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Influence of plasmon resonance on the luminescence of titanium dioxide thin films doped with rare earth ions

M Łapiński¹, J Czubek¹, K Drozdowska², W Sadowski¹, V V Kuznetsov³,
N Charykov³, B Kościelska¹

¹Institute of Nanotechnology and Materials Engineering, Gdansk University of Technology; Advanced Materials Center, ul. Gabriela Narutowicza 11/12, 80-233 Gdańsk, Poland

²Faculty of Electronics, Telecommunications and Informatics; Digital Technologies Center, Gdansk University of Technology, ul. Gabriela Narutowicza 11/12, 80-233 Gdańsk, Poland

³Saint-Petersburg State Electrotechnical University, St.-Petersburg, 197376

e-mail: marcin.lapinski@pg.edu.pl

Abstract. In this work the study of the optical properties of europium doped titanium dioxide thin films (TiO₂:Eu) enhanced by gold plasmonic nanostructures are presented. Plasmonic platforms were manufactured by thermal annealing of thin film of Au, deposited on a Corning glass substrate. As a result of thermal treatment, gold spherical nanostructures with average dimensions of 50 nm were obtained. Luminescent TiO₂:Eu film was deposited by RF magnetron sputtering method, from mosaic target. Morphology of gold nanostructures was investigated by SEM and TEM microscopes, while composition of oxides film was analysed by XPS methods. Luminescence properties were studied on the basis of excitation and emission spectra. Experiments have shown that such structures exhibit interesting luminescent properties and could be potential candidates for optoelectronics applications.

1. Introduction

Integration of the luminescence materials with plasmonic nanostructures may open new applications possibilities. Especially when it leads to enhance of luminescent properties. Such a hybrid structure can be formed by thin oxide layers doped with rare earth ions, deposited on metal nanostructures. Titanium dioxide (TiO₂) seems to be one of the most popular oxide material, as a matrix for rare-earth ions. TiO₂ is an important component in many commercial applications such as electronics, optics, photocatalysis, biotechnology, solar or electrochemical cells, sensors and other fields of materials science [1-5]. Among different techniques for producing rare-earth doped TiO₂ thin films, magnetron sputtering allows a significant control of the layer deposition process. Such type of deposition allows preparation of nanocrystalline films eg. with better mechanical properties and improves their adhesion to the substrate [6-9]. Doping of TiO₂ with rare-earth ions, such as Tb, Eu or Nb ions can be useful in modification of structural, optical and surface properties of titanium dioxide films. Among rare-earth ions, europium (Eu) has been intensely studied for a few decades. Whereas Eu usually assumes trivalent oxidation state (Eu³⁺), divalent one is also stable (Eu²⁺), but characterized by different luminescent properties. As a red light emitter, Eu³⁺ may be employed in various optical devices [10, 11]. In turn, a very special metal, among various plasmonic materials, is gold. This is due to two properties of Au: plasmon resonance in



the visible range of electromagnetic radiation and high chemical stability. Moreover, research shows that Au nanoparticles can positively influence the intensity of rare earth ion luminescence emission [12-15].

In this work the structural and luminescent properties of europium doped titanium dioxide thin films obtained by magnetron sputtering from mosaic target were investigated. Additionally, thin TiO₂:Eu layer was deposited on the gold nanostructures that exhibit surface plasmon resonance phenomenon. The impact of plasmonic platform on optical properties of the luminescent thin film was discussed.

2. Experimental

Investigated structures were deposited on a pre cleaned Corning 1737 glass substrates, which provided flat optical transmission characteristics and high transmission coefficient in a visible light range. Plasmonic nanostructures were formed as a result of thermal annealing. For gold films with thickness of 2.8 nm deposition a table-top dc magnetron sputtering system (EM SCD 500, Leica), equipped with quartz microbalance for in-situ thickness measurements, was used. Films were deposited from a high purity (99.99%) gold target in pure argon (99.999%) plasma. For film deposition with a rate of ca. 0.1 nm/s, ca. 10W of incident power was applied. Annealing of gold thin film, for 15 min at 550 °C in air atmosphere, resulted in forming spherical isolated islands. Two mechanisms could be responsible for spherical island forming. First of them is thermal dewetting, which leads to the formation of nanoislands with various shapes. Second mechanism is melting nanoislands, what leads to formation of spherical drop-like islands. It is well known that melting temperature of the nanostructures is essentially lower than that for bulk material. Spherical gold nanostructures are formed due to poor wettability of glass by gold [16-18]. The formation of gold nanostructures has been described in details in our previous works [18-20]. On that prepared nanostructures dielectric Al₂O₃ ultra-thin film was deposited. Atomic Layer Deposition method (ALD) was chosen as a proper way to deposit ultra-thin films. This method provides precision control of thickness with atomic accuracy. Trimethylaluminum from Sigma-Aldrich and purified water were used as precursors. Deposition of dielectric layer was conducted at 200 °C by Beneq TFS 200 ALD system. On the basis of our previous investigations, film with thickness of 6 nm of aluminum oxide was chosen for investigations [20].

The Eu doped TiO₂ thin film, with thickness of 200 nm, was prepared by radio frequency (RF) magnetron sputtering process, using Omicron NanoScience, four targets sputter system. Ti-Eu mosaic target (both metals with purity of 99.9%) was sputtered in an argon-oxygen atmosphere (Ar:O₂ flow ratio: 5sccm:30sccm, both gasses with purity of 99.999%). Used of RF power of 60W resulted in deposition with a ratio ca. 0.05 nm/s. Substrates with plasmonic nanostructures were heated to 200 °C during TiO₂:Eu film deposition process.

For investigations of plasmonic resonance influence on optical properties, three samples were chosen. Luminescent TiO₂:Eu thin film deposited on Corning Glass, TiO₂:Eu layer on gold plasmonic platform and TiO₂:Eu thin film deposited on plasmonic platform with additional dielectric Al₂O₃ layer. The morphology of gold plasmonic structures was examined by FEI Quanta FEG 250 scanning electron microscope (SEM) operated at 10 kV. Crystal structure of the fabricated luminescent TiO₂:Eu thin films was studied using X-Ray diffraction method (XRD) by Philips X'Pert diffractometer system using Cu K_α radiation, while the chemical composition was analyzed by X-ray photoemission spectroscopy method (XPS). These measurements were performed at room temperature under ultra-high vacuum conditions, at pressures below 1.1×10⁻⁶ Pa by Omicron NanoScience equipment. CASA XPS software package using a Shirley background subtraction and least-square Gaussian-Lorentzian – GL(30) curve fitting algorithm was used for XPS data analysis. The spectra obtained were calibrated to give a binding energy of 285.00 eV for C1s. Optical properties of manufactured structures were investigated using Evolution 220 UV-Visible Spectrophotometer in a range of 200 nm – 1000 nm and Scinco FS-2 spectrofluorometer with excitation and emission wavelength of 394 nm and 591 nm respectively.

3. Results and discussion

The quality of gold plasmonic platforms was examined by SEM microscope. SEM image presented in figure 1 shows a good uniformity of prepared Au nanostructures. Spherical drop-like nanoislands cover whole substrate's surface. The average dimensions of nanoislands are in a range of 20-30 nm, what is in line with our previous works [18, 19].

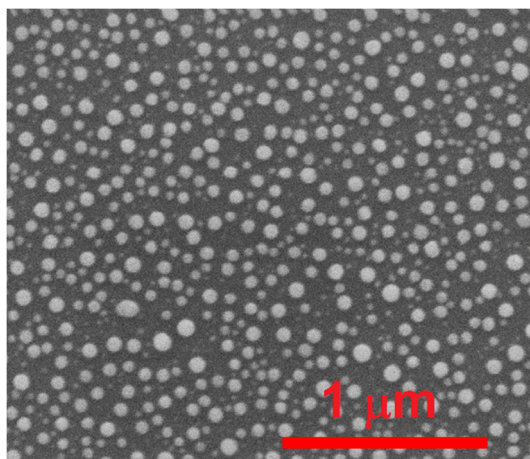


Figure 1. SEM image of gold plasmonic platform.

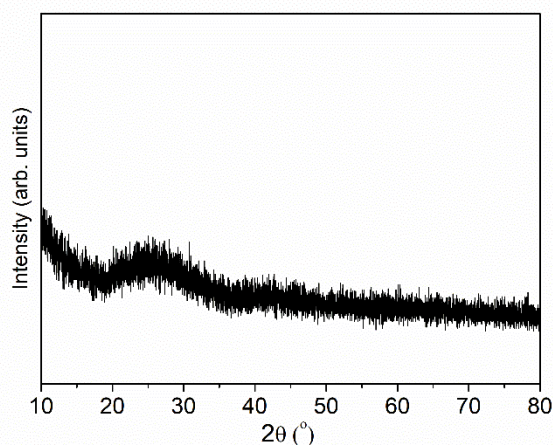


Figure 2. XRD pattern of TiO₂:Eu thin film, deposited on Corning 1737 glass substrate.

XRD results of deposited TiO₂:Eu thin film are presented in figure 2. No peaks are visible. XRD pattern is characteristic for amorphous or nanocrystalline phase. A broad bulge between the 2θ angle 15° and 35° arises from the corning glass substrate. Valence state of titanium and presence of Eu dopant were confirmed by XPS method (figure 3). Recorded spectrum for Ti2p electrons was deconvoluted into two peaks at 458.3 and 464.0 eV, what is characteristic for titanium dioxide [21]. Eu 4d core level electrons spectrum is more complicated. It could be deconvoluted into four peaks. Doublet at 129.5 eV and 135.1 eV, with the energy separation of 5.6 eV corresponds to Eu²⁺ valence state, while peaks at 135.9 eV and 141.6 eV with energy the separation of 5.7 eV correspond to Eu³⁺ [10, 22]. Doublet, which is assigned to Eu³⁺ ions dominates over Eu²⁺ doublet. This led to the conclusion that quantity of Eu³⁺ ions far exceeds Eu²⁺ ions. On the basis peaks' area relative area, calculated ratio Eu³⁺/Eu²⁺ was ca. 9:1. Additionally, on the basis of the survey spectrum, totally percentage content of europium in TiO₂:Eu layer was calculated to be 5%.

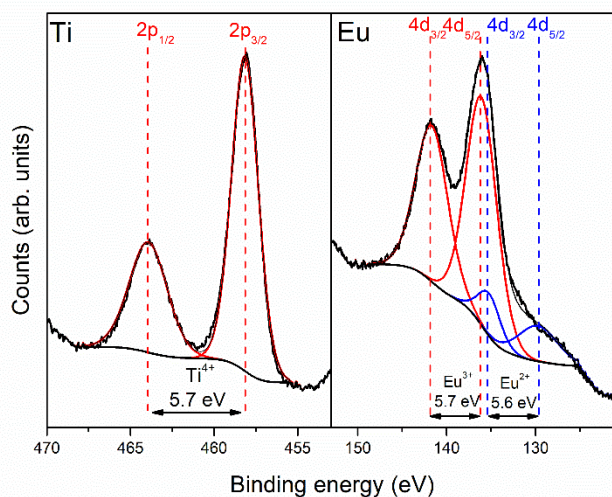


Figure 3. XPS spectra recorded for Ti2p and Eu4d core shell electrons of TiO₂:Eu luminescent thin film.

Figure 4 shows the UV-Vis transmittance spectra for all prepared TiO₂:Eu structures. It can be seen that TiO₂:Eu thin film deposited directly on a glass substrate has a flat transmission characteristic, with a transmittance ca. 85%. For luminescence layer deposited directly on a plasmonic platform, without dielectric film, transmission minimum at 650 nm is visible. On the other hand for structures with additional 6 nm of Al₂O₃ the minimum is at 575 nm. It corresponds to the surface plasmon resonance effect and its strongly shifted towards red in a comparison to plasmon platform characteristics (525 nm). This red shift phenomena is caused by increase of the electric permittivity over the gold nanostructures, in comparison to air. It is directly related to Mie's theory, and was described in literature [20, 23]. Emission and excitation spectra are shown in figure 5. In excitation spectrum, monitored at the wavelength $\lambda_{em} = 615$ nm, in range from 350 to 460 nm only one peak at 394 nm can be observed. Maximum at that peak corresponds to ${}^7F_0 \rightarrow {}^5L_6$ electric dipole transition for Eu³⁺ [24, 25]. Due to low contribution, no characteristic peaks for Eu²⁺ luminescence can be observed. Peaks intensity are strongly enhanced when TiO₂:Eu is deposited on plasmonic platform and is the strongest in a configuration with additional dielectric Al₂O₃ layer. Emission spectra for $\lambda_{ex} = 395$ nm show only one significant peak at 591 nm. It corresponds to the ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition. This type of transition is observed in centrosymmetric structures [10, 24]. This led to the conclusion that there might be some nanocrystal areas in TiO₂:Eu film. One can see, enhanced of intensity of the light emission of TiO₂:Eu layer deposited on a plasmonic platform. The intensity of luminescence is the highest for structures with additional dielectric layer. It must be noted that all optical measurements were carried out under the same physical and geometrical conditions for all samples. Increasing of luminescence for samples with plasmonic platforms could be explained by concertation of electric field, around nanostructures what increases the rate of excitation [20, 26, 27]. Additional Al₂O₃ dielectric layer separate plasmonic gold nanostructures and TiO₂:Eu luminescent film what change the conditions of electromagnetic interaction between plasmons and luminescent material and leads to increasing of the luminescence intensity.

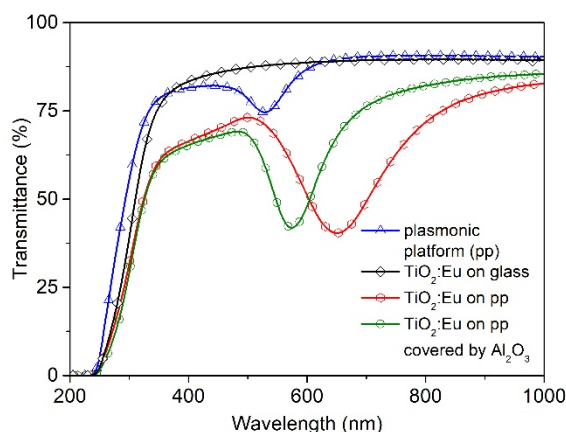


Figure 4. Transmittance spectra for TiO₂:Eu thin film deposited on a Corning glass substrate and TiO₂:Eu film deposited on plasmonic platform in a both configurations, without and with additional dielectric layer. Additionally spectrum for plasmonic platform is presented.

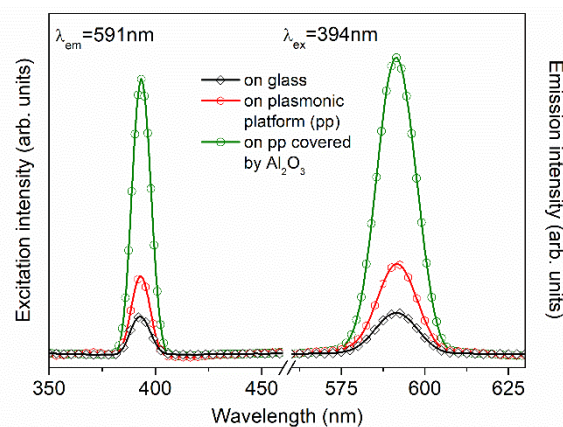


Figure 5. Excitation and emission spectra for TiO₂:Eu thin film deposited on a Corning glass substrate and TiO₂:Eu film deposited on plasmonic platform in a both configurations, without and with additional dielectric layer.

4. Conclusions

Structure with gold plasmonic platform, coated with ultra-thin film of Al₂O₃ and exploiting TiO₂:Eu as a phosphor was successfully designed and tested. The intensity of the luminescence is enhanced by the plasmon resonance from Au nanostructures. Intensity of luminescence can be additionally gain by a thin dielectric film of Al₂O₃, deposited as a separator between metallic nanostructures and a thin layer of

TiO₂: Eu. Interestingly, no transition caused by the electric dipole (615 nm, typical for Eu³⁺ ions) was observed in the emission spectrum. The main emission peak corresponds to the transition occurring via magnetic dipole, which is independent of the host matrix. Such a phenomenon usually takes place in materials in which Eu³⁺ ions are located at sites with higher symmetry, and explaining such behavior in the presented samples would require further research. Anyway, we believe that presented structures could be attractive from optoelectronic applications point of view.

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