

Enhancement of Visible Photoluminescence in ZnO/Ag Thin Films using Nanograting Structures

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ZnO/Ag thin films were deposited on grating structures that were fabricated by nanoimprint lithography. The grating structures exhibited multiple peak features in visible-range photoluminescence (PL), whose intensity was much larger than that of planar thin films. The grating structures also exhibited quite distinctive features, such as several dips in the reflectance, from the planar samples. All of these findings could be understood as a result of plasmon-exciton interaction. Thus, the PL peaks, well matched with the reflectance dips, represent the excited surface plasmon polariton energies, determined by the grating periodicity.

Keywords: ZnO, Ag, Grating, Surface Plasmons, Photoluminescence, Reflectance.

1. INTRODUCTION

ZnO has attracted enormous research attention because it exhibits various physical phenomena, such as electrical, optical, magnetic, and piezoelectric properties.^{1–5} For example, ZnO has a direct bandgap and a large exciton binding energy (60 meV), and hence it is a potential candidate material for ultraviolet light emitting devices. To enhance the light emission efficiency, plasmon effects have been utilized using metal thin layers and nanoparticles.^{6–9} Excitons in ZnO are coupled with surface plasmons (SPs) at the ZnO/metal interface or with localized surface plasmons within the metal particles. In all of these studies, near-UV band-edge emission was enhanced while the visible emission, caused by defects, was suppressed. The plasmons dominantly couple with the near-UV bandgap emission, because the SP resonance peak energies, in planar thin films and nanoparticles, are very close to the bandgap energy of ZnO ($E_g = 3.37$ eV). Periodic metal structures can assist SP radiations (i.e., SP-photon coupling) and the resonant SP energies can be determined by the periodicity of the structure.¹⁰ In such cases, SP excitation should affect optical reflectance as well as light emission behaviors. Thus, photoluminescence (PL) and reflectance spectra can give us valuable information on how SP can influence the optical properties of ZnO thin films.

In this article, we report on the fabrication and optical characterizations of ZnO/Ag nanograting structures. The

experiment data clearly show that the grating structures have largely different optical properties than those of planar thin film samples. In particular, multiple PL peaks and significant enhancement of the intensity are notable. The PL peaks are very indicative of the excited surface plasmon polariton (SPP) energies, comparatively confirmed by the reflectance spectra.

2. EXPERIMENTAL DETAILS

We deposited ZnO and Ag thin films on substrates by sputtering ZnO and Ag targets (two-inch diameter) at room temperature. Prior to the growth, the sputtering system was evacuated to 1×10^{-6} torr. The applied RF power was 50 W and the working pressure of pure Ar ambient was 7.5×10^{-3} torr for both of the ZnO and Ag thin films. In this study, two kinds of samples were prepared: planar samples that were directly grown on Si substrates and grating structures on polymer patterns that were fabricated by nanoimprint lithography. For the planar sample fabrication, 100-nm-thick ZnO and 120-nm-thick Ag layers were deposited on Si substrates. The 100-nm-thick ZnO/50-nm-thick Ag grating structures were grown on polymer patterns that were fabricated by nanoimprint lithography.¹¹ Poly(dimethylsiloxane) (PDMS) with nanoscale features were used as molds. The line (500 nm)/space (500 nm) patterns were printed on the UV-curable polymers that were coated on Si substrates. After printing, the polymer patterns were cured under UV light (wavelength: 365 nm)

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for 30 minutes. The detailed procedures can be found in Ref. [11].

The morphology of the films and the fabricated patterns were examined using a field-emission scanning electron microscope (SEM) (JOEL, JSM-6700F) and atomic force microscopy (AFM) (Digital Instruments, Dimension 3100). The optical properties of the films were studied by PL spectroscopy and UV-visible spectrophotometer (Perkim-Elmer, 750). For the PL measurements, samples were excited by 325 nm photons from a HeCd laser, and the luminescence spectrum was measured by a nitrogen-cooled CCD detector that was attached to a monochromator with a focal length of 275 mm, where the spectral resolution was confirmed to be about 1 nm from the width of the laser lines.

3. RESULTS AND DISCUSSION

Figures 1(a) and (b) show the PL spectra and specular reflectance of the planar ZnO/Si and ZnO/Ag/Si thin films, respectively. The abrupt decrease of the reflectivity at around 380 nm (corresponding photon energy: ~ 3.2 eV) was caused by band-to-band absorption in ZnO. The ZnO/Ag/Si thin films exhibited a reflectivity dip at a wavelength of 450 nm (~ 2.75 eV). This energy corresponds well to the resonance energy of the SP at ZnO/Ag interface, which was expected from the dispersion relation:

$$\hbar k_{sp} = \frac{\hbar \omega}{c} \sqrt{\frac{\epsilon_{Ag} \epsilon_{ZnO}}{\epsilon_{Ag} + \epsilon_{ZnO}}}$$

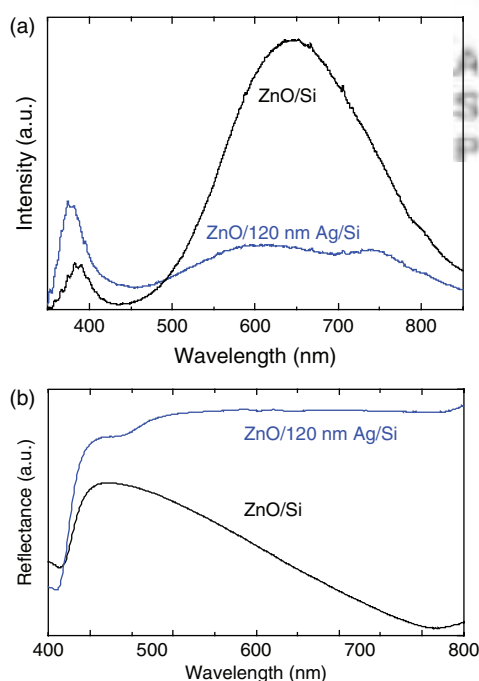


Fig. 1. (a) PL spectra and (b) specular reflectance spectra of ZnO and ZnO/Ag thin films grown on Si substrates.

where k_{sp} is the wave vector of SP, $\hbar \omega$ is the incident photon energy, and ϵ_{Ag} and ϵ_{ZnO} are the dielectric constant of Ag and ZnO, respectively.¹² The ZnO/Si thin film, without SP-induced absorption, showed no dip in the reflectivity. The smaller reflectivity for the longer wavelength indicated that part of the light passed through the underlying Si substrate. Since the SP resonance energy was close to the ZnO bandgap energy, SP-exciton coupling can be expected.⁶⁻⁹ The PL spectra consisted of a relatively sharp peak in the UV region (~ 380 nm) and a broad peak in the visible range, as shown in Figure 1(a). Visible PL, which originated from defect electronic states inside the bandgap region due to atomic vacancy or impurity, has been often observed in wide bandgap semiconducting oxides, such as ZnO and SrTiO₃ thin films.^{8, 13} The excitation via the SP resonance to defect states was less effective than that to the band-to-band excitation. Thus, the PL intensity in the UV region was significantly enhanced and that in the visible region was suppressed in the ZnO/Ag/Si thin films.

Both the PL and reflectance data clearly revealed that the SPPs at the ZnO/Ag interface significantly modified the optical properties of the ZnO thin films. SPs cannot be directly converted to photons because of the momentum mismatch between SPs and photons. Periodic grating structures can assist light emission from the excited SP modes, where the reciprocal space vectors from the periodicity can bridge the SP-photon momentum gap.¹⁰ The resonant SP modes should be determined by the grating period.

We fabricated grating structures by using nanoimprint lithography, as schematically illustrated in Figure 2. The periodicity of the grating was chosen to be 1000 nm and

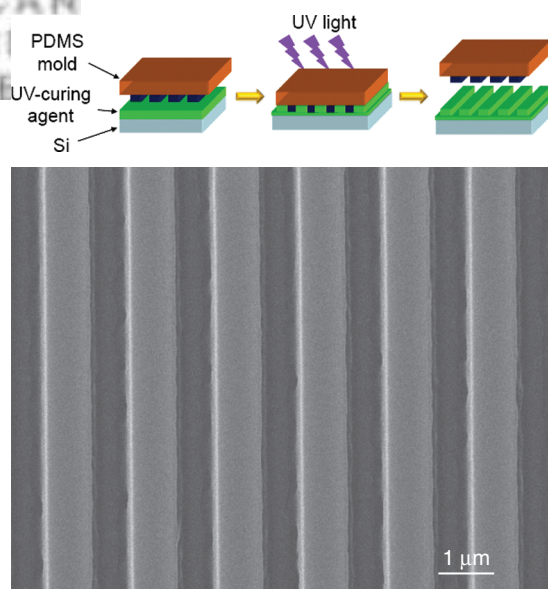


Fig. 2. Schematic illustrations of fabrication procedures of grating structures by nanoimprint lithography and a typical SEM image of the obtained polymer pattern.

the line-and-space ratio was 1:1, as shown in a typical SEM image in Figure 2. The peak-to-valley amplitude of the polymer pattern was estimated to be 760 nm, by AFM measurements. The area of the patterns was 1 cm², which was large enough for conventional optical characterizations.

Figure 3 shows PL spectra of a ZnO/Ag thin film grown on the grating structure and a ZnO film grown on a bare Si substrate. The PL intensity of the grating structure was much larger than that of the planar film. In particular, a drastic enhancement in the visible emission could be noticed. In the planar thin films, the existence of Ag layers suppressed the visible emission as seen in Figure 1(a). It is obvious that the periodic structure can significantly modify the PL spectra. In addition, several peaks in the PL spectra from the grating structure could be seen, as clearly indicated by fitting curves. For one-dimensional grating structures, the coupling of SPPs and photons is governed by the equation:

$$k_{sp} = \frac{\omega}{c} \sin \theta \pm \frac{2\pi}{D} n$$

where θ is the incidence or exit angle of light with respect to the surface normal, D is the grating periodicity, and n is an integer.¹⁰ If the equation above is satisfied, then photons can effectively excite SPPs, and vice versa. The SPPs can generate electron-hole pairs (i.e., excitons) in ZnO, and a subsequent electron-hole recombination will result in the PL intensity enhancement. Thus, the multiple peaks in the PL spectra suggest that the grating structure enables dominant excitation of several SPP modes whose energies can be indicated by the PL peak positions.

Figure 4 shows specular and total reflectance of the ZnO/Ag grating structure. The incident angle of light was 7° from the surface normal. The total reflectance measurements were carried out with an integrating sphere. The

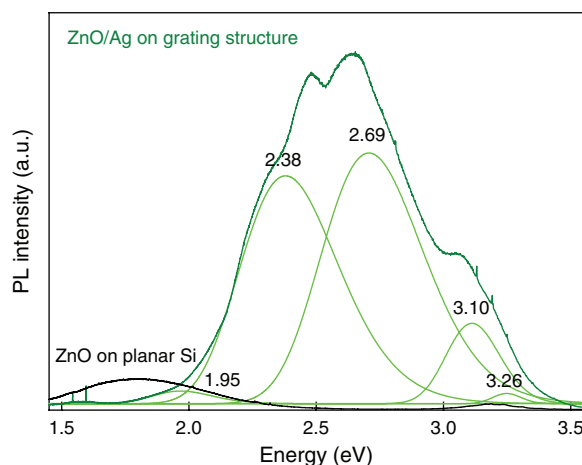


Fig. 3. PL spectra of a ZnO/Ag grating structure and a ZnO/Si film. The fitting curves clearly show that the PL spectra of the ZnO/Ag grating structure consist of several peaks whose positions are indicated as numbers.

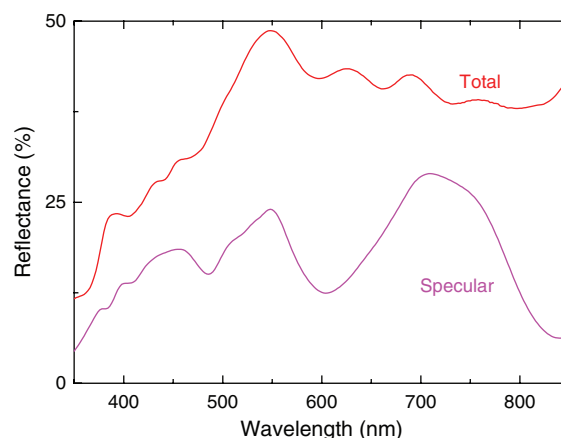


Fig. 4. Total and specular reflectance of a ZnO/Ag grating structure.

reflectance data shows several dips and wiggles, which can be caused by the loss of incident photons including the SPP excitation in the Ag layer, interference, and diffraction. The difference between the specular and total reflectance manifests the diffracted portion of the light in our grating structure. Therefore, the dip positions in the total reflectance, rather than the specular reflectance, can be compared with the PL peak positions. Since the thickness of the Ag layer was only 50 nm, some of the light could be transmitted through the underlying layers due to the incomplete reflection. As a result, the overall reflectance was less than 50%, as shown in Figure 4. Figure 5 shows that the PL peaks well matched the dip location in the total reflectance. Some wiggles in the reflectance, not coincident with the PL peaks, may come from the interference of the thin layers. From such comparison, it is obvious that the incident-photon-to-SPP coupling and the following SPP-exciton coupling can be determined by the grating periodicity. The grating structure can allow wavelength-selective modification of the optical properties of the ZnO thin films, as demonstrated in our experiment results.

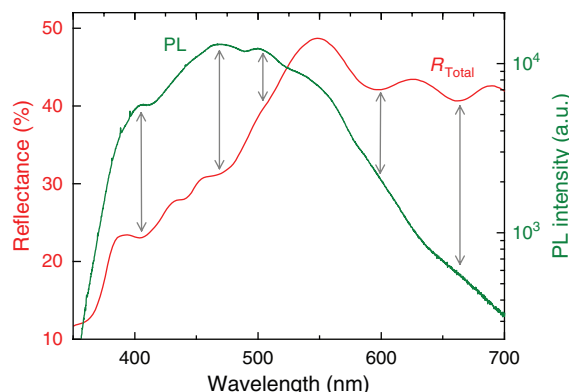


Fig. 5. Total reflectance and PL spectra of a ZnO/Ag grating structure. Arrows indicate that the reflectance dip positions match well with the PL peak positions.

The modification of the optical properties of ZnO thin films using the SPP effects can be useful in many applications. The performance of light emission devices can be improved, as many researchers already have suggested.⁹ Also, there has been increasing interest in ZnO/Ag thin films, as a vital part of photovoltaic systems through the back side reflector.¹⁴ Much of the research has focused on surface texturing, enhancing the light scattering for efficient light trapping in silicon thin-film solar cells. Periodic structures may provide a new way to overcome the limit of the current approaches. It can also be useful for high-efficiency and wavelength-selective photo detectors.¹⁵ By choosing optimal periodicity, photoconductivity (i.e., electron-hole-pair generation yield) can be enhanced at a certain wavelength region. Thus, the photoresponsivity at a specific spectral range can be intentionally improved.

4. CONCLUSIONS

We carried out comparative investigations on ZnO thin films with and without periodic structures. And, we successfully demonstrated the modification of spectral response of the optical properties of ZnO thin films. The experiment results were explained by surface-plasmon (SP)-mediated effects. The periodicity determined the dominant SP energy at which the coupling with the electron-hole pairs in semiconductors can be efficient. Thus, visible range properties that are related to defect states, rather than the near-UV region that is related to bandgap energy, can be significantly altered by choosing the proper periodicity. Our work suggests that introducing periodic structures can be a useful approach to manipulate the optical properties of ZnO thin films. This can provide us with a versatile way to devise novel and high-performance optoelectronic devices.

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