Optical Band Gap Energy of Er-doped TiO_2 Thin Films

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ABSTRACT

Er-doped TiO_2 thin films having Er content in the range of 0 to 1.0 mol% were spin coated onto fluorine-doped SnO_2-coated (FTO) glass substrates by varying polyvinylpyrrolidone (PVP) concentration to evaluate the effect of film thickness on optical band gap energy. Morphology and optical properties of thin films were examined by glancing angle X-ray diffraction (GAXRD) and ultraviolet-visible (UV-vis) spectrophotometer. GAXRD data revealed that thin films consisted of pure anatase and FTO substrate without other phase. Optical band gap energy of Er-TiO_2 decreased gradually with decreasing the film thickness from 1800 nm to 550 nm, and then increased with a further decrease in film thickness. In addition, the band gaps decreased from 3.21~3.25 eV to 2.81~3.03 eV with the increase of Er doping from 0 to 0.7 mol%, but increased to 2.89~3.02 eV when Er doping was 1.0 mol%. The lowest band gap energy of 2.81 eV was observed for the 0.7 mol% Er-TiO_2 having a PVP concentration of 0.0082 g/ml (~550 nm). The film thickness and the dopant ions were considered to be responsible for the reduction in band gap energy.

Keywords: Er-doped TiO_2, polyvinylpyrrolidone (PVP), optical band gap energy, spin coating, film thickness

1 INTRODUCTION

TiO_2-based thin film photocatalysts have been investigated extensively for environmental applications such as air, water treatment and deodorizer, because of its strong oxidizing power, high photocatalytic activity, self-cleaning function, bactericidal and detoxification activity [1-6]. TiO_2 under ultraviolet (UV) illumination has been proposed as the most effective and advanced removal alternative for environmental and biomedical applications due to its efficiency of electron-hole pair separation and its optical absorption property [2]. TiO_2 under UV radiation can be excited to generate charges leading to the production of oxidative radicals, which can mineralize organic pollutants into carbon dioxide and water [4-6]. TiO_2 possessing wide band gap energy of 3.2 eV for anatase limits its uses to those involving UV radiation.

The photocatalytic degradation of organic pollutants by the doped TiO_2 was examined as a function of dopant content to investigate the optical properties of thin films having a thickness of about 500 nm. The suitable doping (Co, Fe, Mn, Zn, Er) has exhibited the enhancement of photoactivity of doped TiO_2 [6-11]. Among them, a lanthanide-modified TiO_2 by doping may effectively retard the electron-hole recombination in the photocatalytic reaction. Lanthanide (rare earth) ions are likely to form complexes with various Lewis bases (e.g., acids, amines, aldehydes, alcohols, thiols, etc) in the interaction of these functional groups with the *f*-orbital of the lanthanides [2-6,12-14]. The incorporation of lanthanide ions into TiO_2 matrix may adsorb dramatically the organic pollutants at the semiconductor surface and facilitate the degradation of organic pollutants [2,6]. In addition, most of the interest in luminescent rare earth ions has concentrated on Er^{3+} due to its unique electronic and optical properties [15,16].

Although the optical indirect band gap energy (E_g) of the doped TiO_2 films is determined to be a function of the dopant content, few studies for the effect of film thickness on the band gap energy of the films are done [6-11]. The optical band gap energy of the films is further scrutinized to elucidate the dependence of film thickness on E_g of the Er-TiO_2 films. In the present study, the Er^{3+}-TiO_2 thin films were synthesized by a sol-gel derived spin coating. The optical band gap energy of the Er-TiO_2 films was examined as a function of PVP and Er content by using an UV-vis spectrophotometer.

2 EXPERIMENTAL

The precursor solution was prepared from 3.5 g of titanium tetrabutoxide ($Ti[O(CH_2)_3CH_3]_4$, 97%, Aldrich, USA) in 3 g of acetic acid by stirring. Polyvinylpyrrolidone (PVP, Mw=1,300,000, Aldrich, USA) dissolved in 5.5 g of ethanol was added to the TiO_2 precursor solution. The amount of PVP was in the range of 0 g to 0.45 g. Then, erbium chloride ($ErCl_3$, Aldrich, USA) was added into the above solution to obtain Er^{3+}-TiO_2 [6,12,13].

FTO glass was first surface cleaned by sonicating using distilled water, alcohol, KOH (1M), followed by rinsing and drying. The FTO glass (25 x 25 mm^2) was used as a substrate. TiO_2 thin films onto the FTO glass were spin coated on the FTO glass at 500 rpm for 8 s and then 3000

rpm for 30 s in air. The thin films were then calcined for 3 h at 500°C in air with a heating rate of 1°C/min. The film thickness was measured by a surface profilometer (SE3500, Kosaka Lab. Ltd., Japan).

The crystalline phase of the films was analyzed by using a glancing angle X-ray diffraction (GAXRD, PW3040-60, PANalytical, Holland). The optical transmittance in the wavelength range of 300 to 800 nm was examined by using an UV spectrophotometer (V-670, Jasco, Japan) to determine the optical indirect energy band gap, as given by Tauc and Menth [17].

3 RESULTS AND DISCUSSION

In order to study the optical band gap energy as a result of the effects of lattice defects rather than the grain boundary light scattering, the thickness of the films should be ~500 nm, which was well-documented by several researchers [7-11]. As the photon mean free path of light in TiO_2 thin films is greater than the grain size, the light scattering is limited to the effects of lattice defects rather than the grain boundary light scattering because the photon mean free path and the wavelength for rutile is found to be a second order relation [18,19]. The greater mean free path may lead to relatively a high and constant light transmission. The film thickness should be less than 1 μm in order to maintain a higher transmission in the wavelength range of 300 to 800 nm. The number of grain boundaries crossed by light should be small to suppress the grain boundary light scattering. The variation of the transmittance and the band gap energy for the TiO_2 thin films having a thickness of about 500 nm might be considered to be responsible for the formation of lattice defects [8,9,11]. In the present study, the Er-TiO_2 film thickness was controlled by varying the PVP amount, as shown in Fig. 1. The film thickness increased gradually from 400±30 nm to 1800±580 nm with increasing the PVP concentration from 0.004 g/ml to 0.082 g/ml, respectively. The 550±30 nm thickness can be obtained for the Er-TiO_2 film having a PVP concentration of 0.0082 g/ml.

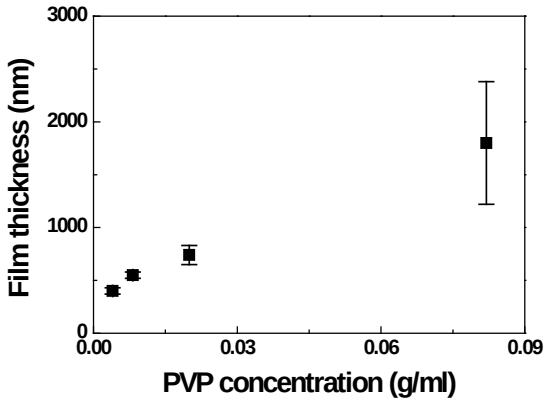

Fig. 1. The variation of 0.5 mol% Er-doped TiO_2 film thickness as a function of PVP concentration.

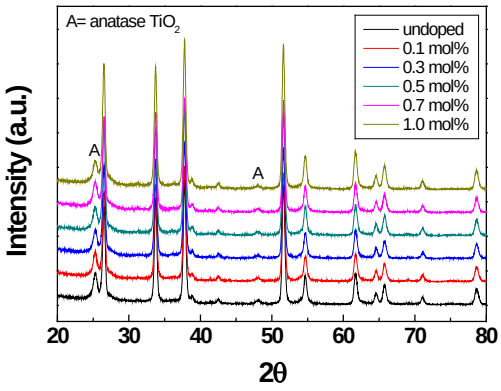

Fig. 2. GAXRD patterns of Er-doped TiO_2 films having a thickness of 400 nm.

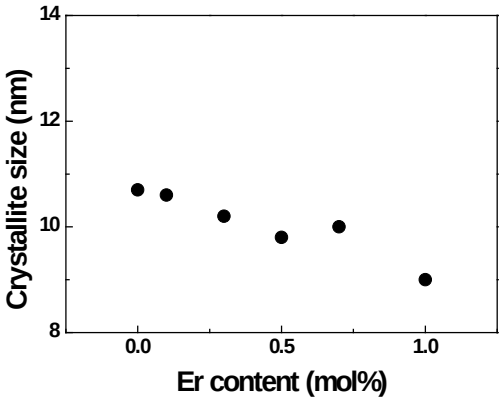

Fig. 3. Crystallite size of Er doped TiO_2 thin films as a function of Er concentration.

GAXRD patterns for thin films are shown in Fig. 2. The films were of the same thickness (400±30 nm). The variation of GAXRD peak intensity was not pronounced because the dopant level was below 1 mol%. The GAXRD results indicate that the films consist of pure anatase (JCPDS-21-1272) and underlying peaks of FTO substrate (JCPDS-41-1445), which are consistent with the well–documented results [8,9,11,13]. No rutile phase (JCPDS-21-1276) was detected. The peak intensity of FTO substrate was not changed with increasing the Er content. On the contrary, the anatase TiO_2 peaks located at 25° and 48° became slightly broader and weaker with increasing the Er concentration due to the disorder caused by the substitution of Er^{3+} for Ti^{4+}, indicative of a reduced grain size and a lower extent of crystallinity [8,9,11]. The crystallite size determined by the Scherrer formula decreased from 10.7 nm to 9.0 nm with increasing the amount of Er from 0 mol% to 1.0 mol%, implying a reduction in crystallinity. Although a slight decrease in crystallinity was detected for the films having a thickness of 400±30 nm as displayed in Fig. 3, the effect of Er content on the crystallinity of Er-TiO_2 was not significant.

TiO_2 under UV radiation can be excited to generate charges leading to the production of oxidative radicals, which can mineralize organic pollutants into carbon dioxide and water. Electrons may be excited from the valence band to the conduction band leaving the holes in the valence band when TiO_2 is irradiated by $h\nu$. Electrons generated by $h\nu$ are transferred from conduction band (CB) of Er to CB of TiO_2 while holes in TiO_2 move to the valence band (VB) of Er. The electron transitions of Er^{3+} (Eg≈2.4 eV) favor the separation of photogenerated electron-hole pairs and the sensitization of TiO_2 by visible light [2,7]. Er^{3+}/Er^{2+} (-3.0 V versus SHE) traps photogenerated electrons (Eq. (2)). Er^{3+} can trap photogenerated holes above the VB edge of TiO_2 (Eq. (3)). Er^{2+} is oxidized by molecular oxygen to form the superoxide anion (Eq. (4), O_2^-). The holes (h^+) were effectively scavenged by the water and generated hydroxyl radicals (Eq. (5), $OH^\bullet$). The superoxides (O_2^-) and the hydroxyl radicals ($OH^\bullet$) may act as active reagents for the mineralization of the organic components [8-11], leading to dramatic improvement of the photocatalytic activity of the Er-TiO_2 catalysts by suppressing the recombination of excited electrons and holes.

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (1)$$
$$Er^{3+} + e^- \rightarrow Er^{2+} \quad (2)$$
$$Er^{3+} + h^+ \rightarrow Er^{4+} \quad (3)$$
$$Er^{2+} + O_2 \rightarrow Er^{3+} + O_2^- \quad (4)$$
$$Er^{4+} + OH^- \rightarrow Er^{3+} + OH^\bullet \quad (5)$$

The optical indirect band gap of thin films can be determined from UV-vis spectra data [8-11]. The transparency of the films exhibits a sharp decrease in the UV region (≤400 nm) due to light absorption, as shown in Fig. 4. The absorption edge shifted to longer wavelengths with increasing Er dopant level. Fig. 4(a) revealed that the transmission decreased gradually with increasing the Er content in visible regions of 400 to 550 nm. The undoped TiO_2 showed the lowest transmission at wavelength in the range of 670 nm to 750 nm. However, the transmittance of the 1.0 mol% Er-TiO_2 increased dramatically as the PVP concentration decreased, as depicted in Fig. 4(c). As the film thickness decreased, the dramatic increase in the transmittance of the 1.0 mol% Er-TiO_2 was detected probably due to the film thickness. It is reported that amorphous phase occurs when the TiO_2 film thickness is less than 100 nm [20].

For the film of approximately same thickness, it is noted that transparency of the film having a smaller crystallite size is better than that of the film having a larger crystallite size [21]. The Er-TiO_2 having a smaller crystallite size, as verified in Fig. 3, should be more transparent. Our results revealed that at lower wavelength region (300-540 nm), the undoped TiO_2 is more transparent compared to Er-TiO_2 but at higher wavelength region (540 nm-800 nm), transparency of Er-TiO_2 is better than that of the undoped TiO_2 for the films having PVP concentration higher than 0.02 g/ml. However, a dramatic increase in transmittance of the 1.0 mol% Er-TiO_2 was observed for the films having PVP concentration less than 0.0082 g/ml. Transparency of thin film may be influenced by dopant concentration and film thickness, however, the reasons behind this phenomenon are not yet understood clearly.

The absorption coefficient (α) above the threshold of fundamental absorption follows the $(E\text{-}E_g)^2$ energy dependence characteristic of indirect allowed transitions as by the $\alpha^{1/2}$ versus photon energy (E) plot in Fig. 5. The optical energy gap changes with the composition, but the slope of the absorption edge changes little. The band gap energy is then estimated by the intercept of the tangent to the inflexion point between the absorption tail and the band states ($\alpha^{1/2}$) with the abscissa (photon energy). The range of values in the literature for the band gaps of anatase are 3.20 to 3.56 eV [6-11]. The energy gap (E_g, 3.21~3.25 eV) of the undoped TiO_2 obtained from Fig. 5 is in good agreement with the literature. The lowest band gaps of Er-TiO_2 are observed for the films containing a PVP concentration of 0.0082 g/ml, as shown in Fig. 5(c). The energy gaps are 3.25, 2.85, 2.85, 2.85, 2.81, 2.89 eV for 0, 0.1, 0.3, 0.5, 0.7 and 1.0 mol% of Er, respectively. The absorption coefficient ($\alpha^{1/2}$) of undoped TiO_2 shifted to lower photon energies dramatically when Er was doped. On the other hand, the absorption coefficient curves of Er-TiO_2 thin films are almost similar regardless of Er dopant content. The lowest E_g of 2.81 eV was observed for the 0.7 mol% Er-TiO_2 thin film, which is in agreement with the photodegradation results of methylene blue (MB) in water [6]. Among Er-TiO_2 catalysts, the 0.7 mol% Er-TiO_2 nanorods showed the highest degradation rate [6]. This effective decrease in the optical indirect band gap could lead to excellent efficiency of the photocatalytic performance of TiO_2. It is interesting to note that the lowest band gap was obtained for the films having a thickness of about 550 nm. Further decrease in film thickness increased the band gap energy, which warranted further studies in order to gain a better understanding of the factors governing the band gap energies of the films.

4 CONCLUSIONS

Er-TiO_2 thin films (≤1.0 mol% Er) were spin coated onto FTO glass by varying PVP concentration to investigate the effect of the film thickness and the dopant content on band gap energy of Er-TiO_2. GAXRD results revealed that the Er-TiO_2 films consisted of anatase phase and FTO. The lowest band gap energy of 2.81 eV was found for the 0.7mol% Er-TiO_2 having a thickness of about 550 nm. The film thickness and the dopant content may be attributed to the band gap energy.

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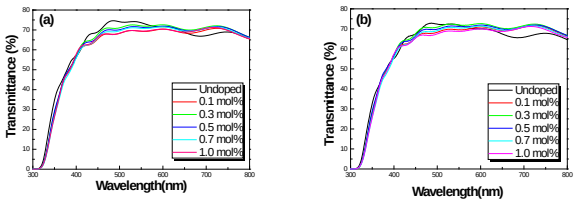

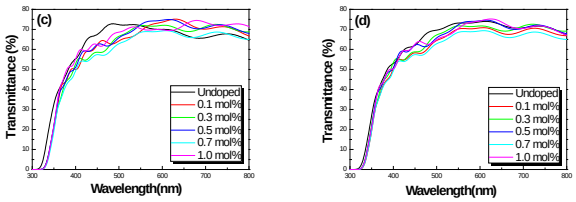

Fig. 4. UV spectra of Er-doped TiO_2 as a function of PVP concentration: (a) 0.082 g/ml, (b) 0.02 g/ml, (c) 0.0082 g/ml and (d) 0.004 g/ml, respectively.

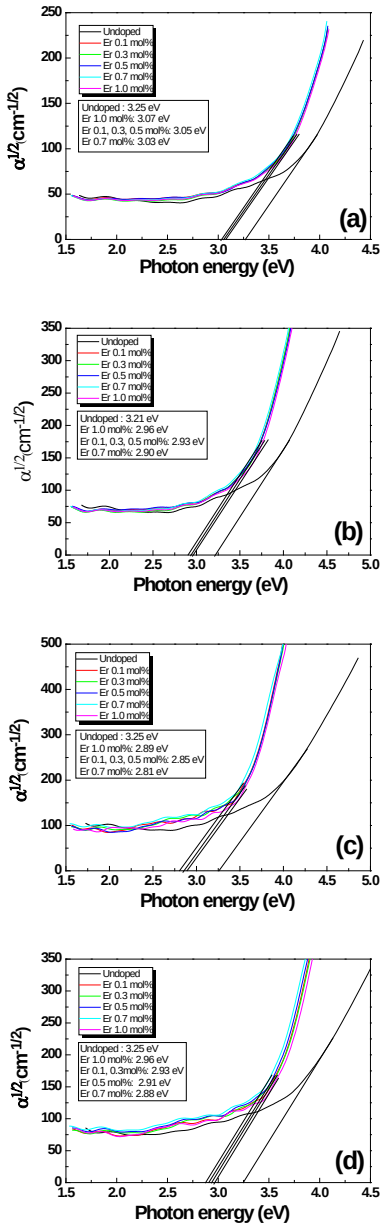

Fig. 5. Optical band gaps of Er-doped TiO_2 thin films after calcination for 3 h at 500°C. Note that PVP concentration is (a) 0.082 g/ml, (b) 0.020 g/ml, (c) 0.0082 g/ml and (d) 0.004 g/ml, respectively.