunctional elements for different devices such as the electrochromic devices, protective antireflecting coatings, solar cells, gate insulator in MOSFETs, etc. [6-9]. Besides, today TiO_2 thin films are known as the most important photocatalytic materials due to the low operation temperature, low cost and low energy consumption [10-12]. Recently good sensing properties of TiO_2 to H_2, CO, ethanol, methane, etc. were reported which makes it a promising material for gas sensors [13-16]. It should be noted that gas sensing properties of nanocrystalline TiO_2 thin films prepared by magnetron sputtering were studied earlier [17].

The variety of applications of TiO_2 thin films requires knowledge of their optical properties. The present paper is devoted to the deposition, structural, ellipsometric, and spectrometric studies of refractive index and extinction coefficient, transmission spectra and absorption spectra as well as investigation of the temperature dependence of Urbach absorption edge parameters in TiO_2 thin films.

II. METHODOLOGY OF EXPERIMENT

TiO_2 thin films were deposited on glass substrates at room temperature by HiTUS technique in reactive $Ar+O_2$ discharges. The plasma source power density was equal of 2000 W while the deposition rate was equal of approximately 1.5 nm/min. Thin films depositions were performed at floating plasma potential.

The structural studies of TiO_2 thin films was carried out by Bragg-Brentano X-ray diffraction (XRD), an URD8 diffractometer with Cu K_α radiation ($\lambda_{CuK\alpha}$= 0.15418 nm) and a graphite curved monochromator were used. The thickness of TiO_2 thin films were measured in cross-section with scanning electron microscope (SEM) TESCAN TS 5136 MM. In the present paper, we investigate TiO_2 films with thickness from 14 nm to 250 nm.

Spectroscopic ellipsometer M-2000V was used for optical constant measurements. Optical transmission spectra of TiO_2 thin films were measured in the temperature range 77–300 K by MDR-3 grating monochromator. For low-temperature studies an UTREX cryostat was applied. Absorption coefficients and refractive indeces of the thin films were calculated using the method which described in Ref. [18].

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III. EXPERIMENTAL RESULTS AND DISCUSSION

XRD patterns for four samples of TiO_2 thin films with the thicknesses of 14.7 nm, 47.9 nm, 75.2 nm, and 222 nm are presented in Fig. 1. It is shown that TiO_2 thin film with the minimal thickness of 14.7 nm (Table 1, sample 4) is amorphous while with increasing thickness nanocrystalline inclusions of anatase and rutile phases of TiO_2 appear (Fig.1). Comparison of the intensities of the X-ray diffraction peaks shows that in thin TiO_2 films with thicknesses of 47.9 nm and 222 nm the fractions of the nanocrystalline inclusions of the anatase and rutile phases are roughly equal (Table 1, sample 1 and sample 3) while in the thin film with thickness of 75.2 nm (Table 1, sample 2) the rutile phase fraction obviously exceeds that of the anatase phase. This fact will be helpful to explain the variation of the optical parameters of TiO_2 thin films.

TABLE 1. ABSORPTION EDGE PARAMETERS FOR TiO_2 THIN FILMS WITH DIFFERENT THICKNESS

Sample	Film thickness (nm)	E_g^{α} (eV) at 300 K	E_U (meV)
1	222	3.527	167.2
2	75.2	3.331	276.5
3	47. 9	3.593	111.5
4	14.7	3.221	199.2

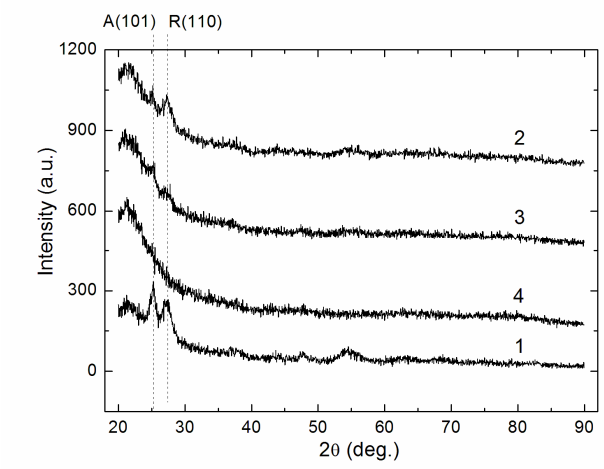

Fig. 1. XRD spectra of TiO_2 thin films with different thickness: (1) 222 nm, (2) 75.2 nm, (3) 47.9 nm, and (4) 14.7 nm.

Refractive indeces n and extinction coefficients k for the TiO_2 thin film (sample 1) were obtained from spectral ellipsometry measurements which carried out in the spectral range of 0.4–1.0 μm (Fig. 2). At λ= 1 μm the refractive index for the thin film is 2.362 while for the crystal refractive index equals 2.582. In the transparency region the slight dispersion of the refractive index is observed, refractive index increases when approaching to the absorption edge. The anomalous dispersion of refractive index is revealed in the region of the extinction coefficient increase.

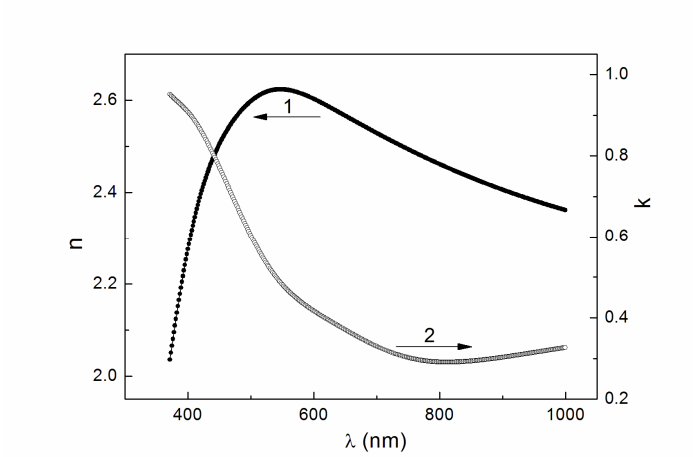

Fig. 2. Spectral dependences of the refractive index n (1) and extinction coefficient k (2) for TiO_2 thin film with d=222 nm.

The optical transmission spectra at room temperature for as-deposited TiO_2 thin films with different thicknesses are shown in Fig.3,a and the spectral dependences of the absorption coefficient for TiO_2 thin films with different thickness are presented in Fig.3,b. The energy pseudogap E_g^{α} for TiO_2 thin films was determined as the energy position of the exponential absorption edge at a fixed absorption coefficient value α=5×10^4 cm^{-1}. The parameters of Urbach absorption edge for the TiO_2 thin films of different thickness are given in Table 1.

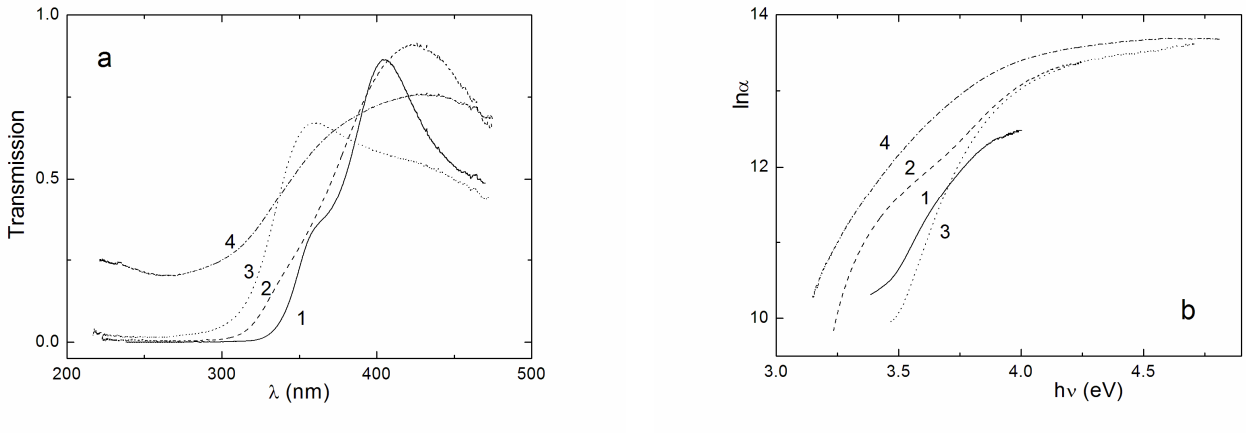

Fig. 3. Spectral dependences of the optical transmission (a) and absorption coefficient (b) of TiO_2 thin films with different thickness: (1) 222 nm, (2) 75.2 nm, (3) 47.9 nm, and (4) 14.7 nm.

It is shown that the highest value of the energy pseudogap is observed for the thin films with approximately equal fraction of the anatase and rutile phases (samples 1 and 3) whereas it decreases with increasing rutile phase fraction (sample 2), and the lowest energy pseudogap is revealed for the fully amorphous thin film (sample 4). The trend of the downward shift of the energy pseudogap in the thin film with excessive fraction of rutile nanocrystal inclusions is in agreement with the results of Ref. [19] where a decrease of the band gap value at the transition from anatase thin film to rutile thin film with phase is observed. Besides, the E_g^{α} value for the amorphous thin film (sample 4) correlates with the results of Ref. [20], in which the optical properties of amorphous TiO_2 thin films deposited by the electron-beam evaporation were studied. It should be noted that Urbach energy which characterises the degree of disorder in a physical

system, is highest for the thin film with the excessive content of rutile nanocrystal inclusions (sample 2), and lowest for the thin film with approximately equal fractions of the anatase and rutile phases (sample 3).

Temperature studies of TiO_2 thin film were performed for the sample with thickness of 222 nm (sample 1). A long-wavelength shift of the short-wavelength part of the optical transmission spectra and the interference maxima with temperature is observed. Figure 4 shows the spectral dependences of the absorption coefficient at different temperatures in the interval 77-–300 K for the TiO_2 thin film. It is revealed that the absorption edge for the TiO_2 thin film in the region of its exponential behaviour is described by Urbach rule [21]

$$\alpha(h\nu,T)=\alpha_0\cdot\exp\left[\frac{h\nu-E_0}{E_U(T)}\right], \tag{1}$$

where $E_U(T)$ is Urbach energy, α_0 and E_0 are the convergence point coordinates of Urbach absorption edge, $h\nu$ and T are the photon energy and temperature, respectively. Constants α_0 and E_0 for TiO_2 thin film (sample 1) are given in Table 2.

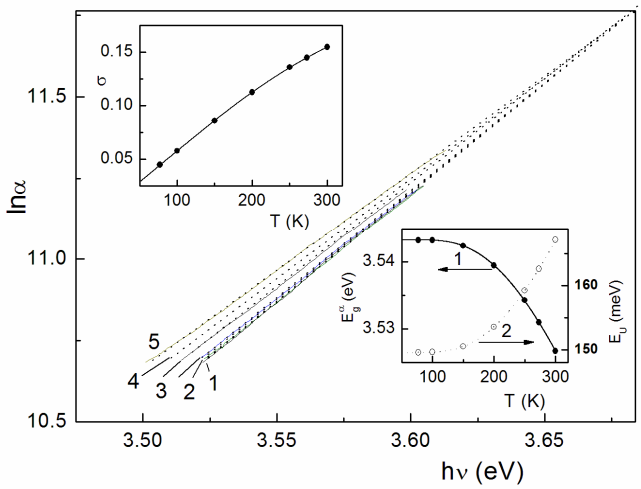

Fig. 4. Spectral dependences of the absorption coefficient of TiO_2 thin film with d=222 nm at various temperatures: (1) 77, (2) 150, (3) 200, (4) 250, and (5) 300 K. The insets show the dependences of the steepness parameter σ, the energy pseudogap E_g^α (α=5×10^4 cm^{-1}) (1) and the Urbach energy E_U (2) on temperature.

The exponential behaviour of the absorption edge is usually explained by the exciton (electron)-phonon interaction (EPI) [20]. Urbach energy $E_U(T)$ is related to the slope of the Urbach absorption edge $\sigma(T)$ as $E_U(T)=kT/\sigma(T)$, where k being the Boltzmann constant. The inset in Fig.4 shows that for the TiO_2 thin film the $\sigma(T)$ dependence is described by the Mahr equqtion [22]:

$$\sigma(T)=\sigma_0\cdot\left(\frac{2kT}{\hbar\omega_p}\right)\cdot\tanh\left(\frac{\hbar\omega_p}{2kT}\right), \tag{2}$$

where σ_0 is a parameter, independent of temperature; $\hbar\omega_p$ is the effective phonon energy in a single-oscillator model, which describing the EPI. For the TiO_2 thin film $\sigma_0 < 1$, which indicates the strong EPI [23]. The values of the effective phonon energy $\hbar\omega_p$ participating in the formation of the absorption edge as well as the σ_0 parameter are listed in Table 2.

The temperature dependences of the energy gap E_g^{α} and the Urbach energy E_U for the TiO_2 thin film are presented in the inset to Fig. 4. For the TiO_2 thin film E_g^{α} and E_U can be described by equations [24, 25]

$$E_g^{\alpha}(T) = E_g^{\alpha}(0) - S_g^{\alpha} k\theta_E \left[\frac{1}{\exp(\theta_E / T) - 1} \right], \tag{3}$$

$$E_U(T) = (E_U)_0 + (E_U)_1 \left[\frac{1}{\exp(\theta_E / T) - 1} \right], \tag{4}$$

where $E_g^{\alpha}(0)$ and S_g^{α} are the energy pseudogap at 0 K and the constant, respectively; θ_E is Einstein temperature, corresponding to the average frequency of phonon excitations of a system of non-coupled oscillators, $(E_U)_0$ and $(E_U)_1$ are constants. The $E_g^{\alpha}(0)$, S_g^{α}, θ_E, $(E_U)_0$, and $(E_U)_1$ parameters obtained for the TiO_2 thin film are listed in Table 2. The temperature dependences of the energy pseudogap E_g^{α} and Urbach energy E_U for TiO_2 thin film obtained from Eqs. (3) and (4) are depicted in the inset to Fig. 4 by solid and dashed lines, respectively.

TABLE 2. ABSORPTION EDGE PARAMETERS AND EPI PARAMETERS FOR TiO_2 THIN FILM WITH *d*=222 nm

Film	TiO_2
E_g^{α} (300 K) (eV)	3.527
E_U (meV)	167.2
α_0 (cm^{-1})	1.28×10^5
E_0 (eV)	3.684
σ_0	0.248
$\hbar\omega_p$ (meV)	74.0
θ_E (K)	859
$(E_U)_0$ (meV)	149.6
$(E_U)_1$ (meV)	290.9
$E_g^{\alpha}(0)$ (eV)	3.543
S_g^{α}	3.68

It appears that the absorption edge of the TiO_2 thin films are highly smeared and characterised by the Urbach tails which leads to the high values of Urbach energy E_U (Table 1). The Urbach behaviour of the absorption edge are explained by the effect of different types of disordering [26], i.e. Urbach energy E_U is described by the relation

$$E_U = (E_U)_T + (E_U)_X, \tag{5}$$

where $(E_U)_T$ and $(E_U)_X$ are the contributions to E_U from temperature-related and structural disordering, respectively. It should be noted that the structural disordering is caused by the high concentration of disordered oxygen vacancies while the temperature-related disordering is caused by the thermal vibrations of the atoms. For the evaluation of the contribution of the different types of disordering into the Urbach energy E_U we applied the procedure described in Ref. [27]. Thus, the contribution of structural disordering into the TiO_2 thin film Urbach energy is shown to be 89.5%.

IV. CONCLUSIONS

TiO_2 thin films are deposited onto silicate glass substrates by means of HiTUS (high target utilization sputtering). XRD studies were performed for structural characterisation of TiO_2 thin films with different thickness. Spectral dependences of the optical constants (refractive index and extinction coefficient) were measured by spectroscopic ellipsometry. Temperature investigations of the transmission spectra for TiO_2 thin film was performed in the interval 77–300 K. A red shift of the absorption edge with increasing temperature was observed, the edge in the range of its exponential behaviour being well described by the Urbach relation. The dependences of the energy pseudogap and Urbach energy on temperature for the TiO_2 thin film were analysed. The temperature-related and structural disorder affect the absorption edge, the contribution of the structural disordering into the Urbach energy for the TiO_2 thin film was estimated.

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