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Low temperature preparation p-CuI/n-ZnO wide gap heterojunction diode

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ABSTRACT

Wide gap diode structures are attractive for various applications including tandem solar cells, light emission devices, UV detectors, and display technology. p-CuI/n-ZnO wide gap heterojunction diode have been prepared at a low cost by chemical method. The prepared hexagonal ZnO and γ-CuI films are polycrystalline nature and observed preferential orientation along the (0 0 2) and (1 1 1) axis aligning with the growth direction, respectively. The heterojunction shows a good rectifying behavior with a I_F/I_R ~600 at 3 V. The turn on voltage (2.05 eV) from *I–V* characteristic is agree with the built-in potential (2.1 eV) from *C–V* characteristic. The current transport mechanism is dominated by the recombination tunneling at low forward bias voltages and by the space-charge limited current (SCLC) conduction at higher forward bias voltages. This heterojunction diode can be good used for light emission devices and UV detectors.

1. Introduction

Wide gap diode structures are attractive for various applications including tandem solar cells, light emission devices, UV detectors, and display technology [1]. Utilization of wide gap semiconductors for fabrication of p–n heterojunctions often fails due to doping limitations in semiconductors having a large band gap [2]. Typical p-type semiconductor is difficult to dope n type, and vice versa. In our material system, as a wide band-gap (3.37 eV) oxide semiconductor material, ZnO has been described as a good candidate for Wide gap diode applications [3]. However, owing to the lack of stable and controllable p-type ZnO films, in most cases, heterojunctions were used to fabricate ZnO-based UV photodiode with a different p-type semiconductor, such as NiO [4], 6H-SiC [5], Si [6–10] and so on. Among all of these p-type semiconductors, the role of the wide gap emitter material plays CuI of p type, having a band gap of 3.1 eV [11]. The injected carrier types are holes and belong to the I–VII semiconductors with Zinkblende structure. Its ability as a transparent hole collector has been successfully demonstrated in solid-state dye-sensitized solar cells [12]. In the following, growth and properties of p-CuI/n-ZnO wide gap diode are studied in detail.

2. Experimental details

In the present paper, we report that wide gap diode of a structure "indium doped tin oxide (ITO) glass/p-CuI/n-ZnO/ITO" (Fig. 1).

The substrate used in the present work was indium doped tin oxide (ITO) glass. ZnO films were grown using a simple two-step process: spin-coating ZnO seeds on the substrate and growth of ZnO films on the seeded substrate by chemical bath deposition (CBD) [13–15]. Then we deposit CuI on n-ZnO/ITO glass substrate at room temperature by the successive ionic layer adsorption and reaction (SILAR) technique [16–18]. All chemicals were used as received without further purification.

In the first step, ZnO seed was prepared by a sol–gel method [19]. Basically, 0.09 g $Zn(CH_3COOH)_2$ and 0.12 g KOH were dissolved into 50 ml methanol, respectively. They were mixed rapidly, and stirring at 60 °C for 5 min, then cooled to room temperature. The resultant solution was transparent with ZnO nanoparticles. The solution was then spin-coated on the substrate at 500 rpm for 15 s, and 3000 rpm for 55 s. After processing, the substrate was heated at 60 °C for 10 min to remove the solvent.

In the second step, ZnO growth was carried out by suspending the substrate in a 200 ml baker filled with an equimolar aqueous solution of zinc nitrate hydrate and methenamine at 90 °C for 3 h. Subsequently, the substrate was removed from the solution, rinsed with deionized water and dried in air at 60 °C.

The deposition of CuI thin films onto n-ZnO/ITO glass substrate was taken at room temperature by SILAR method. We

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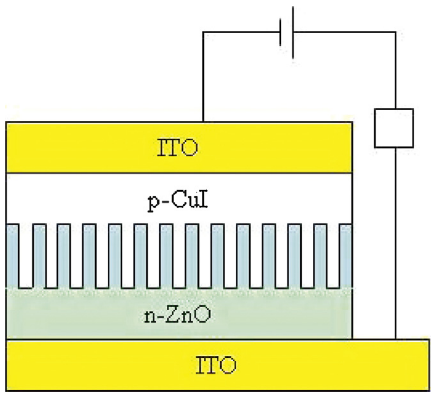

Fig. 1. Schematic structure of fabricated ITO/p-CuI/n-ZnO/ITO diode.

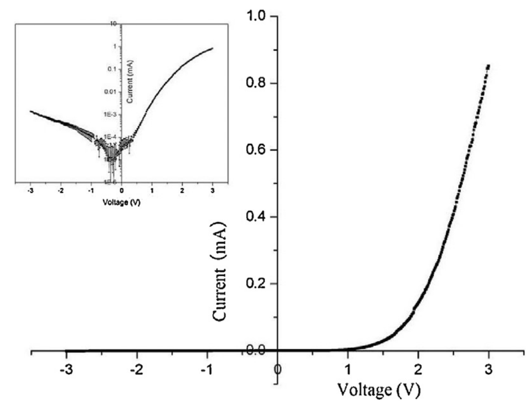

Fig. 3. *I–V* curve for the p-CuI/n-ZnO/ITO heterojunction. *Inset*: semilog plot.

used $CuSO_4{\cdot}5H_2O$ (0.1 mol/dm^3) solution complexed by $Na_2S_2O_3$ (0.1 mol/dm^3) as a cationic precursor. The release of Cu (I) ions is possible via the following reaction $[Cu(S_2O_3)]^- \leftrightarrow Cu^+ + S_2O_3^{2-}$ which acts as a source of cations. The ratio of the $CuSO_4$:$Na_2S_2O_3$ is 5:2. Aqueous solution of KI (0.025 mol/dm^3) is used as an anionic precursor. The ZnO/ITO glass substrate was immersed in a cationic precursor for 5 s. Copper ions ware absorbed on the surface of the substrate and the un-absorbed ions ware removed by rinsing the ZnO/ITO glass substrate in de-ionized water (resistivity ~ 18 MΩ cm) for 5 s. For the reaction with I^- ions, the substrate was immersed in an anionic precursor for 20 s. The powdery material or loosely bounded ions were removed by rinsing the substrate in de-ionized water for 5 s. This completes one SILAR cycle. The number of SILAR cycles is 40.

The ITO/p-CuI contact was obtained simply by pressing a commercial ITO glass on a deposited p-CuI films. The phase composition of the samples was characterized by X-ray powder diffraction (XRD, RINT-2100 V, Rigaku, Cu Kα). Current–voltage (*I–V*) characteristics between two ITO glasses were measured using a Agilent sourcemeter (model 4156C). Capacitance–voltage (*C–V*) characteristics ware measured using an Agilent LCR meter (model 4824A). Electrical resistivity of the films was measured by a four-point method (4 PROBES TECH China RTS-9).

3. Results and discussion

3.1. Structural characterization

Fig. 2 shows the XRD spectra of the as-grown CuI/ZnO films on ITO glass is presented. The observed inter-planer distance "*d*" is compared with JCPDS data which is in good agreement with the standard "*d*" values. Analyses of XRD data reveal peaks corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) planes of the hexagonal ZnO crystal structure, and different peaks of γ-CuI corresponding to planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (4 0 0) of face-centered cubic structure have been identified. The preferential orientation of the ZnO and γ-CuI grains are observed along the (0 0 2) and (1 1 1) axes aligning with the growth direction, respectively. The presence of a number of peaks in XRD pattern is the indication of polycrystalline nature of the ZnO and CuI.

3.2. Electrical characteristics

The resistivity of ITO, n-ZnO and p-CuI are 63 Ω/€, 155 Ω/€ and 230 Ω/€, respectively. The electrical conductivity of p-CuI as well as commercial ITO glass is very high, and the obtained current was stable with time, indicating that a reasonable electrical contact is formed at the ITO/p-CuI interface. The *I–V* characteristic of the heterojunction in Fig. 3 exhibits a good rectifying behavior with a I_F/I_R ~600 at 3 V indicating formation of a diode (I_F and I_R stand for the forward and reverse currents, respectively). The rectification ratio is better than the value (~361 at ~3 V) for the ZnO nanorods/n-Si heterojunction observed by Huang et al. [8], is better than that (~154 at ~2 V) observed by Wu et al. [20] for the n-ZnO nanorods/p-CuSCN heterojunction. This indicates that the electrical property of our p-CuI/n-ZnO heterojunction is comparable to the other junction made by more costly and sophisticated method. The turn on voltage and reverse leakage current values are found to be 2.05 V and 8.52×10^{-4} A at −3 V (equivalent to 2.13×10^{-4} A/cm^2, taking into account the contact).

The $1/C^2$ versus voltage curve of the p-CuI/n-ZnO/ITO heterojunction diode was shown in Fig. 4. The linear relationships imply

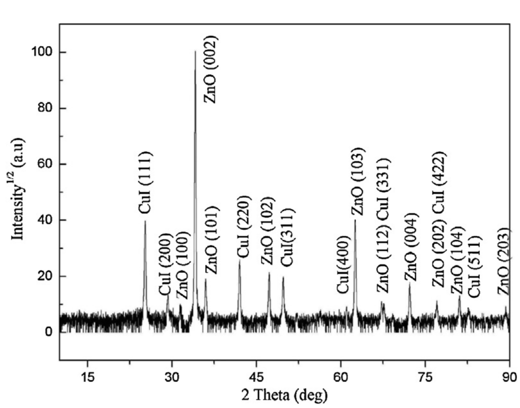

Fig. 2. X-ray diffraction spectra of p-CuI/n-ZnO films on ITO glass.

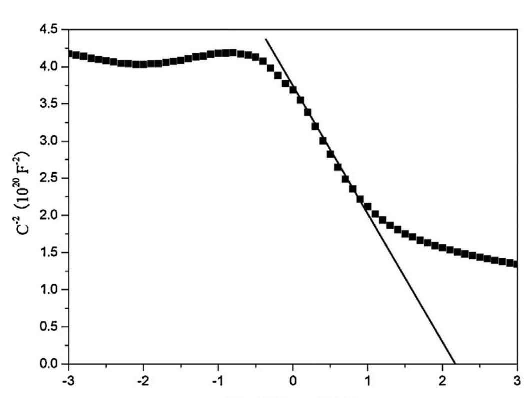

Fig. 4. The $1/C^2$ versus voltage curve of the p-CuI/n-ZnO/ITO heterojunction diode measured at 500 kHz.

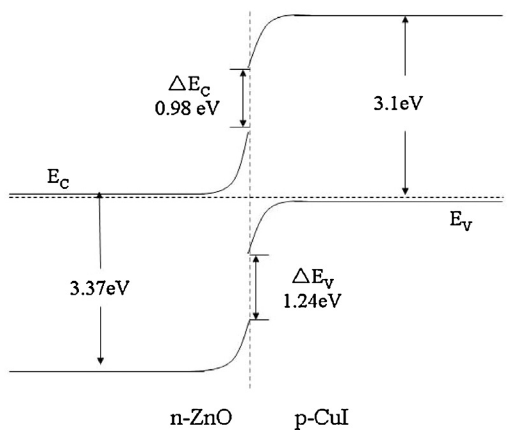

Fig. 5. The energy band diagram of p-CuI/n-ZnO heterojunction.

that the built-in potential V_{bi} of the heterojunction was found to be 2.1 V, which was nearly in agreement with the observed turn on voltage (2.05 V).

3.3. Discussions of energy band diagram

Fig. 5 shows the theoretically expected equilibrium energy band diagram of the p-CuI/n-ZnO heterojunction according to the Anderson model [21]. Under the assumptions that (i) the interface states can be neglected and the Fermi level in the ZnO and CuI lies at the ZnO conduction band edge and CuI valence band edge, respectively. The band gap for ZnO is 3.37 eV [22]. The valence band offset of ZnO/$CuInS_2$ and CuI/$CuInS_2$ are 1.34 eV [23] and 0.1 eV [24], respectively. So the valence band offset of ZnO/CuI can be calculated and the value is 1.24 eV. Using these parameters, as can be seen from Fig. 5, the conduction band offset of p-CuI/n-ZnO heterojunction is 0.98 eV. The model shows the maximum built-in potential V_{bi} of the heterojunction is 2.13 eV, which is nearly in agreement with our *C*–*V* measurement results of Fig. 4.

3.4. Carrier transport mechanism

In Fig. 6, we presented the dark current as a function of junction–voltage in forward bias. At low forward voltage ($V < 1.6$ eV) (region I), the current increased exponentially as the relation of $I \sim \exp(\alpha V)$, which usually observed in wide band gap p–n diodes [25–27], and attributed to the recombination-tunneling mechanism. The constant α has been evaluated to be 5.8 V^{-1} by fitting the experimental data in Fig. 6. From Fig. 5, we know that the conduction band offset (ΔEC) and the value band offset (ΔEV) for

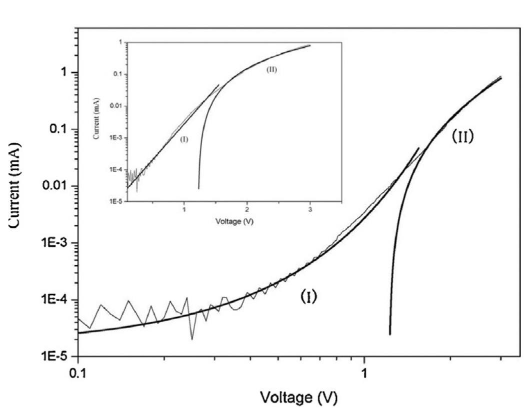

Fig. 6. Log–log plots of the dark current versus voltage in forward bias and inset shows the semilog plot of dark current versus voltage in forward bias.

this heterojunction are very large. The potential barrier for electrons transport from the bottom of conduction band in n-ZnO to the bottom of conduction band in p-CuI and the holes transport from the top of value band in p-CuI to the top of value band in n-ZnO are very large, so the difficulties for transport of electrons and holes in low forward bias is increased. Some defects at the interface providing the recombination tunneling path. That being the case, the recombination-tunneling mechanism dominated the current transport mechanism. When $V > 1.6$ eV (region II), the *I*–*V* characteristic was deviated from the ideal thermionic emission and behaved as $I \sim V^2$ relation, which was attributed to the space-charge limited current (SCLC) conduction [28,29]. This SCLC mechanism is a normal phenomenon in the wide band gap semiconductors due to single-carrier injection [28–30]. Since the difference between ΔE_C and ΔE_V the energetic barrier was much lower for electrons than holes. In the region II, the current is dominated by electrons.

In summary, ITO/p-CuI/n-ZnO/ITO heterojunction diode are prepared at a low cost by chemical method, and shows a good rectifying behavior with a I_F/I_R ~600 at 3 V. The prepared hexagonal ZnO and γ-CuI films are polycrystalline nature and observed along the (0 0 2) and (1 1 1) axis aligning with the growth direction. The turn on voltage (2.05 eV) from *I*–*V* characteristic is agree with the built-in potential (2.1 eV) from *C*–*V* characteristic. The current transport mechanism is dominated by the recombination tunneling at low forward bias voltages and by the SCLC at higher forward bias voltages. This heterojunction diode can be good used for light emission devices and UV detectors.

Acknowledgments

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