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Properties of transparent oxide thin films prepared by plasma deposition

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In this paper, thin films of TiO_2 were deposited onto (100) oriented silicon and glass substrates using low pressure hot target reactive magnetron sputtering (LP HTRS) method. X-ray diffraction (XRD) and optical transmission measurements have been applied to study the influence of substrate type on the microstructure and optical properties of the prepared thin films, respectively. Thin films exhibit the TiO_2-anatase crystalline state, which could be confirmed by the appearance of peaks of (101) orientation.

Keywords: transparent thin film, sputtering process, titanium oxide, hot target.

1. Introduction

To fabricate transparent thin films composed of various metal oxides, different deposition techniques have been employed [1, 2]. In terms of process efficiency as well as microstructural properties, the sputtering methods can be considered as the most effective [3–6].

In this work, a combination of different operation modes used in typical sputtering processes [4], such as: reactive mode without argon, low pressure of pure oxygen and additionally heated target surface were applied. This process has been termed by the authors as low pressure hot target reactive magnetron sputtering (LP HTRS). It has been shown that a modification of sputtering conditions makes it possible to obtain thin oxide layers of TiO_2 with desired structural and optical properties.

2. Experimental procedure

Thin films of TiO_2 were fabricated in the vacuum chamber pumped with diffusion and rotary pumps to the pressure of 10^{-3} Pa. A circular magnetron with 100 mm in diameter and 3 mm thick titanium (purity 99.99%) disc was used. Titanium target was placed at a distance of 1–1.5 mm from the cooling plate. The magnetron was powered by pulsed power supply in the unipolar mode with 165 kHz sinusoidal pulses. The target-to-substrate distance was 90 mm, and the substrates during deposition were additionally heated up to 570–670 K. The titanium oxide thin films were deposited in reactive atmosphere using a high purity (99.999%) oxygen gas. Stable oxygen plasma has been obtained by choosing proper reactive gas pressure (about 10^{-1} Pa) and appropriate level of active power. The rate of the thin film deposition was kept at about 0.1 nm/s.

Thin films were deposited onto monocrystalline (100) oriented silicon wafers (300 μm thick) and glass substrates. The thickness of the films fabricated by LP HTRS was measured by optical interference method with Hg (551 nm) filtered lamp.

3. Results of structural analysis of titanium dioxide thin films

In order to examine the microstructure of manufactured thin films the X-ray diffraction (XRD) was applied. The measurements were performed on a DRON-2 powder diffractometer using Fe- filtered Kα Co radiation. The size of crystallites was measured at the full width at half maximum (FWHM) of the peaks on XRD patterns using Scherrer equation corrected for instrumental and spectral line broadening and $K\alpha_1\alpha_2$ doublet.

In Figure 1, XRD patterns of TiO_2 thin films with the thickness of 415 nm, manufactured by LP HTRS on glass (Fig. 1**a**) and monocrystalline silicon (Fig. 1**b**) substrates have been compared.

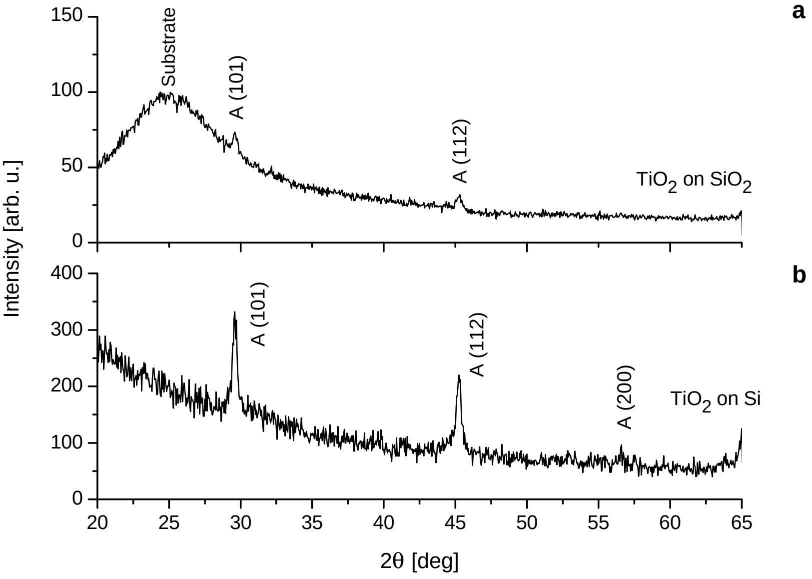

Fig. 1. XRD patterns of TiO_2 thin films with the thickness of 415 nm deposited on glass (**a**) and silicon (**b**).

Table. Structural properties of TiO_2 thin films deposited by LP HTRS determined for the (101) rutile diffraction peak.

Substrate	Film thickness [nm]	Property		References
		D [nm]	*d* [nm]	
Glass	415	20.8	0.3504	Fig. 1**a**
Si	415	35.8	0.3506	Fig. 1**b**
TiO_2-anatase			0.3521	[7]

Both samples were amorphous with weak diffraction lines of titanium oxide-anatase. The wide peak in diffraction pattern, recognizable in Fig. 1**a** in the low range of 2θ angles, results from the kind of applied substrate. It can be seen that the application of a single crystal substrate (Fig. 1**b**) allowed us to obtain thin films with the higher degree of crystallization.

The distribution of intensities of particular lines in diffraction patterns suggests that the microstructure of TiO_2 thin films on silicon exhibits (101) preferential orientation. Based on recorded spectra for both samples being investigated, the lattice distances *d* corresponding to the (101) plane orientation have been determined. The results have been collected in the Table. The lattice distances *d* are comparable for both kinds of applied substrates, but grain size *D* for Si substrate is bigger than that for the glass. Moreover, the obtained spacing values *d* in the fabricated thin films were a little smaller than those of the bulk ones for particular crystallographic plane, *i.e.*, 0.3504 nm and 0.3506 nm for the (101) anatase peak centered at $2\theta \approx 29.5°$ [7]. This implies that the thin films were compressed as compared to the bulk material. Lower content of *d* (compression of structure) indicates that the molecules condensing on the substrate have a higher energy than the energy necessary for the formation of layers on the substrate. In the modification of sputtering method employed by the authors, the excessive energy comes from the hot target heated by plasma discharge, which differs from the typical, high-energy plasma assisted process.

4. Optical properties

The optical properties of manufactured thin films were investigated by means of optical transmission method in the spectral range from 200 to 1400 nm in "so-called" bright configuration.

In Figure 2, the normalized transmission characteristic $T_\lambda(\lambda)$ of the TiO_2 thin films has been presented. The fringes visible in the transmission spectra result from the multiple interference of the light reflected from the two optical interfaces: air–thin film and thin film–substrate. Extrapolation of the linear part of the spectra in the short wavelength range yields the position of the fundamental absorption edge (*i.e.*, $\lambda_{\mathrm{cutoff}}$) at 330 nm.

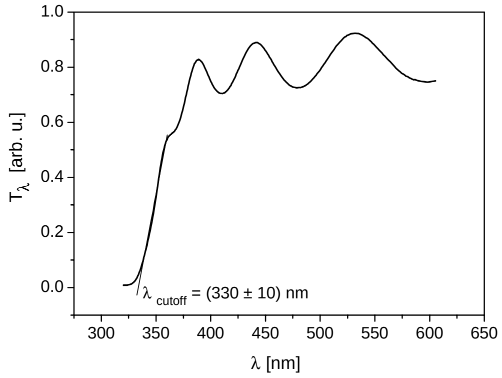

Fig. 2. Normalized transmittance spectra of the TiO_2 thin films, 415 nm thick.

An inclination of the characteristic presented and a small attentuation around 360 nm, which cannot be due to the interferences in the thin film, are clearly seen in Fig. 2. They might come from structural disorder, which is testified by a little contraction of the interplanar distances.

The refractive index *n* (Fig. 3**a**) has been calculated by the well known envelope method [8, 9]. The value of *n* is almost constant in the wide spectral range and is equal to 2.08. This indicates a high quality and dense structure of manufactured TiO_2 thin films. The drop of *n* in the shorter range results from the calculation method applied. Close to the fundamental absorption, transmission characteristics can be converted to the absorption spectra (Fig. 3**b**) using the following relation [1]:

$$\alpha(\lambda) = d^{-1} \ln \frac{1}{T_{\lambda}(\lambda)}$$

where *d* is the thickness of the thin film.

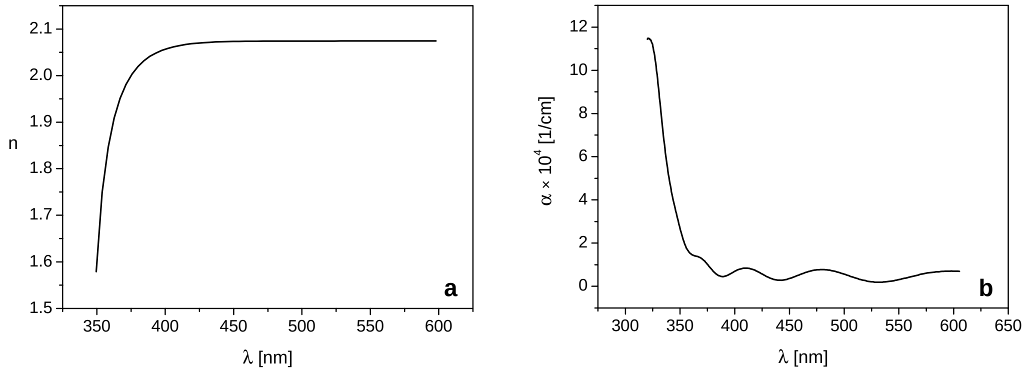

Fig. 3. Characteristics of refractive index (**a**) and absorption (**b**) *vs.* wavelength λ for the TiO_2 thin films.

As it results from Fig. 3**b**, the value of α increases rapidly in the short wavelength range. The effect observed is due to the light absorption in the thin film. That is why most semiconducting and conducting oxides are not transparent for the visible light in the blue region [10].

5. Conclusions

Transparent TiO_2 thin films have been deposited onto (100) oriented silicon and glass substrates using LP HTRS method. In this method oxygen as working gas and the pressure of 10^{-1} Pa was applied.

The results obtained by XRD method confirmed that the TiO_2-anatase phase was formed both on Si (100) as well as glass substrate. It can be seen that the application of a single crystal substrate made it possible to obtain thin films with the higher degree of crystallization and preferred (101) grain orientation.

The fundamental absorption edge ($\lambda_{\text{cutoff}} = 330$ nm) and the absorption spectra have been obtained from optical transmission measurements. The optical properties correspond to the TiO_2-anatase phase and are in agreement with data reported in the literature [11].

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