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Properties of Nanocrystalline TiO_2:V Thin Films as a Transparent Semiconducting Oxides

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In this work the nanocrystalline TiO_2 thin films doped with vanadium in amount of 19 at.% and 23 at.% prepared by magnetron sputtering method have been presented. The transmission measurements shows that *V*-doped TiO_2 thin films were transparent in *ca.* 81% in the visible range of light spectrum. On the basis of electrical examinations it was found that fabricated TiO_2:V thin films are semiconductors at room temperature and have different type of electrical conduction depending on the amount of vanadium dopant applied.

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1. Introduction

Recently, vanadium oxides have attracted much attention in transparent electronics for the sake of their diversified properties depending on the crystal phase. Depending on the oxidation state, vanadium can form different oxides from which the most investigated are V_2O_3, V_2O_5 and VO_2. Because of thermo- and electro-chromic properties vanadium oxides are widely applied in coatings industry for fabrication of smart windows, solar cells, optical switching devices, etc. [1, 2].

In the present work, the properties of TiO_2 thin films doped with different amount of vanadium have been presented. The vanadium dopant was incorporated into TiO_2 during thin film deposition by high energy reactive magnetron sputtering (HE RMS) method. The HE RMS method provides preparation of polycrystalline thin films composed of crystallites in the range of few nanometers in the average size (nanocrystalline structure) with smooth surface and high ordering degree of grains [3, 4].

In this paper the results of structural, optical and electrical investigation of TiO_2:V thin films have been shown.

2. Experimental procedure

Investigated samples were deposited on glass (Corning 7059) and silica (SiO_2) substrates by sputttering of Ti and Ti–V mosaic targets with different amount of V in reactive oxygen plasma. After deposition the amount of 19 at.% and 23 at.% of V dopant in prepared thin films was evaluated using Hitachi S-4700N scanning electron microscope equipped with energy dispersive spectrometer. The thicknesses specified using Taylor Hobson Taly-Surf CCI Lite optical profiler were: 200 nm, 360 nm and 517 nm for TiO_2:V 19 at.%, TiO_2:V 23 at.% and TiO_2 thin films, respectively. The transparency and position of the fundamental absorption edge of the thin films were determined from optical transmission spectra.

The structure and the surface features were examined by using X-ray diffraction (XRD) with Fe-filtered Co K_α radiation and atomic force microscope (AFM) making in contact-mode.

Electrical properties were investigated by thermoelectrical (resistivity (ρ), Seebeck coefficient (S)) measurements. The temperature dependent measurements were performed using air-cooled thermal chuck operated by ERS SP72 controller. For thermoelectrical characterization two parallel Ag/TiW metal electrodes were evaporated through the metallic mask onto the thin films.

3. Results and discussion

Structural properties elaborated based on X-ray diffraction analysis are listed in Table I. The XRD results indicated the nanocrystalline rutile phase in pure TiO_2 with the crystallite size of 9.3 nm. TiO_2 thin films doped with 19 at.% V exhibit an amorphous behavior. From Table I results that the increase in the amount of V only of about 4 at.% (to 23 at.%) was sufficient for modification of TiO_2 thin films and the nanocrystalline V_2O_5 structure was presented. These results are in agreement with Depero et al. who reported the V_2O_5 formation at higher V amount [5].

Figure 1 shows AFM images of TiO_2:V thin films, which reveal densely packed structures with visible grains, especially in the case of TiO_2 thin films doped with 23 at.% of V. Additionally, as it could be seen in Fig. 1a the small grains (too fine for XRD measurements) which may belong to V_2O_5 phase have been detected.

Optical parameters of investigated TiO_2:V films derived from optical transmission measurements are collected in Table II. The average level of transparency (in the visible range of light spectrum) was comparable for both TiO_2:V films and equals to about 81%. However, vanadium doping causes a shift of the fundamental

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TABLE I

Structural parameters of: TiO_2, TiO_2:V (19 at.%) and TiO_2:V (23 at.%) thin films deposited on glass substrates by magnetron sputtering process, derived from XRD measurements.

Thin films	Amount of V [at.%]	Phase	D [nm]
TiO_2	–	rutile	9.3
TiO_2:V	19	amorphous	–
TiO_2:V	23	V_2O_5	32.4

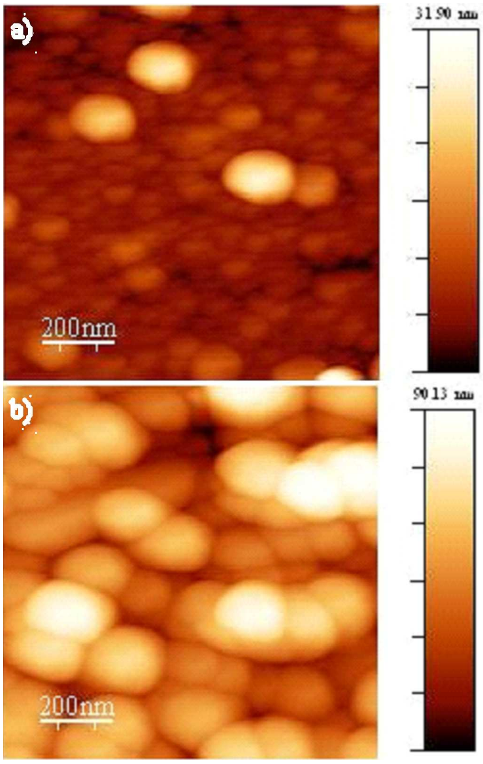

Fig. 1. AFM images of TiO_2:V thin films with the amount of vanadium: (a) 19 at.% and (b) 23 at.%, deposited on SiO_2.

absorption edge, towards the higher wavelengths, from 379 nm for TiO_2:V (19 at.%) to 430 nm for TiO_2:V (23 at.%), respectively. The optical band gaps have also much the same values, about 2.1 eV. The estimated values are smaller than for undoped TiO_2 (3.35 eV).

Electrical resistivity of TiO_2:V thin films was measured in the temperature range from 299 K to 473 K (Fig. 2). The linear dependence of ρ vs. T may be represented by

$$\rho(T) = \rho_0(T) \exp\left(\frac{W_\rho}{k_B T}\right), \quad (1)$$

where ρ_0 — constant, W_ρ — thermal activation energy, k_B — the Boltzmann constant (8.617×10^{-5} eV/K). As it could be seen in Fig. 2 the resistivity dropped with increasing the V amount, from 1×10^5 Ω cm to 4×10^2 Ω cm at room temperature, which implies that TiO_2:V have semiconducting properties at room temperature. From a linear ρ $(1000/T)$ dependence recorded for TiO_2:V thin films the thermal activation energy, W_ρ, was determined. The calculated W_ρ equals to 0.8 eV for TiO_2:V (19 at.%) and 0.57 eV for TiO_2:V (23 at.%).

TABLE II

Optical parameters obtained from transmission measurements of TiO_2:V thin films on SiO_2.

Thin films	T_λ [%]	λ_{cutoff} [nm]	E_g^{opt} [eV]
TiO_2	85	330	3.35
TiO_2:V (19 at.%)	80.76	379	2.11
TiO_2:V (23 at.%)	80.65	430	32.10

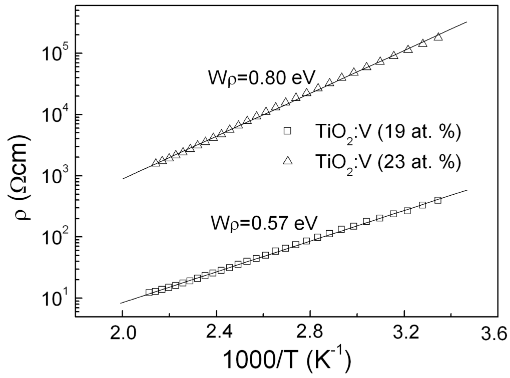

Fig. 2. Electrical resistivity as a function of $1000/T$ for TiO_2:V thin films with different amount of V (19 at.% and 23 at.%).

TABLE III

Electrical parameters determined from thermoelectrical measurements for TiO_2:V thin films.

Thin films	ρ [Ω cm]	W_ρ [eV]	S [μV/K]	Conduction type
TiO_2:V (19 at.%)	8×10^4	0.80	+685	p
TiO_2:V (23 at.%)	6×10^2	0.57	−20	n

In Table III electrical parameters derived from thermoelectrical measurements are collected. Two different types of electrical conduction were obtained at room temperature depending on the V amount: p-type (S = +685 μV/K) for TiO_2:V (19 at.%) thin films and n-type (S = −20 μV/K) for TiO_2:V (23 at.%) ones. Therefore, several percentage change of vanadium dopant makes possible modification of the conduction type.

4. Conclusions

In this work transparent TiO_2:V thin films with semiconducting properties were fabricated by high energy reactive magnetron sputtering. Different amount of vanadium, 19 at.% and 23 at.% allows receiving thin films with diversified structural, optical and electrical properties.

The doping of TiO_2 with V causes that all investigated TiO_2:V thin films have a high (about 81%) transparency in the visible range of light spectrum . Moreover, the films reveals semiconducting properties at room temperature with different type of electrical conduction (p for 19 at.% of V and n for 23 at.% of V).

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