# EVALUATION OF ELECTRICAL PROPERTIES OF Eu AND Pd-DOPED TITANIUM DIOXIDE THIN FILMS DEPOSITED ON SILICON*

Eugeniusz L. Prociow[1], Jarosław Domaradzki[1], Danuta Kaczmarek[1], Karolina Sieradzka[1], Bartosz Michalec[1]

In this work, investigations of electrical properties of Eu and Pd-doped $TiO_2$ thin films have been outlined. Our previous studies [4, 6] of Eu and Pd-doped $TiO_2$ have shown the nanocrystalline structure and high transparency in visible region (about 70%). Now, it has been shown that by incorporation of Pd and Eu dopants into $TiO_2$ matrix, its properties can be modified so as to obtain simultaneously electrically and optically active oxide-semiconductor with specified type of electrical conduction at room temperature. Pd dopant changes the electrical properties of $TiO_2$ from dielectric oxide to conducting oxide. Samples were examined by means of theromelectrical, current-voltage (I-V), transient photovoltage and optical beam induced current OBIC *(Optical Beam Induced Current)*.
I-V measurements showed formation of electrical junctions at the interface of semiconducting thin films of metal oxides and silicon substrate (TOS-Si). The presence of build-in potential has been confirmed by OBIC through created maps of photocurrent distribution generated in the active areas of prepared TOS-Si heterojunctions.

***Key words:*** electrical properties, $TiO_2$:(Eu, Pd), heterojuncion, OPIC

[1)] Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology, Janiszewskiego 11/17, 50-372 Wroclaw, Poland; e-mail: karolina.sieradzka@pwr.wroc.pl
* Praca prezentowana na XXXII International Conference of IMAPS - CPMP IEEE, Poland, Pułtusk 21-24.09.2008

## 1. INTRODUCTION

Transparent oxide semiconductors (TOSs) are very attractive for microelectronics application. Due to their transparency and good conductivity at room temperature they can be considered as active front-electrodes of photodiodes or phototransistors, optical switches, modulators, and so on [1]. Their stability at elevated temperatures and high resistance to harsh environment makes them suitable for realization of optical based gas sensors. Recent progress in silicon technology, including developing of effective light sources based on Si nanocrystals, makes TOSs attractive also for TOS-Si integration. In the present work, modification of electrical properties from $TiO_2$ – insulating oxide to $TiO_2$:(Eu, Pd) – oxide semiconductor has been presented. For the purpose of the work thin films were deposited on standard silicon substrates and photoelectrical investigation provided by (OBIC) technique has been presented. OBIC is a non-destructive, charge collection method and is known a as powerful technique for solar cells, detectors and semiconductor material characterization [2-3].

## 2. EXPERIMENTAL

Thin films were deposited by low pressure hot target reactive magnetron sputtering from mosaic Ti-Eu-Pd target on conventional silicon wafers. The amount of dopants in prepared $TiO_2$:(Eu,Pd) thin film has been evaluated with the help of energy disperse spectrometer to be of Eu – 0.9 at.% and Pd – 5.8 at.%.

The earlier XRD studies [4] have shown the dominating crystal phase $TiO_2$- rutile with crystallites 9.8 nm in size. No separate Pd or Eu phases were found.

For electrical characterization of Eu and Pd-doped $TiO_2$ thin films four parallel Ti metal electrodes were evaporated through the metallic mask onto the thin films.

On the basis of the d.c. electrical resistivity ($\rho_{dc}$) dependence on temperature, in the temperature range from 300 K to 500 K, the activation energy ($W\rho$) was estimated. Negative sign of Seebeck coefficient has been determined what indicates the electron-type (n) conduction. Besides, from the thermoelectric power the activation energy ($W_S$) was calculated. Electrical parameters evaluated from thermoelectrical measurements have been collected in Tab. 1.

Optical properties determined on the basis of optical transmission and photoluminescence measurements have previously been described [5-6]. The prepared $TiO_2$:(Eu,Pd) thin films has proven to be transparent in the visible part of the light spectrum from ca. 450 nm and the optical bandgap of 1.71 eV has been found. PL experiment yields the intense red emission with narrow peak at 615 nm what is consistent with the standard $Eu^{3+}$ emission.

**Table 1.** $TiO_2$:(Eu,Pd) thin films electrical parameters determined from thermoelectrical measurements.
**Tabela 1.** Parametry elektryczne cienkich warstw $TiO_2$:(Eu,Pd) określone na podstawie pomiarów termoelektrycznych

| ρ [Ωm] | $W_\rho$ [eV] | $W_s$ [eV] | Seebeck coefficient at 300 K [μV/K] | Conduction type |
|---|---|---|---|---|
| ~10 | 0.18 | 0.022 | -90 | n |

OBIC investigations have been performed using experimental setup equipped with laser diode as a light source at 650 nm in wavelength. The light beam was focused through optical system down to ca. 30 μm and the locally generated photocurrent was collected using lock-in (PARC 5301A EG&G) phase-sensitive nanovoltmeter equipped with current to voltage converter.

## 3. RESULTS

Current to voltage (I-V) characteristics measured at different ambient temperatures have been presented in Fig. 1 in a semilogarithmic plot.

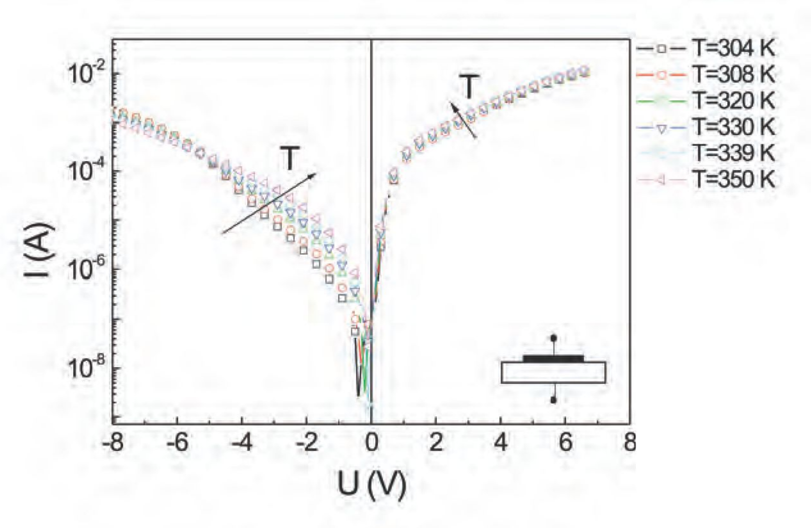


**Fig. 1.** Current to voltage characteristics of $TiO_2$:(Eu,Pd) thin films on Si-p.
**Rys. 1.** Charakterystyki I-V cienkich warstw $TiO_2$:(Eu,Pd) naniesionych na podłoża Si-p.

A strong non-linear effect was observed. For reverse biased structure the presence of unbalanced charge at the interface TOS-Si is clearly visible. The I-V curves shifted, as temperature increased.

For practical application in junction-based devices, such as diodes, a spectral responsivity ($R_\lambda$) is required. $R_\lambda$ is defined as a ratio of the measured photocurrent as a response to the incident light power at a given wavelength. Spectral responsivity characteristics of Me/$TiO_2$:(Eu,Pd)/Si structure have been presented in Fig. 2, together with transmission of $TiO_2$:(Eu,Pd) thin film on $SiO_2$.

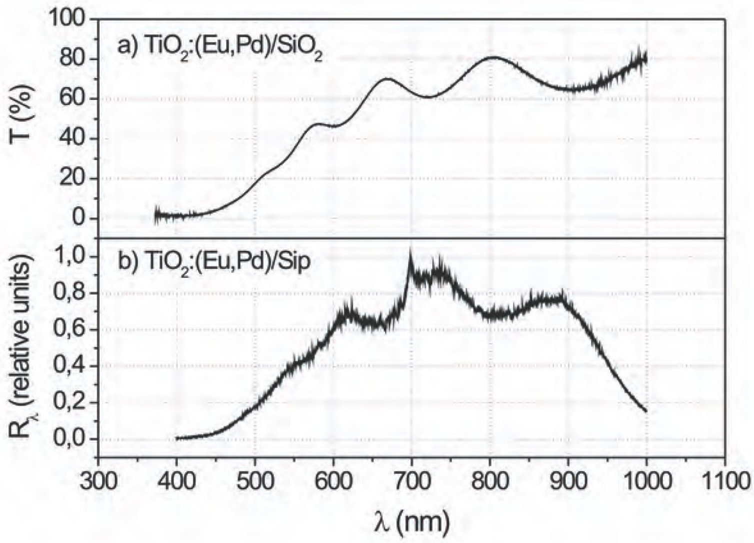


**Fig. 2.** Spectral characteristics of: a) transmittance of $TiO_2$:(Eu,Pd) thin film and b) responsivity of Me/$TiO_2$:(Eu,Pd)/Si structure. Characteristics were measured with illumination of 50 W halogen lamp and the light was dispersed through a ¼ m focal length single grating monochromator.

**Rys. 2.** Charakterystyki spektralne: a) współczynnika transmisji dla cienkich warstw $TiO_2$:(Eu,Pd), b) współczynnika odbicia dla struktury Me/$TiO_{2:}$(Eu,Pd)/Si. Jako źródło światła zastosowano lampę halogenową o mocy 50 W.

The $R_\lambda(\lambda)$ characteristic (Fig. 2b) of prepared structures was shifted from shorter wavelength range to longer one by the light absorption in the thin film itself (Fig. 2a). The limit at the long wavelength range is due to the decrease in photon-electron energy conversion at the interface of TOS-Si structure and is similar to that observed in case of standard silicon devices. Also, in the Fig. 2 the interference fringes visible in Fig. 2a are well reproduced giving local drop of $R_\lambda$.

The transient photovoltage response of $TiO_2$:(Eu,Pd)/Si-p heterojunction to optical excitation with laser diode at 650 nm and 300 Hz square modulation has been presented in Fig. 3.

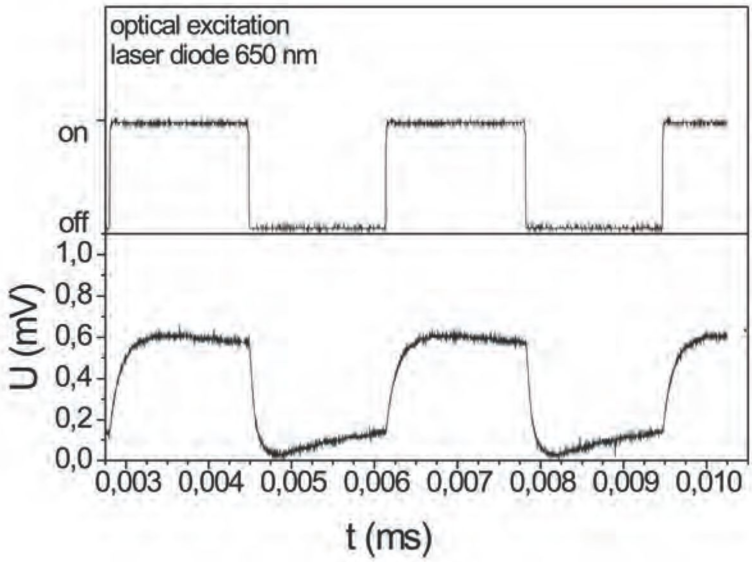


**Fig. 3**. Transient photovoltage response of $TiO_2$:(Eu,Pd)/Si-p heterojunction to optical excitation with laser diode at 650 nm and 300 Hz square modulation.
**Rys. 3.** Pomiar fotonapięcia generowanego w heterozłączu typu $TiO_2$:(Eu,Pd)/Si-p. Jako źródło światła zastosowano diodę laserową o następujących parametrach wiązki świetlnej: długość fali $\lambda$ = 650 nm, częstotliwość modulacji $f$ = 300 Hz.

It can be clearly seen that the photovoltage generated at the active area of prepared TOS-Si heterojunction follows applied optical excitation. Therefore photoelectrical properties of prepared structures could be further investigated using OBIC technique [7]. The measurement of locally generated photocurrent was done at room temperature without any external biasing. The distribution of magnitude and phase (with respect to reference signal) of current generated in the selected area of investigated sample has been presented in Figs. 4 a and b, respectively.

From the maps presented in Fig. 4 it can be seen that both the magnitude and the phase of generated photocurrent are dependent on the position of the light spot on the sample. The highest signal, as it could be expected, is measured near metal electrodes. As the light beam is moved from one side (eg. contact A) at the half distance between electrodes the magnitude of signal drops and the phase reverses in the opposite value range.

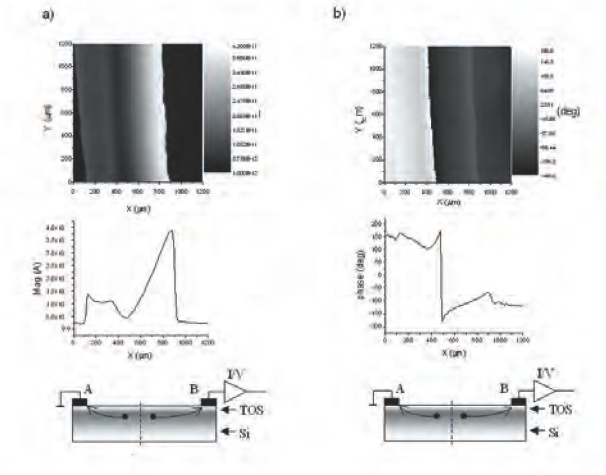


**Fig. 4.** Magnitude (a) and phase (b) distribution of photocurrent generated in the active area (between metal electrodes) of $TiO_2$:(Eu,Pd)/Si-p heterojunction. Light spot 30 µm, step size – 10 µm. At the bottom, schematic drawn of the investigated structures with marked direction of photogenerated carriers depending on the position of the light spot has been included.
**Rys. 4.** Mapa rozkładu: a) amplitudy. b) przesunięcia fazowego fotoprądu generowanego w obszarach międzykontaktowych otrzymana dla heterozłącza typu $TiO_2$:(Eu, Pd)/Si-p. Parametry wiązki świetlnej: średnica 30 µm, krok pomiarowy 10 µm.

## 4. CONCLUSIONS

In this work the influence of Eu and Pd dopants on electrical and optical properties of $TiO_2$ matrix have been presented. Selected dopants resulted that thin films of TOS type in room temperature were obtained with high transparency, about 70% in visible range (at ca. 700 nm), the resistivity of $10^3$ Ωcm and with n-type of electrical conduction. Obtained results are very promising because usually some other dopants usually improves one selected property of $TiO_2$ and simultaneously gets worse another parameters, for example unaccompanied Pd or Eu dopants [8-9].

The electrical I-V characteristics show a strong non-linearity and the presence of junction at the interface TOS-Si is clearly visible. Moreover, the OBIC examinations revealed the electrically active areas of the interface of fabricated heterojunctions. To sum up, it was found that $TiO_2$:(Eu,Pd)/Si-p structures confirm suitability of those oxide-semiconductor heterojunctions for the charge collection applications.

## ACKNOWLEDGMENT

This work was financed from the sources for science development in the years 2007-2009 as a research project No. N N515 4401 33.

## REFERENCES

[1] Ohta H., Nomura K., Hiramatsu H., Ueda K., Kamiya T., Hirano M., Hosono H.: Frontier of transparent oxide semiconductors, *Solid-State Electronics,* 47, (2003), 2261-2267

[2] Galloway S.A., Edwards P.R., Durose K.: Characterisation of thin film CdS/CdTe solar cells using electron and optical beam induced curren, *Solar Energy Materials and Solar Cells,* 57, 1, (1999), 61-74

[3] Castaldini A., Cavallini A., Polenta L., Nava F., Canali C.: *Physics Research, Section A Accelerators, Spectrometers, Detectors and Associated Equipment,* 476, 3, (2002), 550-555

[4] Domaradzki J., Borkowska A., Kaczmarek D., Podhorodecki A., Misiewicz J.: Influence of post annealing on optical and structural properties of Eu and Pd-doped $TiO_2$ thin films *Optica Applicata* XXXVII, 1-2, (2007), 52-56

[5] Domaradzki J., Borkowska A., Kaczmarek D.: VI International Conference on Advanced Semiconductor Devices and Microsystems, ASDAM'06, Smolenice Castle, Slovakia, 16 -18 October, IEEE, (2006), 67-70

[6] Borkowska A., Domaradzki J., Kaczmarek D.: Influence of Eu dopant on optical properties of $TiO_2$ thin films fabricated by low pressure hot target reactive sputtering *Optica Applicata* XXXVII, 1-2, (2007), 117-122

[7] Domaradzki J., Kaczmarek D.: Optical beam injection methods as a tool for analysis of semiconductor structures, *Optica Applicata* XXXV, 1, (2005), 129-137

[8] Prociow E.L., Domaradzki J., Podhorodecki A., Borkowska A., Kaczmarek D., Misiewicz J.: Photoluminescence of Eu-moped $TiO_2$ thin films prepared by low pressure hot target magnetron sputtering, *Thin Solid Films,* 515, (2007), 6344-6346

[9] Sieradzka K., Domaradzki J., Kaczmarek D.: Influence of Eu, Tb, Pd dopants on electric al and optical properties of nanostructured $TiO_2$ thin films, VII International Conference on Advanced Semiconductor Devices and Microsystems, ASDAM'08, Smolenice Castle, Slovakia, 16-18 October, IEEE, (2008), 243-246

## BADANIE WŁAŚCIWOŚCI ELEKTRYCZNYCH CIENKICH WARSTW $TiO_2$ DOMIESZKOWANYCH Eu I Pd NANIESIONYCH NA PODŁOŻA KRZEMOWE

W niniejszej pracy przedstawiono badanie właściwości elektrycznych cienkich warstw $TiO_2$ domieszkowanych Eu i Pd. Pokazano, że wprowadzenie domieszki Eu i Pd do matrycy $TiO_2$ modyfikuje jej właściwości, pozwala otrzymać cienkie warstwy elektrycznie i optycznie aktywne. Dodatkowo, wytworzone tlenki posiadają określony typ przewodnictwa elektrycznego w temperaturze pokojowej. Decydujący wpływ na właściwości elektryczne matrycy $TiO_2$ miała domieszka Pd, która umożliwiła zmianę właściwości cienkich warstw dielektrycznych na półprzewodnikowe.

Próbki badano za pomocą charakterystyk termoelektrycznych, charakterystyk prądowo-napięciowych (I-V) oraz metodą OBIC.

Na podstawie pomiarów I-V zaobserwowano formowanie się złącza na granicy przezroczysty tlenek półprzewodnikowy-podłoże krzemowe (TOS-Si). Mapy rozkładu fotoprądu generowanego w obszarach aktywnych wytworzonego heterozłącza TOS-Si potwierdziły obecność potencjału wbudowanego.

***Słowa kluczowe:*** własności elektryczne, $TiO_2$:(Eu, Pd), heterozłączne, OPIC