Influence of thin metal nanolayers on the photodetective properties of ZnO thin films

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We investigate the photoconductivity properties of ZnO thin films prepared by pulsed laser deposition with and without metals (Au or Pt) on the surface. The covering of nanostructured metals can largely enhance the photocurrent. Meanwhile, the dark currents have been increased significantly due to the increase in carrier concentration and mobility near the surface of ZnO thin film. Although plasmonic effect was observed by the photoluminescence enhancement, the main mechanism of the increase in the dark current and photoresponsivity for ZnO photoconductors has been interpreted by surface states, interface states, and persistent photoconductivity. © 2009 American Institute of Physics. [doi:10.1063/1.3251370]

I. INTRODUCTION

The nanostructured metals have been proven to be an effective approach to improving the quantum efficiency and performance of various optoelectronic devices, such as solar cells, light-emitting devices, and photodetectors, and a number of experimental results have been reported.[1–6] Derkacs *et al.*[5] have improved the performance of InP/InGaAsP quantum well waveguide solar cells via light scattering from Au nanoparticles. The enhancement in photocurrent from metal-semiconductor-metal photodetector has been achieved by integrating a nanoscale metallic grating into its contacts.[4] The observed performance improvement for optoelectronic devices was primarily attributed to scattering and surface plasmonic (SP) effect induced by nanostructured metals.[1,5,6] However, very little information has been reported regarding the photoconductors with metals covering on the surface of the devices.[7] The mechanisms of metals affecting dark current, photoresponse, and response time of photoconductor have been rarely explored. ZnO, as a direct wide band gap semiconductor, has been proposed as a promising material for ultraviolet photon detection. ZnO also possesses unique figures of merit, such as high radiation hardness, intrinsic visible blindness, nontoxic material, and low growth temperature which are crucial for practical optoelectronic devices. In our previous work, we have prepared high performance *p-n* homojunction and metal-semiconductor-metal ZnO-based photodetectors by different methods.[8–10] Motivated by the potential application of metal in ZnO-based photodetectors, we investigate the photoconductivity properties of the ZnO thin films covered with nanostructured metals (Au and Pt). It is shown that the interface states of metal/

semiconductor strongly affect the photoconductive characteristics. Meanwhile, the metals covering on the surface of the devices can also increase the dark current.

II. EXPERIMENT DETAILS

ZnO thin films were deposited on *c*-face sapphire substrates by ultrahigh vacuum ($<2\times10^{-8}$ Torr) pulsed laser deposition (PLD) using a 99.99% pure ZnO target. In our PLD system, a KrF excimer laser with a 248 nm line was used for the ablation of the ZnO target. The laser was operated at 20 Hz under a constant high voltage mode with a voltage of 18.5 kV. The films were grown at substrate temperature of 650 °C with the background O_2 pressure at 0.8 mTorr. High quality epitaxial ZnO films with thickness of 500 nm were fabricated on (0001) sapphire substrates. Atomic force microscopy measurements show that the films are very smooth with the surface roughness of ~0.4 nm. Indium metal contacts were thermally wedded on the ZnO films in a vacuum environment in order to fabricate the photoconductive detector. The schematic of ZnO-based photoconductor with nanostructured metals is shown in Fig. 1(a). The distance of two In electrodes is 0.8 cm and the width of the device is 0.5 cm. Different nanostructured metals (Au and Pt) were sputtered on the surface of the devices between two electrodes (0.5×0.5 cm^2) at the room temperature with the thickness of several nanometers using a dc sputtering system. Au and Pt disks were selected as the targets and the sputtering was carried out at room temperature. The surface of the samples is face-to-face parallel to the targets with the distance of 6 cm. The working pressure in the chamber was kept at 9.0 Pa during the deposition and the dc current was kept at 20 A. Ultrapure (5*N*) Ar gas was selected as sputtering gas. The deposition rates for Au and Pt were around 25 and 20 nm/min, respectively. The thickness of both Au and Pt is ~10 nm. All devices were fabricated on the same ZnO/

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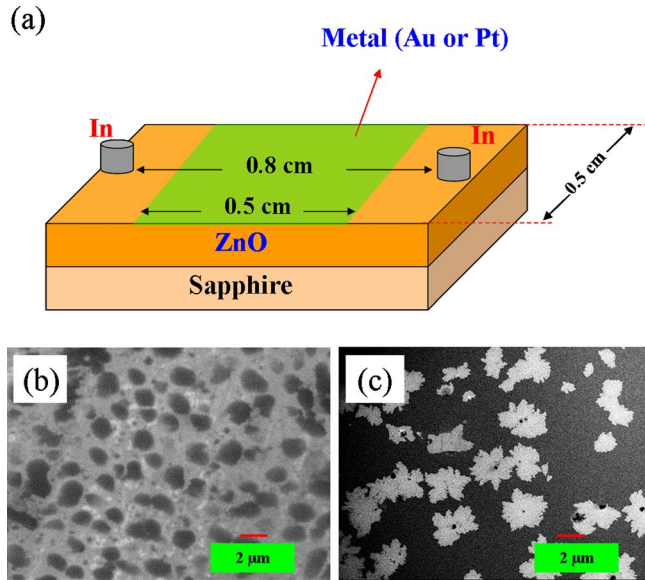b)Author to whom correspondence should be addressed. Electronic mail: hdsun@ntu.edu.sg.

FIG. 1. (Color online) (a) The schematics of ZnO-based photoconductors with nanostructured Au and Pt on the device surface. [(b) and (c)] SEM images of the morphology of Au and Pt nanostructures deposited on the device surface, respectively.

FIG. 2. (Color online) Room temperature PL spectra for ZnO (squares), ZnO with Au (cirlces), and ZnO with Pt (triangles). Inset is the typical *I-V* characteristics of ZnO photoconductors without metal (squares), with Au (cirlces), and Pt (triangles).

sapphire substrates and are identical. The scanning electron microscope (SEM) images of the Au and Pt ultrathin nanolayers are shown in Figs. 1(b) and 1(c), respectively. It can be seen that Au is netlike. Meanwhile, some holes with the diameter around $1-2$ μm can also be clearly observed. As for Pt, it is islandlike and dispersed rather than a continuous film. The size of Pt islands is around 2 μm. The difference in the morphology between Au and Pt may be caused by the nature of the metals. Both Au and Pt do not completely cover the whole 0.5×0.5 cm^2 area and have very rough surface. The photoluminescence (PL) spectra of the samples were performed in a conventional backscattering geometry with the 325 nm line of cw power of 15 mW from a He–Cd laser as the excitation source. The PL signal was collected from the top surface and detected by a photomultiplier tube using standard lock-in technique. The dark current was measured by a semiconductor parameter analyzer.

III. RESULTS AND DISCUSSION

A. Optical properties

Figure 2 shows the room temperature PL spectra from the ZnO films with and without nanostructured metals. The PL was excited and collected from the forward direction by a spectrometer (Acton, SP2750) and all samples were measured at the same conditions. In these PL spectra, all samples showed strong band edge emission around 380 nm and no obvious defect emission was observed. It is found that the integrated PL intensity of ZnO coated with Au and Pt was 3 and 1.5 times stronger than that of bare ZnO, respectively. The enhancement by Au and Pt capping should be attributed to the interaction between the spontaneous recombination in ZnO and surface plasmons arising from metal interfaces.[11] These enhancements should be closely associated with the morphology of Au and Pt because the coupled SP energy can be only converted to free space radiation via scattering by
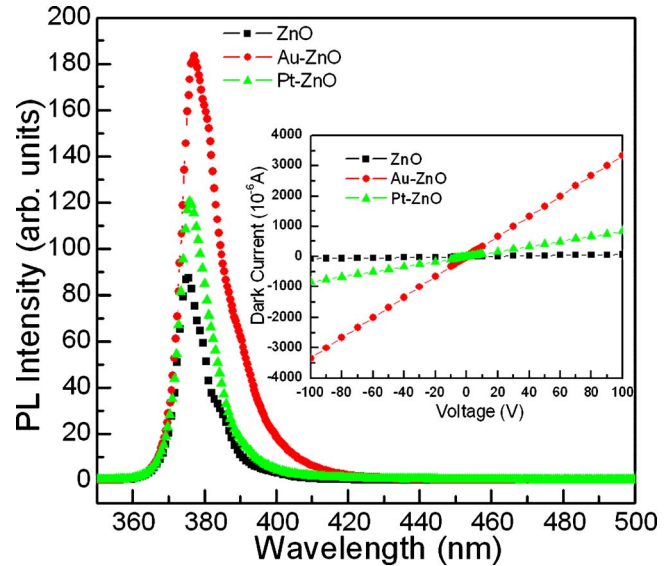
rough surface of metals. These results are in good accordance with the SEM images, confirming that the metals are not continuous films because otherwise the surface plasmon will be dissipated in the metal layers.[12] Meanwhile, the surface modification by covering with metals may be another reason for the enhancement in PL spectra.[13] Furthermore, it should be noted that the PL emission peaks show a little redshift after Au and Pt covering. The energy difference between band gap emission of ZnO and the SP energy of metals should be attributed to this phenomenon.[14]

B. Electronic properties

The typical *I-V* characteristics of ZnO photoconductors with and without nanostructured metals were measured by a sourcemeter (Keithley 2612) at the dark condition, as shown in the inset of Fig. 2. Such a linear relation indicates the Ohmic behavior of In electrodes on ZnO films contact for all devices. Under the constant bias of 5 V, the measured average dark current is 5, 41, and 160 μA for bare ZnO, ZnO with Pt, and Au, respectively. To clarify the reason for the increase in the dark current after covering with metals, the surface states must be considered. It is well known that the unintentionally doped ZnO is a *n*-type semiconductor for its intrinsic defects, such as oxygen vacancies.[15] The defects in the surface layer readily act as adsorption sites. The adsorption of a gas molecule, such as O_2 and H_2O, on the ZnO film surface will trap the free electrons in the films, i.e., $O_2(g) + e^- \rightarrow O_2^-$ (adsorption) and $2H_2O(g) + O_2 + 4e^- \rightarrow 4OH^-$ (adsorption).[16,17] Therefore, the surface states deplete the surface electron states and reduce the free carrier density, which results in the space-charge region and band bending near the surface, as illustrated in Fig. 3. Namely, a low-conductivity depletion layer is formed near the surface. After nanostructured metals covering, the density of surface states is reduced, and the barrier height of the built-in potential is accordingly decreased. It turns out that the concentration of
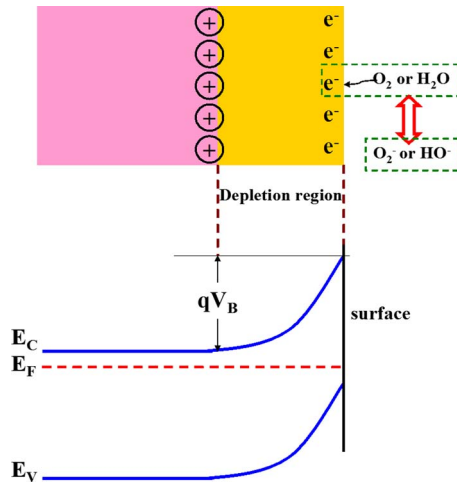
FIG. 3. (Color online) Schematic diagram of the formation of the surface depletion region and the energy band diagrams of the ZnO surface potential. The negative charge is trapped by the adsorbent surface states and the positive charge is produced by the depletion of the free electron. qV_B is the energy of band bending, E_C is the conduction band energy level, E_F is the Fermi level, and E_V is the valence band energy level.

the charge carriers near the surface of ZnO can be increased significantly. Therefore, the dark currents increase after covering with metals (Au and Pt) on the surface of the devices. Meanwhile, the increase in the mobility values in coated samples due to the reduction in electron scattering at their surface should be another reason for the dark current enhancement.[18] On the other hand, it must be noted that the metals can also induce some interface states between metals and ZnO.[19,20] These interface states should have the similar effect with surface states and can partly decrease the dark current. But the overall effects of metals covering on the surface of the devices (both the decrease in surface states and the increase in interface states) could result in the increase in the dark current of the photoconductors. As for the difference between Au-covering and Pt-covering devices, the nature of the metal and its chemistry with ZnO and other parameters may play an important role.[7] Comparing with the thin metal films covering on the surface of the semiconductor, the nanostructured metals should have the similar effect on the dark current. However, thin metal films have a large absorption and reflection due to their flat surfaces, in turn reduce the light-absorption in the semiconductor. But for the nanostructured metals, their rough surface can induce large scattering and increase the absorption in semiconductor.

C. Photoresponse and temporal response of ZnO photoconductors

The spectral responses of the ZnO photoconductors with and without metals are plotted in Fig. 4(a). Spectral responses were performed by a 50 W deuterium lamp with the applied bias of 5 V and the inset of Fig. 4(a) is the measurement configuration. In Fig. 4(a), it was found that the responsivities of ZnO photoconductors with Au and Pt covering are 3.6 and 3.1-times larger than that of bare ZnO photoconductor at the wavelength of 300 nm. Figure 4(b) shows the time response of the photoconductors. The response time of the devices was measured upon 325 nm light illumination by
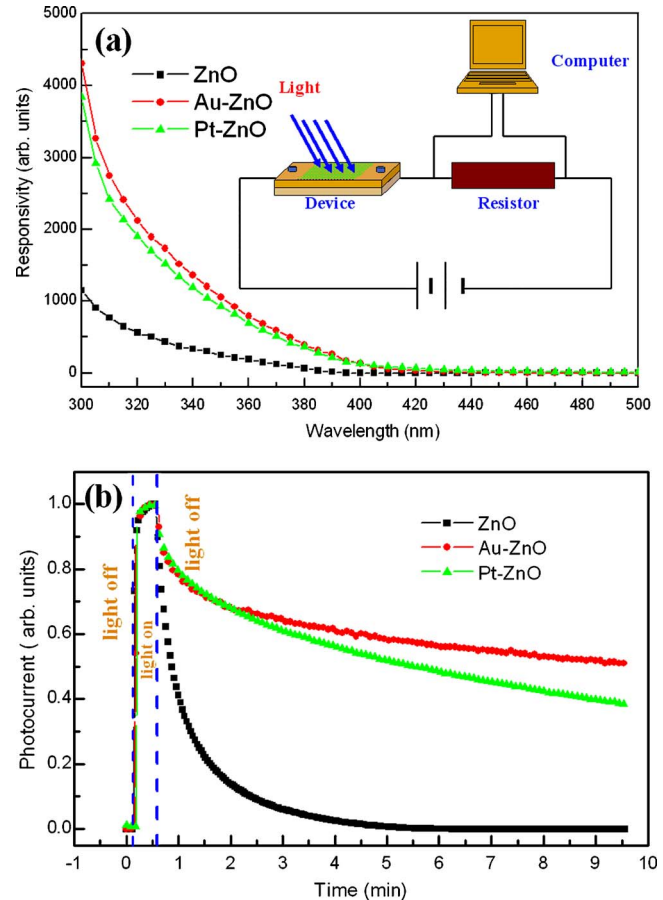

FIG. 4. (Color online) (a) Spectral responses of the ZnO photoconductors without metal (squares), with Au (circles), and Pt (triangles). The measurements were performed by a 50 W deuterium lamp with the applied bias of 5 V. (b) Temporal response of ZnO photoconductors without metal (squares), with Au (circles), and Pt (triangles).

mechanical chopping method and the light spot was expanded to totally cover the region between two electrodes. The conductance of the devices responds quickly to UV laser exposure, and reaches saturation rapidly. However, the photocurrent decays very slowly after the UV laser is turned off. Especially for the devices covered by nanometals, obvious persistent photoconductivity can be observed. According to the previous reports,[18] the persistent photoconductivity for ZnO is usually caused by surface states, which can trap the minority carriers and increase their mean lifetime. In our investigated devices, persistent photoconductivity is quite small for ZnO photoconductor without metals. Furthermore, after covering with metals, the surface states should be reduced and the decay rate of photocurrent should increase. However, it is found that the decay process becomes much slower after covering with Au and Pt, as shown in Fig. 4(b). These phenomena indicate that there must be another reason responsible for the persistent photoconductivity after covering with Au and Pt. As mentioned above, the covering on the devices with nanometals not only reduces the surface states but also induces some interface states between metals and ZnO. These interface states can act as the traps of minority carriers to increase their lifetime, in turn cause persistent photoconductivity. As we know, the photocurrent gain (g) can be expressed as[21]

$$g = \tau_p \mu_n V/L^2, \tag{1}$$

where τ_p is the mean lifetime of minority carrier, L is the distance between two electrodes, V is applied bias voltage, and μ_n is the electron mobility (estimated to be ~ 50 cm^2/V s).[15] The photoresponsivity could be estimated from the equation as[21]

$$R = q\lambda \, \eta g/hc, \tag{2}$$

where λ is the wavelength, h is Planck's constant, c is the light velocity, q is the electron charge, and η is quantum efficiency. According to Eqs. (1) and (2), it can be obtained that long lifetime of minority carriers can cause large photocurrent gain and in turn bring about big responsivity. These results were in good agreement with the response spectra. As for scattering and surface plasmon effect, they can provide the increase in optical absorption and responsivity without largely changing the device speed,[4] so they should partly contribute to the large photocurrent in our work. Therefore, the longer excess lifetime of minority carrier induced by interface states after covering with nanometals should be the main reason for the responsivity enhancement in ZnO photoconductors.

IV. CONCLUSION

In summary, we were able to enhance the photocurrent of ZnO photoconductors by covering nanostructured Au and Pt on the surface of devices. The time response results indicate that nanostructured Au and Pt thin films can induce many interface states which can act as the traps of minority carriers. These traps can increase the lifetime of minority carriers and in turn increase the photocurrent of the devices. Meanwhile, the covering of Au and Pt on the surface of the devices can increase the dark current due to the reduction in electron scattering at their surface and the increase in the free carrier concentration. Our work suggests that rational integration of ZnO and nanostructured metals is a viable approach to enhancing the photoconductive properties of ZnO, which may help to advance optoelectronic devices.

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