Performance Enhancement of ZnO UV Photodetectors by Surface Plasmons

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S *Supporting Information*
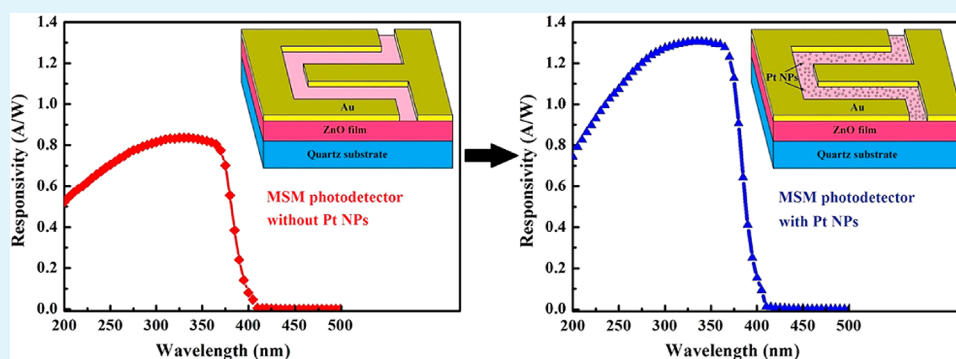
ABSTRACT: Surface plasmons, a unique property of metal nanoparticles, have been widely applied to enhance the performance of optical and electrical devices. In this study, a high quality zinc oxide (ZnO) thin film was grown on a quartz substrate by a radio frequency magnetron sputtering technique, and a metal−semiconductor−metal structured ultraviolet detector was prepared on the ZnO film. The responsivity of the photodetector was enhanced from 0.836 to 1.306 A/W by sputtering metal (Pt) nanoparticles on the surface of the device. In addition, the absorption of the ZnO thin film was enhanced partly in the ultraviolet band. It is revealed that Pt nanoparticles play a key role in enhancing the performance of the photodetectors, where surface plasma resonance occurs.

KEYWORDS: *ZnO film, magnetron sputtering, MSM photodetector, responsivity, surface plasmons, Pt nanoparticle*

1. INTRODUCTION

Over the past decade, zinc oxide (ZnO) has attracted increasing interest for its particular properties, such as a wide band gap of ∼3.37 eV, high radiation endurability, low visible absorption, low cost, and it is environmentally friendly as well, which makes ZnO a promising material for ultraviolet (UV) photodetector applications.[1−4] ZnO-based UV photodetectors have been fabricated from single crystals, thin films and nanostructures in recent years.[5−10] Increasing the performance is still one of the major issues of ZnO-based UV photodetectors, and continuing efforts have been devoted to this issue.[11−17]

Recently, much attention has been paid to surface plasmons (SPs) for their fundamental scientific importance and promising practical applications.[18−24] The SPs can be realized in coatings on the surface of metal nanoparticles (NPs) by magnetron sputtering.[25] The metal NPs on the surface can enhance the scattering of the incident photons and make more photons reach the substrate, and thus the absorption of the photons can be enhanced,[26−28] which provides a novel idea of enhancing the performance of ZnO UV photodetector.

In this paper, we report the growth of ZnO thin films on quartz substrates by a radio frequency (RF) magnetron sputtering technique, and focus on Pt NPs enhancement on the performance of ZnO-based metal−semiconductor−metal (MSM) Schottky UV photodetectors, and then verify the enhanced by FDTD method. Pt NPs on the surface of photodetector make the responsivity significantly enhanced, which demonstrates that this method is a promising route to improve the performance of ZnO-based photodetectors.

2. EXPERIMENTAL SECTION

A high-purity (99.995%) ZnO ceramic was used as the target of the RF magnetron sputtering technique. Before sputtering, the chamber was pumped to a vacuum degree of around 5×10^{-4} Pa. To complement oxygen deficiency of the ZnO thin films, both ultrapure (5 N) oxygen and argon were used as the working gas for the sputtering of ZnO film.

When the pressure was hold at 3.0 Pa, ZnO film began to be deposited. Amorphous structure quartz glass was used as a substrate. The quartz substrate was cleaned by acetone (≥99.5%), absolute alcohol (≥99.7%) and distilled water in an ultrasonic bath. To achieve high crystal quality films, the substrate temperature was kept at 673 K during the sputtering process. The rate of deposition was adjusted to have a thickness of nearly 600 nm with the sputtering time of 2 h (in 0.083 nm/s). Rigaku Ultima VI X-ray diffractometer (XRD) with Cu Kα radiation (λ = ~1.543 Å) was used to make θ−2θ scans to evaluate the crystalline property of the ZnO films. Both optical transmission and absorption spectra were recorded using a PerkinElmer Lambda 950 UV/vis Spectrometer in the wavelength range from 200 to 700 nm.

To fabricate the MSM structure ZnO UV detector, a thin layer of Au was sputtered onto the prepared ZnO films to serve as the metal contact, and the rate of deposition was about 0.33 nm/s for 10 min. Standard UV exposure and wet etching were then performed to define the interdigitated contact pattern. The fingers of the Au contact electrodes were 5 μm in width and 500 μm in length, with an interval spacing of 5 μm, and the sum of finger pairs was 15.

Pt was sputtered on the same device in the chamber of a JEOL JFC-1600 sputter coater for 10 to 50 s at each step measured in periods of 10 s, and the sputtering current was kept at 20 mA. The current−voltage (I−V) (Agilent 16442A test fixture) in the dark and the responsivity (Zolix DR800-CUST) characteristics of the MSM structure ZnO photodetector were measured after each sputtering cycle at room temperature. The applied voltage in the I−V testing was tuned from −15 to +15 V, and the bias voltage in the responsivity testing was 3 V. Furthermore, the surface morphology of the ZnO films from the device was examined by using a Pacific Nanotechnology Nano-R2 AFM in contact mode.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the ZnO thin film without Pt NPs and with sputtering for 50 s with Pt NPs. As shown in
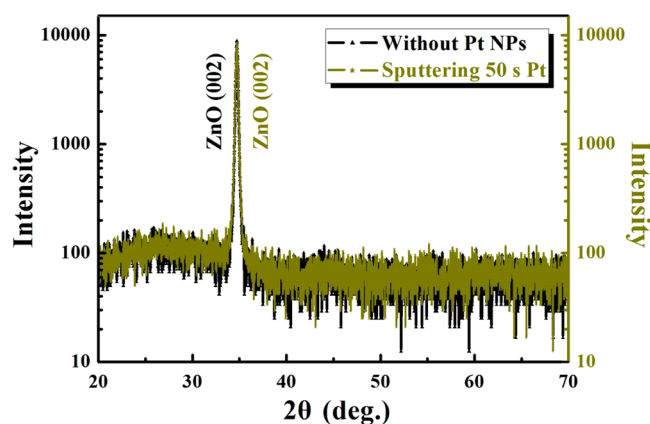
Figure 1. XRD patterns of the pristine ZnO film and another film with sputtering for 50 s with Pt NPs.

the XRD patterns, there is only a diffraction peak located at about 34.4°, which can be indexed to the (002) facet of ZnO, and no other peaks can be found from the XRD pattern like (100) and (101). The intensities of the ZnO peaks are nearly the same, which can prove that the sputtering deposition of Pt just made NPs deposited on the surface of ZnO film, and had no effect on the crystal quality of the films. The absorption spectra of the ZnO films with different sputtering times with Pt NPs are shown in Figure 2, and the inset shows the maximum intensity of absorbance as a function of the Pt NPs sputtering time. It can be observed clearly that NPs can enhance the absorption at opportune sputtering time (particularly at 20 s).
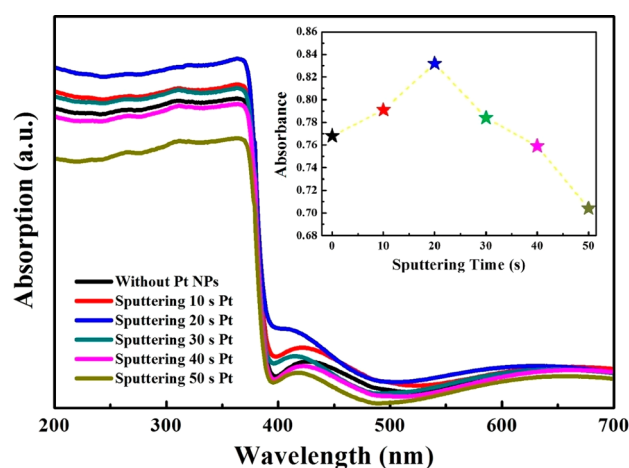
Figure 2. Absorption spectra of ZnO films with different sputtering times with Pt NPs, and the inset shows the maximum intensity of absorbance as a function of the sputtering time.

For the sake of cautiously studying Pt NPs, the ZnO surface with a 20 s sputtering time with Pt NPs was imaged by scanning electron microscopy (SEM), as shown in Figure 3. It
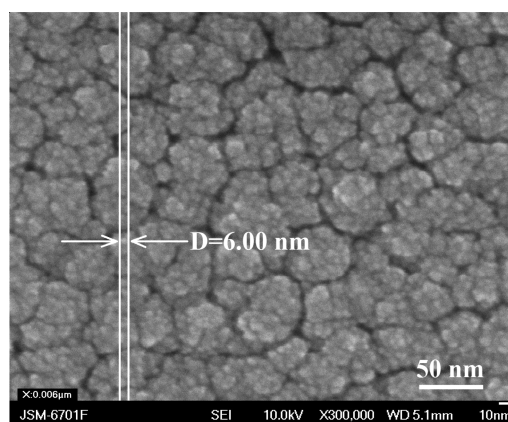
Figure 3. Plane-view SEM image of ZnO surface with sputtering for 20 s with Pt NPs.

was obviously observed that Pt NPs have been deposited onto the ZnO thin films. The average diameter of the Pt NPs is about 6.00 ± 0.50 nm. The refractive index of the ZnO has been measured and the absorption of ZnO thin films with 6.00 nm Pt NPs has been calculated using finite difference time domain (FDTD) (shown in Figure 4). Compared with the pristine ZnO film, the absorption of the ZnO films coating with Pt NPs is enhanced in the spectrum range from 270 to 370 nm, which is consistent with the absorption spectra shown in Figure 2.

The Au−ZnO−Au MSM interdigital configuration was used to evaluate the performance of the UV photodetectors. The I−V characteristics of the photodetector with different Pt NPs sputtering times under dark conditions are shown in Figure 5. The nonlinear I−V characteristics indicate that Schottky contact has been obtained. Meanwhile, the dark current is enlarged with the increased sputtering times of Pt NPs. Due to the small particle size of Pt NPs, the deposited Pt between the adjacent two Au fingers was separated. However, the Pt NPs can promote the transferring probability of electrons, one can
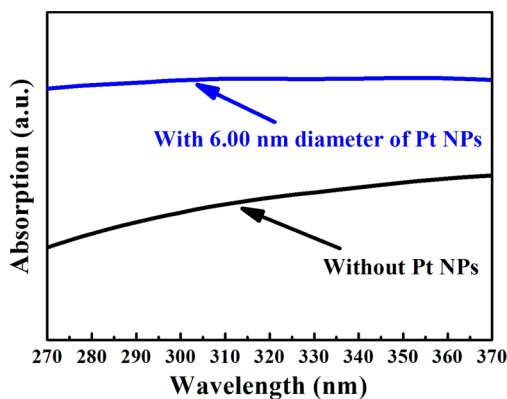
Figure 4. The simulation of absorption of ZnO films with and without Pt NPs by using FDTF method.
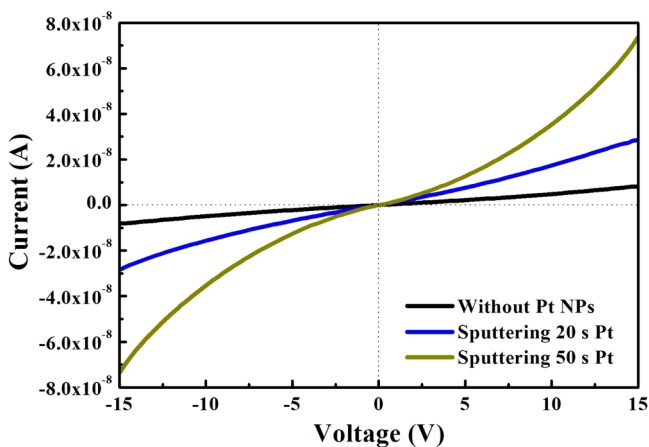
Figure 5. I−V characteristics of the ZnO MSM structure UV photodetectors with different sputtering times with Pt NPs.

see that the electrical conductivity of the ZnO film is enlarged with the Pt NPs.

Figure 6 shows the typical photocurrent spectra of the ZnO MSM UV photodetectors with different Pt NPs sputtering times, and the inset is the schematic illustration of the device with Pt NPs. All the photodetectors were measured under 3 V
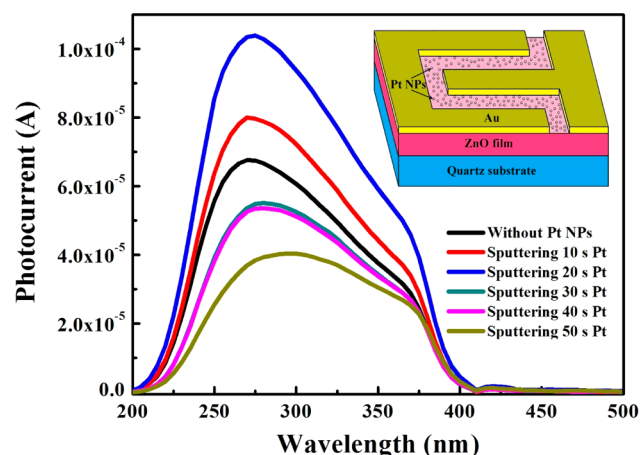
Figure 6. Photocurrent spectra of the ZnO MSM structure UV photodetectors as a function of Pt NPs sputtering time, measured at 3 V bias. The inset shows the schematic illustration of the device with Pt NPs.

bias and calibrated using the standard Si photodetector. The photocurrent is improved with the increased of Pt NPs sputtering times. The optimized sputtering time is 20 s; after that, the photocurrent decreases with the increases to the sputtering time of Pt NPs. Figure 7 shows the responsivity
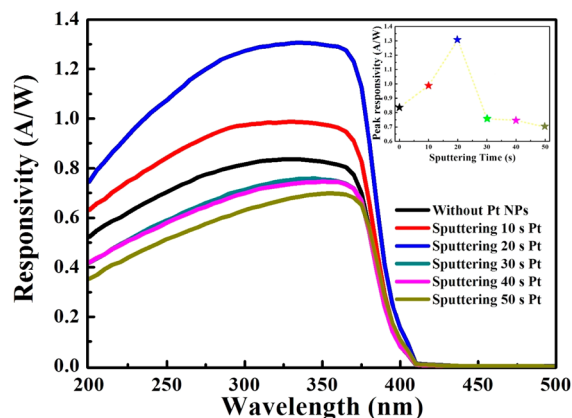

Figure 7. Response spectra of the ZnO MSM structure UV photodetectors with different sputtering times with Pt NPs. The inset shows the variation tendency of the responsivity with sputtering time.

spectra of UV photodetectors, which were transformed from the photocurrent by means of precise count. The maximum responsivity is 1.306 A/W when the NPs sputtering time is 20 s. Furthermore, it is 0.562 times larger than the one without Pt NPs (0.836 A/W). The inset of Figure 7 shows the variation tendency of the responsivity with sputtering time, which is in agreement with the absorption results shows in Figure 2. In theory, the nanoplasmonic scattering effect will result in increasing photon absorption due to the Pt NPs coupling with the incident light. Thus, this may be the dominant reason for the enhanced responsivity. To investigate the effect of Pt NPs on the photon absorption, the surface morphology of the films has been studied by AFM.

Figure 8 shows typical contact mode AFM topographies of the pristine ZnO film, the film with 20 s sputtering time with Pt NPs and the 50 s one. The root-mean-square roughness (R_m) of the films in a 1 μm × 1 μm scan area is 3.117 nm, 3.749 and 7.948 nm, respectively, which means that the roughness increases with the sputtering time of Pt NPs. On the basis of the above analysis, we determine that the Pt NPs play an important role in the increased photon absorption.

Because of surface plasmon resonance (SPR), which occurrs on metal NPs surface, the Pt NPs have been applied to enhance the performance of the ZnO UV photodetectors. The SPR of Pt NPs have enhanced the scattering of incident light, which made more photons scatter on the ZnO thin film, and it is such a result that the light absorption is enhanced. The particle diameter of single Pt NP is about 6.00 nm, which is well below the wavelength of light. As a result, we can describe the absorption and scattering of light well using a point dipole model. The scattering and absorption cross sections are expressed as[26]

$$C_{scat} = \frac{1}{6\pi}\left(\frac{2\pi}{\lambda}\right)^4 |\alpha|^2 \tag{1}$$
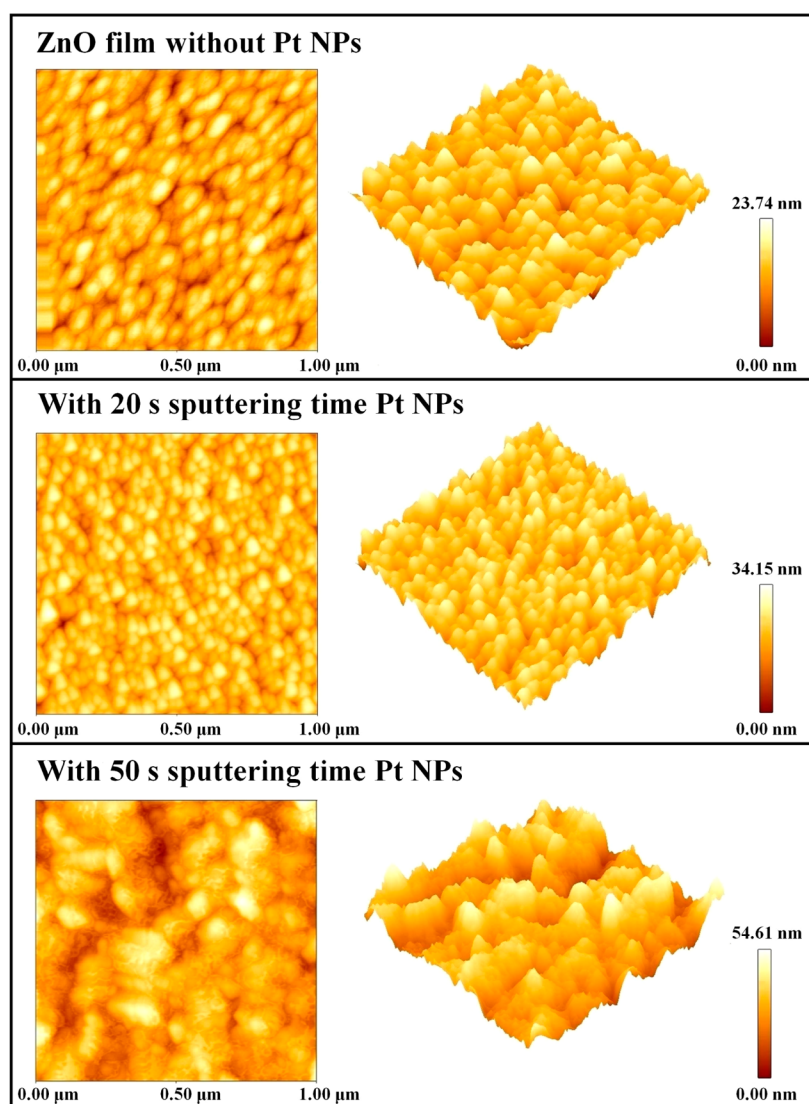
Figure 8. AFM images of the ZnO films without NPs and with 20 s and 50 s sputtering time with Pt NPs.

$$C_{abs} = \frac{2\pi}{\lambda} \text{Im}[\alpha] \tag{2}$$

where α is the polarizability of the particle, which can be calculated from eq 3:

$$\alpha = 3V \left[\frac{\varepsilon_p/\varepsilon_m - 1}{\varepsilon_p/\varepsilon_m + 2} \right] \tag{3}$$

where V is the volume of Pt NPs and ε_p and ε_m are the dielectric function of metal particle and ZnO medium, respectively. Thus, at certain wavelengths, ε_p and ε_m are constant, which makes C_{sact} proportional to the square of the volume. According to eqs 1 and 3, larger size NPs have larger scattering cross-sections than smaller ones. With increases to the sputtering time of Pt NPs, more NPs will cluster together, resulting in larger size NPs. Although we cannot deduce the variation tendency of C_{abs} with the increasing size from eqs 2 and 3, larger scattering cross-sections can ensure that more photon scattering on the ZnO films, which promotes the absorption of photons by the films. When the sputtering time is beyond the optimized value of about 20 s, excessive Pt NPs will cover the ZnO thin films and hinder the absorption of light. Thus, the responsivity of ZnO UV photodetector decreases.

4. CONCLUSIONS

ZnO thin films have been prepared on quartz substrates by a RF magnetron sputtering technique. The metal (Pt) NPs are coated on the surface of ZnO film based MSM structured UV photodetectors. It is found that the responsivity of the device is enhanced by up to 56%. Meanwhile, the absorption of ZnO films with proper sputtering times with Pt NPs (particularly at 20 s) was effectively increased. All of the measurements point to the metal (Pt) NPs, which play a key role in enhancing the performance of photodetectors. FDTF simulation demonstrates that the absorption enhancement is consistent with the result of measurements. We propose that the SPR of Pt NPs have enhanced the scattering of incident light, which made more light scatter on the ZnO thin film, and it is such a result that the light absorption is enhanced.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Photograph of the ZnO MSM structure UV photodetector by Leica DM6000M, transmission spectra of ZnO films with different sputtering times with Pt NPs, and SEM image of ZnO surface with the sputtering time of 20 s with Pt NPs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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