Ultraviolet photodetector composed of ZnO nanosheets/Cu_2O heterostructure fabricated by hydrothermal process

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A highly sensitive ultraviolet detector (UV) sensor composed of ZnO nanosheets/Cu_2O heterostructure was fabricated. It composed of two dimensional ZnO nanosheets and Cu_2O film. The photoresponse results showed that the fabricated UV detector were sensitive to UV light illumination with good stability and reproducibility. The high UV response performance can be attributed to heterojunction formation and large surface area provided by ZnO sheets-like structures. The results indicated the suitability of the simple and low-cost ZnO nanosheets/Cu_2O heterojunction device for optoelectronic applications.

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1. Introduction

With a direct wide band gap (3.37 eV) and relatively large exciton binding energy of (60 meV) ZnO has been widely investigated for many optoelectronic, chemical and biosensing applications [1-10]. Likewise, cuprous oxide (Cu_2O) is another important metal oxide material that has been substantially explored for various fields of applications [11-14]. Till now, the Cu_2O/ZnO heterojunctions that were achieved by direct growth of Cu_2O on ZnO have been demonstrated [15-16]. However, these methods usually need high temperature, high pressure, high cost, especially high energy consumption. Therefore, developing a straightforward, low cost and low energy consumption way to synthesize large-area Cu_2O/ZnO heterojunction is a very important.

Meanwhile, the fabrication of ZnO/Cu_2O heterojunction has attracted optoelectronic and sensor applications. Because it can obtain excellent optical and electrical properties of ZnO and high absorption of Cu_2O in visible region. In recent years, the formation of nanostructured Cu_2O and ZnO by hydrothermal reaction has been attracted considerable attention due to its simplicity and large-scale growth ability [17]. However, it is also not easy to grow ZnO/Cu_2O heterostructure just by using single fabrication technique.

In this study, we reported a novel heterojunction structure composed of ZnO nanosheets and Cu_2O film, which was fabricated by a simple aqueous method. The heterostructure exhibited a prominent performance for UV detection response. It can be attributed to the increased surface area by the ZnO nanosheets and local p-n junction ares. The results indicated the suitability of low-cost Cu_2O/ZnO heterojunction device for optoelectronic applications. Furthermore, it will provide a facile route for large area growth Cu_2O/ZnO heterostructure for low cost UV detector applications.

2. Experimental

Cu_2O film was firstly prepared on pre-cleaned indium tin oxide (ITO) glass plate by two-step growth method. The ITO glass substrate was seeded via spin coating with 0.03M Cu $(CH_3COO)_2.2H_2O$ solution with alcohol as solvent and then annealed at 200℃ to achieve good adhesion between the seeding layer and the substrate. In a typical experiment 0.01 M aqueous solution of Cu $(CH_3COO)_2.2H_2O$ and $C_6H_{12}N_4$ was prepared. The ITO glass was put into the above solution at 90 for 5 h. For the growth of ZnO nanosheets structures, the Cu_2O/ITO substrate was seeded via spin-coating by using zinc acetate solution with alcohol as solvent, then annealing at 200℃ for 30min. Then, 0.03M $(Zn(CH_3COO)_2)$ was prepared. And it was dissolved in alcohol at room temperature. Finally, the seeded Cu_2O/ITO was immersed into the alcohol reaction solution, and the react temperature was kept at 70℃ with 5 h hours.

Structural characteristics of as-grown heterostructures were investigated using X-ray diffraction (XRD). The morphology of the as-deposited material was examined using scanning electron microscopy (FE-SEM, Hitachi S-4800). The current voltage characteristics of the sample were measured using a Keithley 2400 voltage source instrument. The device performance was characterized by current-voltage (I-V) characteristics and time photoresponse measurement was carried out by switching the light from a portable UV lamp (λ = 365 nm, 30 mW/cm^2) on and off. The distance between the sample and the UV lamp was fixed.

3. Results

Fig. 1 showed the XRD patterns of as-grown ZnO/Cu_2O heterojunction structures. All the peaks in the patterns correspond to the hexagonal Wurtzite and cubic type structures of the ZnO and Cu_2O crystallites, respectively. The peaks at 43.9°, 64.4° and 77.4° are originated from (200),(220) and (220) lattice planes of face centered cubic Cu_2O phase [JCPDS card no. 34-1354]. Meanwhile, the peaks observed 31.8°, 34.6°,36.5° and 47.8° which corresponded to the planes (100), (002), (101) and(102) of hexagonal wurtzite ZnO phase (JCPDS 36-1454) . No additional peaks related to other phases such as Zn, $Zn(OH)_2$ were detected suggesting that the grown ZnO nanostructures are of high purity.

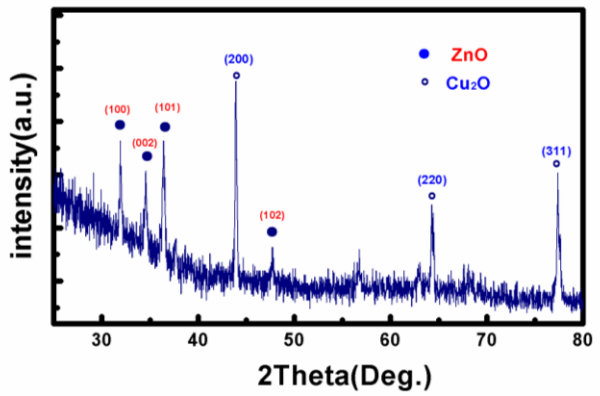

Fig. 1. The XRD patterns of as-grown Cu_2O/ZnO heterojunction structures

Fig. 2 (a) showed the SEM image of the surface morphology of the as-grown Cu_2O film with top view. The film shows grain-like morphology. And it shows densely packed and uniform size crystallites. Meanwhile, it can be seen that he film has a quite uniform surface and the average grain size is about 30 nm. Fig. 2 (b) and (c) displayed the SEM images of ZnO nanosheets prepared on Cu_2O layer with different magnifications. It can be seen that the substrate is covered by hexagonal sheets with almost uniform diameter in a large scale. From the SEM images, we can also observe that these sheets are vertical to the Cu_2O layer. Fig. 2 (d) depicted the cross-sectional SEM of as-grown Cu_2O/ZnO nanosheets heterostructure. It can be seen that as-synthesized ZnO nanosheets merged with each other to form densely packed film, and the thickness is around 150 nm.

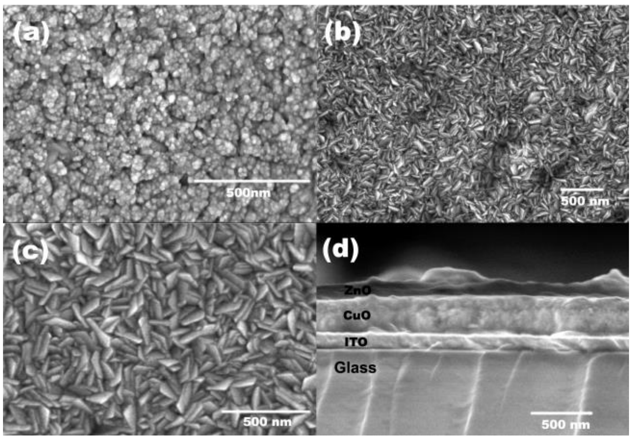

Fig. 2. (a) SEM image of the Cu_2O film grown on ITO/glass substrate. SEM images of Cu_2O/ZnO heterojunction structures with different magnifications. (b)low magnification (c) high magnification. (d) The cross-sectional view of Cu_2O/ZnO hetrojunction structure

The schematic structure of the Cu_2O/ZnO nanosheets heterostructure photodetector was shown in the Fig.3. The ITO film was used to act as top electrodes to increase the contacting the area on the ZnO nanostructures. Then, the as-grown Cu_2O/ZnO nanosheets heterostructure was placed on the prepared ITO/glass substrate. The tip of Cu_2O/ZnO nanosheets heterostructure was directly contacted with the ITO/glass substrate. The UV response of the devices was characterized by a portable UV lamp at room temperature.

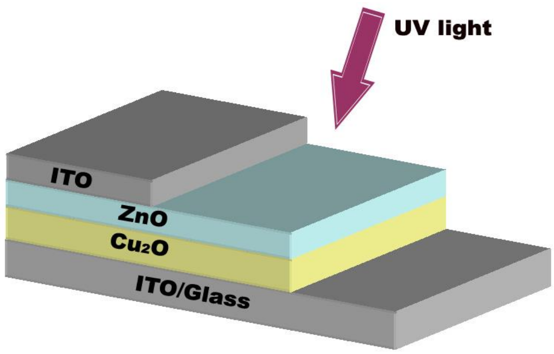

Fig. 3. The schematic diagram of Cu_2O/ZnO heterojunction device structures

The I-V characteristics of the photodetector based on ZnO nanosheets/Cu_2O heterostructure under dark and UV illumination are shown in Fig.4. The I-V curve was measured with bias from -5 to 5 V at room temperature in ambient condition. Clear rectifying behavior can be observed for the sample with and without UV illumination. The current of ZnO nanosheets/Cu_2O heterostructure was increased from 3.4×10^{-7} A to 7.2×10^{-6} A under UV illumination with an applied voltage of 3 V.

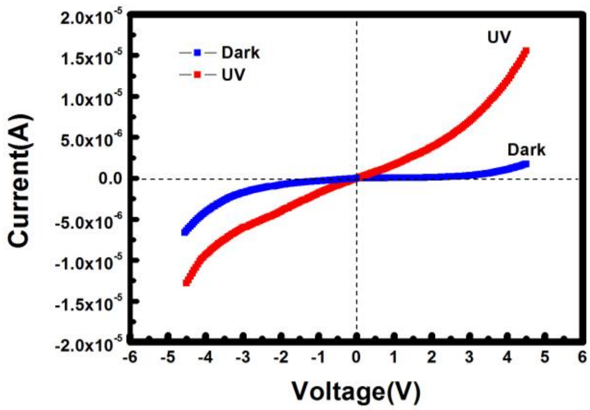

Fig. 4. Current-voltage characteristics of Cu_2O/ZnO heterojunction under dark and illuminated conditions

The repeatability and response speed of the Cu_2O/ZnO nanosheets heterostructure UV detector were measured. Fig. 5 showed the time-dependent response of the ZnO nanosheets/Cu_2O heterostructure structure. The time-resolved photocurrent was measured under 3V bias with multiple UV on/off cycles, in which both the UV light turn-on and turn-off times of the UV light were 30 s. It can be seen that the heterojunction exhibits a nearly identical and repeatable response after multiple illumination cycles. Meanwhile, the photocurrent increases very rapidly upon exposure to UV radiation, stays essentially constant during the UV light exposure, and decays very fast when UV light is turned off.

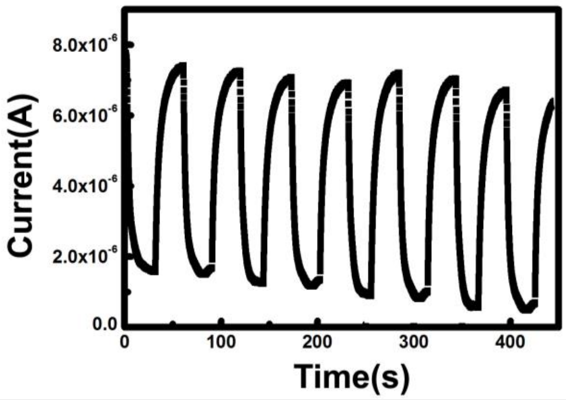

Fig. 5. The time-dependent response curve of the Cu_2O/ZnO heterojunction structures

4. Discussion

For the ZnO/Cu_2O heterojunction structure, in dark conditions, oxygen molecules would adsorb on the ZnO nanosheets surface by capturing free electrons. It will create surface depletion layer with low conductivity. The density of electron-hole pairs in the ZnO nanosheets and Cu_2O film increases significantly when illuminated with UV light. The holes from the Cu_2O film excited by UV light would move to the ZnO nanosheet surface across the ZnO/Cu_2O heterojunction, then take part in the oxidization of the ionized oxygen and release one oxygen gas molecule by an electron-hole recombination process. Meanwhile, it is well known that one dimensional nanostructure can effectively improve the charge transport, but its low surface area limits the enhancement of photocurrent density. In our case, Cu_2O/ZnO nanosheets heterostructure could be one candidate which can simultaneously enhance surface area and charge transport. The high UV response can be attributed that large numbers of ZnO sheet-like structure with high surface-to-volume ratio on the Cu_2O film increased the surface area, and caused more active sites on the surface and high absorption in the UV region. Thus, the fabricated device showed excellent UV sensing properties.

5. Conclusions

In summary, a highly sensitive UV sensor based on Cu_2O/ZnO nanosheets heterostructure was fabricated by using aqueous method. The heterostructure composed of Cu_2O film and ZnO nanosheet structure which exhibited a prominent performance for UV detection response. The results indicated the suitability of low-cost ZnO nanosheets/Cu_2O heterojunction device for optoelectronic applications. Furthermore, it will provide a facile route for large area growth ZnO nanosheets/Cu_2O for low cost UV detector applications.

Acknowledgments

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