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Investigations of electrical properties of Eu- and Pd-doped titanium dioxide thin films on silicon

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In this work, investigations of electrical properties of Eu- and Pd-doped TiO_2 thin films have been outlined. Thin films were deposited by low pressure hot target reactive magnetron sputtering from metallic Ti-Eu-Pd mosaic target on conventional silicon wafers. For electrical characterization of prepared thin films both temperature dependent resistivity and current to voltage (I–V) characteristics have been examined. It has been shown that incorporation of Pd and Eu dopants into TiO_2 matrix modified its properties to obtain *n*-type oxide-semiconductor which is electrically and optically active at room temperature. Additionally from I–V measurements the formation of heterojunction at the interface of thin film–silicon was confirmed.

Keywords: oxide semiconductor, thin film, electrical properties.

1. Introduction

Great progress in oxide engineering makes the transparent oxide semiconductors (TOSs) to take recently its position at the top of the scientific interest. Fabrication of TOS with *n*- and *p*-type of electrical conduction creates the possibility of realization of different kind of heterojunctions [1] as well as offers its applications in the fields of solar energy conversion [2], thin film transistor [3], *etc.*, which have been demonstrated, so far. Major difficulties in the manufacturing of fully functional transparent oxide-based devices still exist due to low electrical performance of TOSs, manifested itself mainly by low charge carrier mobility and limited range for changing the electrical conductivity. Another task is “know-how” to change native type of electrical conduction of oxides using standard microelectronics technology, *i.e.*, by doping. This obviously limits their use in some electrical applications. Thus, the development of methods for modification of electrical properties of thin films of oxides is of great importance.

Our further studies have shown that doping with different transition and noble metals of titanium dioxide as a base oxide, could modify its electrical [4] and optical properties [5]. For example, doping with Pd introduces acceptor levels inside forbidden gap of TiO_2 changing its electrical conductivity from oxide non-conductor to oxide-semiconductor [6]. Additional incorporation of V [7] resulted in change of the type of electrical conduction of prepared thin films.

From literature data [8] it is well known that different oxides could be applied as a host matrix for different rare earth elements, as well. For example, doping of TiO_2 matrix with Eu [9] makes it an efficient red-luminescent material.

In this study thin films of TiO_2:(Eu, Pd) TOS have been deposited from metallic Ti-Eu-Pd target on silicon substrates using low pressure hot target reactive magnetron sputtering (LP HTRS) [10]. The major goal of the work was investigation of electrical properties of the thin film itself, as well as in the conjunction with the standard silicon substrate, *i.e.*, examination of the electrical properties of prepared heterojunction.

2. Experimental procedure

Thin films were prepared by LP HTRS method from metallic Ti-Eu-Pd (mosaic) target and deposited on monocrystalline silicon. The sputtering process was carried out at low pressure (< 0.1 Pa) of pure oxygen as a working gas and with the target additionally heated by reactive plasma up to 873–973 K. The amount of Pd and Eu dopants, determined with energy disperse spectrometer in as-deposited thin films, were 2.8 and 0.3 at.%, respectively.

For electrical characterization, $Ag/Ti_{10}W_{90}$ metal electrodes were evaporated through the metallic mask into the thin films. Measurement of direct current (d.c.) electrical resistivity ρ_{dc} was done using standard four-probe method in a temperature range from 300 to 500 K. The value of Seebeck coefficient S was determined with respect to the standard platinum electrodes, as well. I–V measurements have been performed at room temperature using electrical characterization system based on Keithley's 2000 multimeter and 6517A electrometer.

3. Results

3.1. Temperature dependent electrical measurements

Experimental determination of the temperature dependent electrical resistivity ρ_{dc} is the fundamental step in the recognition of charge transport phenomena and could be applied to a variety of different kind of materials [11]. Figure 1 shows the dependence of d.c. electrical resistivity vs. temperature of prepared TiO_2:(Eu, Pd) thin films.

In the selected range of temperature, experimental data were found to fit straight line and thus the activation energy $W_\rho = 0.18$ eV could be determined.

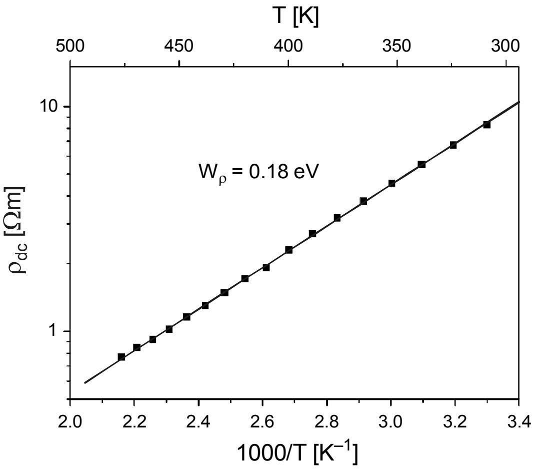

Fig. 1. Dependence of d.c. resistivity vs. temperature of TiO_2:(Eu, Pd) thin films.

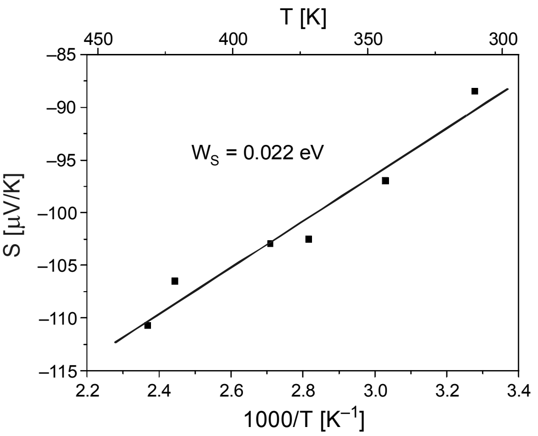

Fig. 2. Dependence of Seebeck coefficient vs. temperature of TiO_2:(Eu, Pd).

In Figure 2, the temperature dependent characteristic of Seebeck coefficient *S* for prepared thin films has been presented. This enables the determination of the type of electric conduction. In the fabricated thin films of TiO_2:(Eu, Pd) negative sign of Seebeck coefficient (Fig. 2) indicates that the conduction is of electron-type (*n*). Additionally, from the slope of $S(T)$ characteristic the thermal activation energy W_S was estimated to be 0.022 eV. An order discrepancy between determined values of activation energies ($W_S = 0.022$ eV and $W_\rho = 0.18$ eV) may reflects complex mechanism of electrical conduction in the prepared thin films [7]. Estimated values could be affected by all thermally activated processes of charge transport occurring in examined films and thus, the distinction of W_S and W_ρ on the basis of plotted curves (Figs. 1 and 2) is difficult.

3.2. I–V measurements

I–V characteristics of *n*-type semiconducting TiO_2:(Eu, Pd) thin films measured when as-deposited on *p*-type silicon have been presented in Fig. 3.

A strong non-linear (diode like) effect could be observed in Fig. 3**a**. The current flowing in the forward direction exhibits the power dependence on the applied voltage ($I \sim U^{3.44}$). Such dependence suggests space charge limited current (SCLC) mechanism of charge transport in the examined structure. SCLC conduction is often

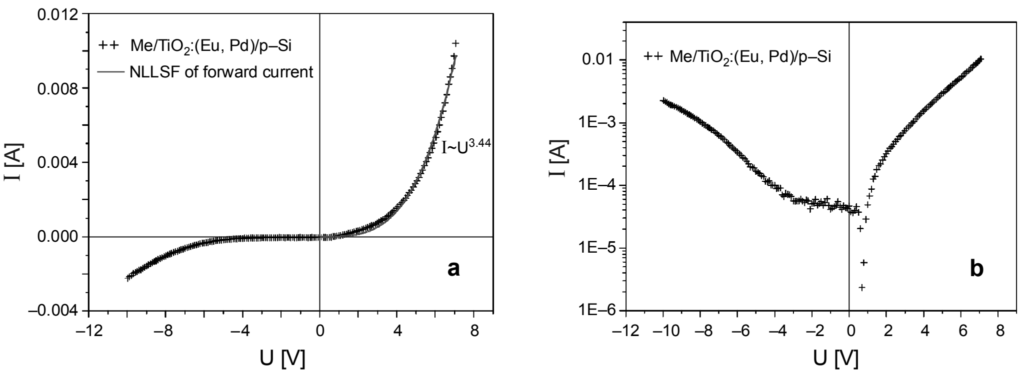

Fig. 3. I–V characteristics of TiO_2:(Eu, Pd) thin films on silicon: linear scale (**a**) and semi-logarithmic co-ordinate system (**b**).

observed in the materials of low concentration of thermally generated carriers. From the shape of the same characteristic, shown in a semi-logarithmic co-ordinate system (Fig. 3**b**), presence of strong depletion for backward biased structure ($U < 0$ applied to silicon substrate) at the prepared heterojunction is clearly seen.

4. Conclusions

From electrical temperature dependent characteristics, the activation energies ($W_\rho = 0.18$ eV and $W_S = 0.022$ eV) were calculated. Estimated values of W_S and W_ρ show that the mechanism of electric conduction in fabricated thin films is complex. The sign of the Seebeck coefficient indicates *n*-type electric conduction in the prepared TOS of TiO_2:(Eu, Pd) thin films.

I–V characteristics showed a strong non-linear behaviour depended on direction of the current flow. Obtained results well correspond to SCLC conduction mechanism in the forward biased structure. Experimental results confirm the formation of electrically active heterojunction and thus offer a possibility of its application to the integrated TOS–Si microstructures.

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