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Optical and electrical properties of TiO_2 doped with Tb and Pd

J. DOMARADZKI*, D. KACZMAREK, E. L. PROCIOW,
A. BORKOWSKA, T. BERLICKI, K. SIERADZKA

Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology,
ul. Janiszewskiego 11/17, 50-372 Wrocław, Poland

Optical and electrical properties of TiO_2 doped with 0.6 at. % Tb and 9 at. % Pd have been investigated. Thin films were deposited by low pressure hot target reactive sputtering from a metallic Ti–Tb–Pd mosaic target on silicon and glass substrates. Total concentration of Tb and Pd was determined using an energy disperse spectrometer. Optical properties were studied by means of optical transmission. It has been shown that Tb dopant does not make any significant changes in the transmission level. Pd dopant shifts the fundamental absorption edge of TiO_2 towards longer wavelengths and decreases the transmission to about 40%. For electrical characterization of the prepared thin films, temperature dependent resistivity and current–voltage (*I–V*) characteristics have been examined. It has been shown that incorporation of Pd and Tb into TiO_2 matrix modifies its properties allowing one to obtain p-type oxide-semiconductor electrically and optically active at room temperature. Additionally, based on *I–V* measurements, the formation of heterojunction at the interface of thin film–silicon was confirmed.

Key words: *terbium; palladium; TiO_2; thin films; transparent oxide semiconductor*

1. Introduction

Transparent oxide semiconductors (TOS) with n- and p-type electrical conduction are of great interest due to fabrication of transparent junction-based devices [1–3]. To form a p–n junction transparent for visible light, oxide semiconductors with band gap wider than 3 eV are needed. A major difficulty in the fabrication of fully functional transparent oxide-based devices is still low electrical performance of TOS. Therefore the development of methods for modification of electrical properties of thin oxide films is of great importance. Another important issue is integration of various TOSs with a standard silicon technology.

*Corresponding author, e-mail: jaroslaw.domaradzki@pwr.wroc.pl

Our previous studies have shown that doping of titanium dioxide, as a base oxide, with various transition and noble metals could modify its certain properties [4]. For example, doping with Pd allows a p-type oxide semiconductor to be obtained [5]. Recently TiO_2 has been reported to be used as a host matrix for various rare earth elements, i.e. Tb [6, 7]. In this paper, optical and electrical properties of TiO_2 doped with Tb and Pd have been described.

2. Experimental procedure

Thin films of TiO_2:(Tb, Pd) were prepared by the low pressure hot target reactive sputtering (LP HTRS) method from metallic Ti–Tb–Pd mosaic target and deposited on silicon and glass substrates. The sputtering process was carried out under low pressure (< 0.1 Pa) of pure oxygen as a working gas and with the additionally heated target (hot target). Optical properties of TiO_2:(Tb, Pd) thin films were studied by means of optical transmission in the spectral range from 250 nm to 1100 nm. Measurements of direct current (d.c.) electrical resistivity (ρ_{dc}) were done using the standard four-point probe method in a temperature range from 300 K to 900 K. Current–voltage (*I–V*) measurements have been performed at room temperature using an electrical characterization system based on a Keithley's 2000 multimeter and 6517A electrometer.

3. Results and discussion

Tb and Pd contents in TiO_2:(Tb, Pd) thin films determined with the energy disperse spectrometer (EDS) amount to ca. 0.6 at. % and 9 at. %, respectively. EDS spectrum of TiO_2:(Tb, Pd) thin film on silicon is shown in Fig. 1. The detected Si signal, visible in the spectra, is due to the substrate.

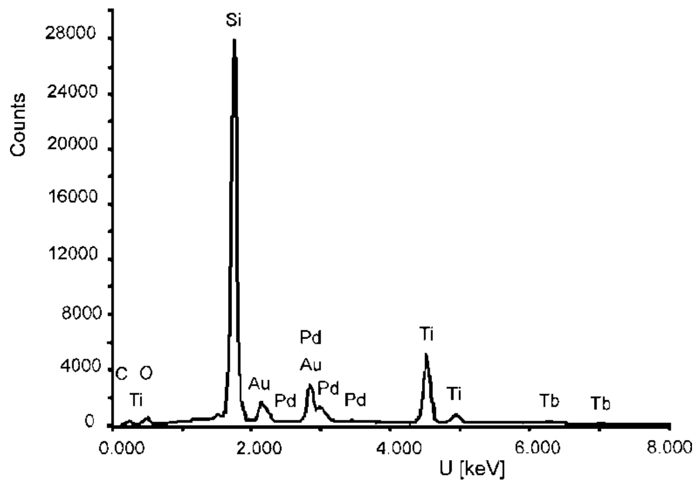

Fig. 1. EDS spectrum of TiO_2:(Tb, Pd) thin films on silicon

Optical transmission characteristics of undoped TiO_2, TiO_2:Tb (0.4 at. %) and TiO_2:(Tb, Pd) thin films are shown in Fig. 2. It has been shown that Tb dopant does not cause any significant changes in the transmission level as compared to pure TiO_2. Incorporation of Pd dopant shifts the position of the fundamental absorption edge (ca. 330 nm) toward longer wavelengths, with the transmission decreasing to about 40 % in the visible region.

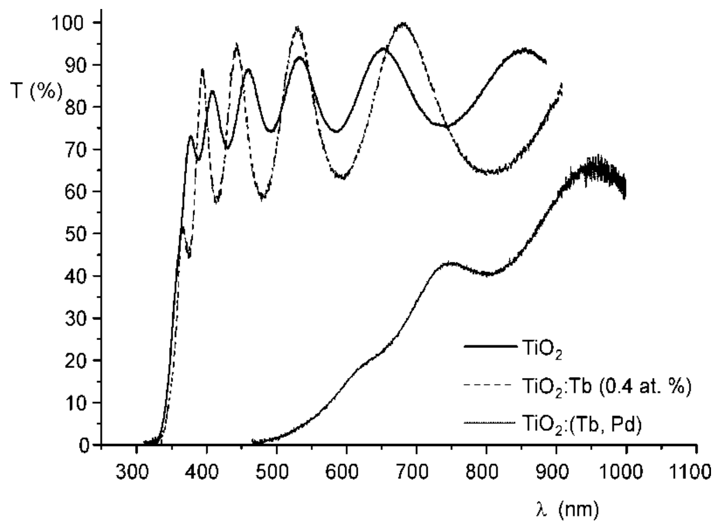

Fig. 2. Optical transmission spectra of undoped TiO_2, TiO_2:Tb (0.4 at. %) and TiO_2:(Tb, Pd) thin films on SiO_2

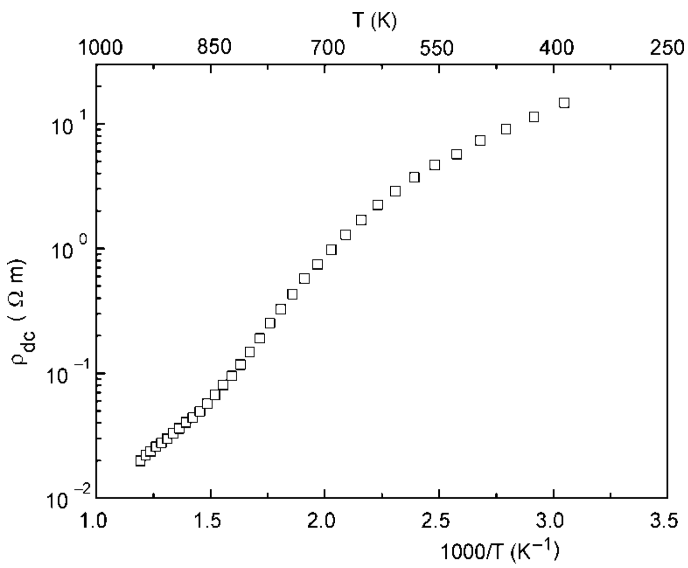

Fig. 3. Dependence of d.c. resistivity of TiO_2:(Tb, Pd) thin films on temperature

Identification of charge transport phenomena requires experimental determination of the temperature dependent electrical resistivity (ρ_{dc}). Figure 3 shows the dependence of d.c. electrical resistivity on temperature of the prepared TiO_2:(Tb, Pd) thin films. A non-linear behaviour can be seen, indicating a complex mechanism of electrical conduction in the films. Thus, determination of the activation energy from the slope is difficult.

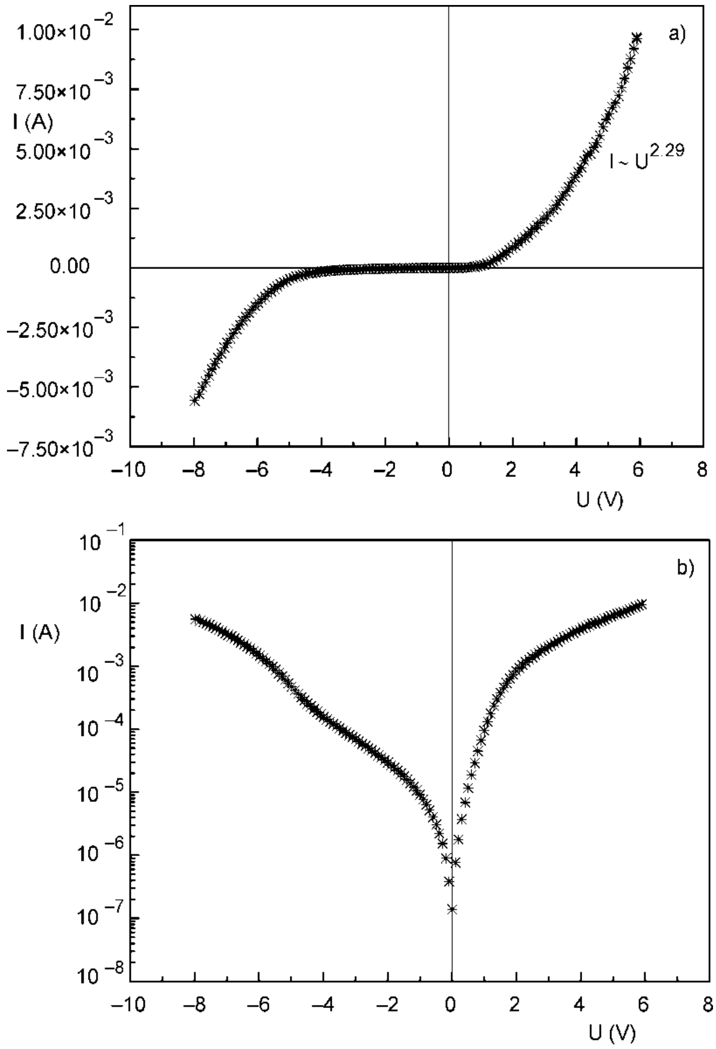

Fig. 4. *I–V* characteristics of TiO_2:(Tb, Pd) thin films on silicon recorded at 300 K: a) linear scale and b) semi-logarithmic co-ordinate system

I–V characteristics of the p-type semiconducting TiO_2:(Tb, Pd) thin films as deposited on p-type silicon recorded at 300 K are presented in Fig. 4. A strong non-linear (diode like) behaviour could be observed in Fig. 4a. The current flowing in the forward direction exhibits the power dependence on the applied voltage ($I \sim U^{2.29}$) which suggests the space charge limited current (SCLC) mechanism of charge transport in the examined structure. SCLC conduction is often observed in materials with low concentration of thermally generated carriers. From the shape of the characteristic, shown in a semi-logarithmic co-ordinate system (Fig. 4b), the presence of strong depletion for backward biased structure ($U < 0$ applied to silicon substrate) at the prepared heterojunction is clearly seen.

4. Conclusions

Optical and electrical properties of TiO_2 doped with Tb and Pd have been presented. It was shown that incorporation of Pd and Tb dopants into TiO_2 matrix modified its properties; a p-type oxide-semiconductor electrically active at room temperature was obtained, although the transparency to visible light was decreased.

I–V characteristics showed a strong diode like behaviour depending on the direction of current flow and revealed a space charge limited current (SCLC) conduction mechanism in the forward biased structure. The obtained results indicate that it is possible to apply TiO_2:(Tb, Pd) thin films to fabricate integrated TOS–Si microstructures.

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