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Influence of rhodamine 6G doping on the optical properties of TiO₂ sol-gel films

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Amorphous titanium dioxide (TiO₂) thin films doped with rhodamine 6G (R6G) were deposited on glass substrates by the sol-gel process. The optical properties of the films were characterized by photoacoustic, excitation, and fluorescence spectroscopies. The absorption spectra of the R6G-doped TiO₂ films exhibited two well-defined absorption regions: an absorption band over 2.0 eV attributed to rhodamine 6G and a band above 3.0 eV corresponding to TiO₂ absorption. While the onset of the R6G absorption band was shifted by 0.06 eV towards lower energies as the R6G doping concentration increased within the interval of 0.01–0.10 mol %, the onset to high absorption (TiO₂ band) for the doped films decreased only by 0.01 eV within the same interval. In addition, the optical absorption of undoped rutile-phase bulk TiO₂ was calculated and compared to the experimental results. The estimated theoretical value of rutile TiO₂ sample was 3.0 eV. This theoretical result shows good agreement when compared with the experimental data of undoped TiO₂ sol-gel films, as well as the undoped TiO₂ film prepared by sputtering. © 2005 American Institute of Physics. [DOI: 10.1063/1.2073972]

I. INTRODUCTION

Since the discovery of the photocatalytic splitting of water by titanium dioxide (TiO₂) in 1972 by Fujishima and Honda,¹ this wide band-gap semiconductor has been proven to have a variety of outstanding properties. These properties have allowed the use of titanium dioxide in a number of applications that include optoelectronic devices,² gas sensors,³ and waveguides.⁴ Another interesting property of this material is its bactericidal activity. Based on the generation of oxidizing species in mechanisms of photodegradation by TiO₂, Matsunaga *et al.*⁵ have claimed that ultraviolet (UV)-irradiated TiO₂ can be used to kill bacteria. Particularly, the strong oxidative power of photogenerated carriers on its surface has made TiO₂ one of the most practical photocatalytic materials for environmental remediation, e.g., for purification and treatment of polluted water and air.⁶ Photocatalytic reactions occur on the surface of TiO₂ particles

when photons are absorbed by this material, creating electron-hole pairs that eventually form redoxing or oxidizing pollutants in water and air.

UV-irradiated TiO₂ represents the benchmark photocatalyst of a large variety of water-bound pollutants, however, the main drawback of this material is that it absorbs light in a small portion of the spectrum in the UV region. A promising approach to overcome this problem is to develop photosensitized materials, which present a more efficient harvesting of optical energy by absorbing light in a wider interval of the spectrum.⁷ Spectral sensitization of TiO₂ with dyes has received special attention for degradation of pollutants in presence of visible light. Dye sensitization has been achieved mostly by coating thin films of dye onto semiconductor surfaces or dispersing dye materials in semiconducting matrices.

In the present study, the optical properties of amorphous TiO₂ thin films prepared by the sol-gel process and doped with rhodamine 6G (R6G) have been studied as a function of R6G doping concentration. The optical characterization of the films was performed by photoacoustic, excitation, and fluorescence spectroscopies. In addition, just for the sake of

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comparison, the optical-absorption coefficient of undoped rutile TiO₂ was calculated with the local-density approximation (LDA), employing the full-potential linearized augmented plane-wave method. A comparison of these calculations with the experimental data of TiO₂ films prepared by the sol-gel process, as well as the TiO₂ film prepared by magnetron sputtering are presented.

II. EXPERIMENTAL METHODS

A. Sample preparation

Titanium dioxide thin films were deposited on Corning's glass substrates by the sol-gel process. The precursor solution consisted of 1 mol of titanium isopropoxide (TIPO, 99.9%, Aldrich Chem. Co.) mixed with 2 mol of acetic acid (Aldrich Chem. Co.) and 2 mol of isopropanol (Baker Co.) at room temperature. Separately, rhodamine 6G (Aldrich Chem. Co.) was dissolved in a mixture of 2 mol of water, 2 mol of acetic acid, and 2 mol of isopropanol. Both solutions were subsequently mixed together under vigorous agitation. With this procedure it was possible to obtain titania sols doped with rhodamine 6G at 0.00 (control), 0.01, 0.02, 0.05, and 0.10 mol % concentrations.

The Corning glass substrates were previously degreased and cleaned by a standard chemical cleaning process based on deionized water and hydrogen peroxide solution. Using the dip-coating technique, the substrates were immersed into and extracted from the titanium sol at a constant velocity of 22.4 mm/min.

For post-annealed samples, undoped sol-gel TiO₂ films were maintained at 400 °C for six days in air. Rutile-phase TiO₂ thin films were prepared by dc-reactive magnetron sputtering, commonly known as rutile sputtering,⁸ and the absorption spectrum was obtained by transmission spectroscopy.

B. Photoacoustic measurements

The optical characterization of R6G-doped titanium dioxide films was performed by photoacoustic spectroscopy (PAS). The photoacoustic spectrometer used in this work consisted of a stabilized 1000 W Xe lamp and a 1/8 m grating monochromator (Oriel, Model 77250). The monochromatic output beam was intensity modulated at 17 Hz with a mechanical chopper (Stanford Research Systems, Model SR540). A quartz optical fiber served to direct the light beam to a photoacoustic (PA) cell containing the sample under study. The PA cell, made of brass, had a cylindrical shape of about 6 mm diameter and 6 mm height. The quartz windows closed the front and rear sides of the PA cell. The PA signal was recorded by an electret microphone and a lock-in amplifier.

C. Excitation and fluorescence measurements

The excitation and fluorescence spectra for the TiO₂ sol-gel films doped with rhodamine were obtained by using a SPEX Fluorolog DM3000F spectrofluorometer with double

grating monochromators and a 450 Xe lamp as the excitation source. The photomultiplier used in all the measurements was an RCA C31034-02.

III. THEORETICAL CALCULATIONS

Calculations for optical absorption of rutile-phase TiO₂ were based on the density-function theory within the local-density approximation, employing the full-potential linearized augmented plane-wave method.⁹ The LDA band-gap energy was corrected self-consistently with an on-site Coulomb potential within the LDA+U approach.¹⁰

In order to obtain the absorption coefficient we calculated first the dielectric functions $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ in the long wavelength limit, $\varepsilon_2(\omega) = \text{Im}[\varepsilon(\mathbf{q}=0, \omega)]$, has been obtained directly from the electronic structure using the joint density of states and the optical matrix overlap,⁹

$$\varepsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{\mathbf{k}n\sigma} \langle \mathbf{k}n\sigma | p_i | \mathbf{k}n'\sigma \rangle \langle \mathbf{k}n'\sigma | p_j | \mathbf{k}n\sigma \rangle f_{\mathbf{k}n} \times (1 - f_{\mathbf{k}n'}) \delta(e_{\mathbf{k}n'} - e_{\mathbf{k}n} - \hbar\omega), \quad (1)$$

where e is the electron charge, m its mass, Ω is the crystal volume, and $f_{\mathbf{k}n}$ is the Fermi distribution. Moreover, $|\mathbf{k}n\sigma\rangle$ is the crystal wave function corresponding to the n th eigenvalue $e_{\mathbf{k}n}$ with crystal momentum \mathbf{k} and spin σ . The summation over the irreducible Brillouin zone in Eq. (1) has been calculated using the tetrahedron interpolation with a \mathbf{k} mesh consisting of about 450 uniformly distributed \mathbf{k} points. The matrix elements, eigenvalues, and eigenvectors are calculated in the irreducible part of the Brillouin zone. The real part of the dielectric function $\varepsilon_1(\omega)$ is obtained from $\varepsilon_2(\omega)$ using the Kramers-Kronig transformation,

$$\varepsilon_1(\omega) \equiv \text{Re}[\varepsilon(q=0, \omega)] = 1 + \frac{1}{\pi} \int_0^\infty d\omega' \varepsilon_2(\omega') \times \left(\frac{1}{\omega' - \omega} + \frac{1}{\omega' + \omega} \right). \quad (2)$$

Finally, the absorption coefficient $\alpha(\omega)$ is obtained directly from the relation⁹

$$\alpha(\omega) = \frac{\omega}{c} (-2\varepsilon_1(\omega) + 2\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2})^{1/2}, \quad (3)$$

where c is the velocity of light.

IV. RESULTS AND DISCUSSION

The photoacoustic spectra of the amorphous TiO₂ sol-gel films doped with rhodamine 6G at 0.00 (control), 0.01, 0.02, 0.05, and 0.10 mol % concentrations are presented in Fig. 1. Two absorption regions can be distinguished. The band just above 2.0 eV is attributed to rhodamine 6G absorption, whereas the band above 3.0 eV corresponds to TiO₂ absorption. At low R6G content, the former band is composed by a broad absorption band centered at 2.3 eV with a weaker shoulder at 2.5 eV. This shoulder is attributed to rhodamine

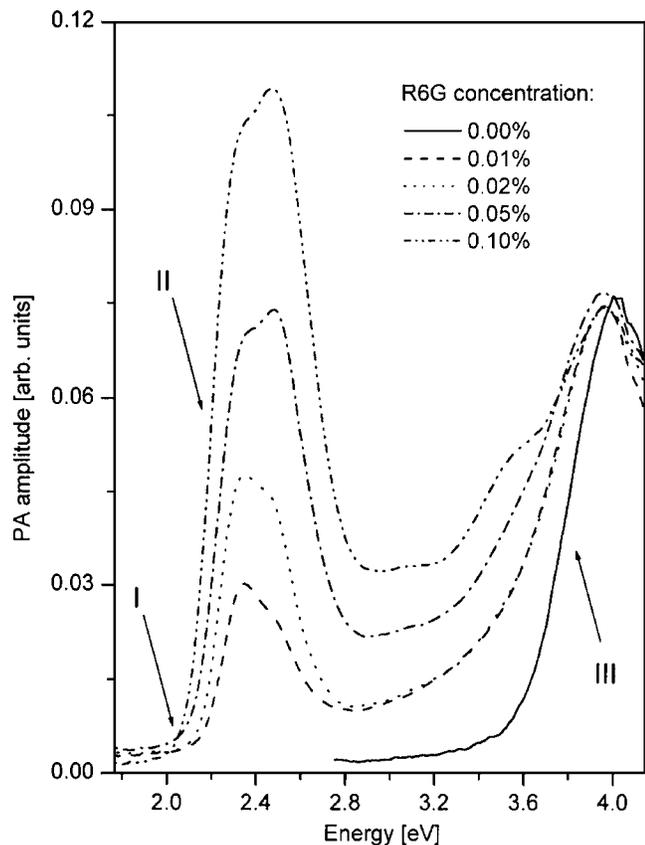


FIG. 1. Photoacoustic spectra for rhodamine 6G-doped TiO_2 thin films. The arrows indicate the analyzed regions.

molecular dimer formation and it becomes more accentuated as the R6G concentration increases. This is in agreement with the aggregative properties of R6G,^{11,12} and it indicates that R6G aggregates relatively easily at concentrations higher than 10^{-5} mol dm^{-3} . At that concentration it has been calculated¹³ that the proportion of dimers present in the sample is nearly 4%, and these aggregates are responsible for the fluorescence quenching of the sample. Additionally, a shoulder about 3.4 eV becomes clearly accentuated in the spectrum of the film doped with R6G at 0.10 mol % concentration. As discussed below, this band yields a strong fluorescence emission band at 2.06 eV.

The influence of R6G doping on the optical properties of the films has been assessed by analyzing three regions of the absorption spectra: regions I and II: indicate the onset to absorption and the inflection point of the R6G absorption band, respectively, and region III: corresponds to the inflection point of the TiO_2 absorption band. The determination of the energy at these points was made according to the derivative method. Regions I and II probably do not define the conventional energy gap of a typical semiconductor. That is, although incident light with these energies is absorbed by the sample, the conduction band of the material is not necessarily influenced by photogenerated carriers, but rather the absorbed energy is used by the dye to undergo a conformational transition. The dependence of regions I and II on the rhodamine concentration is illustrated in Fig. 2(a). Both regions show a similar trend, shifting by ~ 0.06 eV towards lower energies as the rhodamine concentration increases.

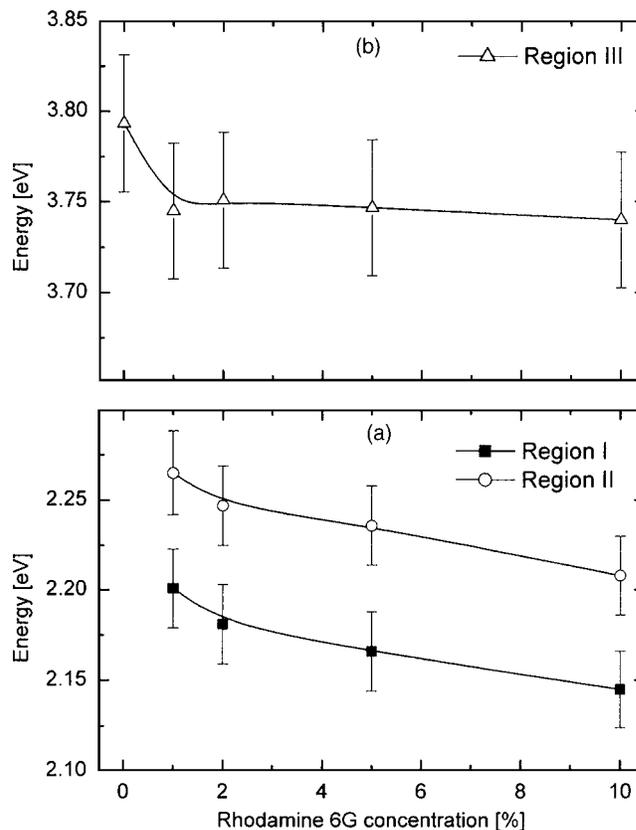


FIG. 2. (a) Energy value at the onset to absorption and at the inflection point of the R6G absorption band (see Fig. 1). (b) Energy value at the inflection point of the TiO_2 absorption band.

Figure 2(b) shows the results for region III. The gap energy for an undoped TiO_2 sample has also been included. The value determined for region III (TiO_2 band) decreased slightly from 3.75 to 3.74 eV by increasing the rhodamine concentration within the interval of 0.01–0.10%. The estimated theoretical value for the undoped TiO_2 sample is ~ 3.0 eV. However, the onset to strong absorption occurs at nearly 3.5 eV which is in agreement with the measured absorption of undoped films (see Fig. 1).

Figure 3 displays the excitation and fluorescence spectra

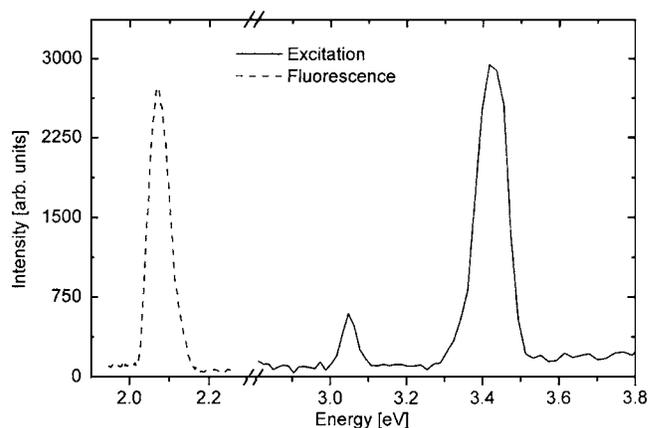


FIG. 3. Excitation and fluorescence spectra for a TiO_2 sol-gel film doped with rhodamine 6G at 0.10 mol % concentration. For the excitation spectrum, the emission photon energy was set at 2.06 eV, whereas fluorescence was measured by setting the excitation photon energy at 3.4 eV.

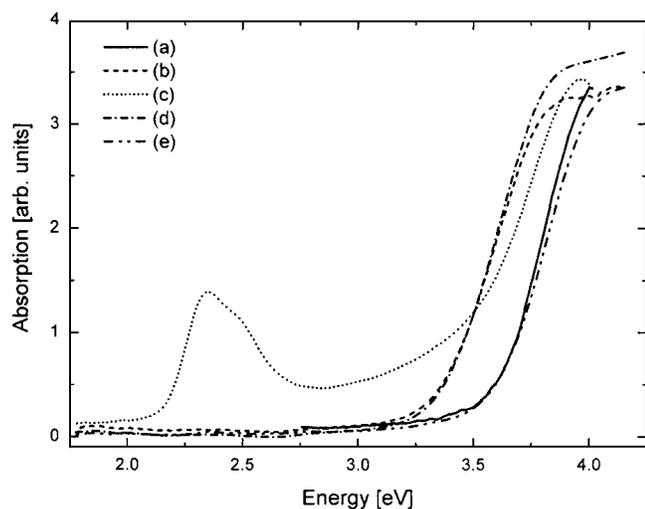


FIG. 4. Curves (a)–(d) show the measured absorption spectra of TiO_2 thin films: (a) an undoped sol-gel film, (b) an undoped sol-gel film post annealed at 400°C for six days in air, (c) a film doped with R6G at 0.01%, and (d) an undoped film prepared by magnetron sputtering. Curve (e) represents the theoretical spectrum for bulk rutile TiO_2 .

for a typical TiO_2 sol-gel film doped with rhodamine at 0.10 mol % concentration. For the excitation spectrum, the excitation photon energy was varied from 2.8 to 3.8 eV and the emission photon energy was set at 2.06 eV. It is observed that besides the absorption band of R6G with peaks at 2.3 and 2.5 eV, two bands with marked difference in intensity appear well defined: the first at 3.0 eV and the second at 3.4 eV. On the one hand, the weakly efficient excitation band at 3.0 eV is probably due either to defect states induced by the interaction of rhodamine 6G with the TiO_2 surface or to the formation of R6B^+ radical, since R6G adsorbed at the surface of TiO_2 gives up one electron to the conduction band.¹⁴ It may also be an enhancement of the very weak band-edge absorption of bulk TiO_2 at about 3.0 eV (Ref. 10) due to the rhodamine 6G doping. On the other hand, the highly efficient energy transfer exhibited by the band at 3.4 eV was confirmed with the aid of fluorescence spectra. In this case, the excitation photon energy was set at 3.4 eV and the emission spectra recorded in the range of 1.95–2.25 eV. This energy transfer might be due to the overlapping of the TiO_2 conduction band and the molecular R6G excited states, yielding a strong fluorescence emission band at 2.06 eV when excited at that energy.

Figure 4 shows the absorption spectra of different types of TiO_2 films: an undoped TiO_2 sol-gel film, an undoped TiO_2 sol-gel film post annealed in air at 400°C for six days, an undoped TiO_2 film prepared by sputtering, and a TiO_2 sol-gel film doped with rhodamine 6G at 0.01 mol % concentration. The theoretical result for a rutile-phase TiO_2 has also been included. It is observed that the theoretical result for absorption compared qualitatively well with the experimental finding.¹⁵ When the undoped TiO_2 sol-gel film is annealed, its absorption band is shifted by ~ 0.15 eV towards

lower energies. In addition, the absorption spectrum of the annealed sol-gel sample coincides with the spectrum of the sample prepared by sputtering. As explained above, the spectrum of the rhodamine-doped sample displays both the band characteristic of rhodamine as well as the shift of the TiO_2 absorption band.

V. CONCLUSIONS

High-quality TiO_2 sol-gel films doped with rhodamine 6G were successfully synthesized on glass substrates. Differently from other processes of adsorption of organic molecules onto TiO_2 , where the particle is already formed, the sol-gel method allows the organic molecule to interact quite strongly with the TiO_2 particles in the formation state of aggregates. The spectroscopic properties presented by the samples strongly suggest that this material has good potential to be applied in catalytic and optoelectronic applications, since we have been able to extend its energy absorption band range into the visible region. For comparison, the results for undoped TiO_2 are compared to other experimental data obtained from the rutile material prepared by sputtering as well as to theoretical calculations. The absorption measurements compared to the theory indicate a similar behavior.

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- ¹A. Fujishima and K. Honda, *Nature (London)* **238**, 37 (1972).
- ²U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, and M. Gratzel, *Nature (London)* **395**, 583 (1998).
- ³I. Hayakawa, Y. Iwamoto, K. Kikuta, and S. Hirano, *Sens. Actuators B* **62**, 55 (2000).
- ⁴A. Bahtat, M. Bouazaoui, M. Bahtat, C. Garapon, B. Jacquier, and J. Mugnier, *J. Non-Cryst. Solids* **202**, 16 (1996).
- ⁵T. Matsunaga, R. Tomoda, T. Nakajima, and H. Wake, *FEMS Microbiol. Lett.* **29**, 211 (1985).
- ⁶P. V. Kamat and K. Vinodgopal, in *Photocatalytic Purification and Treatment of Water and Air*, edited by D. F. Ollis and H. Al-Ekabi (Elsevier, Amsterdam, 1993), p. 8.
- ⁷D. Chatterjee and A. Mahata, *J. Photochem. Photobiol., A* **153**, 199 (2002).
- ⁸T. Lindgren, J. M. Mwabora, E. Avendaño, J. Jonsson, A. Hoel, C. G. Granqvist, and S. E. Lindqvist, *J. Phys. Chem. B* **107**, 5709 (2003).
- ⁹P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K: An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001).
- ¹⁰C. Persson, E. A. de Andrada e Silva, and A. Ferreira da Silva (unpublished).
- ¹¹P. R. Ojeda, I. A. K. Amashta, J. R. Ochoa, and I. L. Arbeloa, *J. Chem. Soc., Faraday Trans. 2* **84**, 1 (1988).
- ¹²F. L. Arbeloa, I. U. Aguirresacona, and I. L. Arbeloa, *Chem. Phys.* **130**, 371 (1989).
- ¹³A. Penzkofer and W. Leupacher, *J. Lumin.* **37**, 61 (1987).
- ¹⁴K. Itoh, Y. Chiyokawa, M. Nakao, and K. Honda, *J. Am. Chem. Soc.* **106**, 1620 (1984).
- ¹⁵S.-D. Mo and W. Y. Ching, *Phys. Rev. B* **51**, 13023 (1995).