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LETTER TO THE EDITOR

Photoluminescence of anatase TiO₂ thin films achieved by the addition of ZnFe₂O₄

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Abstract

We report on the photoluminescence (PL) of anatase TiO₂ thin films caused by the addition of ZnFe₂O₄ nanoparticles prepared by the radio-frequency sputtering method. X-ray diffraction and PL analyses illustrate that there is a very strong band of PL from the anatase TiO₂ thin films caused by the addition of ZnFe₂O₄ at both room and low temperatures; the anatase TiO₂ thin films without this addition show no PL. There is a very weak band of PL from rutile TiO₂ thin films. The strong PL band for the anatase TiO₂ thin films with the addition of ZnFe₂O₄ may be due to increased localization of impurity- and defect-trapped excitons.

1. Introduction

The recent increase in interest in TiO₂ has been prompted 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] for anatase TiO₂ materials have been areas of intensive research activity. TiO₂ is a wide-band-gap semiconductor (3.03 eV for rutile and 3.18 for anatase) and can only absorb about 5% of the sunlight in the ultraviolet light region, which substantially limits its practical application because of the lower degree of utilization of sunlight and hence lower quantum yield. Many studies have been devoted to the enhancement of the photoresponse and improvement of the photoactivity of TiO₂ by dye-sensitizing, additions, surface modification and deposition of noble metals [6–11]. In our previous study it was demonstrated that the addition of ZnFe₂O₄ nanoparticles can sensitize TiO₂ to visible light [12]. In the present letter we will report on the photoluminescence (PL) of TiO₂ thin film with the addition of 2 wt% ZnFe₂O₄ (ZnFe₂O₄/TiO₂ composite film). It was found that anatase TiO₂ thin film with the addition of ZnFe₂O₄ shows significant PL intensity at both room temperature and liquid nitrogen temperature.

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2. Experimental procedure

The sample preparation method is the same as that in the previous study, except that in all cases a quartz substrate was used instead of glass substrate [12]; it is described briefly here. The deposition is carried out in a sputtering unit equipped with a radio-frequency generator. Pure TiO_2 and $\text{TiO}_2 + 2 \text{ wt}\% \text{ ZnFe}_2\text{O}_4$ (all with purity of 99.99%) composite targets of 60 mm diameter fixed on a magnetron-effect cathode were used. The composite target is a mixture of TiO_2 and ZnFe_2O_4 powder prepared by the chemical coordination method; both targets were sintered at 1350°C in air for 2 h. Post-deposition annealing was performed in flowing oxygen at different temperatures for 2 h. The structural properties were assessed by means of x-ray diffraction (XRD) (with a Philips PW 1710 diffractometer, using $\text{Cu K}\alpha_1$ radiation). Room temperature (RT) PL measurements were carried out using an Ar lamp and a wavelength of 320 nm for excitation. Low-temperature PL tests were performed at 77 K (LNT), in which an Ar laser with a wavelength of 413.1 nm was used for excitation.

3. Results and discussion

The XRD analysis indicates that when the annealing temperature is lower than 250°C the TiO_2 thin films are in an amorphous state; upon annealing between 250°C and 800°C the anatase phase forms; on annealing at temperature above 950°C a complete rutile phase forms. The sample that was heat treated at 900°C consists of a major rutile phase plus a minor anatase phase. In contrast, the crystallization temperature of $\text{TiO}_2/\text{ZnFe}_2\text{O}_4$ composite films moves to a higher temperature of about 450°C , the sample that was heat treated at 650°C mainly consists of an anatase phase plus a minor rutile phase and the complete anatase–rutile transformation occurs at 800°C , as shown in figure 1.

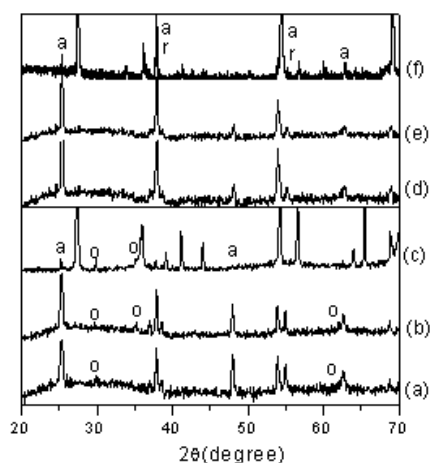


Figure 1. XRD curves for $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ films annealed at (a) 450°C , (b) 650°C and (c) 800°C and for TiO_2 films annealed at (d) 450°C , (e) 800°C and (f) 900°C for 2 h. The labels a, r and o indicate anatase phase TiO_2 , rutile phase TiO_2 and spinel ZnFe_2O_4 respectively. For curves (a), (b), (d) and (e) the unlabelled peaks arise from TiO_2 anatase phase and for (c) and (f) from TiO_2 rutile phase.

Figure 2 shows the room temperature PL spectra of TiO_2 thin film annealed at 900°C (curve (1), major rutile phase) and $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ composite film annealed at 650°C (curve (2), major anatase phase). The rutile TiO_2 thin film shows a weak broad PL band ranging from

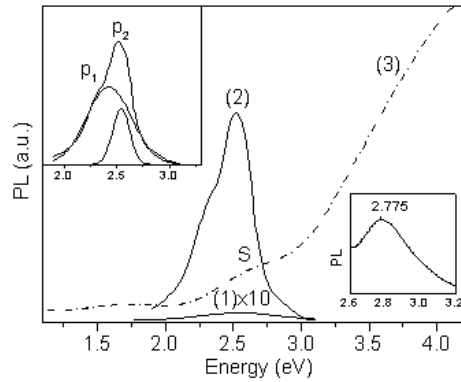


Figure 2. Room temperature PL spectra for TiO_2 film annealed at $900\text{ }^\circ\text{C}$ (curve (1)) and $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ composite film annealed at $650\text{ }^\circ\text{C}$ (curve (2)); the upper left inset shows the corresponding Gaussian fitting of the PL band; curve (3) is the corresponding absorption spectrum and the lower right inset shows the corresponding excitation spectrum (monitored at 488 nm (2.54 eV)).

2 eV to 3 eV with a maximum at 2.54 eV (488 nm). No PL was found for samples annealed at temperatures below $800\text{ }^\circ\text{C}$ (pure anatase phase). But for the anatase TiO_2 thin film with the addition of ZnFe_2O_4 a very strong PL band appears together with a shoulder; see curve (2) in figure 2. The best Gaussian fit of the PL band gives two peaks situated at p_1 , 2.43 eV (510 nm), and p_2 , 2.54 eV (488 nm). It can also be seen that the PL peak for the anatase TiO_2 thin film with the addition of ZnFe_2O_4 is coincident with the absorption shoulder marked S in figure 1 (curve (3)). This result indicates that the strong PL band corresponds to the unusually strong absorption in the same wavelength region. The lower right inset in figure 2 shows the excitation spectrum of the emissions for the composite film, in which the maximum emission occurs at excitation 447 nm (2.774 eV).

Figure 3(a) shows the LNT PL spectra of TiO_2 thin film annealed at $900\text{ }^\circ\text{C}$ (curve (1), major rutile phase) and $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ composite film annealed at $450\text{ }^\circ\text{C}$ (curve (2), pure

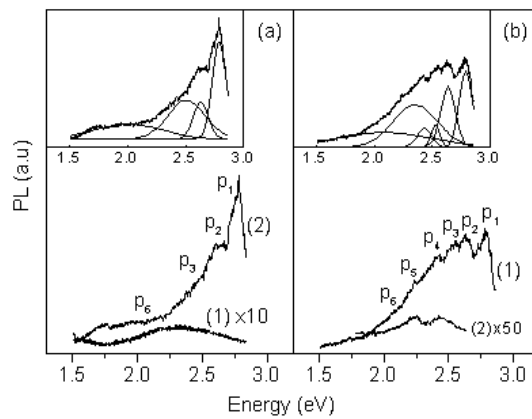


Figure 3. 77 K PL spectra for (a) TiO_2 film annealed at $900\text{ }^\circ\text{C}$ (curve (1)) and $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ film annealed at $450\text{ }^\circ\text{C}$ (curve (2)); the inset shows the corresponding Gaussian fit of the PL spectra), (b) $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ film annealed at $650\text{ }^\circ\text{C}$ (curve (1)); the inset shows the corresponding Gaussian fitting) and at $800\text{ }^\circ\text{C}$ (curve (2)).

anatase phase). From this figure one can see that the PL intensity for rutile TiO_2 thin film is still very weak and broad with a maximum at 2.32 eV (534 nm), while a very strong PL band appears for the anatase TiO_2 thin film with the addition of ZnFe_2O_4 , which consists of two clear peaks and a wider shoulder. The best Gaussian fit gives four peaks marked p_1 , p_2 , p_3 and p_6 situated at 2.78 eV (446 nm), 2.62 eV (473 nm), 2.51 eV (494 nm) and 2.00 eV (620 nm), respectively; see the inset in figure 3(a). When the annealing temperature was increased to 650 °C for $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ composite film (curve (1) in figure 3(b), major anatase phase plus minor rutile phase), the PL peak intensity slightly decreased, but the overall intensity of the PL band slightly increased. The PL peak position hardly changes and two more peaks appear. The best Gaussian fit (the inset in figure 3(b)) gives six PL peaks marked p_1 , p_2 , p_3 , p_4 , p_5 and p_6 situated at 2.79 eV (444 nm), 2.63 eV (471 nm), 2.53 eV (490 nm), 2.43 eV (510 nm), 2.35 eV (528 nm) and 2.10 eV (590 nm), respectively. On further increase of the annealing temperature to 800 °C for $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ composite film (curve (2) in figure 3(b), pure rutile phase), only a very weak PL band appears, which consists of two peaks situated at 2.44 eV (508 nm) and 2.23 eV (556 nm) respectively. It is noted that the separations between p_2 and p_3 , between p_3 and p_4 and between p_4 and p_5 correspond to the energies of 823, 800 and 668 cm^{-1} , respectively, which are nearly the same as those observed in the IR measurement (see figure 4). The IR absorption peaks at 509, 611, 672, 739 and 960 cm^{-1} arise from TiO_2 and those at 556, 611, 672, 814 and 885 cm^{-1} arise from ZnFe_2O_4 . Si (there is a strong IR absorption peak for Si at 640 cm^{-1}) superimposes the peak at 640 cm^{-1} . The relatively strong absorption peaks located at 885, 739 and 611 cm^{-1} in the IR spectrum are very close to the energy positions of 823, 800 and 668 cm^{-1} for the PL peaks in curve (1) in figure 3(b) (the difference is about 60 cm^{-1} , which might be due to the broad PL peaks measured at 77 K). This means that the small PL peaks (p_2 , p_3 , p_4 and p_5) superimposed on the strong PL band (p_1) are phonon replicas. The weak PL peak (p_6) may arise from the minor rutile TiO_2 phase.

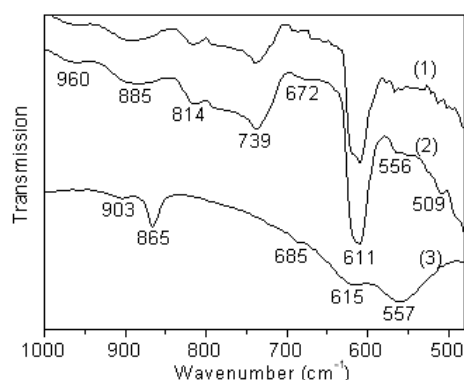


Figure 4. FTIR spectra, measured at room temperature, for anatase TiO_2 with and without the addition of ZnFe_2O_4 and for ZnFe_2O_4 nanopowders deposited on single-crystal Si annealed at 650 °C. Curve (1): pure anatase TiO_2 ; curve (2): anatase TiO_2 with the addition of ZnFe_2O_4 ; curve (3): ZnFe_2O_4 nanoparticles.

De Haart and Blasse [13] studied the PL of TiO_2 rutile single crystals. The corresponding spectrum recorded at 4.8 K under band-gap excitation was seen to start on the short-wavelength side with a sharp line at 412 nm (3.01 eV) followed by two other lines at 419 nm (2.96 eV) and 427 nm (2.90 eV). These emission lines were observed to be superimposed on a broad emission band centred at 485 nm (2.56 eV). De Haart and Blasse attributed the 421 nm line to free-exciton emission and the latter two lines to phonon repetitions of the free-exciton line.

They ascribed the broad PL band to bound-exciton emission due to the trapping of free excitons by titanate groups near defects.

Tang *et al* [14] examined the PL of TiO₂ anatase single crystals and found that the band-gap excitation results in visible broad-band PL, which is interpreted as the emission of self-trapped excitons located or trapped on TiO₆ octahedra.

Saraf *et al* [15] studied the RT PL properties of nanophase TiO₂. They found a narrow PL spectrum at 3.01 eV for anatase TiO₂ powder and a broad band spread over the entire visible range for the anatase and rutile phase mixture. They found that the narrow PL spectrum for the anatase phase compares favourably with the reported anatase spectrum that originated from the excitons self-trapped on TiO₆ octahedra, and they ascribed the broad PL band for the phase mixture to oxygen-related defects in TiO₆ octahedra. They also found that the overall intensity of the broad PL spectrum increases with increasing annealing temperature.

In our case, we found that there is a weak PL band ranging from 2 eV to 3 eV for rutile TiO₂ thin films and that there is no PL for anatase TiO₂ thin film without the addition of ZnFe₂O₄. However, for the anatase TiO₂ thin films with the addition of ZnFe₂O₄ there is a very strong PL band between 2.0 eV and 3.0 eV. This strong PL band has three features:

- (a) superimposed on the PL band are indications of clear PL peaks; the number of peaks increases and the peak position hardly changes with increasing annealing temperature;
- (b) the maximum intensity of the PL band slightly decreases, but the overall intensity of the PL spectrum increases with increasing annealing temperature; this spectrum has the same features as that in reference [12];
- (c) the peak position moves to high energy when the measuring temperature changes from RT to LNT.

A similar PL band has also been observed for TiO₂ ultrafine particles with a surface dipole layer [16].

To discover the origin of the strong PL band for the anatase TiO₂ thin films with the addition of ZnFe₂O₄, some thin-film samples consisting of either SiO₂ + 5 wt% ZnO or SiO₂ + 5 wt% ZnFe₂O₄ were prepared; the PL analysis indicated that there is no PL from the samples annealed at either 450 °C or 650 °C. This result proved that the strong PL band does not arise from either ZnO or ZnFe₂O₄ nanoparticles—it originates from the anatase TiO₂ with ZnFe₂O₄ added.

It has been proved by experiment and theoretical calculations that TiO₂ has a direct forbidden gap, but it is almost degenerate with an indirect allowed transition. The indirect allowed transition in TiO₂ dominates in the optical absorption just above the absorption edge [17–19] and, thus, the photoluminescence intensity of pure TiO₂ is very weak. One way to improve the optical properties of an indirect-band-gap material is by means of spatial localization of the carriers. This increases the uncertainty in momentum and thereby enhances the optical transitions without the use of phonons. The strong PL band for the anatase TiO₂ thin films with the addition of ZnFe₂O₄ is considered to be mainly due to the enhanced localization of impurity- and defect-trapped excitons. Firstly, as an additive, ZnFe₂O₄ can serve as a component in the film and induce impurity levels in the energy gap of the anatase TiO₂ phase. Secondly, due to the interfacial coupling between ZnFe₂O₄ and TiO₂ grains, ZnFe₂O₄ can induce lattice defects on the surface of TiO₆ octahedra, which will serve as centres for bound excitons. Both of these features will enhance the exciton localization.

4. Conclusion

In summary, we have proved that through the addition of ZnFe₂O₄ very intense photoluminescence from the anatase TiO₂ can be achieved at both room temperature and liquid

nitrogen temperature. Furthermore, the absorption edge of TiO₂ thin films can be modified over a large range by the addition of ZnFe₂O₄. ZnFe₂O₄ is an effective sensitizer for the enhancement of the photoresponse and improvement of the photoactivity of TiO₂. We suggest that the strong PL band for anatase TiO₂ thin films with the addition of ZnFe₂O₄ is due to enhanced localization of impurity- and defect-trapped excitons.

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