The Visible Light Photosensitivity Enhancement Of The P-n Type Cu$_2$O/ZnO Heterojunction

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The Visible Light Photosensitivity Enhancement Of The P-n Type Cu$_2$O/ZnO Heterojunction

Chuang Zhao$^1$, Jiaqi Pan$^1$, Shi Li$^1$ and Chaorong Li$^1$,*

$^1$Department of Physics and Key Laboratory of ATMMT Ministry of Education Zhejiang, Sci-Tech University, Hangzhou 310018, China

* Corresponding author: crli@zstu.edu.cn

Abstract: Transparent photosensitive Cu$_2$O/ZnO p-n junction film was prepared by a simple route of co-deposition method and radio-frequency(RF) magnetron sputtering. The results indicate that the Cu$_2$O were well arrayed on the surface of the ZnO film. Further, the transparent Cu$_2$O/ZnO p-n junction film exhibits an obvious photosensitive enhancement compared with pure ZnO films, which could be ascribed to the unique p-n junction and remarkable visible light response of the Cu$_2$O.

1. Introduction
ZnO, with high visible light transparency, stable physical and chemical properties, low cost and environment friendly features, is considered as an ideal transparent conductive material in electronic material field[1-3]. However, it could hardly respond and economize the visible light while maintaining high transparency[4]. So how to improve the responsiveness or utilization of the transparent ZnO in visible light would be one of the main research trends in future optoelectronics field. Up to now, lot of previous works about the transparent conductive ZnO have been reported, including doping or surface modification to provide additional photogenerated carriers. Such as Ebrahimifard et al. have prepared Al and Ga co-doped ZnO film for improving the conductive[5], or fabricate the p-n junction of CdS/ZnO[6], CuAlO$_2$/ZnO[7], etc. to promote the separation of the photon-generated carriers in illumination. However, the photoconductivity of the ZnO-based film would be expected to improve further.

There, the p-type Cu$_2$O, with stable structure, narrow band gap(2.2eV) and easy preparation are considered as the ideal materials[8-10]. Compared with other heterojunction, the p-n junction structure can promote the separation of the photo-generated carriers more efficiently, which is benefit for the photoconductivity[11-13]. In addition, the Cu$_2$O nano-particles arrayed on the surface of ZnO film, can form a special interface to increase the multiple reflections of visible light for increasing the utilization of light energy, which is another advantages for this modification.

In this paper, we prepare the p-n junctions Cu$_2$O/ZnO via a simple route of co-deposition method and radio-frequency(RF) magnetron sputtering. The results show that the p-n junction type Cu$_2$O/ZnO film possesses high transparency, high and quickly photoresponse. In addition, the enhancement mechanism of the photoresponse is studied.

2. Experiment

2.1. Materials
All the chemicals are analytical grade and purchased from Aladdin Industrial Corporation (Shanghai, China), the ZnO target purchased from Crystal Technical Material (Hefei, China).

2.2. Preparation

2.2.1. Preparation of the Cu2O
The Cu2O microcrystals were synthesized as follows: configured 80 ml CuCl2 solution (0.025 mol/L), and 1 g of PVP were added successively with vigorous stirring at 55 °C, then, 20 mL of NaOH solution (16 mmol) was added subsequently. After 30 min, 60 mL of C6H12O6 aqueous solution (0.6 mol/L) was added into the black suspension as the reducing agent[14,15] with stirring for 60 min until the solution turned to brick-red gradually. After cooling the solution to room temperature, the precipitate was separated by centrifugation, and washed by deionized water-alcohol several times, then dried at 60°C for 4 h in the vacuum oven.

2.2.2. Preparation of the ZnO films
ZnO films were prepared by RF magnetron sputtering using high purity ZnO target (99.99%) which has 60 mm diameter and 5 mm thick. A glass slide is used as the substrate and the substrate has a 4 cm distance to ZnO target. The back vacuum was 6×10^-4 Pa and sputtering power was 100 W. The work pressure and deposition time were 1.0 Pa and 1.0 h, respectively. The sputtering gas (40 SCCM) is Ar(99.999%) and the sputtering temperature is 350°C.

2.2.3. Preparation of Cu2O/ZnO heterojunction
First, 10 mg Cu2O was obtained and dissolved in 100 mL water, the concentration of Cu2O solution was 0.1 mg/ml, then the Cu2O was dropped on the surface of the ZnO film directly. The process was as follows: firstly, 0.2 ml Cu2O solution (0.1 mg/ml) was dropped onto the surface of 1×1 cm² ZnO film, and dried at 60°C for 30 min, then repeat adding twice the same volume of Cu2O solution. Finally, the film was dried at 200°C in vacuum for 4 h.

2.3. Characterization
Field-emission scanning electron microscope (FESEM, Hitachi S-4800) was used to investigate the surface morphology of the samples. The X-ray diffraction (XRD, Bruker AXS D8-discover) was used to characterize the crystal structures of the samples. UV-vis absorption spectrophotometer (U-3900 Hitachi) was employed to investigate transparency of the films. The PL spectra were recorded by a Hitachi F-7000 spectrofluorimeter at the excitation wavelength of 360 nm. The photoresponse such as the dark and illuminated currents was gauged by electrochemical workstation.

3. Results and discussions
Fig. 1. the XRD of the ZnO film and Cu$_2$O/ZnO film

Fig. 1 displays the XRD spectrum of the samples with different structure, including the ZnO film and Cu$_2$O/ZnO film. As revealed, the only diffraction peak in the ZnO film is ascribed to the (002) and (004) crystal plane of ZnO (PDF#36-1451). With the introducing of the Cu$_2$O, the obvious diffraction peaks of the Cu$_2$O could be observed and indexed to the (111), (200) and (220) crystal planes of the crystal Cu$_2$O (PDF#05-0667), respectively. No other obvious diffraction peak could be observed, which indicates that the samples are pure.

Fig. 2 is the SEM of the samples at different stage. As shown in Fig. 2a, the surface of the ZnO film is uniform and smooth, which could effectively reduce the boundaries between the crystal grains, thereby reducing the boundary reflection and improving the electrical conductivity of the thin film, the insert is the high resolution SEM. Fig. 2b is the SEM of the Cu$_2$O/ZnO film. As shown in Fig. 2b, the Cu$_2$O intersperse on the surface of the ZnO film, the insert is the corresponding high resolution SEM of the single Cu$_2$O, as shown, the Cu$_2$O is cube and the grain size is about 300 nm.
Fig. 2. The SEM of the samples (a) the ZnO film, insert: the high resolution SEM, (b) the Cu$_2$O/ZnO film, insert: the single Cu$_2$O.

Fig. 3. The optical transmittance spectra (T) of the ZnO film and Cu$_2$O/ZnO film.
Fig. 3 demonstrates the optical transmittance spectra (T) of the ZnO film and the Cu$_2$O/ZnO film. As shown, all of the films systems exhibit a high transparency in the visible light region (around \( \sim 75\% \) in average), the declivity in all curves is ascribed to the band gap of the ZnO[16]. Further, with the introduction of Cu$_2$O nanoparticles, the curves exhibit an obvious decrease and declivity around 600 nm, which causes by intrinsic defect and the band gap of the Cu$_2$O, the high transmittance can help the film applying to the transparent materials, and at the same time, the increasing visible-light utilization rate could increase photo-generated carriers to enhance the photosensitivity.

![Fig. 3: Optical Transmittance Spectra](image)

Fig. 4. The PL of the Cu$_2$O/ZnO film with different Cu$_2$O proportioning
Fig. 5 demonstrates the PL of the ZnO film and Cu2O/ZnO film (Cu2O was added 1 time, 2 time and 3 time respectively) with under the excitation of 360 nm. With the ratio of Cu2O increasing, the intensity of peak is lower and lower. It illustrated the separation of the photo-generated carriers.
become more effective and the higher efficiency of charge immigration with the content of Cu$_2$O increasing. However, with the Cu$_2$O content increasing, transmittance of the Cu$_2$O/ZnO film decreased gradually. Fig. 5 demonstrates the photoelectric properties of the ZnO film and Cu$_2$O/ZnO film. The photoelectronic measurement is carried out in room temperature with the illumination and darkness alternate 5 seconds($\lambda \geq 420$ nm $^*$), and both of the curves under 2 V bias voltage are fitted in uniform coordinate. As seen, the photocurrents of ZnO film is 0.95 $\mu$A, the ZnO films shows weakly photoconductivity, which could be ascribed to the intrinsic defect of ZnO. However, with the introduction of Cu$_2$O nanoparticles, the samples exhibited significant visible light photosensitivity, the photocurrents of Cu$_2$O/ZnO film is 2.33 $\mu$A, through calculation, the photosensitivity of Cu$_2$O/ZnO films is as high as 330%. It’s obvious that, with the introduction of Cu$_2$O, the photoelectric properties has a significant increase.

4. Conclusions
We have successfully prepared Cu$_2$O/ZnO film through a simple process and proved its excellent optical and photosensitivity, which could be mainly attributed to that the remarkable p-n junction of Cu$_2$O/ZnO could take advantage of the visible light efficiently. With the high transmittance and photosensitivity, the Cu$_2$O/ZnO film is regarded as a potential material in transparent-conductive field, and brings us a new vision for the designing of transparent devices and solar energy device.

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