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Tunable Photoluminescence of ZnO Films with Different Surfaces by The Coating of Au Nanoparticles

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Abstract: ZnO films with and without nanorods on the surfaces were prepared by a chemical vapor deposition technique. Au nanoparticles were deposited on the surfaces of ZnO films with and without nanorods by the direct circuit sputtering method. Photoluminescence of the ZnO film with nanorods is tuned by the surface modification of the surface plasmons. Comparing with the ZnO film without nanorods, the near band gap emission from the ZnO film with nanorods is greatly enhanced and visible emission from defects is significantly suppressed. This phenomenon is attributed to the efficient coupling of surface plasmon resonance of Au nanoparticle with ZnO nanorods and the transfer of high energy electrons in Au nanoparticles to conduction band of ZnO.

Key words: ZnO; photoluminescence; surface plasmons

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金纳米颗粒等离子激元对不同形貌氧化锌薄膜 发光性能的调控

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摘要: 采用化学气相沉积法制备了纳米棒状的氧化锌纳米结构薄膜和没有纳米棒的氧化锌薄膜, 通过直流溅射在所制备的有纳米棒和没有纳米棒的氧化锌薄膜上淀积约 3 nm 厚的金纳米颗粒薄膜, 研究了金纳米颗粒对不同表面形貌氧化锌薄膜的发光特性的影响。实验发现金纳米颗粒的存在使具有纳米棒的氧化锌薄膜的紫外发射增强, 但使来自缺陷的可见光发射受到很大的抑制。通过比较有纳米棒和没有纳米棒的氧化锌薄膜在镀金纳米颗粒前后的发光特性, 发现金表面等离子激元对氧化锌发光的调控取决于氧化锌的表面形貌, 纳米棒的存在更有利于金纳米颗粒等离子激元调控氧化锌的发光特性。

关键词: 氧化锌; 光致发光; 表面等离子激元

1 Introduction

Surface plasmons can travel along the interface

between two different media and can be coupled with plane electromagnetic waves^[1]. The resonance frequency of surface plasmons depends on the shapes

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and sizes of noble metal nanostructures and the dielectric layers. Recently, a great deal of attention has been paid to the modification of the light-emitting properties of materials by surface plasmon resonance^[2]. They have been used to mediate light emission and to improve the quantum efficiency of light emitting of materials^[3-4]. ZnO is a semiconductor compound with a wide band gap (3.37 eV) and a large exciton binding energy (60 meV), and it has potential applications in electronic and optoelectronic devices. In general, the photoluminescence (PL) spectrum of ZnO consists of two bands, a near-band-edge excitonic ultraviolet (UV) emission and a defect-related deep-level emission in the visible range. The two carrier recombination routes compete with each other during the luminescence process. However, the visible emission related to defects or impurities usually dominates the luminescence spectra. Therefore, it is important to enhance the near band edge (NBE) emission and suppress the visible emission for the applications in the highly efficient short wavelength optoelectronic devices. Therefore, much effort has been made by highly oriented nanostructures^[5], nanocomposites, microcavity^[6], and surface plasmon resonance^[7]. More recently, the spontaneous emission efficiency of ZnO has been improved by surface plasmon mediated surface emission from rough surfaces of noble metals such as Ag, Au^[8] and Al^[9]. In this paper, it is experimentally demonstrated that the surface plasmons modified emission from ZnO films with nanorods.

2 Experiments

ZnO films with different surfaces were grown on sapphire substrates in a tube furnace by a chemical vapour deposition technique. The Zn powder (purity 99.0%) as a source of material was placed in a quartz boat. The cleaned sapphire substrates were placed at 2 cm downstream from the evaporation center. When the tube furnace was heated at a ramp rate of 10 °C/min, argon as the carrier gas was introduced into the tube furnace with a flow rate of 200 cm³/min. When the temperature of furnace raised to 300 °C, oxygen was introduced into the system at a

flow rate of 40 cm³/min. The two typical experiments were performed at different conditions. For a typical experiment (designated sample A), the temperature was maintained at 650 °C for 30 min. For another typical experiment (sample B), the temperature was maintained at 650 °C for 30 min, and then raised from 650 °C to 900 °C. The temperature of 900 °C was maintained for 20 min. Finally, the furnace was naturally cooled down to room temperature. Au nanoparticles were deposited by a direct current sputtering method. The crystal structures of un-coated ZnO films were analysed by X-ray diffraction (XRD) (Dandong, DX 2500 diffractometer with Cu K α radiation). The surface morphologies were characterized by scanning electron microscopy (SEM, JSM-5600LV JEOL). PL spectra of the Au-coated and un-coated ZnO films were measured at room temperature with a Fluorolog Tau-3 spectrofluorometer (Jobin Yvon/SPEX Horiba). The 320 nm line of a 450-W Xe lamp was used as the excitation source. The UV-Vis absorption spectra of Au-coated ZnO nanostructured films were measured by UV-Vis photo-spectrometer (Cary 5000, America Varian Company).

3 Results and Discussion

Fig. 1 shows the XRD patterns of the as-grown ZnO films. It can be seen that two strong peaks at 34.6° and 36.6° correspond to (002) and (101) planes of hexagonal ZnO, respectively. The peak at 42° is attributed to (006) plane of sapphire substrate. The strongest peak of (002) indicates that the film is formed in an effective equilibrium state which gives enough surface mobility to impinge atoms at the deposition temperature of 650 °C and 900 °C. No peaks from Zn or other impurities can be observed.

The SEM images of samples A and B grown at 650 °C and 900 °C are shown in Fig. 2 (a) and (b), respectively. It can be seen that the surfaces of both ZnO films are considerably rough. For sample A, it shows that there are plentiful ZnO nanorods on its surface. For sample B, it has only a rough surface and no nanorods on its surface.

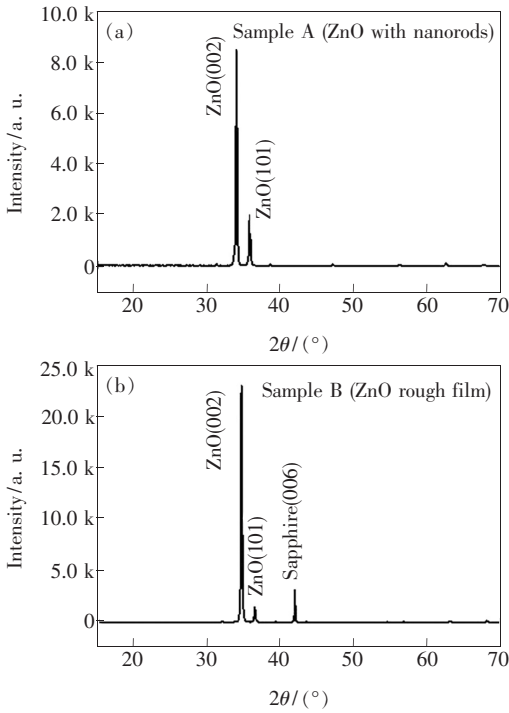


Fig. 1 XRD patterns of ZnO films grown at different temperatures. Sample A grown at 650 °C, and sample B at 900 °C.

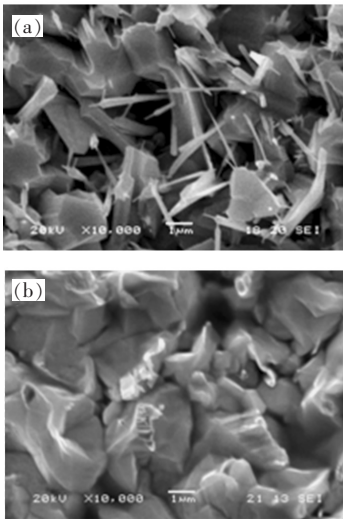


Fig. 2 SEM images of ZnO nanostructured films. (a) Sample A with nanorods grown at 650 °C. (b) Sample B without nanorods grown at 900 °C.

Fig. 3 shows the PL spectra of Au-coated ZnO and un-coated ZnO nanostructured films. For sample A, with nanorods on the surface, after Au nanoparticles were deposited, UV emission from sample A is greatly enhanced, while the visible emission at ~ 500 nm is suppressed significantly. For sample B without nanorods, PL spectrum of un-coated ZnO

film shows a strong UV peak at the 380 nm and another strong visible peak centered at 600 nm. However, after Au nanoparticles were deposited, UV is not enhanced significantly, but the visible emission was almost completely quenched.

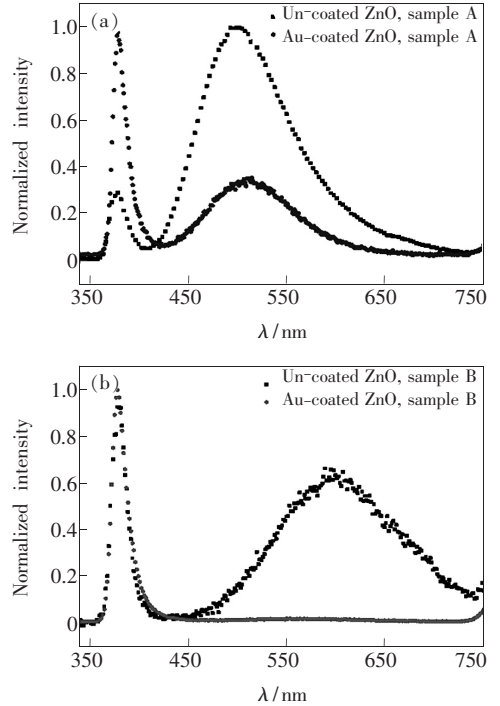


Fig. 3 (a) PL spectra of Au-coated and un-coated ZnO nanostructured films with nanorods (sample A). (b) PL spectra of Au-coated and un-coated ZnO films without nanorods (sample B).

By comparison the PL spectra of un-coated and Au-coated ZnO films with different surfaces, it is found that the pronounced changes in PL of ZnO films are related to the presence of Au nanoparticles as well as the surface structure. In particular, the visible emission depends on the surface structure. In sample A, the visible emission is around 494 nm. For the sample B without nanorods, the visible emission is around 600 nm.

As is well known, there are many defect states on ZnO surface. For Au-coated ZnO film with nanorods, the NBE emission is enhanced and the visible emission is reduced. Because the energy of green emission from the ZnO film with nanorods is the same with the surface plasmon resonance of Au nanoparticle, the visible emission is transferred to the surface plasmons. Meanwhile, those resonant electrons

with higher energy can escape from the interface to conduction band of ZnO, which leads to the enhancement of NBE emission and the suppression of defect related emission of ZnO. The electrons in defect states transfer to Au nanoparticles by two processes. One is the increase of the resonant electron density; the other is the strong couple between the electrons in the defect states and the field of the localized surface plasmons created energetic electrons in higher energy states^[10]. As for sample B without nanorods was deposited by Au nanoparticles, its NBE emission in PL spectra is not significantly enhanced while the visible band emission is suppressed to the noise level. This suggests that the visible emission at 600 nm from ZnO film with rough surface is related to the surface defect. After the rough surface was coated by Au nanoparticles, the concentration of surface defect of sample B is reduced greatly. Thus, the visible emission at 600 nm of Au-coated ZnO rough film is suppressed.

The UV-Vis absorption spectra of Au-coated ZnO nanostructured films with or without nanorods on surface are shown in Fig. 4. There is a strong peak at ~ 494 nm in the visible region of sample A with nanorods. The peak at ~ 494 nm is due to the surface plasmon resonance which comes from the interface of Au nanoparticles and ZnO nanorods. This is very fit to the reported plasmon resonance absorption of the Au nanoparticles^[11-12]. For sample B, a peak at ~ 470 nm occurs in the visible region and the strong peak at 364 nm is in the UV region. The peak at ~ 470 nm is attributed to the surface plasmon resonance on the interface of Au nanoparticles and ZnO rough surface, while the peak at 364 nm is due to the band edge absorption of ZnO^[13-14]. The strong absorption at 494 nm is very close to the wavelength of the visible emission of ZnO films having nanorods. Thus, the charges in defect states maybe couple with the surface plasmon resonance mode on the interface between Au nanoparticles and ZnO nanorods. PL spectrum of ZnO film having nanorods is mediated by the surface plasmon resonance.

The near band gap emission of ZnO film is enhanced, and the defect emission is suppressed significantly. For sample B, the absorption peak of surface plasmon resonance at ~ 470 nm does not match the emission wavelengths (380 and 600 nm). At the same time, the concentration of surface defect of sample B is reduced greatly due to the coating by Au nanoparticles. Therefore, PL spectrum of ZnO film without nanorods is not mediated significantly by the surface plasmon resonance. Its near band gap emission is not enhanced compared with un-coated ZnO film without nanorods.

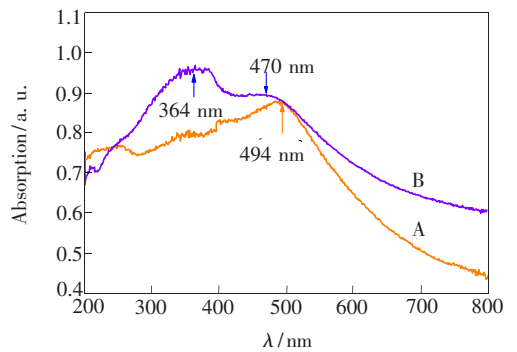


Fig. 4 UV-Vis absorption spectra of Au-coated ZnO nanostructured films. Sample A has a rough surface with nanorods, and sample B has a rough surface without nanorods.

4 Conclusion

In conclusion, ZnO nanostructured films with different surface morphologies were prepared by a chemical vapor deposition technique. PL properties of ZnO films with different surface morphologies are mediated by the coating of Au nanoparticles. The NBE emission of ZnO films with nanorods is enhanced by Au nanoparticles, and its defect emission is significantly suppressed. It is suggested that PL properties of ZnO films can be tuned to the surface plasmon resonance of Au nanoparticles. This modification of emissions from ZnO nanostructured films has a greater potential for practical applications in further development of nanophotonics in short wavelength optoelectronic devices.

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