Vol 10 No 2, February 2001
1009-1963/2001/10(02)/0148-04

Chinese Physics

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and IOP Publishing Ltd

EFFECT OF $ZnFe_2O_4$ DOPING ON THE OPTICAL PROPERTIES OF TiO_2 THIN FILMS

Li Guang-hai(李广海), Wu Yu-cheng(吴玉程), and Zhang Li-de(张立德)
Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, *China*

(Received 31 July 2000)

Amorphous TiO_2 thin films and $ZnFe_2O_4$-doped TiO_2 composite films were deposited by radio frequency magnetron sputtering. The effect of $ZnFe_2O_4$ doping on the optical properties of TiO_2 thin films was reported. Our results show that the absorption edge of TiO_2 thin films and composite films exhibits a blueshift with decreasing annealing temperature. The absorption edge of composite films has moved to a visible spectrum range, and a very large redshift occurs in comparison with TiO_2 thin films. An enhanced photoluminescence was observed in $ZnFe_2O_4$-doped anatase TiO_2 thin films at room temperature.

Keywords: sputtering, titanium oxide, optical properties
PACC: 6855, 7865

Recent interest in TiO_2 has been motivated by its key role in the injection process in a photochemical solar cell with a high conversion efficiency.[1] Size confinement effects,[2,3] and optical properties[4,5] based on anatase TiO_2 materials have been the subject of intensive research. TiO_2 is a wide band gap semiconductor (3.03 eV for rutile and 3.18 for anatase) and can only absorb about 5% of sunlight in the ultraviolet region, which greatly limits its practical applications because of the lower utility of sunlight and quantum yield. Many studies have been devoted to the extension of the photoresponse and improvement of the photoactivity of TiO_2 by dye-sensitizing, doping, surface modification and depositing noble metals.[6,7] In recent years, it has been found that spinel $ZnFe_2O_4$ is another semiconductor (band gap 1.9 eV) that has potential application in the conversion of sunlight. Nevertheless, because of the lower valence band potential and poor property in photoelectric conversion, $ZnFe_2O_4$ cannot be used directly in the photocatalytic destruction of toxic organic compounds.[8]

Nanosized TiO_2 has high photoactivity and superior property in photoelectric conversion, while nanosized $ZnFe_2O_4$ is sensitive to visible light. So the compound of these two semiconductors in nanoscale, which utilizes the special properties of nanoparticles and the coupling between them, will be a new type of composite that will have a high utility of sunlight, high photoactivity and high efficiency of photoelectric conversion.

This paper aims to report on the elaboration of TiO_2 thin films and $ZnFe_2O_4$-doped TiO_2 thin films prepared by radio frequency (rf) sputtering and on the effect of post-deposition annealing upon optical properties of the films.

The deposition was carried out in a sputtering unit equipped with an rf generator. Pure TiO_2 and TiO_2+2wt% $ZnFe_2O_4$ (purity 99.99%) composite of 60 mm in diameter were used as targets to prepare TiO_2 thin films and $ZnFe_2O_4$-doped TiO_2 thin films. The detailed preparation procedures can be found elsewhere.[9–11] Post-deposition annealing was performed in flow oxygen at temperatures ranging from 200–1000°C. X-ray diffraction (XRD), Raman scattering and atomic force microscopy (AFM) were used to assess the structural properties. The optical absorption spectra were recorded with a Cary-5E spectrophotometer. Photoluminescence (PL) measurements were carried out at room temperature, in which an Ar lamp with a wavelength of 320 nm was used for excitation.

XRD and Raman spectra analyses indicate that when the annealing temperature is lower than 250°C the TiO_2 thin films are in an amorphous state, annealing between 250–800°C the anatase phase forms, higher than 950°C a pure rutile phase forms. The sample heat-treated at 900°C consists of a major rutile phase plus a minor anatase phase. In contrast, the crystallization temperature of $ZnFe_2O_4$-doped TiO_2 thin films moves to a higher temperature of about 450°C, while the sample heat-treated at 650°C con-

sists mainly of an anatase phase plus a minor rutile phase, and the complete anatase–rutile transformation occurs at 800°C. The typical Raman spectra of $ZnFe_2O_4$-doped TiO_2 thin films are shown in Fig.1. AFM observation indicated that the particle size of anatase TiO_2 increases almost linearly with an annealing temperature below 600°C, (the particle size is 25 and 32 nm after the samples are annealed at 400°C and 600°C, respectively), and it quickly increases to about 120 nm at 800°C in TiO_2 thin films. Particle sizes as large as 200 nm were formed in the phase mixture of anatase and rutile in TiO_2 thin films annealed at 900°C. The average particle size of TiO_2 in $ZnFe_2O_4$-doped TiO_2 thin films is always smaller than that in TiO_2 thin films under the same annealing temperature. The size distribution of TiO_2 particles in composite films is narrow whether it is in anatase phase or in anatase and rutile phase mixture, and in rutile phase.[11]

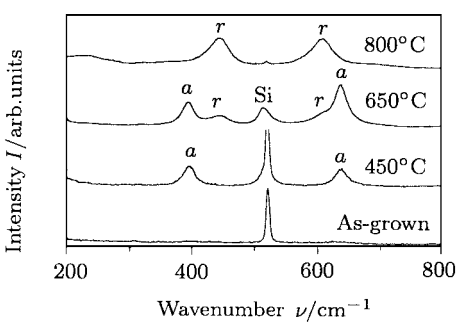


Fig.1. Raman spectra of $ZnFe_2O_4$-doped TiO_2 thin films annealed at different temperatures. The labels *a* and *r* refer to anatase and rutile phase TiO_2, respectively.

Figure 2 shows the absorption spectra of TiO_2 thin films and $ZnFe_2O_4$-doped TiO_2 thin films annealed at different temperatures. It is seen that with increasing annealing temperature the absorption edge shifts to the longer wavelength direction in both films, particularly in the composite films. A broad diffusion absorption band forms around 500 nm for $ZnFe_2O_4$-doped TiO_2 thin films. This result proves that, upon addition of $ZnFe_2O_4$ particles to TiO_2, the absorption edge of the composite films moves to the visible spectrum range. This indicates that the composite films are sensitive to visible light. The optical band gap E_g can be determined from the absorption coefficient α, and has been investigated by plotting $(\alpha h\nu)^{1/2}$ versus $h\nu$ (for indirect allowed transitions) and $(\alpha h\nu)^2$ versus $h\nu$ (for direct allowed transitions). In the present study, the best straight line plot extended over most data points is $(\alpha h\nu)^2$ vs $h\nu$, as shown in Fig.3. Plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ show no linear relationships near the optical absorption edge for TiO_2 and $ZnFe_2O_4/TiO_2$ films. The optical energy gaps for direct transition range from 3.64–3.78 eV for TiO_2 thin films, and from 3.14–3.56 eV for $ZnFe_2O_4$-doped TiO_2 thin films when the annealing temperature decreases from 700°C to 300°C. The obvious blueshift of the optical energy gap is seen in both films.

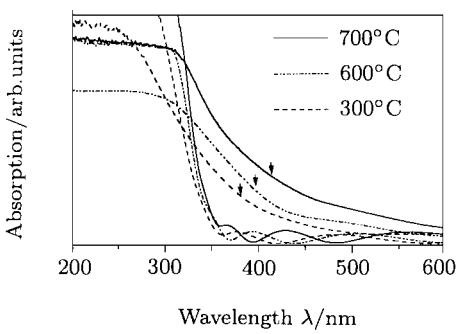


Fig.2. Optical absorption spectra for TiO_2 thin films and $ZnFe_2O_4/TiO_2$ composite films (arrows) annealed at different temperatures.

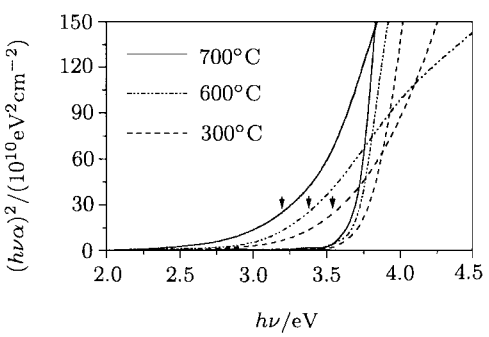


Fig.3. Plots showing the fit for the absorption edge of TiO_2 thin films and $ZnFe_2O_4/TiO_2$ composite films (arrows) annealed at different tmeperatures when $(\alpha h\nu)^2$ is plotted versus hν.

The blueshift in the absorption band edge has been claimed as a consequence of exciton confinement with decreasing particle size (the so-called quantum-size effect) in TiO_2. Serpone *et al.*[12] indicated that the blueshifted absorption thresholds for TiO_2 small particles are direct (Franck–Condon type) transition in an otherwise indirect band gap semiconductor instead of quantum-size effect. Deloach *et al.*[13] recently reported that the blueshift of the optical energy gap is due to the change of the energy gap of the disordered crystals in TiO_2 films. The particle size of TiO_2 in anatase TiO_2 films increases from 25–120 nm when the annealing temperature increases from 300°C

to 700°C, while the corresponding optical energy gaps only vary for about 0.14 eV. From this result, it is believed that the blueshift of absorption band edge might be due to the change of the energy gap of the disordered crystals in TiO_2 films. Nevertheless, the particle size of TiO_2 in $ZnFe_2O_4$-doped anatase TiO_2 thin films increases from 15 to 30 nm when the annealing temperature increases from 300°C to 600°C, while the corresponding optical energy gaps increase from 3.21 to 3.56 eV, the difference being 0.35 eV. The large blueshift is believed to be due mainly to the exciton confinement effect of $ZnFe_2O_4$ particles embedded in the anatase TiO_2 matrix in the composite films.

A comparison of optical energy gaps between TiO_2 and $ZnFe_2O_4$-doped TiO_2 shows an obvious redshift in $ZnFe_2O_4$-doped TiO_2 thin films at the same annealing temperatures. The redshifts are 0.21, 0.45 and 0.50 eV for samples annealed at 300°C, 600°C and 700°C, respectively. The large redshift of optical energy gaps is considered to be due to two factors. One of these comes from the mixing effect of band gaps of the composite semiconductor. When anatase TiO_2 with a relatively high band gap mixed with a low band gap $ZnFe_2O_4$, the band gap of the $ZnFe_2O_4$-doped TiO_2 composite semiconductor will be located between the band gaps of these two semiconductors, i.e., it shifts to a lower energy, as compared with that of TiO_2. Since the added amount of $ZnFe_2O_4$ is only 2 wt%, it cannot cause such a large shift of the band gap. The other factor is considered to be the interface effect between $ZnFe_2O_4$ and TiO_2 particles, because TiO_2 particles are isolated by small $ZnFe_2O_4$ particles, and the increased dielectric confinement effect at the interface can also cause the redshift.

Figure 4 shows the room temperature PL spectra of the TiO_2 thin film annealed at 900°C (curve (1), mainly of rutile phase) and $ZnFe_2O_4$-doped TiO_2 thin film annealed at 650°C (curve (2), mainly of anatase phase). The rutile TiO_2 thin film shows a weak broad end PL band ranging from 400–700 nm with the maximum at 488 nm. No PL was found for samples annealed at temperatures below 800°C (pure anatase phase). But for the $ZnFe_2O_4$-doped anatase TiO_2 thin film a very strong PL band appears together with a shoulder marked by the arrow, curve (2) in Fig.4. With a further increase in the annealing temperature to over 800°C (pure rutile phase), a very weak PL band appears for the $ZnFe_2O_4$-doped anatase TiO_2 thin film, similar to curve (1) in Fig.4. This result indicates that the strong PL band only occurs in the $ZnFe_2O_4$-doped anatase TiO_2 thin film. From Fig.4, one can see that the PL peak for the $ZnFe_2O_4$-doped anatase TiO_2 thin film is coincident with the absorption shoulder marked S in Fig.4 (curve (3)). This result indicates that the strong PL band corresponds to the unusual strong absorption in the same wavelength region. As the annealing temperature increases, the unusual strong absorption band also disappears for the $ZnFe_2O_4$-doped anatase TiO_2 thin film, see Fig.2.

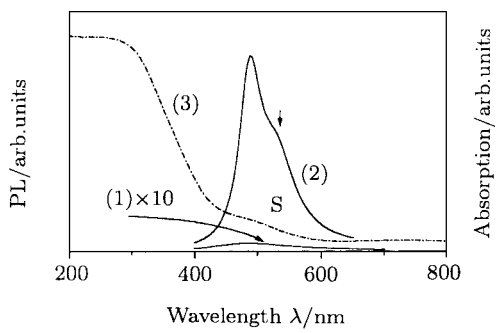


Fig.4. PL spectra for curve (1) TiO_2 thin film annealed at 900°C and curve (2) $ZnFe_2O_4/TiO_2$ composite film annealed at 650°C and the corresponding absorption spectrum (curve 3).

Tang *et al.*[14] examined the PL of TiO_2 anatase single crystals and found the band gap excitation results in visible broad band PL, which is interpreted as the emission of self-trapped exitons located or trapped on TiO_6 octahedra.

Saraf *et al.*[15] studied the room temperature PL properties of nanophase TiO_2. They found a narrow PL spectrum at 3.01 eV with anatase TiO_2 powder and a broad band spread over the entire visible range with the anatase and rutile phase mixture. The narrow PL spectrum in anatase phase compares favourably with the reported anatase spectrum originating from the self-tapped exitons on TiO_6 octahedra. The broad PL band in phase mixture is ascribed to oxygen-related defects in TiO_6 octahedra.

The strong PL band in $ZnFe_2O_4$-doped anatase TiO_2 thin films is considered mainly due to the radiative recombination of impurity and defect trapped excitons versus self-trapped excitons. Firstly, as a dopant, $ZnFe_2O_4$ can serve as a component in the composite film and induce impurity levels in the energy gap of the anatase TiO_2 phase. Secondly, due to the interfacial coupling between $ZnFe_2O_4$ and TiO_2 grains, $ZnFe_2O_4$ can induce lattice defects on the surface of TiO_6 octahedra, which will serve as the centres of bound excitons. All these factors will increase the

probability of exciton formation and radiation transition.

In summary, we have studied the effect of $ZnFe_2O_4$ doping on the optical properties of TiO_2 thin films. We found that the absorption edge of TiO_2 thin films and $ZnFe_2O_4$-doped TiO_2 composite films exhibits a blueshift with decreasing annealing temperature. The absorption edge of composite films has moved to the visible spectrum range. A very large redshift of the absorption edge of $ZnFe_2O_4$-doped TiO_2 composite films occurs in comparison with TiO_2 thin films. The redshift is considered to be mainly induced by the interface effect between $ZnFe_2O_4$ and TiO_2 particles. The absorption edge of TiO_2 thin films can be modified in a large range upon the addition of $ZnFe_2O_4$ nanoparticles and post-deposition annealing. We demonstrated that the doping of $ZnFe_2O_4$ can enhance the photoluminescence of the anatase TiO_2 thin films at room temperature, and we believe that the strong PL band in anatase TiO_2 thin films doped with $ZnFe_2O_4$ is due to radiative recombination of impurity and defect trapped excitons versus self-trapped excitons.

References

[1] O'Regan B and Gratzel M 1991 *Nature (London)* **353** 737

[2] Anpo M, Shima T, Kodama S and Kubokama Y 1987 *J. Phys. Chem.* **91** 4305

[3] Kavan L, Stoto T, Gratzel M, Fitzmaurice D and Shklover V 1993 *J. Phys. Chem.* **97** 9493

[4] Serpone N, Lawless D and Khairutdinov R 1995 *J. Phys. Chem.* **99** 16 646

[5] Tang H, Berger H, Schmid P E and Levy F 1993 *Solid State Commun.* **87** 847

[6] Kocher H, Däubler T K *et al.* 1998 *Appl. Phys. Lett.* **72** 650

[7] Arango A C, Carter S A and Brock P J 1999 *Appl. Phys. Lett.* **74** 1698

[8] Yuan Z H, You W and Zhang L D 1998 *Chin. Phys. Lett.* **15** 535

[9] Liu F M and Zhang L D 2000 *Chin. Phys. Lett.* **17** 142

[10] Yang L, Li G H, Zheng M J and Zhang L D 2000 *Chin. Phys. Lett.* **17** 592

[11] Li G H, Yang L, Jing Y X and Zhang L D 2000 *Thin Solid Films* **368** 164

[12] Serpone N, Lawless D and Khairutdinov R 1995 *J. Phys. Chem.* **99** 16646

[13] Deloach J D, Scarel G and Aita C R 1999 *J. Appl. Phys.* **85** 2377

[14] Tang H, Berger H, Schmid P E and Levy F 1993 *Solid State Commun.* **87** 847

[15] Saraf L V, Patil S LI and Ogale S B 1998 *J. Mod. Phys.* **12** 2635