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Ultraviolet detectors based on ZnO films by thermal oxidation of Zn metallic films

Research Article

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Abstract: Metallic Zn films were deposited on glass substrates by electron-beam evaporation. ZnO films were synthesized by thermal oxidation of Zn metallic films in air. At the annealing temperature of 550°C, ZnO nanowires appeared on the surface, which mainly result from the decrease of oxidation rate. A ZnO ultraviolet photodetector was fabricated based on a metal-semiconductor-metal planar structure. The detector showed a large UV photoresponse with an increase of two orders of magnitude. It is concluded that promising UV detectors can be obtained on ZnO films by thermal oxidation of Zn metallic films. The ways of performing spectral response measurements for polycrystalline ZnO films are also discussed.

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Keywords: ZnO • Ultraviolet detectors • nanowires • thermal oxidation

1. Introduction

As a wide bandgap semiconductor, ZnO is a promising material for potential applications such as ultraviolet (UV) light emitting diodes, laser diodes, and photodetectors [1–6]. UV detection has many applications, such as air quality monitoring, gas sensing, missile plume detection, etc. [7–9]. There are reports on the studies of UV detectors based on ZnO films grown by many different techniques, such as metal-organic chemical vapor deposition (MOCVD) [1, 3], pulsed laser deposition (PLD) [10], etc. Actually, it is more essential to find an effective way to fabricate UV detectors with high sensitivity and low cost. As we know, high-quality ZnO films with low intrinsic defect concentrations could be prepared by thermal oxidation [11–15]. However, there are few reports on the UV detectors based on ZnO films grown by thermal oxidation.

Low-dimensional systems such as quantum dots, nanotubes, and nanowires have promising applications in nanoscale optoelectronic devices. Recently, many techniques have been employed to synthesize ZnO nanowires. For instance, ZnO nanowires were synthesized by chemical vapor deposition [16, 17], or through thermal oxidation of Zn nanowires grown by RF magnetron sputtering [18]. It was also reported that ZnO nanowires were obtained by lowering the oxidation rate of Zn vapor on the surface of Zn particles [19]. In this study, ZnO films whose surface

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was covered with ZnO nanowires were prepared on glass substrates by thermal oxidation of metallic Zn films, and high-sensitivity ZnO UV detectors based on such composite structure were also reported.

2. Experimental details

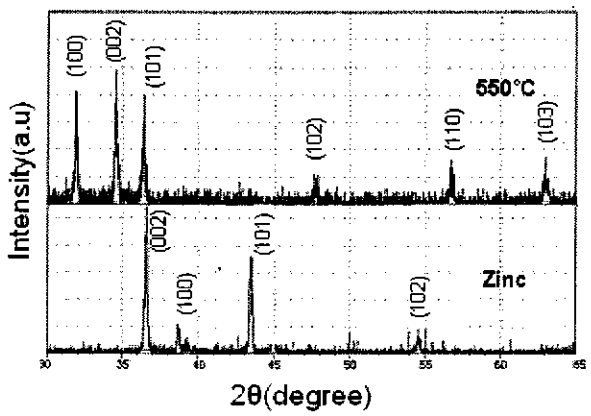


Figure 1. XRD patterns of the zinc films and the ZnO films prepared by oxidation at 550°C for 1h.

Zn films were deposited by electron-beam evaporation of a Zn target (99.99%) on glass substrates. The target-to-substrate distance was 24 cm. The base pressure of the growth chamber was 10^{-6} Torr. During deposition, the substrate temperature was maintained at 150°C at a growth rate of 0.5Å/s. The film thickness was measured to be about 600 nm thick. After deposition, the substrate was cut into several small pieces for oxidation. The Zn samples were placed in the bottom of an oven in an open-air environment. The annealing temperature was 550°C and the annealing time was 1 h. The annealed samples were cooled naturally to room temperature in the oven.

ZnO UV photodetectors were fabricated based on metal-semiconductor-metal planar structures. Two 200-nm-thick aluminum contacts were patterned on the ZnO surface with a shadow mask by electron beam evaporation. The distance between two electrodes is 0.1 mm.

The crystal structure and morphology of the films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Photoresponse measurements were performed using a 150 W Xe-arc lamp and a monochromator covering the range of 300 nm to 1050 nm. The bias voltage was 5 V.

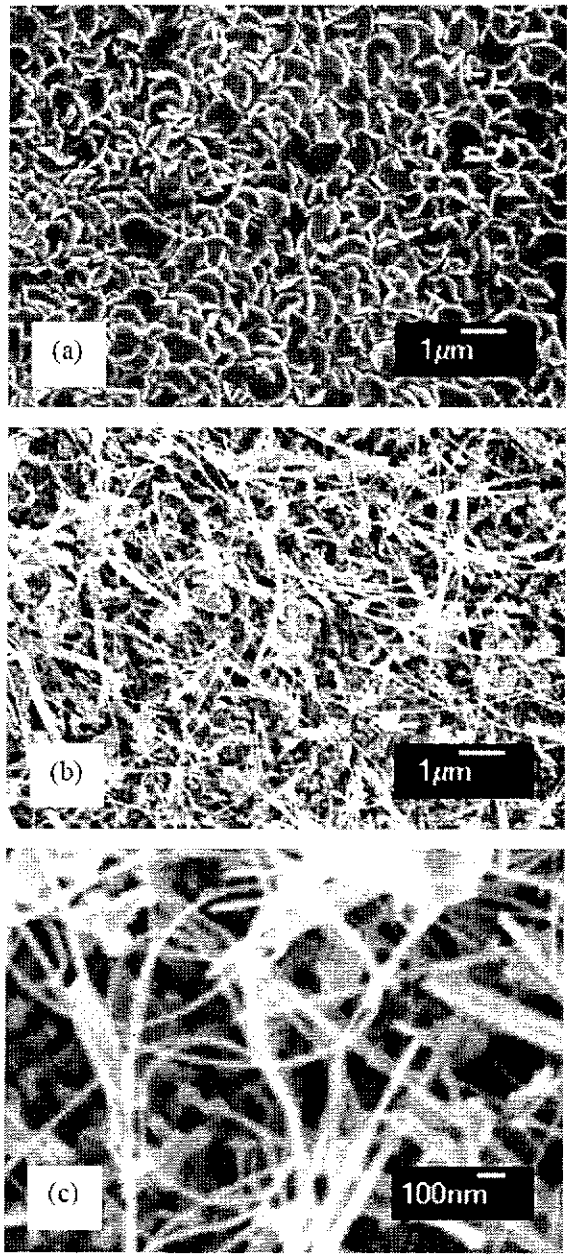


Figure 2. SEM images: (a) Zinc film. (b) ZnO film after thermal oxidation at 550°C for 1 h. (c) a high-magnification SEM image of Fig. 2(b).

3. Results and discussion

Fig. 1 shows the XRD pattern of the Zn film and ZnO film prepared by oxidation at 550°C for 1 h. The XRD measurements were conducted using the CuKα radiation with $\lambda = 1.54$ Å. The Zn film is polycrystalline with hexagonal

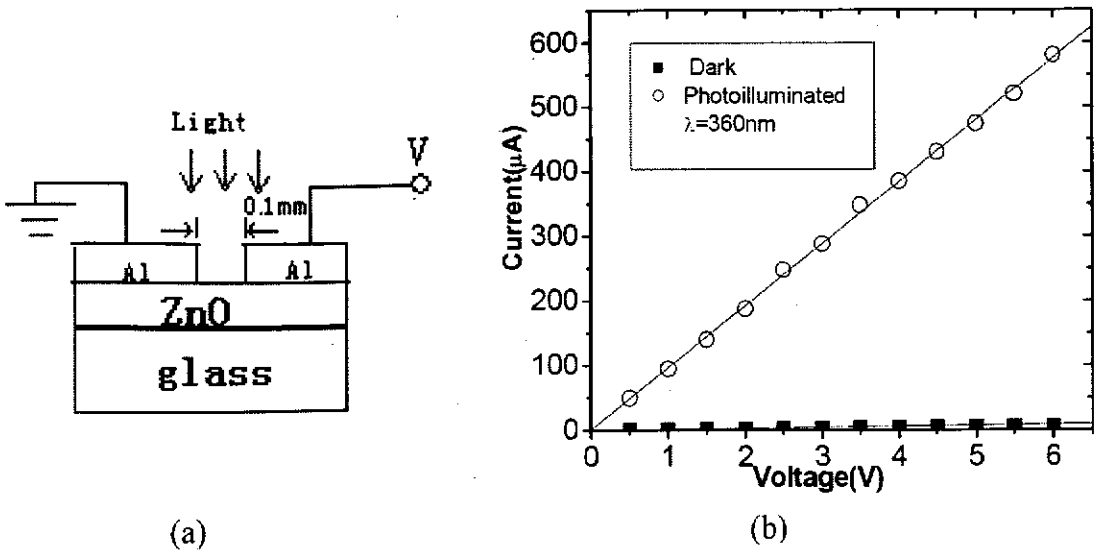


Figure 3. (a) Cross-sectional view of the ZnO UV detector. (b) Dark (diamonds) and photoilluminated (circles) I-V characteristics.

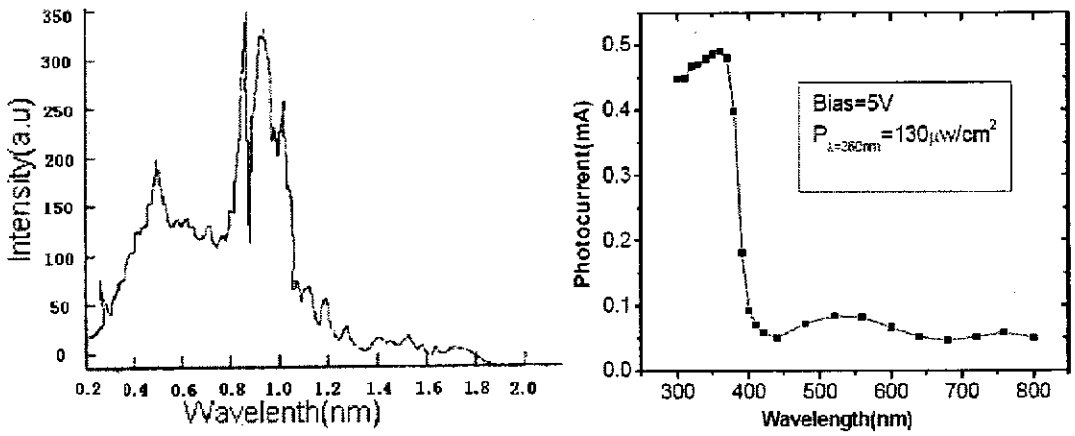
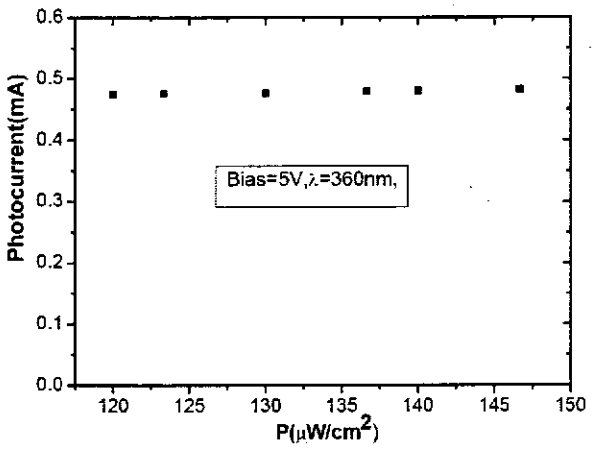


Figure 4. (a) Spectrum of Xe-arc lamp. (b) Spectral-response of the ZnO detector.

crystal structure. After oxidation, the Zn diffraction patterns disappear. Alternatively, several ZnO characteristic peaks appear, which corresponds to the (100), (002), (101), (102), (110), and (103) diffraction patterns of the hexagonal crystal structure. This suggests that Zn is totally transformed to ZnO after thermal oxidation at 550°C for 1h.

Fig. 2 shows SEM images of the Zn film and ZnO film after thermal oxidation at 550°C for 1 h. The Zn film is composed of sheet-like particles. After oxidation, the surface morphologies of the ZnO film change greatly. Nanowires with the length of about 10 micrometers are observed on the surface, which is very surprising. In order to attain more detailed surface structure information, An SEM image with high-magnification image is shown in Fig. 2(c). The mean diameter ranges from 10 nm to 30 nm, indicating the aspect ratio ranges from 300 to 1000.

It has been found that the low oxidation rate of Zn vapor on the surface of Zn particles contributes to the synthesis of ZnO nanowires. Zhou *et al.* [20] suggested a gas



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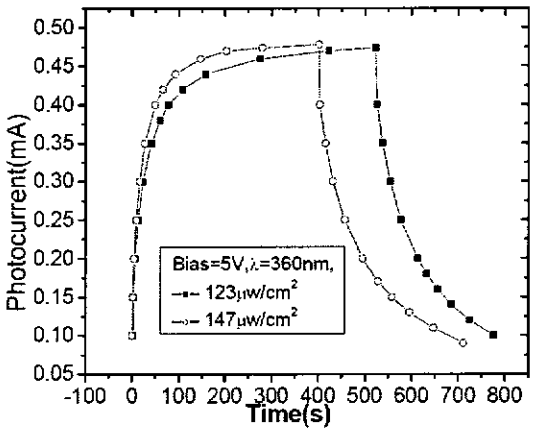

b

Figure 5. Under 360 nm light illumination: (a) Saturation photocurrent. (b) Photocurrent transients.

expansion method to decrease oxygen partial pressure to lower the oxidation rate. The principle is to decrease oxygen density by increasing the reaction chamber inner temperature. They synthesized ZnO nanomaterials successfully using this method. In our experiments, the reaction chamber is an open-air environment, and the oxygen partial pressure varied with the chamber inner temperature. When the oxidation reaction was carried out at 550°C, the oxygen partial pressure in the chamber can be 0.36 times of that before the oxidation. Consequently, the oxidation rate of Zn is low.

In the past, the studies of ZnO films by thermal oxidation were mainly focused on the crystal structure and PL characteristics, and seldom investigated the UV detection properties. In this study, ZnO ultraviolet (UV) detectors were fabricated based on ZnO films. Fig. 3(a) shows the cross-sectional view of the ZnO UV detector. Fig. 3(b) is the dark and photoilluminated I-V characteristics of the ZnO detector. The wavelength of the illuminated light is 360 nm. In this experiment, ohmic contact between the Al-electrode and ZnO film is crucial to ensure that I-V characteristics belong to the ZnO film itself. As can be seen from Fig. 3(b), both the dark and photoilluminated I-V relation are linear, indicating the ohmic contact between Al-electrode and ZnO film. The dark current for a bias voltage of 5 V is only 4.7 μA, indicating the high resistivity of the ZnO film after thermal oxidation of Zn metallic films at 550°C for 1 h.

In the spectrum of a Xe-arc lamp, optical power density varies with wavelength, as shown in Fig. 4(a). The power density of the ultraviolet wavelength of 360 nm is 130 μW/cm^2. Fig. 4(b) shows the spectral response of the ZnO detector. The photocurrent becomes maximum at around 360 nm and then falls in the visible range. This can be explained as follows [7]: When a photon of energy greater than the band-gap energy is absorbed in the ZnO film, an electron-hole pair is produced, changing the electrical conductivity of the film. Therefore, the band-gap energy is confirmed to be about 3.2 eV. Under a bias of 5 V, the dark current of the detector is 4.7 μA, while the photocurrent of 360 nm is 0.49 mA. The conductivity rises by a factor of 100. Moreover, the UV photoconductivity is more than 10 times the photoconductivity in the visible range. The results indicate that a photoconductive UV detector with high sensitivity has been prepared. Earlier high-quality ZnO UV detectors are mainly based on epitaxial films grown by expensive deposition techniques [1, 3, 10]. Our results might open up the possibilities for low-cost ZnO UV detectors. Fig. 4(b) also shows that there is a small rise from 450 nm to 600 nm, which is due to the photo-generated carriers excited from the deep-level traps [6].

The photoresponse of polycrystalline ZnO films deposited on glass substrates is mainly due to a two-step process [1]:

(a) Oxygen is adsorbed by taking a free electron from the film in the dark: $O_2(g)\ e \rightarrow O_2$

(b) Photogenerated holes discharge the negatively charged oxygen ions and the oxygen is desorbed: $h\ O_2 \rightarrow O_2(g)$

Adsorption and photodesorption of oxygen molecules play a great role in the polycrystalline ZnO photoconductivity. In this report, the high UV sensitivity is attributed to the large specific surface area of the film surface, because the film is covered with snaky nanowires. The composite structure has a large specific surface area and is favorable to oxygen adsorption in the dark. So the dark conductiv-

ity is very low. While under UV light illumination, a large amount of chemisorbed oxygen is photodesorbed, leading to the high UV photoconductivity. In this sense, our ZnO ultraviolet detector can also be employed as a gas (oxygen) detector.

We also performed photocurrent measurements with 360 nm light illumination, as shown in Fig. 5(a). The photocurrent is nearly invariable, while the input optical power density varies from 120 $\mu W/cm^2$ to 147 $\mu W/cm^2$, indicating the photocurrent of the detector is saturated. Shown in Fig. 5(b) are the photoconductivity transients with 360 nm light illumination. The input optical power density is 123 $\mu W/cm^2$ and 147 $\mu W/cm^2$, respectively. While under UV light illumination, the photocurrent increases slowly and ultimately reaches the peak value. When the incident power density increases from 123 $\mu W/cm^2$ to 147 $\mu W/cm^2$, it takes much less time for the photocurrent to become mostly unchanged. However, the peak value (saturation photocurrent) is the same.

For polycrystalline ZnO films, oxygen is adsorbed by taking a free electron in air in the dark, which lowers carrier the density and introduces a potential barrier. While under UV light illumination, photogenerated holes are captured by the negatively charged oxygen ions and leave excess conduction-band electrons. The neutralization prevents holes from recombining with electrons and increase the photogenerated electrons' life, causing the accumulation of conduction electrons. The oxygen photodesorption also lowers the barrier height of the grain boundaries and increases the carrier mobility. Consequently, the conductivity increases. As a conclusion, the photocurrent mainly results from the conduction-band accumulation of electrons and the gradual reduction of the grain-boundary barrier height during oxygen adsorption [10]. In our opinion, it is not appropriate to calculate the photoconductivity (R_λ) of photoconductive detectors based on polycrystalline ZnO films using $R_\lambda = I_{ph}/P_\lambda$, (where I_{ph} is the photocurrent and P_λ is the incident power) [6]. It is also not appropriate to perform spectral response measurements on normalizing light-power density at different wavelengths [2]. For polycrystalline ZnO films, it is a suitable way to perform spectral response measurements under saturation light illumination.

4. Conclusions

We prepared ZnO nanowires on a film surface by thermal oxidation of Zn metallic films in air on glass substrates and studied the formation mechanisms. The aspect ratio of nanowires ranges from 300 to 1000. We also demonstrated photoconductive UV detectors on such ZnO films. The UV photoconductivity of 360 nm increases two orders of magnitude compared to dark conductivity. For polycrystalline ZnO films, it is a suitable way to perform spectral response measurements under saturation light illumination. Our results provide another way to fabricate UV detectors or gas detectors with high sensitivity and low cost.

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