



Influence of annealing temperature on the photoluminescence property of ZnO thin film covered by TiO₂ nanoparticles

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ABSTRACT

In this work, ZnO thin films covered by TiO₂ nanoparticles (labeled as TiO₂-ZnO thin films) were prepared by electron beam evaporation. The influence of annealing temperature on the photoluminescence property of the samples was studied. The structures and surface morphologies of the samples were analyzed by X-ray diffraction (XRD) and atomic force microscope, respectively. The photoluminescence was used to investigate the fluorescent properties of the samples. The measurement results show that the ultraviolet emission of ZnO thin films is largely enhanced after they are covered by TiO₂ nanoparticles, while the green emission is suppressed. However, when the annealing temperature is relatively high (≥ 500 °C), the intensity of ultraviolet emission drops off and a violet emission peak along with a blue emission peak appears. This is probably connected with the atomic interdiffusion between TiO₂ nanoparticles and ZnO thin film. Therefore, selecting a suitable annealing temperature is a key factor for obtaining the most efficient ultraviolet emission from TiO₂-ZnO thin films.

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1. Introduction

With the advance of information society, the demand for short-wavelength optoelectronic devices becomes more and more urgent at present. As an important semiconductor material, ZnO has a wide direct band-gap of 3.37 eV and a large exciton binding energy of 60 meV. Such a large exciton binding energy makes its excitons very stable and many research results also show that ZnO materials have high-efficiency exciton emission at room temperature or even at higher temperatures. Therefore, ZnO is an ideal material for the fabrication of short-wavelength optoelectronic devices, especially for the fabrication of ultraviolet light-emitting devices such as ultraviolet light-emitting diodes [1], ultraviolet lasers [2], etc. So far, a variety of nanostructured ZnO materials such as nanodots, nanorods, nanobelts, nanotubes, etc. have been fabricated, but ZnO thin film is still the ZnO material, which is studied most widely and most deeply at present. That is because the preparation technology of one- and three-dimensional nanostructured ZnO materials is usually complicated and consequently these ZnO nanostructured materials are difficult to be massively produced under present conditions. Compared with ZnO nanostructured materials, ZnO thin film has some advantages like the relatively simple preparation technology, good crystalline

quality, being able to be massively produced, etc., which are very important for commercial application of ZnO materials. As for the fabrication of ultraviolet light-emitting devices based on ZnO thin film, one problem which should be solved first is how to improve ultraviolet emission of ZnO thin film and quench its visible emissions at the same time. To solve this problem, two methods have been adopted. One is optimizing the preparation parameters to improve the crystalline quality of ZnO thin film, the other is adopting surface modification [3,4] or doping [5]. For example, some researchers utilized metal layer to cap the ZnO thin film; the ultraviolet emission can be enhanced when the emission energy of ZnO matches closely with the surface plasma of metal layer. What is more, other researchers adopted some metal oxides to modify the surface of ZnO materials [6–8] and the ultraviolet emission is also enhanced. In these metal oxides, TiO₂ is an important material, which has some characteristics similar to ZnO [9]. TiO₂-ZnO compound materials can be used in many applications [10,11]. In our previous work [9], our group studied the effect of TiO₂ buffer layer on the structural and optical properties of ZnO thin film and found the ultraviolet emission was enhanced to some degree after a TiO₂ buffer layer was used. Furthermore, we also noticed that Lin et al. [6] utilized TiO₂ nanoparticles to modify the surface of ZnO nanorods and the ultraviolet emission of ZnO nanorods was greatly enhanced. In this work, in order to more deeply understand the effect of TiO₂ on the luminescent property of the ZnO thin film, we prepared ZnO thin film covered by TiO₂ nanoparticles and investigated the

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effect of annealing temperature on the photoluminescence property of the samples.

2. Experiment

ZnO thin films and TiO₂ capping layer were deposited by electron beam evaporation (PMC90S, Protech Korea Ltd.). The deposition process was similar to that described in literature [9]. The raw materials are high-purity (99.999%) ZnO and TiO₂ particles. The substrate material is glass. Before deposition, the deposition chamber was evacuated to a base pressure of 2.66×10^{-3} Pa. First, ZnO thin films were deposited on glass substrates which had been cleaned thoroughly and dried. After ZnO thin films reached a desired thickness, TiO₂ capping layer was then deposited directly on ZnO thin films. Some deposition parameters are listed in Table 1. Under the same conditions, a bare ZnO thin film (150 nm) and a TiO₂ thin film (170 nm) were also deposited on glass substrates; and they were annealed in air at 300 °C for 30 min. The as-grown TiO₂-ZnO thin films were annealed in air at 300, 400 and 500 °C for 30 min.

The crystal phase and crystalline orientation of the samples were analyzed by an X-ray diffractometer (Bruker D8 Advance). The surface morphologies were observed by an atomic force microscope (CSPM4000) in contact mode; the scanning area was $8 \mu\text{m} \times 8 \mu\text{m}$. The transmittance was measured by a UV-visible spectrophotometer (Lambda 950). The photoluminescence spectra were recorded by a fluorophotometer (FluoroMax-2) with an excitation wavelength of 325 nm.

3. Results and discussion

3.1. The influence of annealing temperature on the microstructure of TiO₂-ZnO thin film

Fig. 1 shows the XRD patterns of TiO₂-ZnO thin films annealed at different temperatures. From Fig. 1, it can be seen that all the samples have a strong diffraction peak located at 34.46° or so, which corresponds to the diffraction of the (0 0 2) plane of ZnO. It means the deposited ZnO thin films are hexagonal wurtzite structures and have a preferential orientation along the *c*-axis perpendicular to the substrate surface. Besides the (0 0 2) peak, they also have a weak diffraction peak located at 48.3° , which corresponds to the (2 0 0) diffraction peak of anatase-structured TiO₂ [12]. This indicates that the TiO₂ layer is composed of anatase-structured TiO₂ crystals. It should be pointed out that besides the (2 0 0) peak, the TiO₂ layer also has a very weak (1 0 1) peak (not shown here). In most cases, the (1 0 1) peak is stronger than the (2 0 0) peak for anatase-structured TiO₂ thin films. However, here the (1 0 1) peak is weaker than the (2 0 0) peak. It is similar to the XRD pattern of TiO₂ thin film deposited by Iida et al. at total gas pressure 266 Pa [12]. It is well-known that the variation of the diffraction peaks of TiO₂ thin films mainly depends on the deposition conditions, annealing treatment and substrates. For our samples, that the (1 0 1) peak is weaker than the (2 0 0) peak is thought to be mostly connected with the deposition conditions, namely the working pressure and substrate

temperature. With the increase of annealing temperature (up to 400 °C), the intensity of the (0 0 2) peak is gradually increased and the full width at half maximum (FWHM) is somewhat decreased, indicating the crystalline quality of ZnO thin film is improved. The FWHM of the (0 0 2) peaks of the samples is shown in Fig. 2. However, when the annealing temperature is raised up to 500 °C, the intensity of the (0 0 2) peak drops a little. Similarly, the intensity of the (2 0 0) peak is also increased when the samples are annealed at 300 and 400 °C, and dropped when annealed at 500 °C. This means the crystalline quality of ZnO thin film and TiO₂ capping layer decline after annealed at 500 °C. It is probably connected with the enhanced atomic diffusion between ZnO thin

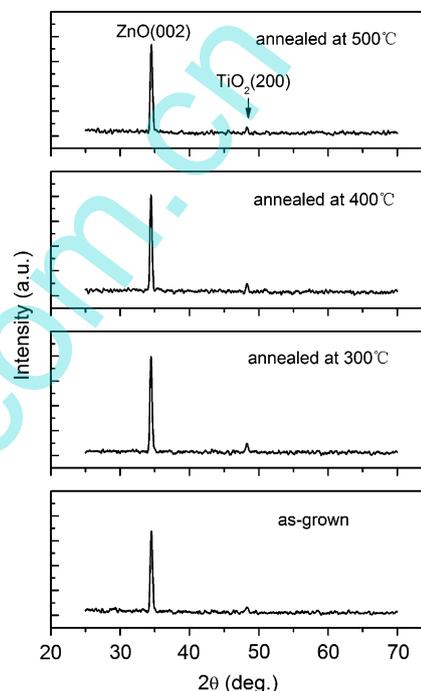


Fig. 1. XRD patterns of TiO₂-ZnO thin films.

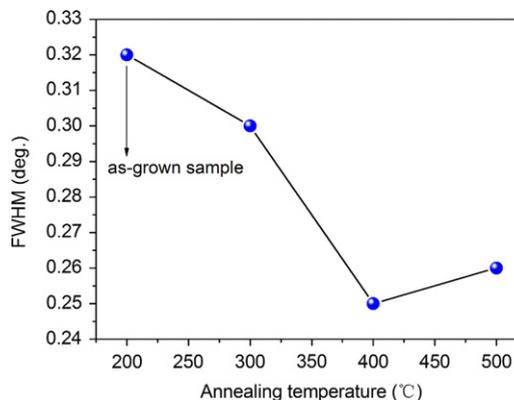


Fig. 2. The FWHM of the (0 0 2) peak of the samples.

Table 1
The deposition parameters.

	Substrate temperature (°C)	Working pressure	Thickness (nm)	Pressure ratio (Ar/O ₂)	Electron gun voltage (kV)	Working current (mA)
ZnO	250	3.0×10^{-2} Pa	150	1:2	7.11	78
TiO ₂	250	1.7×10^{-2} Pa	20	0 (no Ar)	7.11	246

film and TiO₂ capping layer. When TiO₂-ZnO thin film is annealed at 500 °C, due to the high temperature, the atoms can obtain enough energy to move. As a result, the interdiffusion motion between ZnO thin film and TiO₂ capping layer is strengthened. Some Ti atoms probably move into ZnO thin film and enter lattices to replace Zn²⁺. Because the ionic radiuses of Zn²⁺ and Ti⁴⁺ are different, excess Ti⁴⁺ replacing Zn²⁺ will lead to lattice distortion, which will give rise to stress in ZnO thin film and consequently deteriorate the crystallization quality. The research result of Lin et al. [13] also indicates that Ti-doping deteriorate the crystalline quality of ZnO thin film. In addition to the above reason, the increased interface defects may be another reason for the decline of the crystalline quality of ZnO thin film and TiO₂ capping layer.

Fig. 3 presents the surface morphologies of the bare ZnO thin film (a) and TiO₂-ZnO thin films ((b), (c) and (d)). Obviously, the surface morphologies of TiO₂-ZnO thin films are different from that of the bare ZnO thin film. This is a result of TiO₂ capping. Comparing Fig. 3(a) with (b), we can see that the ZnO thin film is covered by a layer of TiO₂ nanoparticles. When the TiO₂-ZnO thin film is annealed at 400 °C, its surface morphology is a little changed. However, after TiO₂-ZnO thin film is annealed at 500 °C,

its surface morphology is much changed. On the one hand, it seems that the TiO₂ nanoparticles grow up; on the other hand, compared with the sample annealed at 300 °C, its average surface roughness decreases from 4.29 to 2.56 nm. These changes are all associated with atomic migration.

3.2. The influence of annealing temperature on the photoluminescence property of TiO₂-ZnO thin film

Fig. 4 shows the photoluminescence spectra of TiO₂-ZnO thin films and the bare ZnO thin film. For the bare ZnO thin film, it has an ultraviolet emission peak centered at 384 nm, which originates from the recombination of free exciton [14,15]. Besides this ultraviolet emission peak, it also has a wide and weak green emission band. Although the green emission behavior of ZnO materials has been widely studied, its emission mechanism is unclear as yet. Some researchers suggest that the green emission is probably connected with oxygen vacancy defects [16–18] in ZnO materials. Compared with the bare ZnO thin film, the ultraviolet emission of TiO₂-ZnO thin films is largely enhanced and the green emission is suppressed. With the increase of

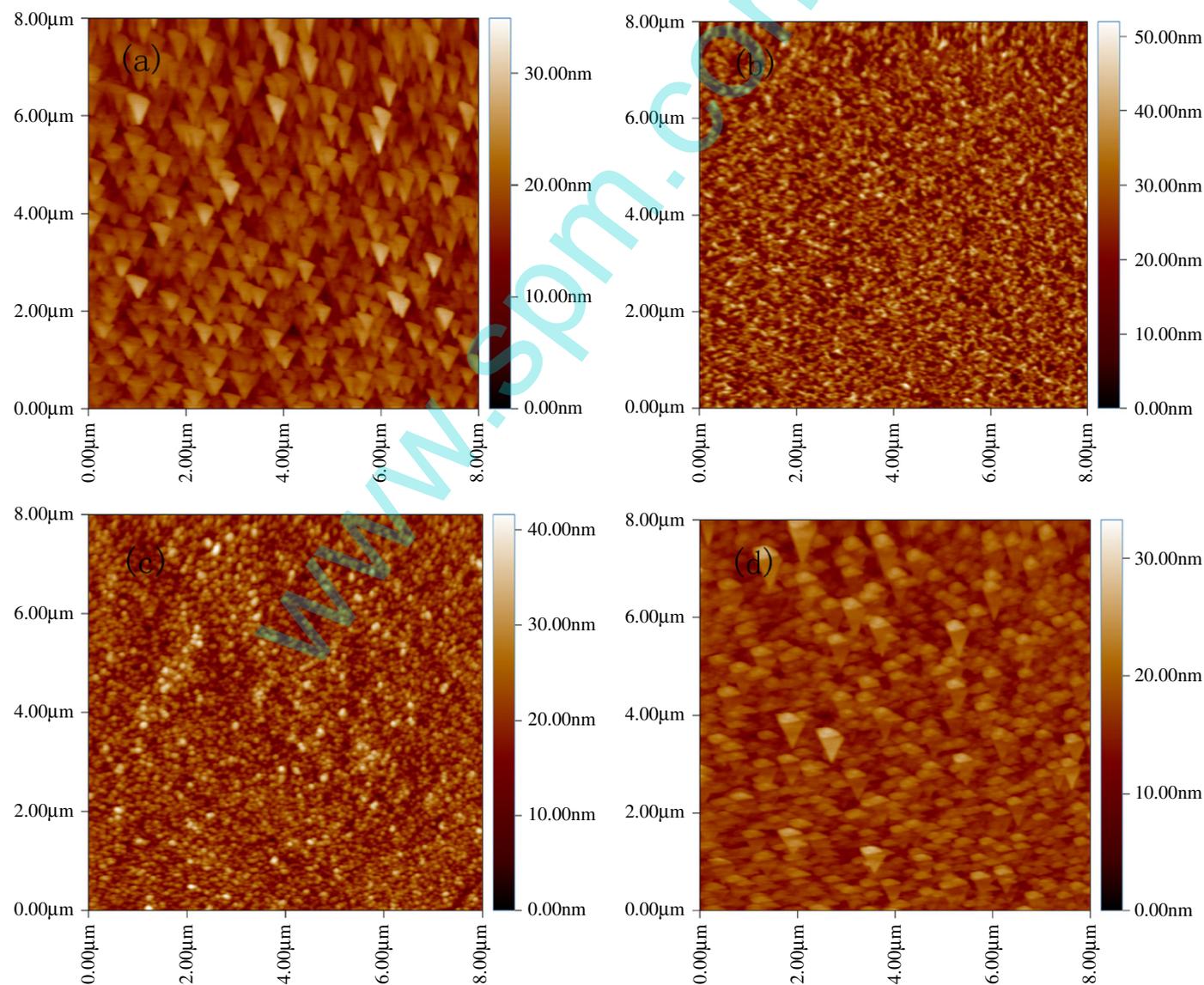


Fig. 3. Surface morphologies of the bare ZnO thin film (a) and TiO₂-ZnO thin films annealed at 300 °C (b), 400 °C (c) and 500 °C (d).

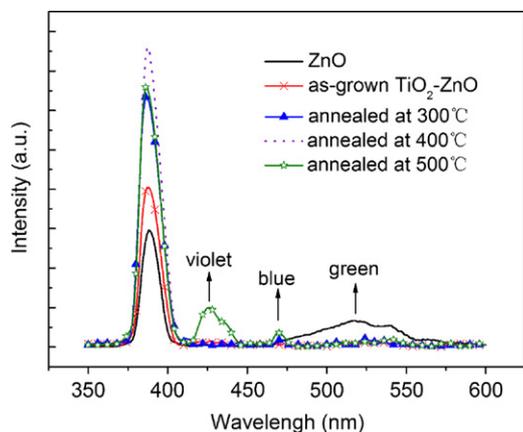


Fig. 4. Photoluminescence spectra of the bare ZnO thin film and TiO₂-ZnO thin films.

annealing temperature, the ultraviolet emission of TiO₂-ZnO thin film gradually increases until 400 °C. However, it is reduced when the annealing temperature increases up to 500 °C and a violet emission peak along with a blue emission peak occurs. As for the violet and blue emissions of ZnO materials, they have been reported previously [19–22]. Some research results show that the violet emission of ZnO may be resulting from the interface traps near grain boundaries [19,20] and the blue emission is probably connected with Zn interstitial defects [22]. The above microstructure analyses show that when TiO₂-ZnO thin film is annealed at 500 °C, the atomic interdiffusion between ZnO thin film and TiO₂ capping layer is strengthened, which may lead to more interface defects and at the same time some interstitial Zn or/and Ti atoms occur in ZnO thin film. As a result, these defects result in the visible emissions.

Here, the enhanced ultraviolet emission of TiO₂-ZnO thin film is connected with the following three factors: (1) the surface passivation effect due to TiO₂ nanoparticles capping; (2) the improved crystalline quality owing to annealing; (3) the fluorescence resonance energy transfer (FRET) between TiO₂ nanoparticles and ZnO thin film [6]. Comparing the photoluminescence spectrum of the bare ZnO thin film with that of TiO₂-ZnO thin film annealed at 300 °C, it is clearly seen that the ultraviolet emission of TiO₂-ZnO thin film is largely enhanced, while the green emission is suppressed. This indicates that the TiO₂-nanoparticle capping plays an important role for the enhanced ultraviolet emission and an FRET plays a dominant role [6] in the first and third factors.

FRET is an important fluorescence technique and has been widely used in biological and supramolecular studies [23,24]. The occurrence of an FRET has to satisfy the following three conditions [6,23]: (1) donor and acceptor have to be close enough; (2) the absorption spectrum of acceptor has to overlap with the fluorescence spectrum of donor; (3) donor and acceptor transition dipole orientation should contain a parallel component. Here, the donor and acceptor are TiO₂ and ZnO, respectively. The first and third conditions can be satisfied. Fig. 5 gives the transmittance spectra of ZnO, TiO₂, and TiO₂-ZnO thin films (the inset is the photoluminescence spectrum of TiO₂ thin film). From Fig. 5, it can be seen that the outline of the transmittance spectrum of TiO₂-ZnO thin film has some change compared with that of the bare ZnO thin film. This is the result of the modulation of TiO₂ capping layer. But its absorption edge does not shift and still lies at ~370 nm. The fluorescence emission center of the TiO₂ layer is located at ~365 nm. The absorption spectrum of ZnO thin film just has some ranges to overlap with the fluorescence spectrum of the TiO₂ capping layer. This means the second

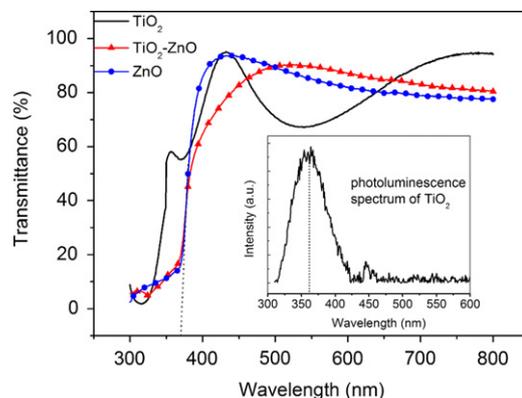


Fig. 5. Transmittance of the bare ZnO thin film, TiO₂-ZnO thin film and TiO₂ thin film (the inset is the photoluminescence spectrum of TiO₂ thin film).

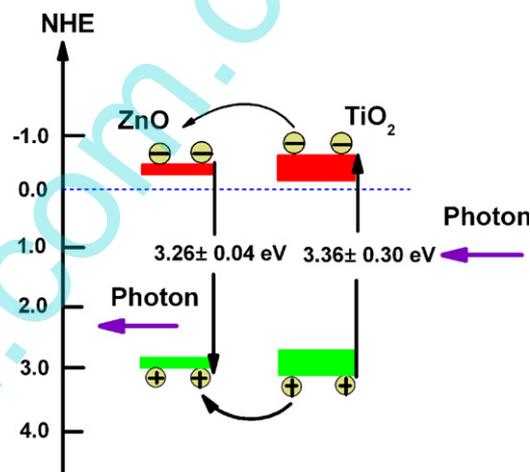


Fig. 6. Energy band alignment of TiO₂-ZnO composite.

condition for the occurrence of an FRET is also satisfied. Therefore, it is reasonable that the FRET is mainly responsible for the enhanced ultraviolet emission.

Fig. 6 shows the band alignment diagram of TiO₂-ZnO [6]. After the excitation of electron-hole pairs in TiO₂ nanoparticles, through the resonance effect, the energy is easily transferred to ZnO thin film. As a result, the ultraviolet emission of ZnO thin film is largely enhanced. The more detailed explanation about the FRET process is described in literature [6].

4. Conclusion

In this work, the bare ZnO thin film and TiO₂-nanoparticle capped ZnO thin film were prepared by electron beam evaporation. The authors mainly studied the influence of annealing temperature on the photoluminescence property of TiO₂-ZnO thin film. The results show that TiO₂-nanoparticle capping largely enhances the ultraviolet emission of ZnO thin film and suppresses its green emission. However, when the annealing temperature reaches a relatively high temperature like 500 °C, an ultraviolet emission decreases and violet and blue emissions appear. This is probably connected with the atomic interdiffusion between TiO₂ nanoparticles and ZnO thin film, which leads to more interface defects and internal point defects. Therefore, it is very important to select a suitable annealing temperature for obtaining the most efficient ultraviolet emission from TiO₂ to ZnO thin film.

This TiO₂–ZnO composite thin film can be used to fabricate high-efficiency ultraviolet light-emitting devices.

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