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

Gasochromic Effect in Nanocrystalline TiO_2 Thin Films Doped with Ta and Pd

J. Domaradzki*, E. Prociow, D. Kaczmarek, D. Wojcieszak, D. Gatner and M. Lapinski

Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology

Janiszewskiego 11/17, 50-372 Wrocław, Poland

In this work gasochromic effect in TiO_2 thin films doped with palladium and tantalum (without catalyst film) have been described. The results have shown that in nanocrystalline TiO_2:(Ta, Pd), with anatase structure, the film colorization effect in alcohol presence was observed. Both colorization and also bleaching effect were stable and thermally activated.

PACS numbers: 68.43.−h, 68.47.Gh, 78.20.Ek

1. Introduction

Recently, crystalline thin films with gasochromic properties have attracted great interest because of wide application possibility. Such layers can be used as optically switchable coatings like displays, smart windows or optical hydrogen sensor, which is one of the alternative sources of energy [1–4]. Literature reports that the gasochromic properties can be found in materials based on tungsten oxide, vanadium oxide and magnesium oxide coated with very thin layer of catalyst such as platinum or palladium [2–7]. However, there were also few research works concentrated on gasochromic films consisting of pure titanium oxide coated Pd catalyst film. Novel achievement presented in this work was to obtain gasochromic effect in thin nanocrystalline layers prepared from TiO_2 doped by palladium and tantalum.

2. Thin films manufacturing

Nanocrystalline TiO_2 thin films doped with Ta and Pd (TiO_2:(Ta, Pd)) were deposited on Corning 7059 and SiO_2 substrates by magnetron sputtering process. Thin films were sputtered from metallic, mosaic Ti–Ta–Pd target in oxygen reactive atmosphere. The pressure of working gas was kept at 10^{-1} Pa. The energy disperse spectroscopy (EDS) measurements performed with Hitachi S-4700N scanning electron microscope equipped with the EDS attachment (Noran Vantage) have shown that there were 2.54 at.% of Ta and 12.36 at.% of Pd in the prepared tin film, respectively.

* corresponding author; e-mail: jaroslaw.domaradzki@pwr.wroc.pl

3. The structure of the films

The structure of prepared thin films was determined on the basis of the X-ray diffraction results (XRD) performed with DRON-2 powder. In Table the XRD results have been collected. The thin film had anatase structure and was nanocrystalline. The average crystallite size D was 16.1 nm. The comparison of measured interplanar distance d with standard one (d_{PDF}) [8] have shown that the structure of the film is tense.

TABLE

The XRD results of TiO_2:(Ta, Pd) thin film as-deposited on Corning (7059) glass.

Thin film	Structural properties					
	Phase	D [nm]	d [nm]	d_{PDF} [nm]	Δd [%]	Type of stress
TiO_2:(Ta, Pd)	anatase	16.1	0.3530	0.3520	+0.3	tension

D — average crystallite size, d — interplanar distance, d_{PDF} — standard interplanar distance [8], $\Delta d = \frac{\mathrm{d}-d_{\mathrm{PDF}}}{\mathrm{d}_{\mathrm{PDF}}} \cdot 100\%$

4. Gasochromic effect in TiO_2:(Ta, Pd)

The study on gasochromic effect of the TiO_2:(Ta, Pd) thin film was made by comparison of the level of light transmitted through the layer in an ambient air and after presence of the ethylic alcohol. Optical transmission spectra of samples over the spectral range from 200 to 2600 nm at normal incident were acquired using Ocean Optics spectrophotometers (QE65000 and NIR-256-2.1). Analysis of the measured data was covered by SpectraSuite Spectrometer Operating Software.

The experiment showed that both colorization and bleaching effects were thermally activated. That is why after sputtering of the film it is needed to form it by annealing at proper temperature. In case of TiO_2:(Ta, Pd) the forming temperature was 500 °C when irrevocable 10% decrease of transmission was observed. The gasochromic effect reveal at 300 °C. At temperature higher than 350 °C presence of alcohol caused homogeneous layer colorization. The observed process was dynamic and proceeded in few seconds. Normally total colorization of the sample with gasochromic properties lasts from tens of seconds [9] to tens of minutes [3]. Optical transmission spectra of sample in colorization (colorization at temperature 350 °C) and bleached state was shown in Fig. 1. Decrease in transmission ΔT_λ measured for wavelength 630 nm was about 45%. Repeating of experiment at higher temperature demonstrates that the tested sample shows stable and repetitious response at temperatures in the range of 350–500 °C.

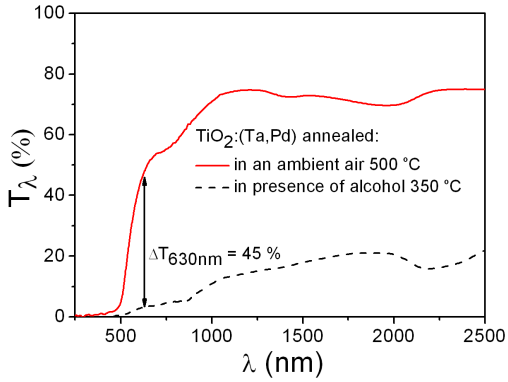

Fig. 1. Optical transmission spectra of TiO_2:(Ta, Pd) thin film annealed in an ambient air at 500 °C and in presence of alcohol at 350 °C.

The change of the optical density at 630 nm calculated according to formula $\Delta\mathrm{OD} = \log(T_{\mathrm{bleached\,(633\ nm)}}/T_{\mathrm{coloured\,(633\ nm)}})$ [4] is 1 which puts it in the upper part of typical range for gasochromic layers WO_3 0.1–1 [4]. In ambient air and room temperature the colored state of film remains permanent. The change of sample transmission kept in such conditions for a month was not observed. Bleaching is obtained by holding temperature of sample at 500 °C in ambient air. Total return to initial state at that temperature occurs after about 30 min.

5. X-ray photoelectron spectroscopy analysis

The analysis of gasochromic effect in the films was performed with the aid of X-ray photoelectron spectroscopy (XPS). The TiO_2:(Ta, Pd) thin film colorization, which was observed in alcohol presence, was connected with surface reaction of the ethanol thermal decomposition products with the thin film surface.

The XPS results have not shown meaningful change on the titanium, oxygen, tantalum and palladium spectra (Ti 2*p*, O 1*s*, Ta 4*d* and Pd 3*d* region, respectively). However, in case of carbon spectra (C 1*s* region) there was significant change of C 1*s* peak shape. In Fig. 2 the XPS spectra of the C 1s region annealed in an ambient air at 500 °C and annealed in the ethanol presence at 350 °C thin films have been showed. The C 1*s* peaks region spectra deconvoluted into surface functional groups. The estimated peaks at 285.8 eV, 287.2 eV and 289.1 eV are coming from the amorphous C–C bond, –C–OH and –C=O, respectively [10]. The results of peaks estimation have shown that the adsorption of –C–OH groups increase almost twice (from 34% to 54%), while the adsorption of the –C=O particles on the film surface is on the similar level. The percentage quantity of C–C bond on the TiO_2:(Ta, Pd) surface decreased almost twice after annealing in alcohol presence.

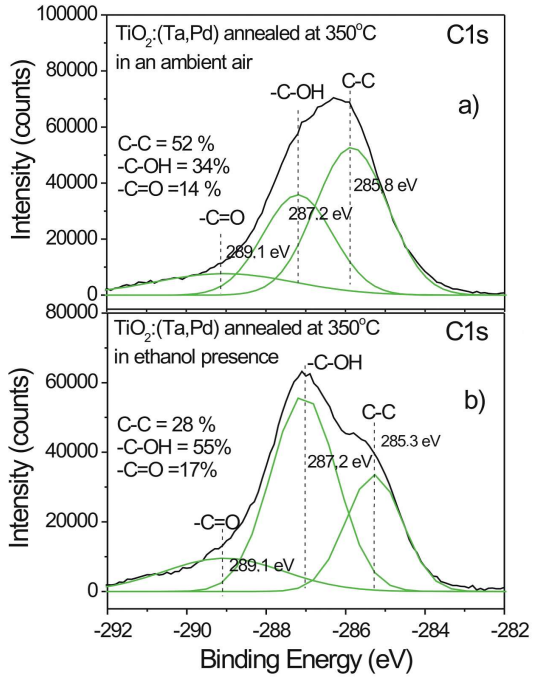

Fig. 2. The XPS spectra of the C 1*s* region of thin films annealed in ambient air at 500 °C and in the ethanol at 350 °C.

For the temperature range of 330 ÷ 360 °C ethanol starts to convert into H_2, CO, CO_2 and CH_4 [11]. Our experiment have shown that the thin film colorization process starts at 300 °C, but the fastest colorization is observed at 350 °C. This means that the gasochromic change of TiO_2:(Ta, Pd) resulted from adsorption of the decomposition products. The chemically bounded ethanol decomposition products (–C–OH) with the film surface results in the long-time stability of the colorization effect. Nearly chemical character of the surface adsorption testifies also the necessity of TiO_2:(Ta, Pd) film annealing at 500 °C (in an ambient air) for the film bleaching.

6. Conclusions

The TiO_2 thin films exhibit gasochromic properties, but they need top Pd layer as a catalyst. In this work gasochromic effect in nanocrystalline TiO_2 thin film doped with Ta and Pd have been described. The film colorization was thermal activated and long-term stable. The gasochromic change of TiO_2:(Ta, Pd) properties was induced by reaction of ethanol thermal decomposition products with thin film surface and caused by adsorption of decomposition products on the surface.

Acknowledgments

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

References

[1] J. Okumu, F. Koerfer, C. Salinga, T.P. Pedersen, M. Wuttig, *Thin Solid Films* **515**, 1327 (2006).

[2] V. Wittwer, M. Datz, J. Ell, A. Georg, W. Graf, G. Walze, *Solar Energy Mater. Solar Cells* **84**, 305 (2004).

[3] M. Ranjbar, A. Iraji Zad, S.M. Mahdavi, *J. Phys. D, Appl. Phys.* **41**, 055405 (2008).

[4] H. Chen, N. Xu, S. Deng, D. Lu, Z. Li, J. Zhou, J. Chen, *Nanotechnology* **18**, 205701 (2008).

[5] M. Ranjbar, S.M. Mahdavi, A. Iraji Zad, *Solar Energy Mater. Solar Cells* **92**, 878 (2008).

[6] S. Yamamoto, K. Takano, A. Inouye, M. Yoshikawa, *Nucl. Instrum. Methods Phys. Res. B* **262**, 29 (2007).

[7] X.Q. Xu, H. Shen, X.Y. Xiong, *Thin Solid Films* **415**, 290 (2002).

[8] Powder Diffraction File, Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, 1967, Card 21-1276.

[9] B. Orel, N. Groselj, Opara-U. Krasovec, M. Gabrscek, P. Bukovec, R. Reisfeld, *Sensors Actuators* **50**, 234 (1998).

[10] J. Li, Y. Huang, Z. Xu, Z. Wang, *Mater. Chem. Phys.* **94**, 315 (2005).

[11] V. Galvita, V.D. Belyaev, V.A. Semikolenov, P. Tsiakaras, A. Frumin, V.A. Sobyanin, *React. Kinet. Catal. Lett.* **76**, 343 (2002).