

## Optical emission from Eu, Tb, Nd luminescence centers in TiO<sub>2</sub> prepared by magnetron sputtering

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This work presents the results of optical emission from Eu<sup>3+</sup>, Tb<sup>3+</sup> and Nd<sup>3+</sup> luminescence centers in TiO<sub>2</sub> thin films. Thin films were prepared by magnetron sputtering from metallic Ti-Eu, Ti-Tb, Ti-Nd targets, respectively. Optical properties were examined by means of photoluminescence and optical transmission measurements. The total content of dopants was analyzed using an energy disperse spectrometer. It has been shown that doping of TiO<sub>2</sub> thin films using selected lanthanides results in the visible (Eu, Tb) and near-infrared (Nd) light emission, upon ultraviolet radiation. Additionally, transparency range and optical band gap of prepared thin films were determined, in comparison to pure TiO<sub>2</sub>.

Keywords: luminescence, rare earth elements, TiO<sub>2</sub>, magnetron sputtering.

### 1. Introduction

Due to the effective emission in the visible and near infrared region, doping of TiO<sub>2</sub> with rare earth (RE) elements has recently attracted much attention [1–3]. For nanocrystalline TiO<sub>2</sub> the emission center can be formed by the surface state, such as surface trapped state, defect state and oxygen vacancy. For fabrication of lanthanide-doped TiO<sub>2</sub> thin films different methods have been applied so far, including magnetron sputtering [2, 4, 5]. Since there are not many reports about sputtering from metallic targets, mostly powder targets are used [1, 4].

In this work, the investigations into optical emission from Eu<sup>3+</sup>, Tb<sup>3+</sup> and Nd<sup>3+</sup> luminescence centers in TiO<sub>2</sub> thin films have been reported.

## 2. Experimental procedure

Thin films of  $\text{TiO}_2\text{:Eu}$ ,  $\text{TiO}_2\text{:Tb}$  and  $\text{TiO}_2\text{:Nd}$  were deposited on  $\text{SiO}_2$  and Si substrates by the magnetron sputtering method in oxygen atmosphere from metallic targets: Ti-Eu, Ti-Tb and Ti-Nd, respectively.

Optical transmission measurements were performed in a spectral range from 200 nm to 1000 nm. Samples were illuminated by a coupled deuterium-halogen lamp at normal incidence. The fundamental absorption edge and optical band gap of the thin films were determined from transmission characteristics. For photoluminescence measurements UV argon laser with the excitation wavelength of 302 nm was used. All samples were measured at room temperature.

Thin films of lanthanide doped  $\text{TiO}_2$  with the strongest emission lines were chosen for investigations. Elemental analysis made using EDS (OXFORD Link-ISIS) yields the amount of RE-dopants in the selected samples of: 0.1 at.%, 2.6 at.% and 0.3 at.% in the prepared  $\text{TiO}_2\text{:Eu}$ ,  $\text{TiO}_2\text{:Tb}$  and  $\text{TiO}_2\text{:Nd}$  thin films, respectively. Additional post-annealing at 200 °C and 600 °C of  $\text{TiO}_2\text{:Eu}$  and  $\text{TiO}_2\text{:Nd}$  thin films, respectively, improved their luminescence properties. From X-ray diffraction measurements (not shown in the paper) all samples were found to be nanocrystalline with  $\text{TiO}_2$  crystallite size less than 10 nm.

## 3. Results and discussion

### 3.1. Undoped $\text{TiO}_2$ thin films

Optical properties of RE-doped  $\text{TiO}_2$  thin films have been investigated in comparison to pure  $\text{TiO}_2$ -anatase prepared in similar technological conditions. Transmission characteristic of  $\text{TiO}_2$  thin film has been presented in Fig. 1a. The fundamental

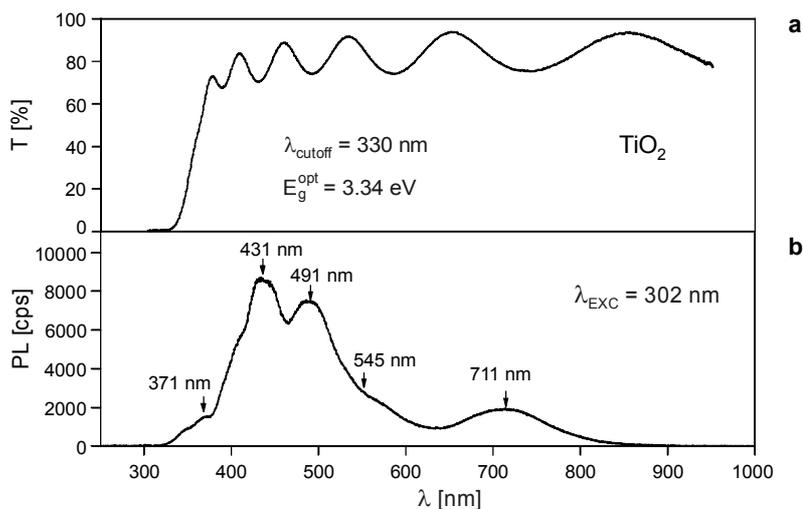


Fig. 1. Transmission (a) and photoluminescence (b) spectra of as-deposited  $\text{TiO}_2$  thin films on  $\text{SiO}_2$ .

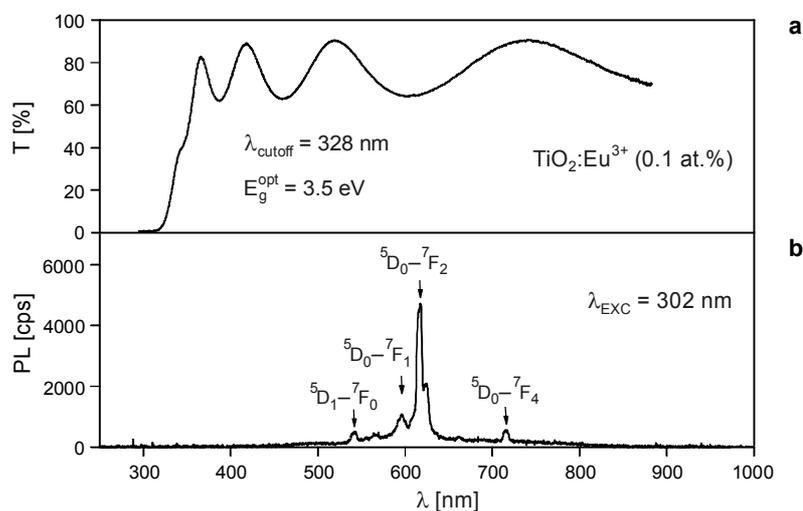


Fig. 2. Transmission (a) and photoluminescence (b) spectra of  $\text{TiO}_2:\text{Eu}$  (0.1 at.%) thin films deposited on  $\text{SiO}_2$  (a) and Si (b), additionally annealed at 200 °C.

absorption edge ( $\lambda_{\text{cutoff}}$ ) has found to be about 330 nm and the optical band gap energy ( $E_g^{\text{opt}}$ ) for the allowed indirect transition has been estimated to be of 3.34 eV.

Photoluminescence of  $\text{TiO}_2$  thin films on  $\text{SiO}_2$  has been presented in Fig. 1b. PL spectrum, measured at room temperature exhibits the broad emission band between 350 nm and 580 nm with the most intense peaks around 431 nm and 491 nm. The peak situated at 431 nm corresponds to the emission band of self-trapped excitons of the  $\text{TiO}_2$  nanoparticles [6]. As it has been reported by LIU *et al.* [7], a strong emission at 491 nm could be attributed to the indirect recombination via defect states with the interaction of phonons in  $\text{TiO}_2$  lattice. There are also visible two shoulders around 371 nm and 545 nm: the peak with the center at 371 nm could be attributed to the intrinsic emission of the  $\text{TiO}_2$  and that at 545 nm corresponds to  $\text{TiO}_2$ -anatase emission itself [8]. The origin of the broad peak with the center around 711 nm is not known and, to our knowledge, has not been reported for  $\text{TiO}_2$  thin films so far.

### 3.2. $\text{TiO}_2:\text{Eu}^{3+}$ thin films

From optical transmission measurements (Fig. 2a) the position of the fundamental absorption edge, similar to undoped  $\text{TiO}_2$  (Fig. 1a), was found to be about 330 nm. Although, doping with Eu 0.1 at.% did not make any essential changes in transmission characteristic as compared to pure  $\text{TiO}_2$ , there is a band gap widening from 3.34 eV to 3.5 eV due to Eu doping. The transparency of Eu-doped  $\text{TiO}_2$  thin films is in a range of about 80%.

PL spectra, measured at room temperature, show a dominating strong red luminescence corresponding to  ${}^5D_0-{}^7F_2$  transition at ~617 nm and ~623 nm. The remaining emissions are visible at 565 nm, 596 nm and 715 nm, and they correspond to the intrashell transitions between the first excited state  ${}^5D_0$ , and the  ${}^7F_0$ ,

${}^7F_1$ ,  ${}^7F_4$  levels [2, 9]. The strong splitting of  ${}^5D_0-{}^7F_2$  transition indicates that  $\text{Eu}^{3+}$  ions existing in at least two different structural environments differ from each other in the symmetry.

### 3.3. $\text{TiO}_2:\text{Tb}^{3+}$ thin films

Optical transmission study has shown a slight red shift of the fundamental absorption edge of  $\text{TiO}_2$  after Tb-doping at the amount of 2.6 at.% (Fig. 3a). Also, the transparency of the thin film decreased.

This photoluminescence experiment shows broad unresolved spectra with dominating green luminescence at 545 nm (Fig. 3b) corresponding to the intra-4f  ${}^5D_4-{}^7F_5$  transition of  $\text{Tb}^{3+}$ . Other remarkable emissions visible in the spectrum are positioned at 431 nm, 491 nm and 619 nm. They can be attributed to the transitions between  ${}^5D_3-{}^7F_4$ ,  ${}^5D_4-{}^7F_6$ ,  ${}^5D_4-{}^7F_3$ , respectively [6, 10].

According to the literature [3],  $\text{Tb}^{3+}$  ions embedded in  $\text{TiO}_2$  need an excitation energy higher than that of  $\text{TiO}_2$  defect states and thus sensitized luminescence for terbium in  $\text{TiO}_2$  was rarely observed. The reason of effective green photoluminescence in our samples may be that the  $\text{Tb}^{3+}$  emission centers are mainly excited through the photon absorption of  $\text{TiO}_2$  host and the energy transfer process directly from the conduction band of the  $\text{TiO}_2$  to  $\text{Tb}^{3+}$  ions without relaxation to defect states of titania [10].

### 3.4. $\text{TiO}_2:\text{Nd}^{3+}$ thin films

Optical transmission measurements (Fig. 4a) show the position of the fundamental absorption edge at 320 nm (Fig. 1a). The optical band gap was found to be about

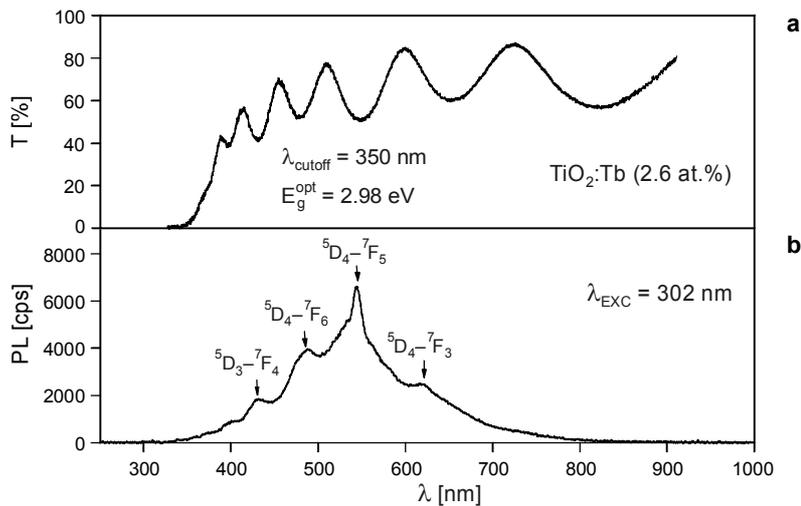


Fig. 3. Transmission (a) and photoluminescence (b) spectra of as-deposited  $\text{TiO}_2:\text{Tb}$  (2.6 at.%) thin films on  $\text{SiO}_2$ .

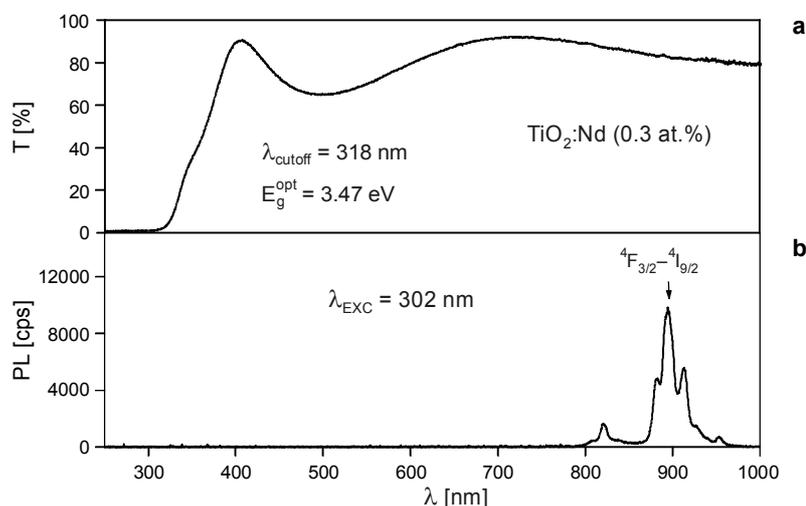


Fig. 4. Transmission (a) and photoluminescence (b) spectra of  $\text{TiO}_2:\text{Nd}$  (0.3 at.%) thin films deposited on  $\text{SiO}_2$ , additionally annealed at 600 °C.

3.47 eV what indicates band gap widening which is often observed in the case of nanostructured materials.

The prepared neodymium-doped thin films exhibit characteristic  $\text{Nd}^{3+}$  photoluminescence with the strongest broad near-IR luminescence bands between 875 nm and 930 nm, corresponding to  ${}^4F_{3/2} - {}^4I_{9/2}$  transitions (Fig. 4b). The emission band is composed of four peaks centered at 882 nm, 895 nm, 912 nm and 925 nm [5]. In the spectrum the weaker emission at about 825 nm could be also observed.

#### 4. Conclusions

RE-doped nanostructured titania prepared by co-sputtering of metallic RE-Ti mosaic target has been found as an excellent host for trivalent  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Nd}^{3+}$  rare earth ions. Due to the strong UV light absorption in the intrinsic band gap of titania nanocrystallites, followed by the relaxation to surface-defect states, an efficient energy transfer to the crystal field states of the  $\text{Eu}^{3+}$  and  $\text{Nd}^{3+}$  rare earth ions could occur and a strong red and near-IR luminescence was observed, respectively. The observed green photoluminescence from  $\text{Tb}^{3+}$  emission centers is mainly due to the energy transfer directly from the excited  $\text{TiO}_2$  host to  $\text{Tb}^{3+}$  ions without relaxation to defect states of titania.

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## References

- [1] QI J., MATSUMOTO T., TANAKA M., MASUMOTO Y., *Europium silicate thin films on Si substrates fabricated by a radio frequency sputtering method*, Journal of Physics D: Applied Physics **33**(16), 2000, pp. 2074–8.
- [2] PROCIOW E.L., DOMARADZKI J., PODHORODECKI A., BORKOWSKA A., KACZMAREK D., MISIEWICZ J., *Photoluminescence of Eu-doped TiO<sub>2</sub> thin films prepared by low pressure hot target magnetron sputtering*, Thin Solid Films **515**, 2007, pp. 6344–6.
- [3] FRINDELL K.L., BARTL M.H., ROBINSON M.R., BAZAN G.C., POPITSCH A., STUCKY G.D., *Visible and near-IR luminescence via energy transfer in rare earth doped mesoporous titania thin films with nanocrystalline walls*, Journal of Solid State Chemistry **172**(1), 2003, pp. 81–8.
- [4] CHANG C., MAO D., *Long lasting phosphorescence of Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> thin films by magnetron sputtering*, Thin Solid Films **460**(1–2), 2004, pp. 48–52.
- [5] MACDONALD A.C., HRYCIW A., LI Q., MELDRUM A., *Luminescence of Nd-enriched silicon nanoparticles glasses*, Optical Materials **28**(6–7), 2006, pp. 820–4.
- [6] MOON B.K., JEONG J.H., YI S., KIM S.C., CHOI H., KIM J.H., *Anomalous Tb<sup>3+</sup> luminous spectrum in the TiO<sub>2</sub> nanocrystals*, Optical Materials **28**(6–7), 2006, pp. 676–80.
- [7] LIU B., ZHAO X., ZHAO Q., HE X., FENG J., *Effect of heat treatment on the UV-vis-NIR and PL spectra of TiO<sub>2</sub> films*, Journal of Electron Spectroscopy and Related Phenomena **148**(3), 2005, pp. 158–63.
- [8] MELNYK V., SHYMANOVSKA V., PUCHKOVSKA G., BEZRODNA T., KLISHEVICH G., *Low-temperature luminescence of different TiO<sub>2</sub> modifications*, Journal of Molecular Structure **744–747**, 2005, pp. 573–6.
- [9] ZENG Q.G., DING Z.J., ZHANG Z.M., *Synthesis, structure and optical properties of Eu<sup>3+</sup>/TiO<sub>2</sub> nanocrystals at room temperature*, Journal of Luminescence **118**(2), 2006, pp. 301–7.
- [10] JIA CH., XIE E., PENG A., JIANG R., YE F., LIN H., XU T., *Photoluminescence and energy transfer of terbium doped titania film*, Thin Solid Films **496**(2), 2006, pp. 555–9.

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