

Enhanced ultraviolet emission from ZnO thin film covered by TiO₂ nanoparticles

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Received December 22, 2008

A ZnO thin film covered by TiO₂ nanoparticles is prepared by electron beam evaporation. The structure and surface morphology of the sample are analyzed by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. Photoluminescence is used to investigate the fluorescent property of the sample. The results show that the ultraviolet (UV) emission of the ZnO thin film is greatly enhanced after it is covered by TiO₂ nanoparticles while the green emission is suppressed. The enhanced UV emission mainly results from the fluorescence resonance energy transfer (FRET) between ZnO thin film and TiO₂ nanoparticles. This TiO₂-ZnO composite thin film can be used to fabricate high-efficiency UV emitters.

OCIS codes: 240.6675, 250.5230, 260.5740.

doi: 10.3788/COL20090710.0953.

ZnO is an important II-VI group compound semiconductor. At room temperature, it has a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV. Such a large exciton binding energy makes ZnO have a strong excitonic emission performance at room temperature or even at higher temperatures. Therefore, it is an ideal material for the fabrication of ultraviolet (UV) light-emitting devices. Zu *et al.* reported the excitonic stimulated emission from ZnO thin films at room temperature^[1,2], which made ZnO become a worldwide research focus rapidly. In the past decade, the preparation techniques and the optical and electrical properties of ZnO thin films have been widely studied. However, for the fabrication of UV light-emitting devices based on ZnO thin films, there are still some problems needing to be solved. Among these problems, how to improve the UV emission of ZnO thin films is the most important one. It is well known that ZnO thin films usually exhibit relatively strong visible emissions due to various surface states and intrinsic point defects such as oxygen vacancy, Zn interstitial, etc. The visible emissions decrease the excitonic emission at a large extent. Therefore, in order to obtain excellent UV light-emitting devices, it is necessary to enhance the UV emission of ZnO thin film and quench its visible emissions at the same time. To solve this problem, some methods have been adopted, such as improving the quality of ZnO thin films through optimizing the preparation technology or doping^[3]. Although these methods can improve the UV emission to some degree, more enhancements are still needed. In recent years, some groups utilized metal layer^[4,5] or metal oxides^[6–8] to modify the surface of ZnO thin films or ZnO nanostructures and found that the UV emission of ZnO materials could be greatly enhanced. Among these metal oxides used to modify ZnO materials, TiO₂ is an important semiconductor material. The compound materials made up of ZnO and TiO₂ can be used in many fields^[9,10]. In our previous work^[11], it was found that TiO₂ buffer layer could improve the crystalline quality and enhance the UV emission of ZnO thin films to some

extent. At the same time, it was also noticed that Lin *et al.* adopted TiO₂ nanoparticles to modify the surface of ZnO nanorods and the UV emission of ZnO nanorods was greatly enhanced^[6]. In this letter, in order to more deeply understand the influence of TiO₂ on the luminescent property of ZnO thin films, we prepare a bare ZnO thin film and a TiO₂-nanoparticles-capped ZnO thin film (labeled as TiO₂-ZnO thin film) and contrastively investigate their photoluminescence (PL) properties.

The ZnO thin film and TiO₂ layer were deposited by electron beam evaporation (PMC90S, Protech Korea Ltd.). The thickness of TiO₂ capping layer was 20 nm. The deposition process was similar to that described in Ref. [11]. The substrate materials were Si (100) and glass. Some deposition parameters are listed in Table 1. A TiO₂ thin film of 170-nm thickness was also deposited on a glass substrate. All the samples were annealed in air at 300 °C for 30 min.

The crystal phase and crystalline orientation of the samples were analyzed by an X-ray diffractometer (XRD, Bruker D8 Advance). The surface morphologies were observed by an atomic force microscope (AFM, CSPM4000) in contact mode. The transmittance was measured by an UV-visible spectrophotometer (Lambda 950). The PL spectra were recorded by a fluorophotometer (FluoroMax-2) with the excitation wavelength of 325 nm.

Figure 1 shows the XRD patterns of the bare ZnO thin film and the TiO₂-ZnO thin film deposited on Si substrates. It can be seen that both of them have a

Table 1. Deposition Parameters

Film	Substrate Temperature (°C)	Working Pressure (Pa)	Thickness (nm)	Pressure ratio (Ar:O ₂)
ZnO	250	3.0×10^{-2}	150	1:2
TiO ₂	250	1.7×10^{-2}	20/170	0(no Ar)

diffraction peak located at 34.6° or so, which corresponds to the diffraction of (002) plane. This means that the prepared ZnO thin films are hexagonal wurtzite structures and preferentially oriented along the c -axis perpendicular to the substrate surface. In Fig. 1(b), there is a weak diffraction peak located at 48.3° . It corresponds to the (200) diffraction peak of TiO_2 with anatase phase. This suggests the TiO_2 covering layer is composed of anatase-structured TiO_2 crystals. Figure 2 shows the surface morphologies of the samples. It is clear from Fig. 2(b) that the ZnO thin film is covered by a layer of uniform TiO_2 nanoparticles.

Figure 3 shows the PL spectra of the samples deposited

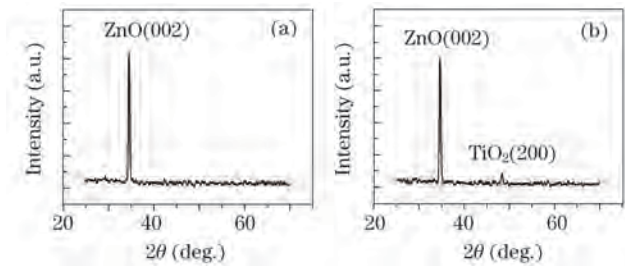


Fig. 1. XRD patterns of (a) the bare ZnO thin film and (b) TiO_2 -ZnO thin film.

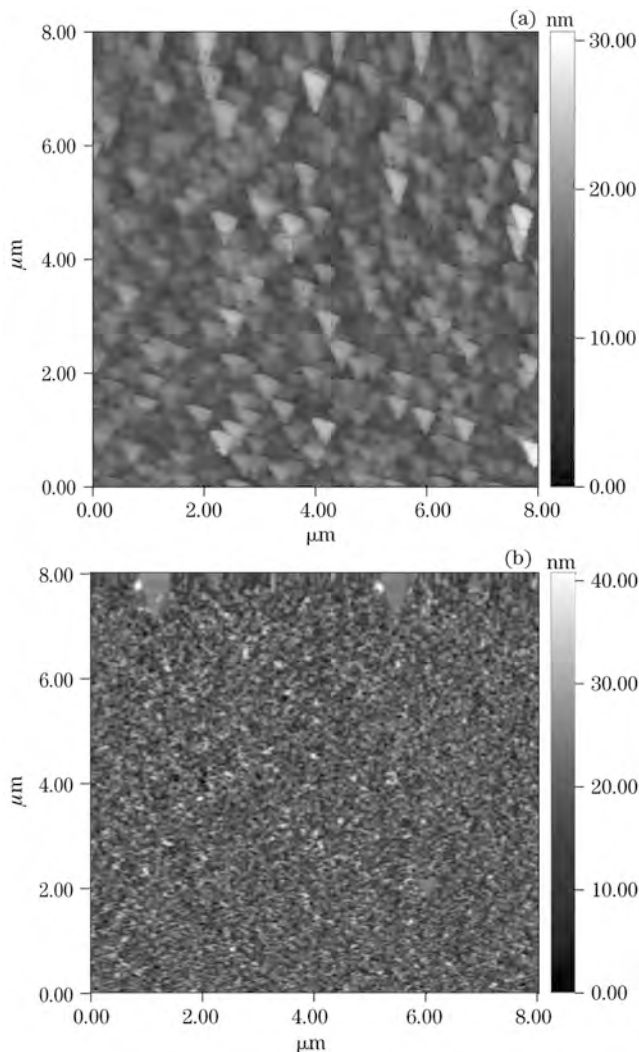


Fig. 2. Surface morphologies of (a) the bare ZnO thin film and (b) TiO_2 -ZnO thin film.

on Si substrates. For the bare ZnO thin film, it has an UV emission peak centered at 385 nm, which originates from the recombination of free excitons^[12,13]. Besides the UV emission peak, it also has a wide green emission band. The green emission of ZnO materials has been widely investigated. A lot of researchers think the green emission is mainly connected with oxygen vacancy defects^[14,15]. Compared with the bare ZnO thin film, the UV emission of TiO_2 -ZnO thin film is greatly enhanced while the green emission is suppressed. According to the explanation of Lin *et al.*^[6], the enhanced UV emission can be ascribed to two factors: the surface passivation effect due to TiO_2 nanoparticles capping, and the fluorescence resonance energy transfer (FRET) between TiO_2 nanoparticles and ZnO thin film. And the FRET plays a dominant role. The suppressed green emission is possibly attributed to the surface passivation effect due to the covered TiO_2 nanolayer^[6].

FRET is the radiationless energy transfer from an excited donor to a suitable ground-state acceptor^[16]. As an important fluorescence technique, it has been widely used in biological and medical studies^[16,17]. The occurrence of FRET has to satisfy the following three conditions^[6,17]. 1) The separation of donor and acceptor has to be close enough. 2) The absorption spectrum of acceptor has to overlap with the fluorescence spectrum of donor. 3) The donor and acceptor transition dipole orientation should contain a parallel component. Here the donor and acceptor are TiO_2 and ZnO, respectively. The first and third conditions can be satisfied. From Fig. 4, it

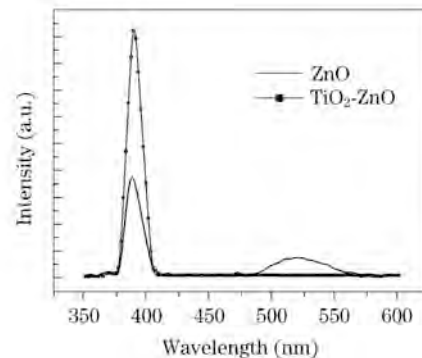


Fig. 3. PL spectra of the bare ZnO thin film and TiO_2 -ZnO thin film.

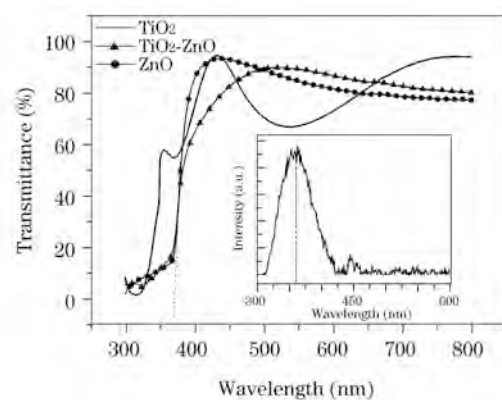


Fig. 4. Transmittance of the bare ZnO thin film, TiO_2 -ZnO thin film, and TiO_2 thin film. Inset shows the PL spectrum of TiO_2 thin film.

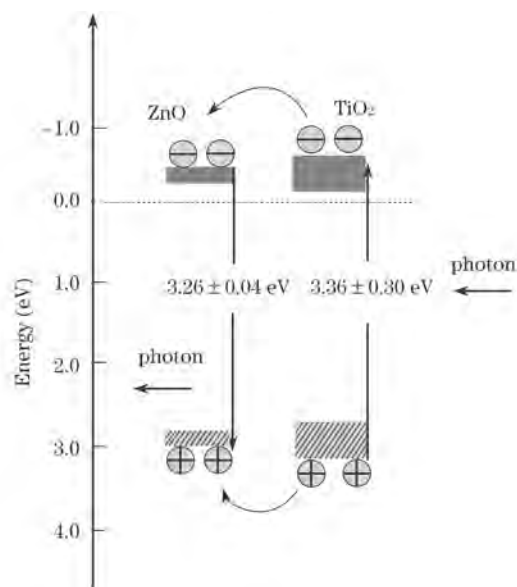


Fig. 5. Energy band alignment of ZnO/TiO₂ composite.

is clear that the absorption spectrum of ZnO thin film just has some ranges overlapping with the fluorescence spectrum of TiO₂ thin film. The positions of the dashed lines in Fig. 4 correspond to the absorption edge of ZnO thin film and the fluorescence center of TiO₂ thin film, respectively. Therefore, the second condition is also satisfied. It is reasonable to attribute the enhanced UV emission mainly to TiO₂ nanoparticles capping.

Figure 5 presents the band alignment diagram of ZnO-TiO₂^[6]. After the excitation of electron-hole pairs in TiO₂ nanoparticles, through the resonance effect, the energy is easily transferred to ZnO thin film^[6]. As a result, the UV emission of ZnO thin film is greatly enhanced. The more detailed explanation about FRET process can be found in Ref. [6].

In conclusion, the ZnO thin film covered by TiO₂ nanoparticles is prepared by electron beam evaporation. The measurement results show that the UV emission of the ZnO thin film is greatly enhanced while the visible emission is suppressed. The enhanced UV emission is mainly ascribed to the FRET between TiO₂ nanoparticles and ZnO thin film. This TiO₂-ZnO composite thin film can be used to design high-efficiency UV light emitting devices. Considering that annealing tempera-

ture and growth temperature have an important effect on the crystallinity and optical properties of ZnO thin films^[18,19], in the following work, we will study the influence of annealing temperature and growth temperature on the PL property of TiO₂-ZnO thin films.

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