Vanadium-doped nanocrystalline TiO_2 layer prepared by spin coating pyrolysis

KYU-SEOG HWANG*
Department of Applied Optics and Institute of Photoelectronic Technology, Nambu University, 864-1 Wolgye-dong, Gwangsan-gu, Gwangju 506-824, Republic of Korea
E-mail: khwang@nambu.ac.kr

JUN-HYUNG AHN, BYUNG-HOON KIM
Department of Materials Science and Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500–757, Republic of Korea

TiO_2 thin films have received great attention in recent years because of their excellent optical and electrical properties [1–3]. Roles of electron-hole pairs generated by the ultraviolet (UV) light irradiation have been studied in the basic and application field. The band gap energy requires that near-UV light be used to photoactivate this very attractive photocatalyst. Unfortunately, in solar energy applications only ~3 % of the solar light is absorbed. It would be advantageous, therefore, if TiO_2 could be photosensitized by visible light.

Many studies have been devoted to the extension of the photoresponse and improvement of the photoactivity by dye-sensitizing, doping, surface modification, and depositing noble metal [4–6]. Doping with metal cations has been attempted for photo-catalytic applications by shifting the threshold for photonic excitation of the TiO_2 towards the visible. All metal dopants are conveniently substituted into the TiO_2 lattice, if their ionic radii are identical or nearly identical to that of the Ti^{4+}. These systems are being prepared in the form of thin films due to the advantages of their use as electrodes, transparent coatings, etc. [7, 8].

Vanadium (V) doping increases carrier lifetime and apparently also extends the absorption range of TiO_2 [7]. Herein, we examine the crystallographic and spectroscopic behavior of V-doped TiO_2 thin films prepared by spin coating-pyrolysis process. Metal naphthenate precursor was used as a starting material because of stability in air and ease of handling.

Ti- and V-naphthenates (Nihon Kagaku Sangyo Co. Ltd., Japan) were used as a precursor in the spin coating-pyrolysis process and by diluting the sol with toluene (molar ratio of $V:Ti = 9:95$). The concentration of metal ions in coating solution was about 4 wt.%.

Thin films were fabricated by spin coating onto 2.5 cm × 2.5 cm × 1 mm substrates of the soda lime silica glass [SLSG, Corning 2947, O (60 at.%), Si(24.5 at.%), Na (10 at.%), Ca (2.5 at.%), Mg (2 at.%), Al (1 at.%)] at a roation speed of 1500 rpm for 10 s. After each deposition, the coating film was pyrolyzed in air at 500°C for 10 min to decompose organic species. For multiple coatings, the above-mentioned processes were repeated five times to obtain the resulting films with a thickness of approximately 0.6–0.7 μm. The resulting films were directly annealed into a preheated furnace with temperature at 550 °C for 30 min in air.

The phase evolution of the films was examined by an high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands) using a CuK_α radiation. The thickness of the films was measured by observations of fractured cross-section using a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi Co., Japan). The microstructure of the films after annealing was examined using a FE-SEM. Spectroscopic analysis of the films was performed by using a UV-Visible-NIR spectrophotometer (Cary 500 Scan, Varian Co., Australia, its wavelength range is 300–900 nm).

Fig. 1 shows the XRD pattern of the film after annealing at 550 °C. An anatase phase with a strong (110) reflection ($2\theta = 25$–$26°$) appeared when the temperature reached 550 °C, although the films after prefiring at 500 °C for 10 min exhibit amorphous character, not shown here. There was no peaks for rutile of TiO_2, vanadium oxide, and vanadium titanate. Of the two crystal forms of TiO_2 catalysts, the anatase invariably exhibits a higher photoactivity than rutile does [9]. Therefore, the higher the anatase-to-rutile ratio the crystal has, the more photoactive the catalyst is. Metal dopants, such as Fe and Cr, would be increasing oxygen vacancies in TiO_2 crystal lattice. These oxygen vacancies are responsible for the enhancement of transformation from anatase to rutile [10]. Rutilisation was already induced at 400 °C in Fe-doped TiO_2 sample

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* Author to whom all correspondence should be addressed.

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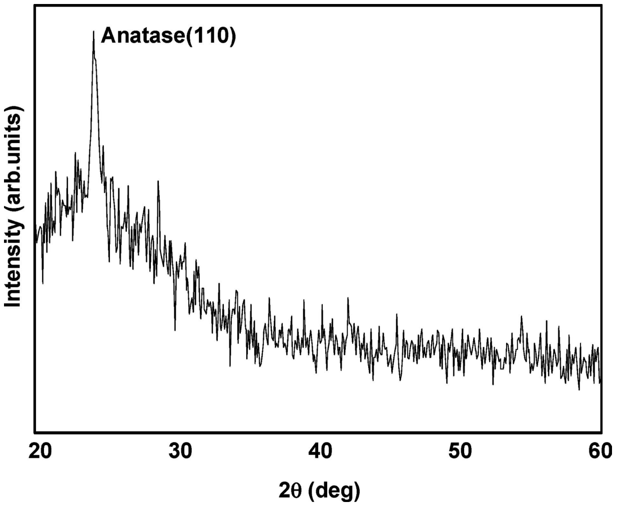

Figure 1 XRD spectra of the 5 mol% V-doped TiO_2 thin film on SLSG substrate after annealing at 550 °C.

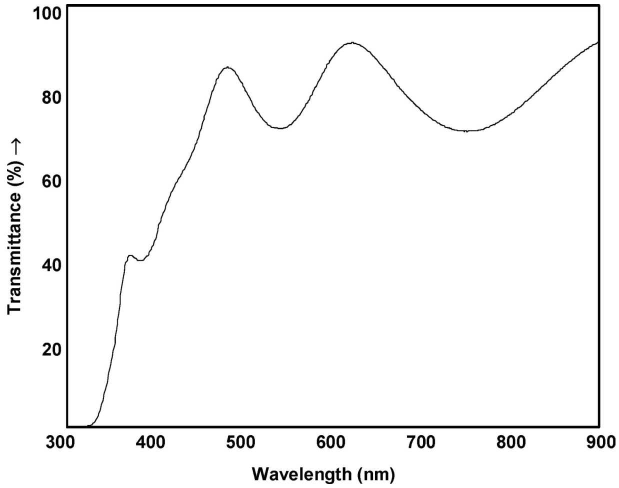

Figure 3 Transmittance in visible wavelength range of the 5 mol% V-doped TiO_2 thin film on SLSG substrate after annealing at 550 °C.

[5]. This would be for the acceptor dopants. However, in this work, V-doped TiO_2 thin films fully crystallized into anatase structure at high annealing temperature, 550 °C. We assume that V would act as a donor dopant in TiO_2 lattice [11].

Fig. 2 shows surface microstructure (a) and fractured cross-section (b) of the film after annealing at 550 °C. The film exhibits a dense microstructure with a nano grain size, as shown in Fig. 2a. No evidently aggregated particles are present. The fractured cross-section of the layer of about 0.6–0.7 μm thickness appears dense and uniform.

Fig. 3 shows the visible spectra in the wavelength range 300–900 nm of the film on SLSG substrate after annealing at 550 °C. Relative high transmittance at visible range and a clear absorption edge of the film were observed. The high transmittance of the film is attributed to the small particle size which eliminate light scattering [12]. From this spectrum, it is apparent that films present relatively high optical quality, with an absorption in the visible region that is characterized by the typical interference pattern found when a transparent thin film is deposited onto a substrate of different refractive index. Furthermore, the film containing V showed a shift towards the visible in the absorption threshold.

Furthermore, we calculated the band gap values of the films from their transmission spectra using the following equation [13]:

$$a = (h\nu - E_g)^{1/2}$$

where α is the absorption coefficient, E_g is the band gap and $h\nu$ is the photon energy. The intersection of the linear region on the $h\nu$ axis of the plot of α^2 versus $h\nu$ gives the band gap of the ZnO films deposited on SLSG substrates. As shown in Fig. 3, using this method [14] the band gap value of the films is found to be 3.41 eV. The estimated value of the band gap for the present film, V-doped TiO_2, is much smaller than that of previous TiO_2 film (3.70 eV) [15]. Generally, the film consisting of fine crystallites show 'blue shift' [16]. A comparison of optical energy gaps between pure TiO_2 and V-doped TiO_2, thin films shows an obvious red shift in V-doped TiO_2 films.

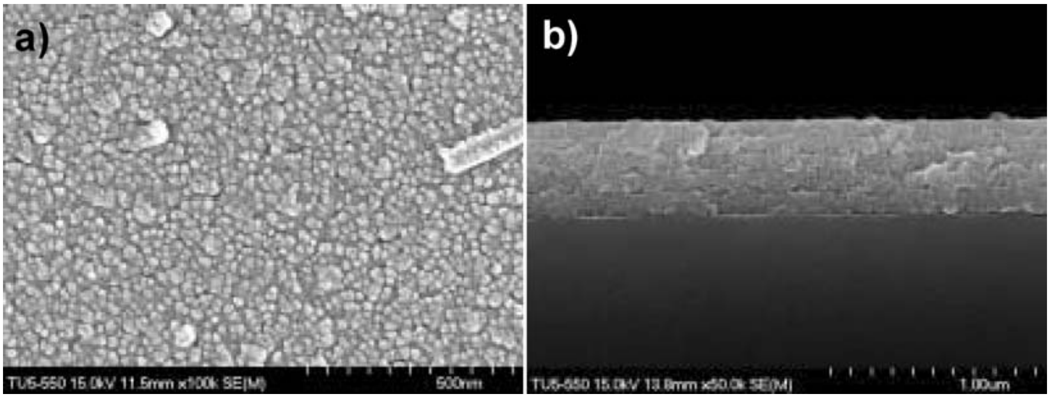

Figure 2 FE-SEM photographs of the surface morphology (a) and fracture cross-section (b) of the 5 mol% V-doped TiO_2 thin film on SLSG substrate after annealing at 550 °C.

In summary, V-doped TiO_2 thin films were prepared on SLSG substrates at 550 °C from metal naphthenates precursor. Only anatase phase with a strong (110) reflection appeared when the temperature at 550 °C. The film exhibits a dense microstructure with a nano grain size by FE-SEM observation. The estimated value of the band gap for the V-doped TiO_2, is much smaller than that of previous pure TiO_2 film (3.67 eV).

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