Hydrothermal growth of quasi-crystalline ZnO thin films and theirs application in ultraviolet photodetectors

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Abstract

The use of a quasi-crystalline ZnO film grown by hydrothermal growth (HTG) method for the fabrication of Cu₂O/ZnO heterojunction (HJ) UV photodetectors is demonstrated. The HJ were formed via the sputtering deposition of a p-type Cu₂O layer onto the HTG ZnO film. The optoelectronic properties of Cu₂O/ZnO film with different Cu₂O thickness (250-750 nm) under UV (365 nm) light intensities (3 mW/cm²) were investigated and discussed. The prepared photodetectors based on HTG ZnO films show a much better UV sensitivity (I_{UV}/I_{dark}) as high as 22 (at 365 nm) as compared with that of 1.2 obtained from the one based on sputtering deposition.

1. Introduction

Zinc oxide (ZnO) is a well-known semiconductor material with a direct wide band gap of 3.37 eV and a large excition binding energy of about 60 meV at room temperature, which make it very suitable for UV-PDs application[1-2]. ZnO-based UV-PDs with nanowires (NWs) have attract a lot of attentional due to their ease of fabrication, low-temperature processing, and unique properties, such as higher aspect ratio, surface-to-volume ratio and carrier confinement in two dimensions that could improve device performance[3]. However, UV-PDs based on ZnO NWs usually suffer from reduced junction area for photo detection, in addition, integration of ZnO-NWs into working device still remains a complicated, time-consuming and uneconomic process to avoid possible short-circuit problem for ZnO-NWs-based UV-PDs [4]. In this study, the fabrication of ZnO film with a quasi-crystalline structure by hydrothermal growth (HTG) method is reported. Optoelectrical properties of UV-PDs based on the proposed and conventional sputtering deposited ZnO film quasi-crystalline ZnO film are compared and discussed.

2. Experiments

The present study demonstrates the fabrication and characterization of p-Cu₂O/n-ZnO film HJ for UV detection with improved performance. The key fabrication processes are schematically shown in Fig. 1. At first, a 100-nm-thick aluminum-doped-zinc-oxide (AZO) film was sputtered on indium tin oxide (ITO)-glass substrates to serve as a seed layer for the growth of ZnO film by HTG [5, 6]. Then the samples were placed in a solution of 0.04 M zinc nitrate hexahydrate and Hexamethylenetetramine at 70°C for 4 hour (Fig. 1(a)). After HTG, a p-Cu₂O film was sputtered onto the ZnO film and the p-Cu₂O/n-ZnO film HJ were formed (called HTG-device, Fig. 1(b)). Finally, an ohmic-contact electrode with 200-nm-thick Pt film electrodes was deposited on the surface of the p-Cu₂O layer through e-gun evaporation (Fig.

1(c)). For comparison, photodetectors based on the sputtering deposited (SD) ZnO film of the same thickness (called SD-devices) were also fabricated.

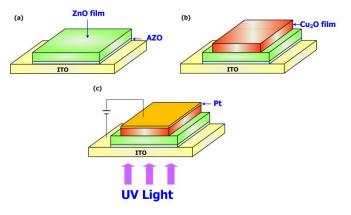


Fig. 1 Schematics of the process flow for the fabricaiton of $p-Cu_2O/ZnO$ film.

3. Results and discussion

The surface morphologies of the grown ZnO film and p-Cu₂O/n-ZnO film were characterized by scanning electron microscopy (SEM). Fig. 2(a) and 2(b) show that the quasi-crystalline ZnO films with a controllable thickness (300 nm) by hydrothermal and the tops of the ZnO films are covered with Cu₂O films (500 nm), respectively. The material properties were further analyzed by XRD (Fig 3). Based on the diffraction peak of (002) plane, ZnO films are indexed to be of hexagonal wurtzite structure according to the standard JCPDS card. It indicates that ZnO films are mainly composed of crystalline ZnO film (002), with c-axis vertical to the substrate surface.

The fabricated p-Cu₂O/n-ZnO (HTG) HJs with different Cu₂O thicknesses all exhibit well-defined rectifying behaviors in dark as shown in Fig. 4. Note that the sample with 250-nm-thick Cu₂O film exhibits the highest forward current. It possible be attributed to the fact that the thickness of the Cu₂O layer is so thin that the build-in voltage and depletion region is smallest than other devices. Similarly, the decrease in the forward current of the 750-nm-thick Cu₂O device might be due to the series resistance of the thicker Cu₂O layer. Among them, the sample with 500-nm-thick Cu₂O film might be most suitable for UV-PDs because it could have a wide enough depletion region and the lowest series resistor as compared with other samples. The possible band diagram of p-Cu₂O/n-ZnO film HJ under thermal equilibrium condition is shown in the inset of Fig. 4.

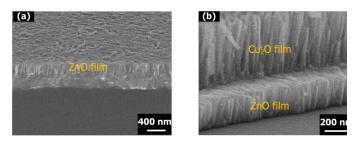


Fig. 2 SEM images of (a) HTG-ZnO film (300 nm) and (b) after Cu2O layer (500 nm) deposition.

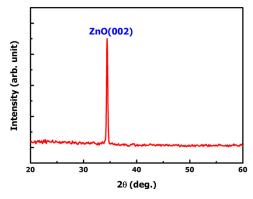


Fig. 3 XRD pattern of the ZnO film prepared by HTG.

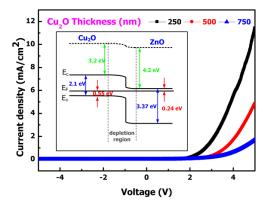


Fig. 4 The J-V curves of the p-Cu₂O/HTG-ZnO films HJs in dark. The inset shows the energy band diagram of the p-Cu₂O/n-ZnO HJ under thermal equilibrium.

Fig. 5(a) and (b) show the dynamic photoresponses of the fabricated HTG- and SD-devices. Note that the thickness of the p-Cu₂O and ZnO layer is 500 and 300 nm, respectively. The response times of the SD- and HTG-device are about 2 and 2 sec and the recovery times were about 60 and 3 sec, respectively, and the measured responsivities are 1.2 and 22 times, respectively. The HTG-device shows a 25-fold increase in the current at -5 V as irradiated by 365-nm UV light with a power density of 3 mW/cm^2 . The enhanced photoresponse of the HTG-device should be mainly attributed to the superiority of the optoelectronic properties of the quasi-crystalline ZnO film prepared by HTG. Although further investigation is still ongoing, it is speculated that the n-ZnO film grown by HTG has better crystal (quasi-crystalline) and optoelectrical characteristics than those of based on ZnO film prepared by SD.

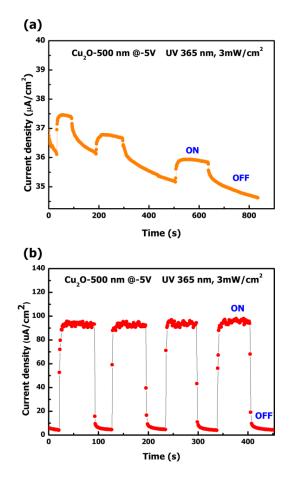


Fig. 5 Transient response of photocurrent density. (a) SD-device and (b) HTG-device.

4. Conclusion

In summary, p-Cu₂O/HTG-ZnO films HJs with good UV sensitivity have been demonstrated. Experimental results reveal that the Cu₂O/HTG-ZnO films HJs have fairly good response to UV light (3 mW/cm² at 365 nm) with an increase in the photocurrent of about 22 times. It is expected that the present HJs could provide a simple and effective mean for future optoelectronic applications.

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