Proceedings of the III National Conference on Nanotechnology *NANO 2009*

Thin Films Based on Nanocrystalline TiO_2 for Transparent Electronics

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In this work, investigations of structural, optical and electrical properties of transparent oxide semiconductor thin films based on TiO_2 doped with Eu, Pd and Tb, Pd have been presented. The transparent oxide semiconductor nanocrystalline thin films were prepared by magnetron sputtering process. It was shown that doping with selected elements results in semiconducting properties of prepared thin films of oxides with p-(TiO_2:(Tb, Pd)) or n-type (TiO_2:(Eu, Pd)) of electrical conduction.

PACS numbers: 73.61.Ey, 78.66.−w, 71.20.Nr

1. Introduction

Development of transparent electronic devices like transparent diodes or transistors demands fabrication of transparent heterojunctions based on thin films with specific properties. Especially important aspect in junction based devices is photovoltaic effect which was focused by many authors because of its meaningful function in promising application for transparent solar cells [1]. For example, Baik and Cho [2] investigated UV-sensing ZnO/n-Si junction solar cells prepared by sol-gel method and devices fabricated by spray pyrolysis method were described by Kobayashi et al. [3]. Moreover, Tonooka et al. [4] have reported photovoltaic effect observed in transparent oxide semiconductor (TOS) heterojunctions based on n-ZnO/p-$CuAlO_2$, while Levy et al. in their report concerned TiO_2/SnO_2 heterojunction [5].

The latest achievements in the thin films technology showed that TiO_2 doped with some rare earth elements or transition metals provides interesting and unique properties. Such TOS material could be applied as an active component of transparent heterojunction for optoelectronic devices [6]. Former practical and theoretical investigations on transition metals and rare earth elements simultaneously introduced to the same thin film, showed that the connection of their optoelectronic properties is possible. Therefore, in this paper, the results of structural, optical and electrical properties of TiO_2 doped with Eu–Pd and Tb–Pd have been studied. Eu^{3+} and Tb^{3+} are well known for their luminescent properties [7], while Pd in TiO_2 works as an electrical modifier which makes non-conductive TiO_2 a semiconductive thin film [8].

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2. Experimental procedure

Thin films were prepared by reactive magnetron sputtering method [9] using mosaic target in the form of Ti–Eu–Pd and Ti–Tb–Pd. The thin TOSs films were deposited on glass (Corning 7059) substrates for structural and thermoelectrical characterization and on silicon substrates for X-ray photoelectron spectroscopy (XPS) and optical beam induced current (OBIC) measurements. During deposition process low pressure (< 0.1 Pa) of pure oxygen as a working gas, and conditions of the magnetron powering have been precisely selected. Thanks to that, particles deposited during the film growth had enhanced energy. In consequence, thin films with nanocrystalline, densely packed structure could be obtained [9].

The dopants amount in prepared thin films, determined by energy disperse spectrometer (EDS) were: Eu — 0.9 at.%, Pd — 5.8 at.% in TiO_2:(Eu, Pd) thin film and Tb — 0.6 at.%, Pd — 9 at.% in TiO_2:(Tb, Pd) one. Thicknesses, specified using standard Fizeau interferometer were 396 nm and 420 nm, respectively.

3. Results and discussion

Investigations of structural parameters were carried out by X-ray diffraction (XRD) in our previous works [10, 11]. The XRD patterns revealed the presence of the TiO_2-rutile phase directly in both investigated as deposited TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films. The investigated thin films were nanocrystalline with the grain size about 10 nm for both investigated samples. Neither Pd nor Eu or Tb crystal forms were detected.

Composition of the prepared TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films deposited on silicon was investigated by XPS with the excitation of Mg K_α (1253.6 eV) source. In Table the XPS Ti $2p$, O $1s$ and Pd $3d$ core level

spectra of the fabricated thin films have been presented. The position of Ti $2p$ doublet and separation of 5.76 eV and 5.75 eV for TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films, respectively, between the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks indicate a Ti^{4+} oxidation state [12]. The binding energy of 529.5 eV and 529.45 eV for TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films, respectively, recorded for O $1s$ peak corresponds to the normal O^{2-} oxidation state.

TABLE

Binding energy for Ti $2p$, O $1s$, Pd $3d$ peaks and separation energy between Ti $2p_{1/2}$–Ti $2p_{3/2}$, Ti $2p_{3/2}$–O^{2-} and Pd $3d_{3/2}$–Pd $3d_{5/2}$ photoelectron peaks for TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films.

Sample	Ti $2p$		ΔBE	O $1s$		ΔBE	Pd $3d$		ΔBE
	Ti $2p_{1/2}$ [eV]	Ti $2p_{3/2}$ [eV]	(Ti $2p$) [eV]	O^{2-} [eV]	OH^- [eV]	(Ti–O) [eV]	Pd $3d_{3/2}$ [eV]	Pd $3d_{5/2}$ [eV]	(Pd $3d$) [eV]
TiO_2:(Eu, Pd)	−464.0	−458.2	5.76	−529.5	−531.4	2.11	−343.5	−338.1	5.36
TiO_2:(Tb, Pd)	−463.8	−458.1	5.75	−529.4	−531.1	2.01	−344.5 −342.8	−339.4 −337.4	5.41

For TiO_2:(Eu, Pd) sample the Pd $3d$ photoelectron peaks have been centered at 343.5 eV and 338.1 eV indicating presence of PdO_2 in the thin film. In the case of the TiO_2:(Tb, Pd) sample, 342.8 eV and 337.44 eV photoelectron peaks have been assigned to PdO_2 and the additional ones at 344.5 eV and 339.4 eV to PdO. Neither Tb nor Eu photoelectron peaks were detected. This could be the reason that the amounts of selected Tb and Eu dopants (0.6 and 0.9 at.%) were under detection limit of applied equipment.

For electrical investigations of TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films four parallel metal electrodes were evaporated through the metallic mask into the sample. Measurements of dc electrical resistivity (ρ_{dc}) was done in the temperature range from 300 K to 500 K (Fig. 1a). Doping of TiO_2 matrix, especially with Pd, which is often used as an electrical activator, caused clear decreasing of ρ_{dc} comparatively to the undoped TiO_2 ($\rho \approx 10^8$ Ω cm). Based on the slope of $\log \rho_{dc}$ $(1000/T)$ dependence the thermal activation energies W_ρ have been calculated from exponential Arrhenius formula [13] and were 0.18 eV and 0.11 eV for the TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films, respectively.

In Fig. 1b, the temperature dependent characteristics of Seebeck coefficient (S) for prepared thin films have been presented. This allows the determination of the type of electrical conduction. From Fig. 1b results that addition of the rare earth elements (Eu and Tb) makes possible to prepare the thin films with different type of electrical conduction: p for TiO_2:(Eu, Pd) and n for TiO_2:(Tb, Pd). Additionally, the thermal activation energies (W_S) were calculated from the $S(T)$ curve, in the same way as W_ρ and were equal to 0.022 eV for the TiO_2:(Eu, Pd) and 0.038 eV for the TiO_2:(Tb, Pd).

In order to complete the study it was necessary to confirm that prepared thin TOSs films can form heterojunction with silicon (p-type) substrate. The photoelectrical characteristics $I_{ph}(x)$ were recorded using the OBIC measurements performed at three different wavelengths of 399 nm, 632 nm and 928 nm (Fig. 2). The measurements were curried out at room temperature, with the light beam *ca.* 30 μm in diameter and frequency of square modulation $f = 181$ Hz. The highest photocurrent vs. scanning beam position was recorded between 3–4 contacts separated with 300 μm at the wavelength of

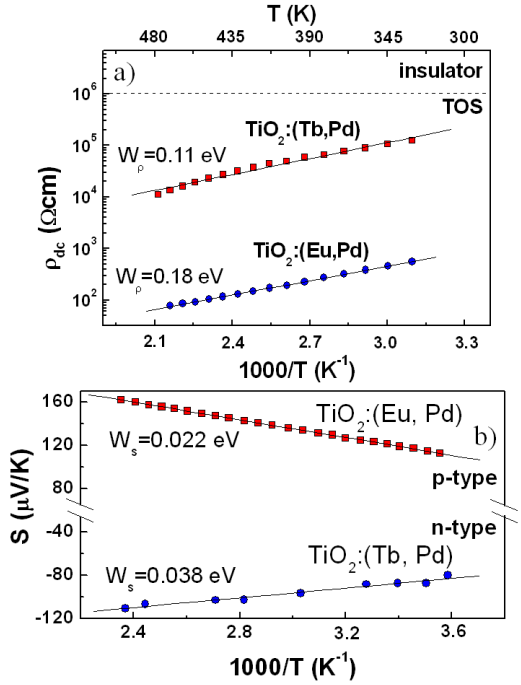

Fig. 1. Electrical characteristics of: (a) resistivity and (b) Seebeck coefficient for TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films deposited on glass substrates.

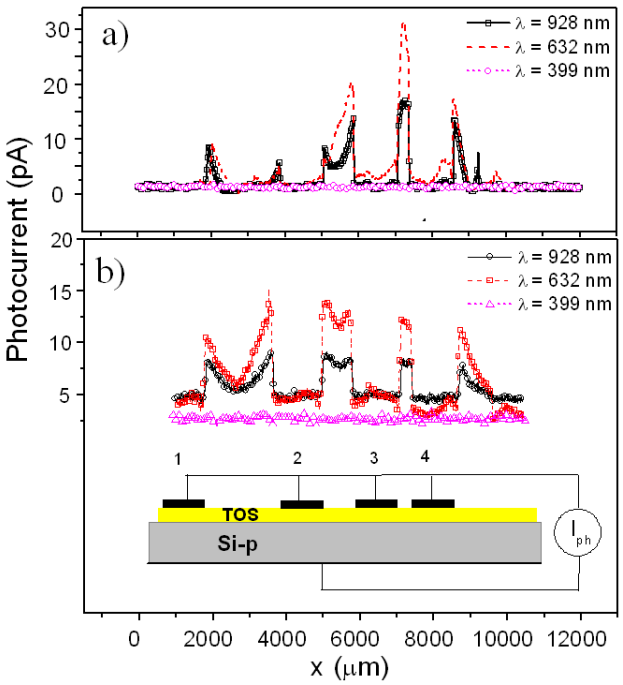

Fig. 2. Characteristics of photocurrent $I_{ph}(x)$ obtained in effect of single scan "in line" of light beam across the area between the electrodes on: (a) TiO_2:(Eu, Pd)/Si and (b) TiO_2:(Tb, Pd)/Si with the different light wavelength.

$\lambda = 632$ nm both for TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) (Fig. 2). However, in the case of TiO_2:(Eu, Pd) thin films (Fig. 2a) the quantity of photocurrent is approximately 30% higher than for TiO_2:(Tb, Pd) one (Fig. 2b). The results shows that amplitude of generated photocurrent was directly proportional to distance between particular contacts and incident light beam wavelength.

4. Conclusions

In this work study of the thin films consisting of: TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) has been shown. The thin films modificated by Eu, Pd and Tb, Pd dopants allowed to obtain nanocrystalline TiO_2-rutile thin films with PdO and PdO_2 phases in both cases.

Electrical results shows that TiO_2:(Eu, Pd) and TiO_2:(Tb, Pd) thin films reveals semiconducting properties at room temperature and different type of electrical conduction (n for TiO_2:(Eu, Pd) thin films and p for TiO_2:(Tb, Pd)). The OBIC measurements confirms that prepared thin films were also optically active and could form transparent heterojunction which gives the possibility of their application for realization of the integrated TOS–Si microstructures.

Acknowledgments

This work was financed from the sources by the NCBiR in the years 2008–2010 as a development research project number N R02 0019 04.

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