STUDY OF STRUCTURAL AND OPTICAL PROPERTIES OF TiO_2:(Eu, Pd) THIN FILMS DEPOSITED BY MAGNETRON SPUTTERING*

Danuta Kaczmarek[1], Jaroslaw Domaradzki[1], Eugeniusz L. Prociow[1], Damian Wojcieszak[1], Bartosz Michalec[1]

In this study the results on TiO_2 thin films doped with europium and palladium at the amount of 0.9 at. % and 5.8 at. % respectively have been presented. For thin films deposition the high energy (HE) magnetron sputtering method was used. Some samples were subjected to the post-processed annealing. X-Ray Diffraction (XRD) results have shown that after deposition nanocrystalline TiO_2 - rutile structure was obtained. After additional annealing at 800°C average crystallites sizes increased about twofold (from 9 to 16 nm). The XRD results were confirmed using atomic force microscope. Optical properties of thin films were examined using optical transmission method. They have shown that doping with Eu and Pd has decreased the transmission level by about 15% and shifted absorption edge to the longer wavelength range (from 330 to 450 nm) compared to pure TiO_2. The width of optical bandgap of TiO_2:(Eu, Pd) thin film decreased to ca. 1.7 eV, i.e. twofold, when compared to 3.35 eV of undoped-TiO_2. The photoluminescence results have shown that examined thin film has strong red luminescence from standard Eu^{3+} emission lines.

Key words: TiO_2, thin films, magnetron sputteing
Słowa kluczowe: TiO_2, cienkie warstwy, rozpylanie magnetronowe

1. INTRODUCTION

The thin films based on TiO_2 doped with transition and rare earth (RE) elements exhibit great potential for developing their properties. TiO_2 is a semiconducting oxide

[1)] Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology, Janiszewskiego 11/17, 50-372 Wroclaw, Poland damian.wojcieszak@pwr.wroc.pl

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with preferred n- or p-type electrical conduction, insulating at room temperature. Doping with Nb, V, Pd enhances electrical conduction, but decreases the transparency range of the prepared doped-TiO_2 thin films. Doping of TiO_2 with some RE elements, such as Er, Eu, Nd, Tb makes it an attractive material for (photo) luminescence applications [3-5]. Combining above by processing, thin films based on TiO_2 co-doped simultaneously with transition and RE elements must result in promising, electrically and optically active material, with great potential for further applications.

In this paper structural and optical properties of TiO_2 co-doped with Pd (modifier of electrical properties) and Eu (optical properties modifier) have been presented. The properties of prepared TiO_2:(Eu, Pd) thin films have been analyzed in comparison to undoped TiO_2 which was prepared in similar technological conditions.

Thin films of oxides can be prepared using different deposition techniques. One of the method which is commonly used nowadays is sputtering. The method enables fabrication of wide variety of different materials and with different physical and chemical properties.

2. EXPERIMENTAL

Titanium dioxide thin films were deposited on silicon substrates by High Energy (HE) magnetron sputtering process [6]. In HE process thin films were sputtered from mosaic Ti-Eu-Pd target in oxygen plasma. The oxygen was used as a working and reactive gas, which pressure was kept at 10^{-1} Pa. The energy of sputtered particles in HE process was enhanced, compared to standard sputtering process. It was achieved by limiting of heat flow in physical contact between target and water-cooled magnetron and by increase of unipolar pulses voltage (up to 1800 V) which supply magnetron [7]. Due to enhanced energy, molecules approaching the substrate have enough energy to order themselves and sublimate in the TiO_2-rutile form right during deposition. To make thing better, the as-deposited thin films were also subjected to the post-processing annealing at 1070 K in ambient air.

Structural properties of fabricated thin films were examined using DRON-2 powder diffractometer with Fe-filtered Co Kα radiation. The images of surface topography were taken by atomic force microscopy method using Veeco Picco Force microscope, which was working in contact mode. The dopants amount (Eu and Pd) in processed films were estimated using energy dispersive spectroscopy (EDS) method. The EDS measurements were recorded on scanning electron microscope, which was equipped with EDS attachment (Hitachi S-4700N, Noran Vantage).

Optical properties were examined with the use of by optical transmission method. The optical measurements were preformed in a spectral range of 200 nm – 1100 nm with the help of CCD spectrophotometer and a coupled deuterium – halogen lamp as a light source. The photoluminescence (PL) properties were obtained using UV argon laser with the excitation wavelength of 302 nm. The PL signal has been detected by Ocean Optics HR4000 spectrometer.

3. RESULTS

3.1. Amount of Eu and Pd dopants

Titanium dioxide thin films were sputtered from mosaic Ti-Eu-Pd target on silicon substrates. The EDS results have shown that in as-deposited TiO_2:(Eu, Pd) thin film there was 0.9 at. % of Eu and 5.8 at. % of Pd-dopant. The EDS spectra of processed TiO_2:(Eu, Pd) thin film is presented in Fig. 1. Except peaks of Ti, O, Eu and Pd there were also peaks of Si, C and Au in this spectrum. The presence of silicon comes from the substrate, on which the thin films were deposited. The carbon peak is quite usual in EDS spectra and it comes from the air pollutants, as samples cannot avoid the contact with ambient. The spectral line of Au is due to the thin film of gold which was applied to cover the sample surface to eliminate the charge effect during the EDS measurement.

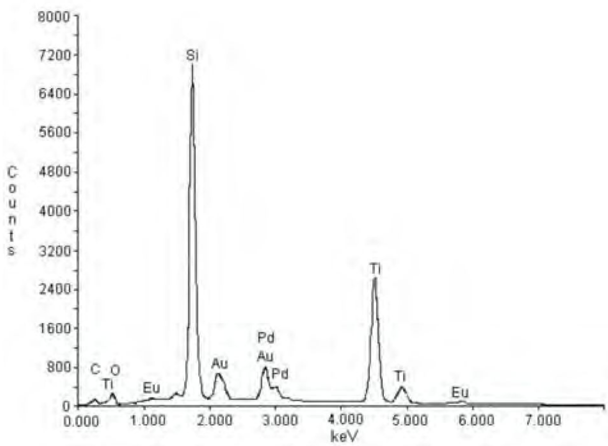

Fig. 1. EDS spectrum of TiO_2:(Eu, Pd) thin film on silicon.
Rys. 1. Widmo EDS cienkiej warstwy TiO_2:(Eu, Pd) na krzemie.

3.2. Structure

Parameters, like crystal phases, average crystallite sizes, interplanar distances or type of stress in the film were determined on the basis of XRD patterns. In the Fig. 2 the XRD-patterns of TiO_2 and TiO_2:(Eu, Pd) thin films, as-deposited and annealed at 1070 K are presented. The as-deposited thin films (Figs. 2a-b) grew in crystalline

TiO_2-rutile form. This is quite unusual because usually, the as-deposited thin films prepared by magnetron sputtering display the anatase or amorphous form and an additional post-processing heat-treatment is required for transformation into thermodynamically stable rutile phase. Therefore the fact that we have got the rutile form must result from the peculiarity of the high energy magnetron sputtering and that is HE process that allows to obtain nanocrystalline TiO_2 thin films with rutile form after deposition. The additional post-process annealing at 1070 K (Fig. 2c) brings

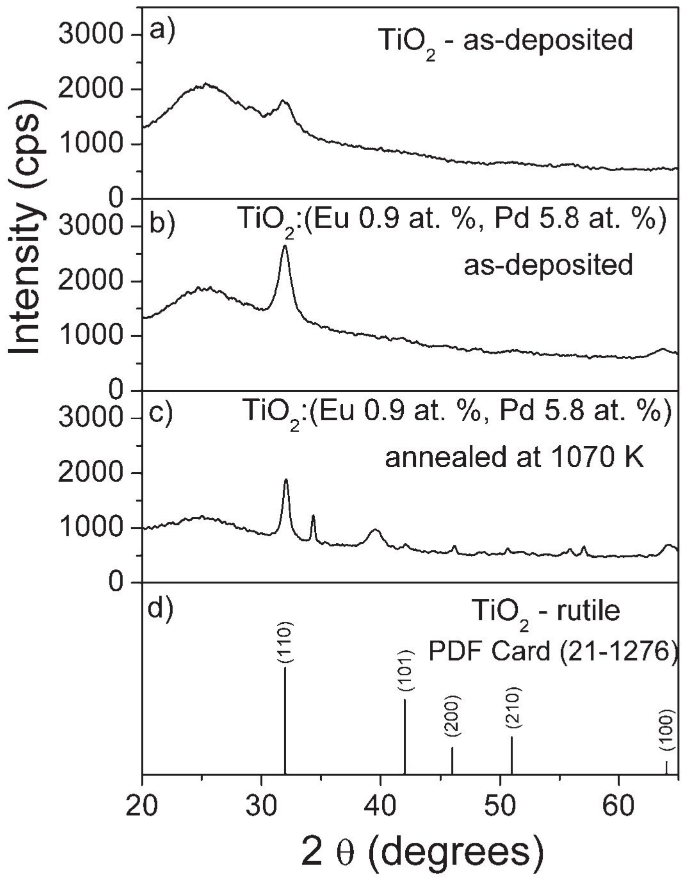

Fig. 2. XRD-patterns of as-deposited TiO_2 (a) and TiO_2:(Eu 0.9 at. %, Pd 5.8 at. %) (b) and annealed at 1070K TiO_2:(Eu 0.9 at. %, Pd 5.8 at. %) (c) thin films deposited on SiO_2, compared to standard pattern of the TiO_2-rutile (d) [8].

Rys. 2. Dyfraktogramy XRD cienkich warstw naniesionych na SiO_2: TiO_2 po naniesieniu (a), TiO_2:(Eu 0,9 % at., Pd 5,8 % at.) po naniesieniu (b), wygrzewanej w temperaturze 1070 K TiO_2:(Eu 0,9 % at., Pd 5,8 % at.) (c), porównane do danych standardowych dla TiO_2- rutylu (d) [8].

about an increase of the doped thin film crystallinity what makes the narrowing of the most intense (110) rutile peak and appearance of additional diffraction peaks which originate from crystallites with other plane orientations (Fig. 2c).

The structural parameters of examined thin films, which were evaluated for the most intense (110) diffraction peak of the rutile have been collected in Tab. 1.

Table 1. Structural parameters of TiO_2 and TiO_2:(Eu 0.9 at. %, Pd 5.8 at. %) thin films (derived from the most intense (110) TiO_2-rutile diffraction peak). D – average grain size, d – interplanar spacing, Δd – relative difference in d, where $\Delta d = (d-d_{PDF})/d_{PDF}$ (%).
Tabela 1. Parametry strukturalne cienkich warstw TiO_2 i TiO_2:(Eu 0,9 % at., Pd 5,8 % at.) (względem najintensywniejszego piku dyfrakcyjnego (110) dla TiO_2-rutylu). D – średni rozmiar krystalitów, d – odległość międzypłaszczyznowa, Δd – względna różnica d, gdzie $\Delta d = (d-d_{PD}F)/d_{PDF}$ (%).

Sample	Property			
	phase	*D* (nm)	*d* (nm)	Δ*d* (%)
TiO_2 as deposited	rutile	9.3	0.3263	+0.49
TiO_2:(Eu, Pd) as deposited	rutile	8.8	0.3353	+3.26
TiO_2:(Edu, Pd) anne-aled at 1070 K	rutile	15.8	0.3243	-0.12
bulk rutile [8]	–	–	0.3247	–

The thin films of both pure TiO_2 and TiO_2 doped with Eu and Pd exhibited the similar crystallite sizes, about 9 nm, at average (Tab. 1). The tension stress took place in as-deposited thin films, however, doping by Eu and Pd brought about the higher rate of tension. The compression rate was determined by comparing the values of interplanar distances (d), measured and that of standard bulk TiO_2-rutile (PDF Card 21-1276) [8]. This behavior can be ascribed to the differences in the ionic radii of Ti^{4+} (0.056 nm), Eu^{3+} (0.108 nm) and Pd^{2+}(0.100 nm). The XRD pattern (Fig. 2b) of as-deposited TiO_2:(Eu, Pd) film do not reveal any crystal form of Eu or Pd. The dopants (or their ions) must be located in the interstitial positions of the TiO_2 matrix and thus influence its tension. Different oxidation state and disproportionate sizes of dopants make that substitution of lattice Ti^{4+} in TiO_2 matrix by Eu^{3+} or Pd^{2+} is rather less probably. Zeng et. al. [9] reported that the Eu^{3+} may be located at the surface of the TiO_2 nanocrystallites and can form Eu-O-Ti bonds. In our previous works [10], we have found Pd dopant to be an effective modifier of electrical properties of insulating TiO_2. Due to the shallow energy levels introduced by nanocrystalline Pd and PdO phases (not detected by XRD in as- deposited films) being close to the valence band of TiO_2, the prepared Pd-doped TiO_2 are oxide semiconductors at the room temperature.

The post-processing annealing of TiO_2:(Eu, Pd) film at 1070 K (Fig. 2c) brought about the increasing of crystallite sizes up to 16 nm and it also resulted in change of type of stress in the thin film – on compression one (Δd = -0.12) (Tab. 1).

3.3. The surface topography

The AFM images have confirmed the XRD results and also have shown that deposited thin films were nanocrystalline. The AFM images of as-deposited pure TiO_2-matrix, as-deposited and annealed at 1070 K TiO_2:(Eu, Pd) thin films, which were deposited on Si substrates are presented in the Fig. 3. It can be seen that all the processed and examined films have homogeneous structure. However doping with Eu and Pd resulted in increase of surface diversification. Also, the additional

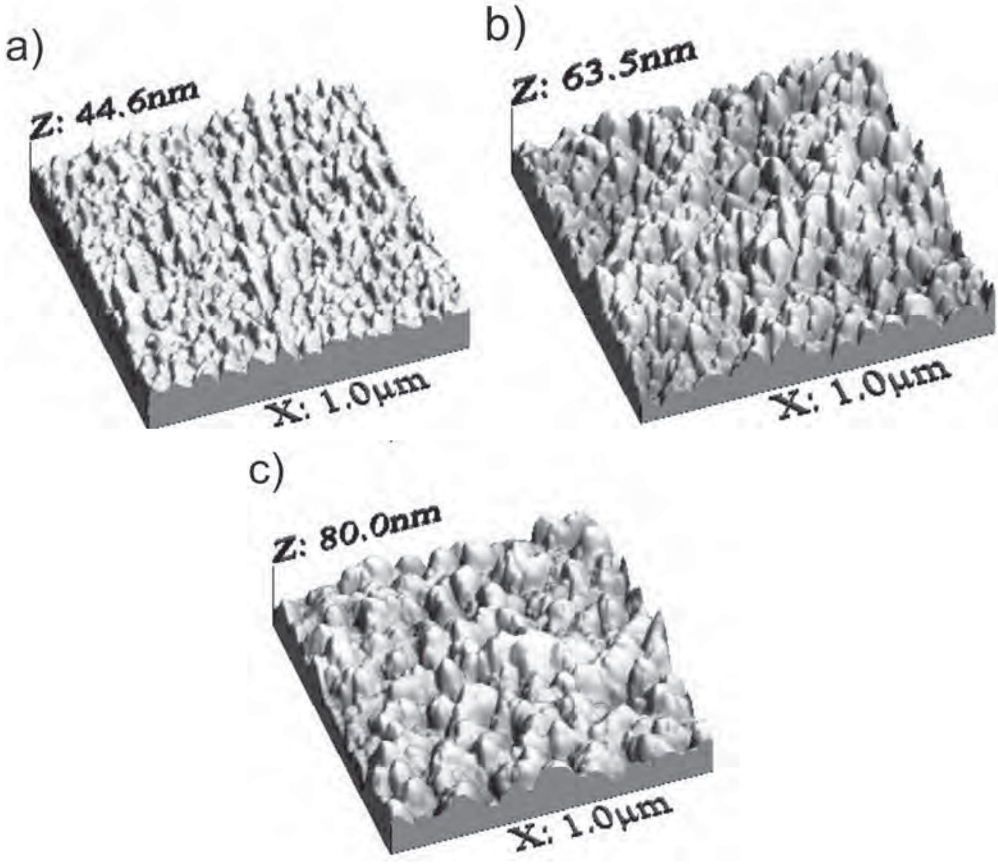

Fig. 3. AFM images of as-deposited TiO_2 (a), as-deposited TiO_2:(Eu, Pd) (b) and annealed at 1070 K TiO_2:(Eu, Pd) (c) thin films, which were deposited on Si (100) substrates.
Rys. 3. Obrazy AFM cienkich warstw TiO_2 po naniesieniu (a), TiO_2:(Eu, Pd) po naniesieniu (b) i wygrzewanej w 1070 K TiO_2:(Eu, Pd) (c), naniesionych na podłoża krzemowe Si (100).

post-processing annealing triggered the increase of grain sizes, but the thin film was still nanocrystalline.

3.4. Optical properties

Optical properties of processed and examined TiO_2 thin films were estimated from optical transmission characteristics. The transmission spectra of TiO_2:(0.9 at. %Eu, 5.8 at. % Pd) thin films, as-deposited and annealed at 1070 K, deposited on SiO_2 substrates, are presented in Fig. 4. The characteristic of Eu and Pd-doped were compared with undoped TiO_2-rutile thin film.

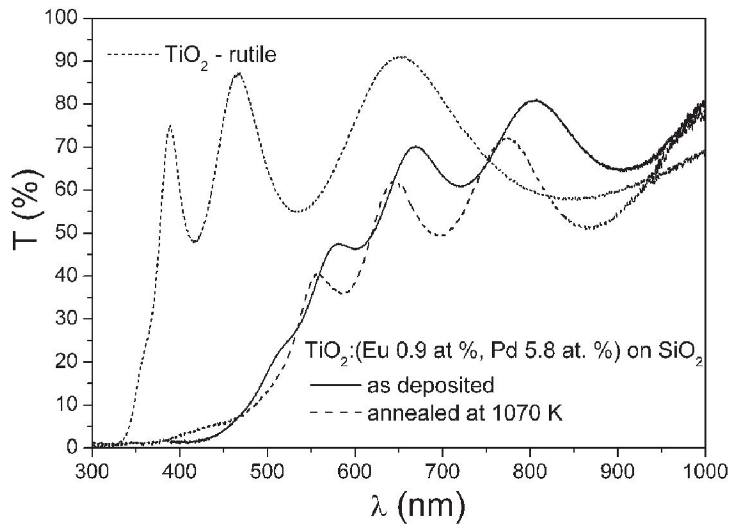

Fig. 4. Optical transmission spectra of deposited on SiO_2 the undoped TiO_2 and TiO_2:(Eu 0.9 at. %, Pd 5.8 at. %) thin films, as-deposited and additionally annealed at 1070 K.

Rys. 4. Charakterystyki transmisji cienkich warstw, naniesionych na podłoża SiO_2, niedomieszkowanego TiO_2 i TiO_2:(Eu 0,9 % at., Pd 5,8 % at.), po naniesieniu i dodatkowym wygrzewaniu w temperaturze 1070 K.

The results have shown that doping TiO_2-matrix with Eu and Pd caused 15% decrease of transparency level. It revealed also that incorporation of selected dopants into TiO_2, shifts the position of its fundamental absorption edge from ca. 330 nm toward the longer wavelength region widening the optical transmission range to ca. 450 nm. This behavior is mainly due to the light absorption by Pd inclusions. In our previous works [12], it has been shown that thin films of TiO_2 doped with Eu at different concentration were still transparent, similarly to the pure TiO_2. On the other hand doping with Pd, which result in good electrical conduction of TiO_2:Pd thin films [10] makes that thin films becomes opaque.

Optical properties of prepared samples were analyzed applying the well known envelope method [13]. The optical band gap energy (E_g^{opt}) for the allowed indirect transition together with the Urbach energy (E_u) have been calculated and the selected optical parameters are summarized in Tab. 2.

Table 2. Optical properties obtained from transmission measurements of undoped TiO_2 and TiO_2:(Eu 0.9 at.%, Pd 5.8 at.%) thin films on SiO_2.
Tabela 2. Właściwości optyczne uzyskane z pomiarów metodą transmisji światła cienkich warstw niedomieszkowanego TiO_2 i TiO_2:(Eu 0,9 % at., Pd 5,8 % at.), naniesionych na SiO_2.

Sample	Property			
	T (%)	λ_{cutoff} (nm)	E_g^{opt} (eV)	E_u (eV)
TiO_2 as deposited	75	330	3.35	0.05
TiO_2:(Eu, Pd) as deposited	60	450	1.71	0.38
TiO_2:(Eu, Pd) annealed at 1070 K	55	470	2.31	0.06

The optical band gap of the undoped-TiO_2 (E_g^{opt} = 3.35 eV) is wider than that reported in the literature [14] for the bulk rutile (3.02 eV). That can result from the nanocrystalline structure of prepared thin films. The small size of particles invokes the optical bandgap widening. The width of E_g^{opt} of thin films deposited from co-sputtered Ti-Eu-Pd target decrease down to ca. 1.7 eV. As it was already mention, this is mainly due to the incorporation of Pd (PdO) which introduces the energy levels in the band gap of TiO_2 matrix. Simultaneously, the decrease in E_g^{opt} is accompanied by the increase in the width of absorption tail, given by the Urbach energy (E_u) (Tab. 2). The additional post-process annealing, resulting in the rutile crystals expansion (section 3.1), makes the sharpness of the mobility edges (i.e. conduction band minimum and valence band maximum edges), manifested by the narrowing of the width of absorption tails down to 0.06 eV.

3.5. Photoluminescence properties

In the Fig. 5 photoluminescence spectrum of TiO_2:(Eu, Pd) thin film, as-deposited on silicon substrate has been presented. The PL spectrum, which was measured at room temperature, shows the strong red luminescence from standard Eu^{3+} emission lines what is connected with the light conversion in short wavelength range (excitation wavelength 302 nm). The most intense peaks on the spectrum can be observed around 615 nm and 700 nm (Fig. 5) and they correspond to $^5D_0$-$^7F_2$ transition at ~617 nm and $^5D_0$-$^7F_4$ transition at ~700 nm. The wavelengths of those peaks correspond to working range of typical silicon devices. That gives opportunity on application of TiO_2:(Eu, Pd) thin films to form junction-based devices on silicon substrates.

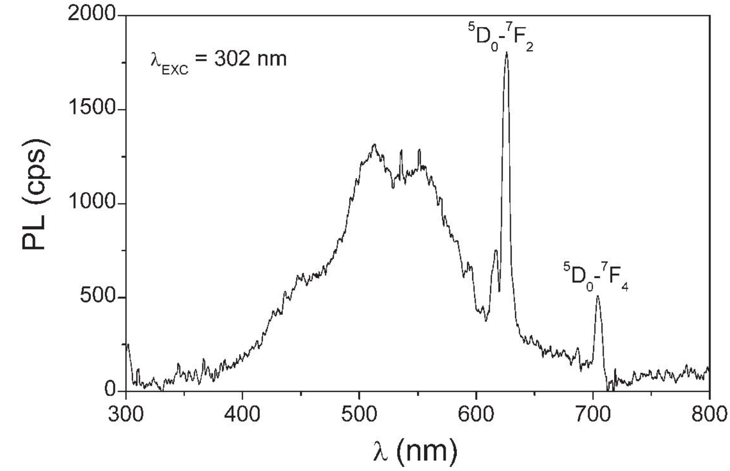

Fig. 5. Photoluminescence spectrum of TiO_2:(0.9 at. % Eu, 5.8 at. % Pd) thin film, as-deposited on silicon substrate.
Rys. 5. Widmo fotoluminescencji cienkiej warstwy TiO_2:(0,9 % at. Eu, 5,8 % at. Pd) naniesionej na podłoże krzemowe.

4. CONCLUSIONS

The structural and optical properties of TiO_2:(Eu, Pd) thin films, which were fabricated using High Energy magnetron sputtering method have been presented. The results of the investigation have shown that HE process allowed to obtained homogenous and nanocrystalline thin films. The additional post-processing annealing of TiO_2:(Eu, Pd) thin films results in the further TiO_2-rutile crystals growth from ca. 8 nm up to ca. 16 nm. The optical bandgap significantly decreased from 3.35 eV for the undoped-TiO_2 to ca. 1.7 eV for TiO_2:(Eu, Pd) thin films. The PL results have shown that examined thin films have also good photoluminescence properties - strong red luminescence, corresponds to working range of standard silicon devices.

5. ACKNOWLEDGMENTS

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BADANIE WŁAŚCIWOŚCI STRUKTURALNYCH I OPTYCZNYCH CIENKICH WARSTW TiO_2:(Eu, Pd) WYTWARZANYCH METODĄ ROZPYLANIA MAGNETRONOWEGO

W pracy przedstawiono wyniki badań cienkich warstw TiO_2 domieszkowanych europem i palladem, w ilości odpowiednio 0,9 % at. i 5,8 % at. Do nanoszenia

cienkich warstw zastosowano wysokoenergetyczny proces (High Energy) rozpylania magnetronowego. Wybrane próbki poddano dodatkowemu poprocesowemu wygrzewaniu. Wyniki dyfrakcji rentgenowskiej (X-Ray Diffraction – XRD) wykazały, że bezpośrednio po naniesieniu otrzymano nanokrystaliczną warstwę TiO_2 o strukturze rutylu. Po dodatkowym wygrzewaniu w temperaturze 800 °C średnia wielkość krystalitów wzrosła około dwukrotnie (z 9 do 16 nm). Wyniki badań XRD zostały potwierdzone za pomocą badań wykonanych za pomocą mikroskopu sił atomowych. Właściwości optyczne cienkich warstw określono na podstawie wyników badań metodą transmisji światła. Uzyskane wyniki wykazały, że domieszkowanie Eu i Pd spowodowało spadek przezroczystości warstwy o ~ 15% i przesunięcie krawędzi absorpcji optycznej w stronę dłuższych fal (z 330 do 450 nm) w porównaniu do warstwy niedomieszkowanego TiO_2. Szerokość optycznej przerwy zabronionej dla cienkiej warstwy TiO_2:(Eu, Pd) po naniesieniu wynosiła 1,7 eV i była około dwukrotnie mniejsza w porównaniu do 3,35 eV dla warstwy TiO_2. Wyniki badań fotoluminescencji pokazały, że badana warstwa wykazuje silną czerwoną luminescencję odpowiadającą standardowym linią emisyjnym Eu^{3+}.