

THE SEEBECK COEFFICIENT OF TiO₂ THIN FILMS

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Undoped and doped TiO₂ thin films were deposited onto glass substrates, by r.f. sputtering technique, at different substrate temperatures. The films were heat treated in order to stabilize the structure of the samples and to decrease the structural defects. The dependence of the Seebeck coefficient, α , versus inverse temperature, has been studied in the range 300 K–425 K. From the slope of the linear decrease of these dependences, Fermi energies have been obtained. The values of parameter r , which depend on the nature of the scattering mechanism of the current carriers, have been also determined.

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1. Introduction

Thin films like titanium dioxide are very attractive materials due to their unique properties: high thermal and chemical stability in hostile environments, good durability, high transmittance in the visible spectral range, high refractive index and high dielectric constant.

Doping is an useful method to induce substantial modifications in electrical and optical properties of semiconductor materials. The influence of In, Ce, Fe, or Nb doping on the structure of TiO₂ thin films is already reported in literature [1-6].

In a series of previous papers [1, 3, 5, 7, 8] we have studied the optical, electrical and dielectric properties of doped and undoped TiO₂ sputtered thin films.

The aim of this paper is to obtain information on the change of the conduction type in TiO₂ thin films by Nb or Fe doping.

2. Experimental

Undoped and doped TiO₂ thin films were deposited onto glass substrates, by r.f. sputtering technique. The substrate temperature varied from room temperature to 250 °C. The dopants were: 0.35at.% Nb and 1 at. % Fe. Details on the deposition parameters are given elsewhere [1].

The study includes four different types of samples labelled as: A_{gl}, E_{gl}, C_{gl} and D_{gl}. The deposition conditions and the characteristics of the samples are summarized in Table 1.

A profilometer (Alpha-Step 500, Tencor) was used in order to determine the thickness of the thin films. The values are also given in Table 1.

Table 1. Dopant, weight percentage of the anatase phase (W_A), substrate temperature (T_S), film thickness (d), surface roughness determined by AFM (R_{AFM}) of the studied TiO₂ thin films.

Sample	Dopant (% at.)	W_A (%)	T_S (°C)	d (nm)	R_{AFM} (nm)
A _{gl}	-	60	250	300	5.5
E _{gl}	-	-	≤100	100	2.0
C _{gl}	0.35 at. % Nb	100	250	300	-
D _{gl}	1 at. % Fe	0	250	250	9.2

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X-ray diffraction (XRD) measurements have been performed in grazing incidence geometry at 5° (Geigerflex, Rigaku). The diffractometer settings were: Cu K_α radiation, $U = 40$ kV and $I = 30$ mA [1].

The films were heat treated in order to stabilize the structure of the samples and to decrease the structural defects [3]. The heat treatment consisted in two successive heatings and coolings ($10^\circ\text{C}/\text{min}$) within a temperature range $\Delta T = 300$ K - 700 K.

In our experiments, the apparatus allows for determining the Seebeck voltage, ΔU , between two points of the film, having the temperature difference $\Delta T = T_2 - T_1$ [9]. The temperatures T_1 and T_2 were measured at the surface of the thin film, with the help of two thermocouples. Because of the high resistance of TiO_2 films [3], a Keithley 6517A electrometer was used, in order to obtain the Seebeck voltage.

3. Results and discussion

In another paper [1], we have shown that, being deposited at 250°C , sample A_{gl} (pure TiO_2 thin film) has a mixed anatase/rutile structure with anatase predominating over the rutile phase (Table 1). Adding 0.35 at. % Nb (C_{gl}), pure anatase TiO_2 films have been obtained. For sample D_{gl} (TiO_2 doped with 1 at. % Fe) the rutile reflection R(110) is the only one detected. Thin films deposited onto unheated substrates (E_{gl}) have an amorphous structure and they are smoother than the polycrystalline films (see Table 1) [1,7].

The dependences of the Seebeck coefficient versus inverse temperature, $\alpha = f(10^3/T)$ were studied in the temperature range 300 K - 425 K for all the samples: A_{gl} , E_{gl} , C_{gl} and D_{gl} (Fig. 1).

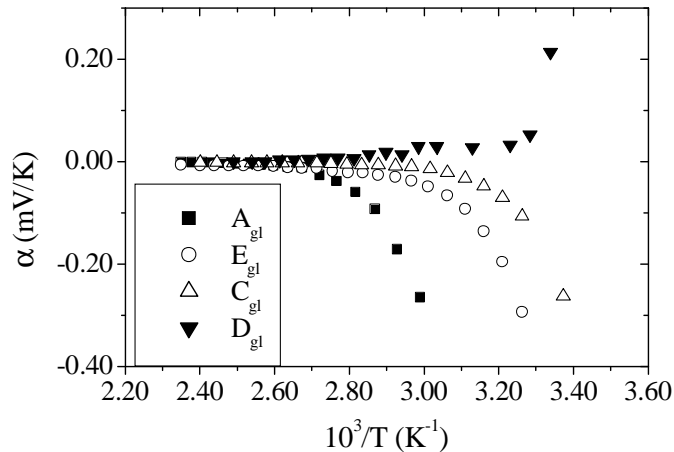


Fig. 1. The dependences $\alpha = f(10^3/T)$ in the temperature range 300 K - 425 K.

It is known that, in n-type semiconductors [10, 11], the warm end of the sample has a positive charge and the cold end has a negative charge, because of the diffusion of the electrons from the warm end to the cold one. For a p-type semiconductor, the holes diffuse from the warm end to the cold end, so the Seebeck voltage has an opposite sign.

The Seebeck coefficient (thermoelectric coefficient), α , at a temperature $T = (T_2 + T_1)/2$, is given by:

$$\alpha = \Delta U / \Delta T \quad (1)$$

For undoped semiconductors, or for weakly doped semiconductors, the dependence $\alpha = f(T)$ could be described using the theory of energy bands. When the scattering of the current carriers is produced by only one scattering mechanism, the following relations correspond to non-degenerate semiconductors of n-type and of p-type, respectively [10]:

$$\alpha_n = -\frac{k}{e} \left(r + \frac{5}{2} - \frac{E_F}{kT} \right) = -\frac{k}{e} \left(r + \frac{5}{2} + \ln \frac{N_c}{n} \right) \quad (2)$$

$$\alpha_p = \frac{k}{e} \left(r + \frac{5}{2} + \frac{E_F + E_g}{kT} \right) \quad (3)$$

Here, k is the Boltzmann constant, e is the absolute value of the electron charge, E_F is the energy of the Fermi level (the energy is measured from the inferior limit of the conduction band, E_c), E_g is the energy bandgap, n is the concentration of the electrons, N_c is the density of the states in the conduction band, r is a parameter which depend on the nature of the scattering mechanism of the current carriers. One can see the dependence of Seebeck coefficient on the temperature and on the semiconductor nature. Because $n < N_c$, the sign of α is given by the sign of the current carriers.

The relations (2) and (3) have been obtained in the hypothesis that E_F slowly depends on the temperature. Also, the lower limit of the conduction band, E_c , is assumed to be $E_c = 0$, and the upper limit of the valence band E_v is $E_v = -E_g$.

From Fig. 1, one can observe the negative values of the Seebeck coefficient for A_{gl} , C_{gl} and E_{gl} samples, which indicate the n-type conduction in these semiconductors. The positive values of the Seebeck coefficient for D_{gl} sample indicate p-type conduction. The values of the Seebeck coefficient at 400 K, are given in Table 2. The highest value for α , belongs to the sample E_{gl} .

Oxygen vacancies and impurities influence electrical properties of TiO₂ thin films. While Fe impurities act as acceptors [12], Nb impurities, as well as oxygen vacancies, act as donors [13]. In Fe doped films, Fe impurities determine a decrease of the electron concentration, while the oxygen vacancies increase it. Bally et al. [6] established that for an iron concentration higher than 0.13 at. % the ratio between vacancies and Fe impurities concentration is lower than 0.5 and the conductivity switches from n to p-type.

Comparing our data with those obtained for TiO₂ single crystals at 310 K, we have found for E_{gl} the value $\alpha_{310K} = 0.2$ mV/K, very closed to $\alpha_{310K} = 0.28$ mV/K, obtained by Forro et al. [14] for anatase single crystals. For Nb doped sample and for Fe doped sample we have found 0.07 mV/K and 0.03 mV/K respectively. Thurber et al. [15] found for Nb doped rutile single crystals, $\alpha_{310K} = 0.7$ mV/K, ten times higher than ours. Cristea [16] obtained, at the same temperature, $\alpha_{310K} = 0.4$ mV/k – 0.6 mV/K, for Nb doped rutile single crystals, depending on Nb concentration.

Table 2. Seebeck coefficients at 400 K (α_{400K}), Fermi energies (E_F), parameter r and the correlation coefficients (R) of the linear dependences.

Sample	α_{400K} (μ V/K)	E_F (eV)	r	R
A_{gl}	-3,50	-0,033	-1,54	0,97
E_{gl}	-7,50	-0,018	-2,01	0,94
C_{gl}	-1,20	-0,0054	-2,35	0,99
D_{gl}	1,07	-2,970	-1,64	0,97

For all the studied samples, the absolute value of the Seebeck coefficient presents a sharp decrease with the increasing temperature, near room temperature. Then, it follows a slow linear decrease, in higher temperature range (Fig. 2). On this range, from the slope of the linear decrease, Fermi energies have been obtained. The correlation coefficients, R , and the values of Fermi energies, E_F , are given in Table 2.

So, for an n-type semiconductor, the energy of the Fermi level, E_F , can be obtained from the slope of the linear dependence, $\alpha_n(1/T)$ which is observed in the higher temperature range. In that range, we can choose a small domain, $T''-T'$, on which r and E_F do not depend on the temperature:

$$\alpha'_n = -\frac{k}{e} \left(r + \frac{5}{2} - \frac{E_F}{kT'} \right), \quad (4)$$

$$\alpha''_n = -\frac{k}{e} \left(r + \frac{5}{2} - \frac{E_F}{kT''} \right). \quad (5)$$

For an n-type semiconductor, the energy of the Fermi level E_F is given by:

$$E_F = e \frac{\alpha''_n - \alpha'_n}{\frac{1}{T''} - \frac{1}{T'}} \quad (6)$$

Analogously, for a p-type semiconductor, using the relation (3), one gets:

$$E_F = e \frac{\alpha''_p - \alpha'_p}{\frac{1}{T''} - \frac{1}{T'}} - E_g \quad (7)$$

The Fermi energy decreases from -0.035 eV for the undoped sample, to -0.0054 eV by doping with Nb impurities, and the Fermi level approaches to the bottom limit of the conduction band, E_c . For sample D_{gl} , $E_F = 2.97$ eV, so, Fe doping determines an approach of the Fermi level to the the upper limit of the valence band, at a distance of 0.030 eV, if we consider $E_g \cong 3$ eV, a characteristic value for rutil phase which is present in the Fe doped sample [1].

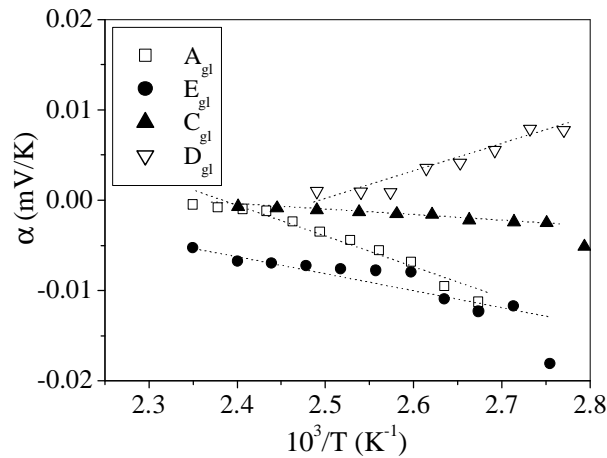


Fig. 2. The dependences $\alpha=f(10^3/T)$ in the range 355 K - 425 K.

The free term in the relations (2) and (3) offers the value of parameter r , which depend on the nature of the scattering mechanism of the current carriers (see Table 2). We found out that, in the undoped sample, on the temperature range 375 K - 425 K and in Fe doped sample on the range 355 K - 400 K, prevails the carrier scattering on acoustic longitudinal phonons ($r \cong -3/2$). By Nb doping, r becomes -2.35 , in the range 360 K-415 K. This value may indicate a simultaneous action of scattering mechanisms.

4. Conclusions

In this paper we have shown that the undoped samples and Nb (0.35 at. %) doped sample, have a n-type conduction, indicated by the negative values for the Seebeck coefficient, while positive values for α , obtained for Fe (1 at. %) doped sample, indicate a p-type conduction. While Nb doping determines an approach of the Fermi level to the bottom limit of the conduction band, Fe

doping determines the shift of the Fermi level towards the upper limit of the valence band. The carrier scattering on the acoustic longitudinal phonons prevails in the undoped sample, in the temperature range 375 K-425 K, and in Fe doped sample in the range 355 K-400 K.

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