

## Enhanced ultraviolet emission due to surface plasmon resonance in ZnO/Ag

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**Abstract:** To improve the photoluminescence intensity of ZnO, the optical properties of ZnO/Ag structures were systematically investigated. The radio-frequency magnetron sputtering technique was adopted to deposit ZnO and Ag thin films on Si substrates. The optical properties of ZnO/Ag structures that significantly different from those of pure ZnO thin films at different sputtering time were demonstrated in detail. The photoluminescence intensity of ZnO/Ag films was carried out compared with that of the pure ZnO. The results reveal that, the photoluminescence spectra of bare ZnO film showed a weak bandgap emission at around 378 nm and a broad defect-related emission band centered at 470 nm. After adding Ag film, it resulted in an increase and decrease of the near band edge, meanwhile, the position of UV peak has as lightred-shift compared with that of pure ZnO thin film. The optical features can be influenced by the evolution of the Ag film varied with the deposition time. The reasons for the enhancement of the band edge emission which caused by the surface plasmon resonance coupling of the near band edge emission between Ag and ZnO was detailed discussed.

**Key words:** PL spectrum; surface plasmons; ZnO; magnetron sputtering

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## 表面等离子体共振增强 ZnO/Ag 薄膜发光特性研究

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**摘 要:** 为了提高氧化锌光致发光强度,以磁控溅射氧化锌/银复合薄膜为研究对象,系统地研究了氧化锌薄膜的光学性质。实验中首先在硅衬底上用射频磁控溅射的方法沉积氧化锌/银复合薄膜,作为对比,同时沉积了一层氧化锌薄膜。通过扫描电子显微镜和原子力显微镜对样品的形貌及成份进行表征,并且在室温下测试样品在 300~800 nm 波长范围内的光致发光光谱。实验结果表明:所制得样品为均匀分布的氧化锌纳米薄膜,纯氧化锌光致发光光谱结果显示有波长位于 378 nm 左右的紫光、470 nm 左右的蓝色发光峰存在,加入银薄膜后,氧化锌可见光区和紫外光区的光致发光光谱强度均有所增强,而且紫外光峰位出现了红移。实验结果结合样品吸收谱对光致发光机理的分析作了进一步的分析。

**关键词:** 光致发光光谱; 表面等离子体共振; 氧化锌; 磁控溅射

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## 0 Introduction

In recent years, ZnO has attracted a great deal of attention as one of the most interesting semiconductors due to its large band gap of 3.37 eV at room temperature and high excitonic binding energy of 60 meV<sup>[1-3]</sup>. Thus, the application of ZnO includes photodetectors, fluorescent biosensors, light-emitting diodes, and back reflectors for thin-film solar cells. In all these studies, the plasmonic effects in the ZnO/metal structures play major roles in improvement of the device performance.

These properties have made it a promising material in the development of optoelectronic devices, especially in the fabrication of UV light emitting diodes and laser diodes. A wide variety of nanostructures of ZnO have been prepared by earlier researchers by using different synthesis procedures<sup>[4-6]</sup>. Surface plasmons (SPs) have attracted more and more attention in the enhancement of luminescence efficiency of light emitting materials and devices due to scientific interest and applications in optoelectronic devices<sup>[7]</sup>. In many studies of ZnO/metal structures, near-UV emission is enhanced because the SP resonance is close to the bandgap energy of ZnO. Generally speaking, the PL spectrum of ZnO thin films are influenced by the deposition method and preparing conditions. There are many preparation methods to fabricate ZnO thin films, such as metal organic chemical vapor deposition (MOCVD), sputtering, electron beam evaporation (EBE), pulsed laser deposition (PLD) and so on, among of them, there are many advantages by using magnetron sputtering to form ZnO thin films, such as good adhesion, good thickness uniformity, high density of films, so we take advantage of this method in our experiment<sup>[8-10]</sup>.

In this study, the radio-frequency (RF) magnetron sputtering technique is adopted to deposit ZnO and Ag thin films on Si substrates. The band edge emission enhancement from ZnO/Ag films by using PL spectrum have been investigated, and the PL intensity of the ZnO/Ag was larger than that of the ZnO sample,

and the UV emission increases more significantly, meanwhile, the position of UV peak has as light red-shift compared with that of pure ZnO thin film.

## 1 Experimental procedure

We deposited 70 nm Ag and 120 nm ZnO thin films on Si substrates at room temperature using a RF magnetron sputtering technique. The base pressure of the sputtering system was  $1 \times 10^{-4}$  Pa, and the working pressure of pure Ar was 0.1 Pa during thin-film growth. The applied RF power was 50 W and 75 W for the Ag and ZnO films respectively. For comparison, pure ZnO thin film was also prepared on planar Si substrate under the same condition.

The morphology of the ZnO/Ag and ZnO films on Si were measured using an atomic force microscopy (AFM) system (\_BYM-018) and a field-emission scanning electron microscope (SEM) (Hitachi SU8020). The crystal structures of the films were analyzed by an X-ray diffractometer (D/max-2200PC). The optical reflectance of the films were studied using a UV-visible spectrophotometer (SHIMADZU UV-2501PC), and for PL measurements, samples were excited by a fluorescence spectrophotometer (SHIMADZU RF-5301PC) with an excitation wavelength of 320 nm.

## 2 Results and discussion

Figure 1 shows the XRD patterns and a scanning electron microscopy (SEM) image of the ZnO/Ag and ZnO thin films deposited on Si substrates. In Fig.1(a), there is two diffraction peaks located at  $38.2^\circ$  and  $44.47^\circ$  which corresponds to the (111) and (200) diffraction peaks of Ag with the fcc structure. Similarly, it can be seen that there is a diffraction peak located at  $34.6^\circ$  or so, which corresponds to the diffraction of (002) plane of ZnO. This means that the prepared ZnO thin films are hexagonal wurtzite structures and preferentially oriented along the c-axis perpendicular to the substrate surface. Figure 1 (b) and

(c) show the surface morphologies of ZnO and Ag samples. The diameters of the ZnO and Ag nanoparticles are in the range of 20 nm and 30 nm respectively, and the grain size distribution of the films are with good uniformity without obvious defect.

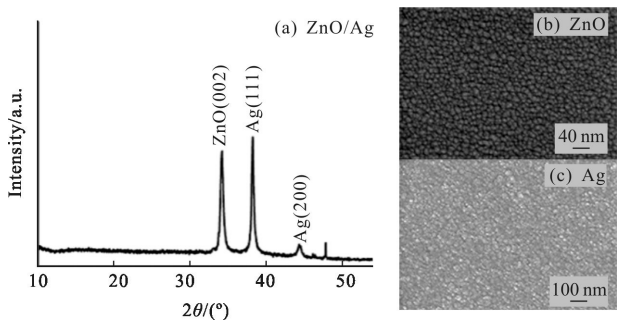


Fig.1 XRD spectra of (a) ZnO/Ag film and SEM images of (b) ZnO and (c) Ag

The AFM image (scanning area was  $10\ \mu\text{m} \times 10\ \mu\text{m}$ ) of ZnO(120 nm)/Ag(70 nm) film is shown in Fig.2. It is clear that the as-prepared ZnO/Ag film reveals a coarse surface with the root mean square (RMS) roughness of 6 nm at  $10\ \mu\text{m} \times 10\ \mu\text{m}$  scan size, and obvious ZnO dense surface arrangement with the size distribution above 20 nm.

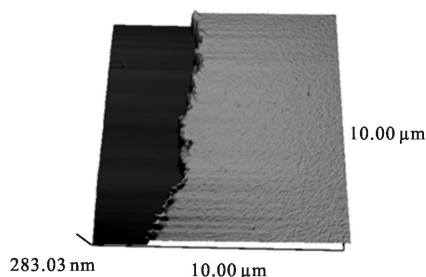


Fig.2 AFM image of ZnO/Ag film

In general, a rougher surface means that bigger particles experience greater scattering so as to further enhance of luminescent efficiency. In addition to the effects of surface roughness, structure characteristics (metal layer, crystallization) are another factor that affects the luminescent efficiency, so we deposited a 70nm Ag film in our experiment.

Figure 3 presents the reflectance spectra of pure ZnO and ZnO/Ag thin films. As for the two samples. Obviously, the reflectance spectrum of ZnO/Ag is different from pure ZnO. The most obvious feature of

ZnO/Ag is that there is a strong absorption band centered at 440 nm, which is often attributed to surface plasmon resonance (SPR) absorption of Ag nanoparticles. The optical features can be influenced by the evolution of the Ag film varied with the deposition time. As shown in Fig.4(a) and (b), at the beginning of sputtering deposition, Ag particles were deposited as islands with various sizes and randomly distributed on substrate, and the separated island would scatter the incident light thus reducing the light transmittance. As sputtering was carried further, the gap between aggregated particles was decreased, thus the scattering property was decreasing. Finally, the Ag islands coalesced to a continuous film, which would work as a reflection film and the reflectance would increase gradually.

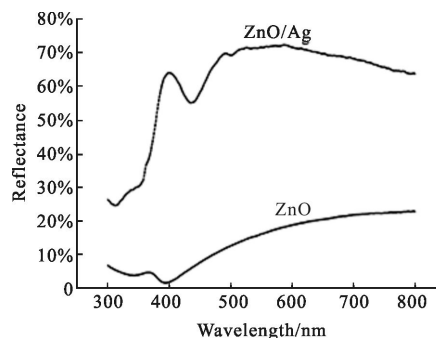
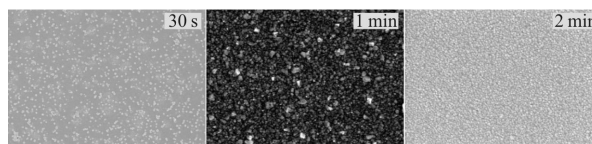
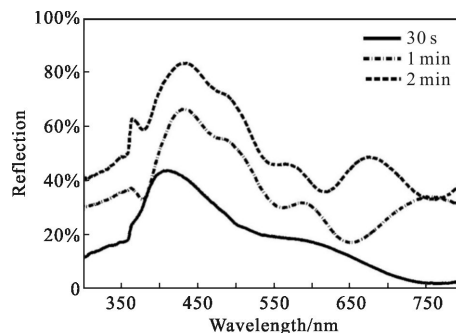


Fig.3 Reflectance spectra of pure ZnO and ZnO/Ag



(a) SEM of ZnO/Ag film with different sputtering time of Ag



(b) Reflectance spectra of ZnO/Ag film with different sputtering time of Ag

Fig.4 Optical features influenced by Ag film varied with deposition time

Figure 5 exhibits the photoluminescence spectra of ZnO/Ag and pure ZnO thin films. All the samples show two luminescent regions, namely a strong, narrow UV emission peak and a wide, weak visible emission band. The UV emission results from the recombination of free excitons while the visible emission is considered to be connected mainly with different kinds of defects. Apparently, the bare ZnO film exhibits a band edge emission around 378 nm and a visible emission near about 470 nm. After added a 70 nm Ag layer, the ZnO/Ag sample enhances both the UV and the visible emission at the same time compared to that of the pure ZnO. However, the intensity of UV emission increases more significantly, and the position of UV peak has as light lightred-shift compared with that of pure ZnO thin film.

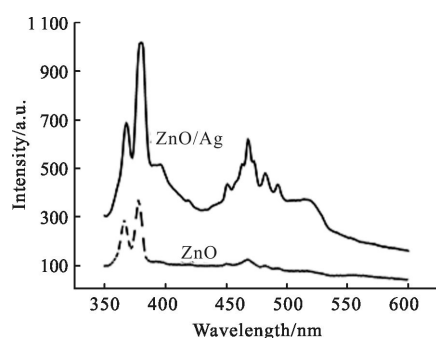


Fig.5 Photoluminescence spectra of ZnO/Ag and pure ZnO

### 3 Conclusion

In this work, we demonstrated that the optical properties of ZnO/Ag structures were significantly different from those of pure ZnO thin films. The PL intensity of the ZnO/Ag was larger than that of the ZnO sample, and the UV emission increases more significantly, meanwhile, the position of UV peak has as lightred-shift compared with that of pure ZnO thin film.

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