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Electrical conduction mechanism in polycrystalline titanium oxide thin films

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ABSTRACT

Titanium oxide thin films were deposited onto glass substrates by a d.c. reactive sputtering technique. The temperature dependence of the electrical conductivity was studied using surface type cells, in a wide temperature range (120 K–570 K). The experiments showed that, after a heat treatment within the high temperature range 300 K–570 K, the temperature dependence of the electrical conductivity became reversible. The structural analysis of the heat-treated films indicated a polycrystalline anatase or/and rutile structure. The mechanism of the electronic transport in the studied samples was explained by applying models elaborated for films with polycrystalline (discrete) structure. Some characteristic parameters of these models were calculated: the energy barrier, $E_B = (0.046–0.082)$ eV and the constant interface-state distribution, $N_{SS} = (3.02\times10^{12}–1.23\times10^{13})\,cm^{-2}\,eV^{-1}$.

1. Introduction

Titanium dioxide (TiO_2) has been regarded as materials with many attractive properties such as large band gap, high electrical resistivity, high dielectric constant, high oxidative power etc. [1,2]. Consequently, this oxide offers an important number of applications (optical thin film devices, capacitors in microelectronic devices, high-density dynamic-memory applications, gas sensors, etc.) [3–6]. There are different advantageous methods used to obtain TiO_2 thin film with different desired properties: reactive sputtering, sol–gel method, spray pyrolysis, etc. [1–7]. Reactive sputtering is indicated to obtain uniform and dense films, with well-controlled stoichiometry [2,6,8–13], desired in electronic applications. Understanding the electronic properties of the transition-metal oxides is a precondition required in electronic device application. Many efforts have been performed in this direction [8–14], but the picture of the electrical transport mechanisms of these materials is not very clear yet.

TiO_2 thin films, deposited by d.c. reactive sputtered, have been chosen to be studied in this paper. Their electrical conduction mechanism is explained in the temperature range 120 K–570 K, by applying some models elaborated for films with polycrystalline (discrete) structure.

2. Experimental

The studied titanium oxide films, were deposited onto heated glass substrates by a reactive d.c. sputtering technique. Argon, used as sputtering gas, has the partial pressure of 1.4×10^{-3} mbar, while the reactive gas (water vapors) has the partial pressure of 0.6×10^{-3} mbar. The target to substrate distance was about 15 cm. The deposition rate was 0.03 nm/s. Details on other deposition parameters are indicated in Table 1.

Thickness measurements, performed with a Surface Profiler, revealed very close values for the samples under study, as presented in Table 1.

To obtain a clear image on the phase composition of the studied TiO_2 thin films, we have chosen the Grazing Incidence Angle geometry in a computer-controlled diffractometer (Cu K_α radiation, $\lambda = 1.54$ Å). The small angle (here 5°) made by the incident beam with the surface sample, determines an increase in the path length of the X-ray beam through the film, having as an effect the increase in the intensity peaks from the film and a decrease in the diffracted signal from the substrate. In a θ–2θ conventional geometry, some of the peaks, like the most intense peak of anatase, A(101), could be hidden by the amorphous "shoulder" of the glass substrate.

For electrical resistance measurements, gold rectangular electrodes, placed parallel one to each other at a distance of 0.5 mm, have been deposited onto titanium oxide films, by thermal evaporation under vacuum. The electrical measurements were performed at high temperatures (300 K–570 K) with a Keithley 617 electrometer and at low temperatures (120 K–320 K) with a Keithley 196 multimeter. For the high temperature measurements, the samples were heat-treated in air. The heat treatment consisted in two successive heatings and coolings (20 K/min) in the temperature range $\Delta T =$ (300 K–570 K), resting 5 min at the highest temperature. For low temperature measurements, the samples were cooled in a continuous He flow cryostat (Cti-Cryogenics-Helix Technology Corporation).

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Table 1
Thickness of the films (d), substrate temperature (T_S), weight percentage of the anatase phase (W_A), average crystallite sizes for the anatase phase (D_A) and for the rutile phase (D_R), the temperature range in which the energy barrier height has been determined (ΔT_1), the energy barrier height (E_B) in the low temperature range, relative permittivity (ε_r), impurity concentration calculated from Eq. (6) (N_G), correlation coefficient R and standard deviation SD of the straight-line fits.

Film	d (nm)	T_S (K)	W_A (%)	D_A (nm)	D_R (nm)	ΔT_1 (K)	E_B (eV)	ε_r	N_G ($\times 10^{18}$ cm^{-3})	R	SD
S_A	280	523	100	13.9	–	120–290	0.046	31	3.27	0.9972	0.067
S_R	245	723	0	–	20.3	133–300	0.082	100	8.82	0.9996	0.040
$S_{A.R}$	260	543	46	19.6	14.5	150–285	0.058	66	6.80	0.9992	0.047

3. Results

The structural analysis of the heat-treated films indicates a polycrystalline anatase or/and rutile structure (Fig. 1). The studied samples were labeled: S_A, S_R and $S_{A.R}$ according to its content of anatase and rutile phases, respectively. The weight percentage of the anatase phase, W_A, was determined using the equation [15]:

$$W_A = 1/(1 + 1.265 I_R / I_A) \quad (1)$$

where I_R is the intensity of the strongest rutile peak R(110), and I_A represents the intensity of the strongest anatase peak A(101).

The average crystallite size, D, was obtained, for each phase, from the diffraction peaks A(101), R(110) using the Debye–Scherrer formula [16]:

$$D = \frac{k\lambda}{B_{2\theta}\cos\theta} \quad (2)$$

where k is the Scherrer's constant ($k = 0.9$ [16]), λ is the X-ray wavelength corresponding to CuK$_\alpha$, $B_{2\theta}$ denotes the full-width at half-maximum of the peak, and θ is the Bragg angle. Some structural parameters, obtained after the heat treatment of the investigated samples, are listed in Table 1.

It is known that the thermal energy band gap of TiO_2 crystals is about 3.65 eV and has been calculated at high temperatures (over 1200 K) [17,18]. At room temperature, values of about 3.0 eV–3.2 eV can be obtained (depending on the different phases content) using the optical transmittance spectra [2,9,18].

Fig. 2 illustrates the typical transmittance spectrum for one of the studied titanium oxide films (S_A), the one which contains only the anatase phase. It can be observed that the film is transparent in the visible region (one of the most important properties of titanium oxide) and its transparency exhibits a sharp decrease in the UV region, at a wavelength which corresponds to the forbidden energy band gap of the studied oxide.

For wavelengths close to values where loss scattering are dominated by the fundamental absorption of light, the absorption coefficient α can be calculated using the expression [2]:

$$\alpha = d^{-1} \ln(1/T_\lambda) \quad (3)$$

where d is the thickness of the film and T_λ is the optical transmittance at wavelength λ.

In the vicinity of fundamental absorption, we may consider that the indirect allowed transition dominates over the optical absorption, according to the relation [19]:

$$(\alpha h\nu)^{\frac{1}{2}} = A_i\left(h\nu - E_{g0}\right) \quad (4)$$

where $h\nu$ is the photon energy, A_i is a characteristic parameter independent of photon energy for respective transitions and E_{g0} is the optical band gap. In Fig. 3, a typical $(\alpha h\nu)^{1/2} = f(h\nu)$ dependence, for the same sample S_A, is presented. The values of E_{g0} for the studied samples, determined by extrapolating the linear part of $(\alpha h\nu)^{1/2} = f(h\nu)$ dependence to $(\alpha h\nu)^{1/2} = 0$, ranged from 3.15 eV to 3.22 eV. These values are in good agreement with those reported in literature (3.11 eV for the rutile phase [20] and 3.2 eV for the anatase phase [2,9]). Generally, the effects of the crystallite boundaries on the optical absorption are small [19] and this was the reason why we have obtained the energy band gap from optical measurements.

Some important parameters of the semiconducting thin films can be determined by using the temperature dependence of the transport coefficients (electrical conductivity, Seebeck coefficients, etc.). The mechanism of the electrical conduction was explained by studying the temperature dependence of the electrical conductivity.

By heat treatment, the structural characteristics of TiO_2 films may modify and, consequently, the electronic transport properties of the respective films (particularly, electrical conductivities) may vary too. To obtain films with stable structure, all samples were subjected to a heat treatment consisting of two successive heating/cooling cycles

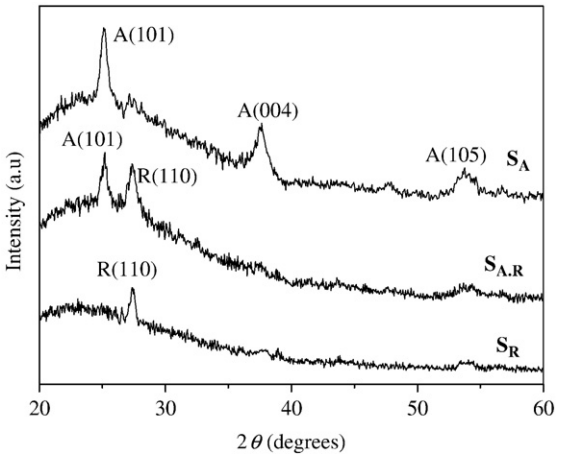

Fig. 1. XRD patterns of the investigated samples (CuK$_\alpha$ radiation, $\lambda = 1.54178$ Å).

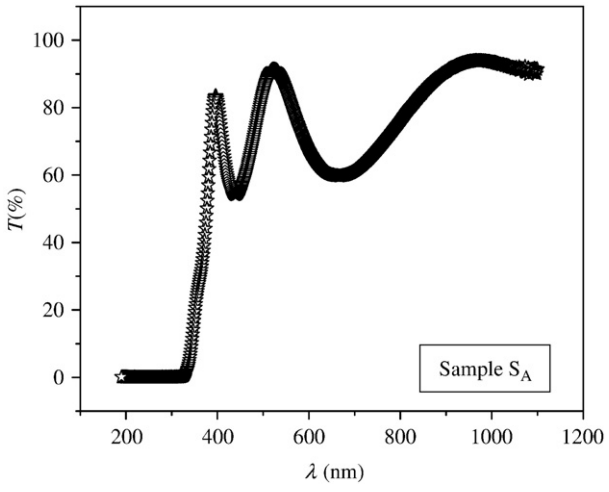

Fig. 2. Transmittance spectrum of the anatase TiO_2 sample, S_A.