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On the optical constants of TiO_2 thin films. Ellipsometric studies

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Abstract

TiO_2 thin films were obtained on unheated glass substrates by a DC reactive magnetron sputtering method. The as-deposited films exhibit an amorphous structure as observed from X-ray diffraction (XRD) patterns. The structure changes to a mixed one of 70% anatase and 30% rutile after heat treatment in air in the temperature range 293–673 K. Using ellipsometric measurements, and a computer to solve the corresponding equations, a modeling technique was used to find the optical constants of the studied thin films. A sensitivity analysis was performed. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Titanium dioxide thin films are extensively used in optical device applications, as anti-reflection coatings [1], multilayer optical coatings [2], optical waveguides [3], etc., owing to their good durability, high transmittance in the visible spectral range, and high index of refraction. The structure of the films can be modified by different processing (changing the deposition parameters, heat treatment) [4–7] or by doping with different impurities (In, Ce, Nb, or Fe) [8–10]. As a consequence, the optical constants of the thin films change. In this paper, we present the influence of heat treatment on the TiO_2 film structure and, as a consequence, on its optical constants.

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2. Experimental

TiO_2 films were deposited onto unheated glass substrates by DC reactive magnetron sputtering. The substrate temperature reached 373 K without heating, because of sputtering. Metallic titanium (99.5%) of 50 mm diameter was used as a sputtering target. Pure argon (N5.7) and oxygen (N4.8) were used as the sputtering and reactive gases, respectively. Sputtering pressure was kept at 10^{-3} Torr (10% argon and 90% oxygen). Sputtering current and voltage were kept at 400 mA and 450 V, respectively. The target-substrate distance was 15 cm. The sputtering time was 30 min.

As-deposited samples were heat-treated in the temperature range 293–673 K. The heat treatment, performed in air, consisted of two successive heatings and coolings (20°C/min).

An Alpha-Step 500 Surface Profiler was used for measuring the thicknesses of the samples. X-ray diffraction measurements were performed in grazing incidence geometry at 5° (Geigerflex, Rigaku). The diffractometer settings were Cu Kα radiation, $U = 40$ kV, and $I = 30$ mA.

For ellipsometric measurements, an IFTAR ellipsometer with a high-pressure mercury-vapor lamp and a monochromatic filter was used in the PCSA variant (polarizer P/quarter wave plate C/sample S/analyzer A/photomultiplier). All the angles are reported in regard to the incidence plane, the sensitivity of the readings being of 1 min.

3. Results and discussion

Depositing thin films onto unheated substrates leads to an amorphous structure because the adatom mobility is negligible, thus the atom condensation takes place near the point of impingement [11]. With heat treatment, a crystalline structure develops. XRD patterns (Fig. 1) show that the structure is a mixed one of anatase and rutile. The weight percentage of the anatase phase is 70%, as calculated with a formula given by Spurr [12].

To obtain the optical constants of thin films, we considered a system (i.e., substrate covered with a film) placed in an ambient assumed to be homogeneous, isotropic, and transparent with the index of refraction n_1. The complex indices of refraction $\bar{n}_3 = n_3 - jk_3$ and $\bar{n}_2 = n_2 - jk_2$ characterize the substrate and the film, respectively.

The expression of the fundamental equation of ellipsometry is [13]

$$\bar{\rho} = \mathrm{tg}\Psi \exp(j\Delta) = \frac{\bar{r}^p_{12} + \bar{r}^p_{23}\exp(-2j\delta)}{1 + \bar{r}^p_{12}\bar{r}^p_{23}\exp(-2j\delta)} \cdot \frac{1+\bar{r}^s_{12}\bar{r}^s_{23}\exp(-2j\delta)}{\bar{r}^s_{12} + \bar{r}^s_{23}\exp(-2j\delta)} \qquad (1)$$

Here, Δ is defined as the relative phase difference and $\tan\Psi$ is the change in the amplitudes ratio upon reflection. The complex variables $\bar{r}^p_{ij}$ and $\bar{r}^s_{ij}$ depend on the optical constants of the ambient (medium 1), thin film (medium 2), and substrate (medium 3) and also on the propagation angles φ_i ($i, j = 1, 2, 3$) in each medium. δ is the change in phase of the beam of vacuum wavelength λ, caused by traversing the film of thickness d and complex index of refraction $\bar{n}_2$.

By introducing into Eq. 1, the expressions of $\bar{r}^p_{ij}$, $\bar{r}^s_{ij}$, φ_i, and δ [13], then separating the