Study on the Synthesis, Characterization of p-CuSCN/n-Si Heterojunction

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Abstract: The p-CuSCN/n-Si heterojunction is fabricated by depositing CuSCN films on n-Si (111) films substrate using successive ionic layer adsorption and reaction (SULAR). CuSCN films show β-phase structure by virtue of X-ray diffraction (XRD) spectroscopy. ZnO/CuSCN heterojunctions exhibit good diode characteristics and photovoltaic effects with illumination form its current-voltage (I-V) measurements. The linear relationship of $1/C^2$ versus voltage curve implies that the built-in potential V_{bi} and the conduction band offset of the heterojunctions were found to be 2.1eV and 1.5eV, respectively. The forward conduction is determined by trap-assisted space charge limited current mechanism. At forward bias voltages, the electronic potential barrier is larger than holes in the p-CuSCN/n-Si heterojunction interface. In this voltage area, a single carrier injuction is induced and the main current of p-CuSCN/n-Si heterojunction is hole current. In addition, a band diagram of ZnO/CuSCN heterojunctions is also proposed to explain the transport mechanism. This heterojunction diode can be well used to light emission devices and photovoltaic devices.

Keywords: Heterojunction diode, p-CuSCN/n-Si, the current transport mechanism.

1. INTRODUCTION

Wide gap semiconductor films/Si heterojunction structures have been intensively studied these days for various applications including solar cells, light emission devices, UV detectors, and display technology [1-3]. Interface states of the heterojunction is difficult to overcome. Among all of these p-type semiconductors, CuSCN of p-type plays an role in the wide gap emitter material, having a band gap of 3.6 eV, which has been used in extremely thin absorber solar cells (ETAs) as a p-type hole conducting material [4-8]. Additionally, as an economically viable optoelectronic device material and preparation of CuSCN films at low temperature, p-CuSCN films have drawn intensive attention [7-11]. Literatures [6] and [7] focused on filling of CuSCN on ZnO rod arrays by the electrodeposition method to form p-CuSCN/n-ZnO rod array interpenetrating heterojunctions. Aé *et. al.* [8] reported a hybrid flexible vertical nanoscale diodes, which formed by n-type ZnO and p-type CuSCN embedded in polymer foil, by using electrochemical deposition technique. In Ref. [9], they presented a light-emitting diodes consisting of n-ZnO nanorods and p-CuSCN prepared by electrochemical method. However, there are few reports to research for p-CuSCN/n-Si heterojunctions recently.

In this paper, p-CuSCN/n-Si heterojunctions are fabricated by using simple solution method at low temperature. CuSCN thin films are deposited on n-Si substrate by SILAR. This method fabricating p-CuSCN/n-Si heterojunctions has not been seen in previous reports. The current transport properties of the heterojunctions are also investigated by means of current-voltage measurements and capacitance voltage method.

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2. EXPERIMENT

2.1. Deposition of CuSCN Films Using SILAR

The deposition of CuSCN thin films onto n-Si substrate was taken at room temperature by SILAR method. Here, we used $CuSO_4{\cdot}5H_2O$ (0.02 mol/L) solution complexed by $Na_2S_2O_3$ (0.08 mol/L) as a cationic precursor. The release of Cu (I) ions is possible *via* the following reaction

$$[Cu(S_2O_3)]^- = Cu^+ + S_2O_3^{2-} \quad (1)$$

which acts as a source of cations. The ratio of $CuSO_4$:$Na_2S_2O_3$ is 5:2. Aqueous solution of KSCN (0.025 mol/dm3) was used as an anionic precursor. The n-Si substrate was immersed in a cationic precursor for 10s. Copper ions were absorbed on the surface of the substrate and the un-absorbed ions were removed by rinsing the n-Si substrate in de-ionized water (resistivity ~18 MΩ cm) for 5s. For the reaction with SCN^- ions, the substrate was immersed in an anionic precursor for 20s.

$$[Cu(S_2O_3)]^- + SCN^- = CuSCN\downarrow + S_2O_3^{2-} \quad (2)$$

The powdery material or loosely bounded ions were removed by rinsing the substrate in de-ionized water for 5s. Thus, we complete one SILAR cycle, and this SILAR cycle need attain 100.

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2.2. Characterization and Measurements

The samples were frozen in liquid nitrogen and sliced by freezing slicer. The phase composition of the samples was characterized by X-ray powder diffraction (XRD, RINT-2100V, Rigaku, Cu Kα). In Fig. (**1**), we present wide gap diode of a structure "indium doped tin oxide (ITO) glass/p-CuSCN/n-Si". The ITO/p-CuSCN contact was obtained simply by pressing a commercial ITO glass on a deposited p-CuSCN films. Current-voltage (I-V) characteristics between two ITO glasses were measured using an Agilent sourcemeter (model 4156C). Capacitance-voltage (C-V) characteristics were 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).

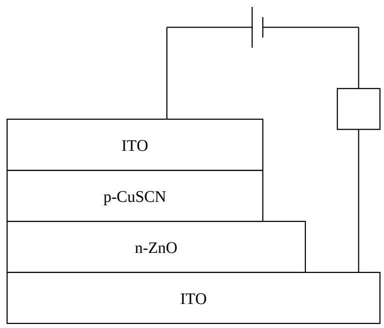

Fig. (1). Schematic structure of fabricated n-Si/p-CuSCN /ITO heterojunction.

3. RESULTS AND DISCUSSIONS

3.1. Structural Characterization

Fig. (**2**) shows the XRD spectra of the as-grown CuSCN films on n-Si. 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 (111) and (101) planes of the Si crystal structure, and different peaks of β-CuSCN corresponding to planes (003), (101), (006), (104), (015), (110), (113) and (021), are identified as wurtzite structure. The preferential orientation of the β-CuSCN grains is also observed along the (003) axis aligning with the growth direction. The presence of a number of peaks in XRD pattern is the indication of polycrystalline nature of the CuSCN.

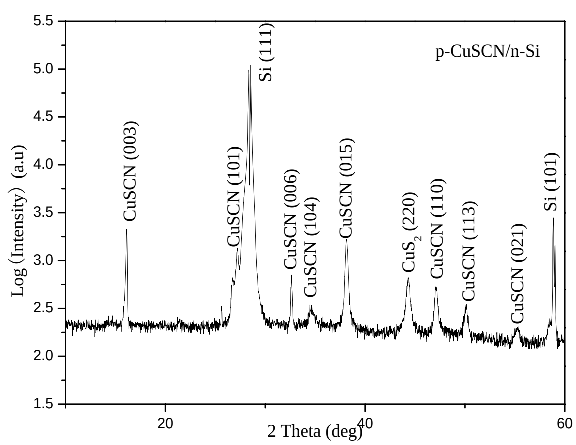

Fig. (2). X-ray diffraction spectra of p-CuSCN films on n-Si.

3.2. Electrical Characteristics

The resistivities of ITO and p-CuSCN are 63 Ω/□ and 230 Ω/□, respectively. The electrical conductivity of p-CuSCN 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-CuSCN interface. The I-V characteristic of the heterojunction in Fig. (**3**) exhibits a good photoelectric effect and rectifying behavior with a IF/IR ~6 at 5V, indicating formation of a diode (IF and IR stand for the forward and reverse currents, respectively). The turn on voltage can be observed and is about 1.0V from Fig. (**3**). Under light irradiation, when forward current increases, the reverse current hardly changes.

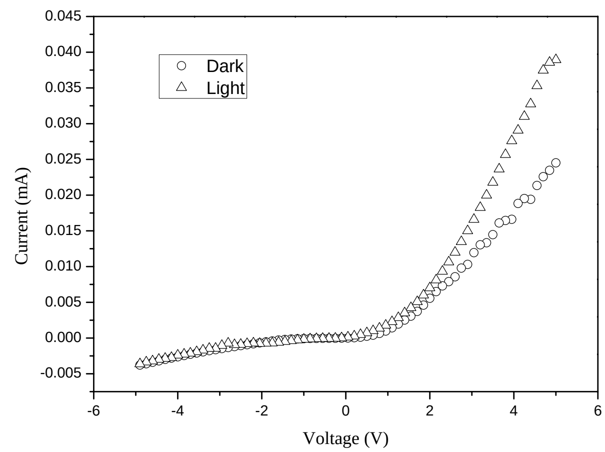

Fig. (3). I-V curve for the p-CuSCN/n-Si heterojunction with illumination and no illumination.

The $1/C^2$ versus voltage curve of the p-CuSCN/n-Si heterojunction diode is shown in Fig. (**4**).

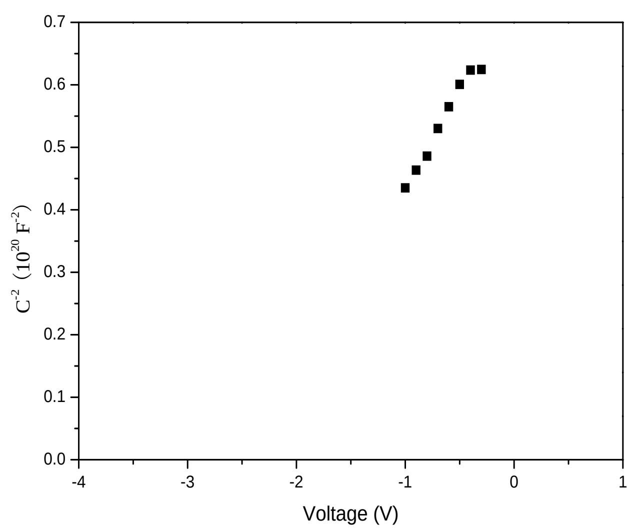

Fig. (4). The $1/C^2$ versus voltage curve of the p-CuSCN/ n-Si heterojunction diode measured at 500 kHz.

If the influence of the interface states is ignored at the p-CuSCN/n-Si heterojunction interface, the relationship of the capacitance and the applied voltage is expressed as

$$.\, C^2 = \frac{qN_A N_D \varepsilon_1 \varepsilon_2}{2(N_A \varepsilon_1 + N_D \varepsilon_2)} \frac{1}{(V_D - V)} . \quad (3)$$

where N_A is the donor concentration of the p-CuSCN, and N_D is the acceptor concentration of n-Si, respectively. N_A and N_D can also be viewed as net effective space charge density in the space charge region (assuming impurities completely ionized). $\varepsilon_1, \varepsilon_2$ denote mediated dielectric constant of Si and CuSCN, respectively. V stands for bias voltage application, V_D is sized for the built-in potential barrier.

Fig. (**4**) shows the linear relationship of $1/C^2$ versus voltage curve of the p-CuSCN/ n-Si heterojunction in the case of ignoring interface state. It is found that the built-in potential V_{bi} of the heterojunction is 2.1eV.

3.3. Carrier Transport Mechanism

In Fig. (**5**), we give the dark current as a function of junction-voltage in forward bias. At forward voltage, 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 [12-15]. This SCLC mechanism is a normal phenomenon in the wide band gap semiconductors due to single-carrier injection [14,15].

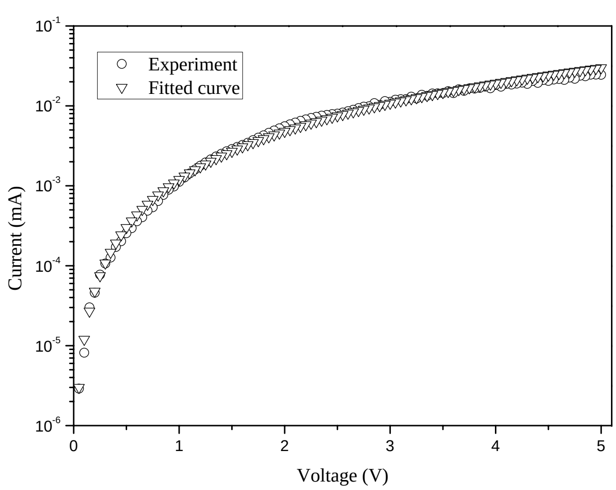

Fig. (5). The I-V curve for the p-CuSCN/n-Si heterojunction in forward bias.

Fig. (**6**) shows the theoretically expected equilibrium energy band diagram of the p-CuSCN/ n-Si heterojunction according to the Anderson model. Suppose that the interface states can be neglected and the Fermi level in the Si and CuSCN lies at the Si conduction band edge and CuSCN valence band edge, respectively. The model shows the maximum built-in potential V_{bi} of the heterojunction is 2.1 eV, which can be seen from the C-V measurement results of Fig. (**4**). As can be seen from Fig. (**6**), it can be approximated estimation that the conduction band offset (ΔE_C) and value band offset (ΔE_V) of p-CuSCN/ n-Si heterojunction are 1.5eV and 0.98eV, respectively.

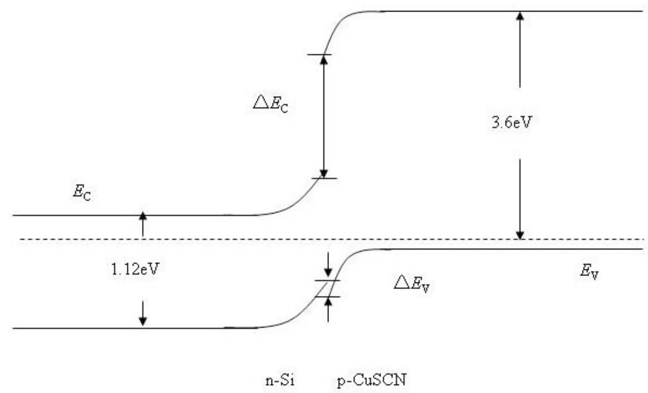

Fig. (6). The energy band diagram of n-Si /p-CuSCN heterojunction.

From Fig. (**6**), we know that the ΔE_C and ΔE_V for this heterojunction are very large. The potential barrier for electrons transport from the bottom of conduction band in n-Si to the bottom of conduction band in p-CuSCN and the holes transport from the top of value band in p-CuSCN to the top of value band in n-Si is very large, so the difficulties for transport of electrons and holes in forward bias is increased. Since the difference between ΔE_C and ΔE_V, the energetic barrier is much lower for holes than electrons. In the region II, the current is dominated by holes, which agrees with the observed turn on voltage (1.0 V).

4. CONCLUSIONS

In summary, p-CuSCN/n-Si heterojunction diode is prepared at a low cost by chemical method, and shows a good photoelectric effect and rectifying behavior with an IF/IR ~6 at 5V. The prepared β-CuSCN film is polycrystalline nature. The built-in potential is 2.1eV from C-V characteristic. The conduction band offset and value band offset of p-CuSCN/n-Si heterojunction are 1.5eV and 0.98eV, respectively. The current transport mechanism is also dominated by the SCLC at forward bias voltages. This heterojunction diode can be well used for photoelectric devices and detectors.

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CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

The work was financially supported by the Natural Science Foundation of Changzhou Institute of Technology, China (No. YN1105), the Science and Technique Foundation of Changzhou, China (No. CJ20120001), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (No.12KJD510001), as well as the Special Fund for Theoretical Physics from the National Natural Science Foundation of China (No.11247323).

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Received: July 9, 2013 Revised: August 7, 2013 Accepted: August 7, 2013