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Fabrication and characterization of CdS-Cu_2S thin film heterojunction diode using chemical bath deposition technique

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Various methods have so far been used to fabricate and characterize CdS-Cu_2S heterojunction thin film devices. In this paper a chemical bath deposition technique was used to synthesize the same on a non-conducting glass substrate. In this fabrication process a cadmium sulfide (CdS) layer was formed by depositing a chemical compound consisting of cadmium chloride, ammonium acetate, thiourea and ammonium hydroxide solution on the glass surface. The copper sulfide (Cu_2S) layer was grown by dipping a small portion of the CdS sample into a cuprous chloride solution. Different doping concentrations of the heterojunction diode were achieved by using boric acid solutions of different molarity. Aluminium dots were deposited on the samples by using a vacuum coating system for measurement of different characteristics through computer interfacing. Both forward and reverse bias I-V and C-V characteristics of the resultant n-CdS and p-Cu_2S heterojunction diode were measured and analyzed for various doping concentrations.

Keywords: Semiconductor devices; heterojunction; chemical bath deposition technique; doping concentration; diode characteristics.

INTRODUCTION

Fabrication and characterization of thin film heterojunction devices has become a subject of interest by the researchers [1, 2]. Among various thin film devices CdS-Cu_2S heterojunction is one of the most interesting devices [3, 4]. Cadmium sulfide (CdS) is a material with a large absorption coefficient and copper sulfide (Cu_2S) is suitable for generating a large amount of photocurrent. Cu_2S is also a very promising agent for different photovoltaic applications because of its unique structure and stoichiometric composition. Thin layer of Cu_2S (0.1 μm to 0.3 μm) has a bandgap of 1.2 eV which is suitable to exhibit high luminescence efficiency [5]. It is a very useful material to act as a p-type semiconductor for solar cells. On the other hand, cadmium sulfide (CdS) is a suitable material for acting as a n-type semiconductor [5]. CdS is a direct bandgap semiconductor having a band gap of 2.4eV in the visible region [5-8]. CdS is a potential absorber for thin film photovoltaic cells and also acts as an efficient window material which can form a heterojunction with a bandgap material like Cu_2S. CdS thin film (8 μm to 20 μm) was deposited by various research groups [9, 10] using different techniques, namely, vacuum evaporation, spray parolysis, electro deposition technique, etc. In this work a CdS-Cu_2S thin film heterojunction was formed by using chemical bath deposition technique (CBDT). CBDT is a very useful method for growing thin film compound semiconductors using different chemical solutions [2]. Using this method different deposition characteristics such as film thickness, deposition rate, etc. could be controlled easily by varying solution molarity, pH, temperature, etc. This technique is simple and not too expensive also.

THEORY

When two semiconductors of different band gaps are joined together, the atoms of the heterojunction form chemical bonds at the interface. Due to mismatch of lattice constants across the hetero interface there exists a region of crystal dislocation and crystal imperfections which spans over many crystalline layers. This dislocation acts as a scattering center and recombination center for electrons and holes, limiting their mobilities and recombination life time as well. These effects may result in a poor-quality device formation. Device performance can significantly be improved by (a) using materials with nearly equal lattice constants, (b) using alternative layers of semiconducting material, producing a structure called superlattice which reduces the number of dislocations, and (c) choosing the substrate crystal plane that is slightly offset from the major crystal plane so that the distance between the atoms on the substrate surface approximates the distance between the atoms in the deposited film of another semiconductor material [11].

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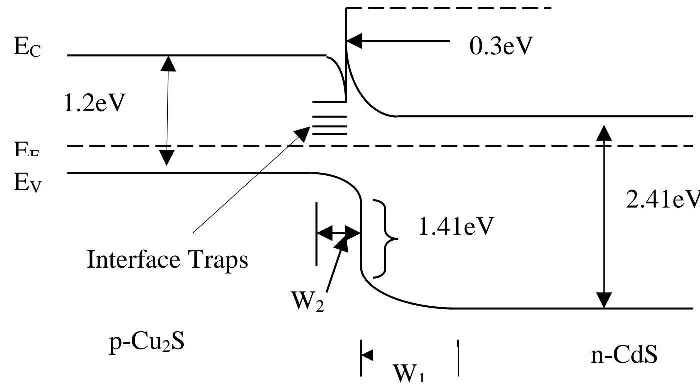


Fig. 1. Energy band diagram of Cu_2S-CdS heterojunction

Fig. 1 shows the energy band diagram of Cu_2S-CdS heterojunction [12]. The built-in barrier potential is shown in Eqn. (1):

$$V_{bi} = \frac{qN_{dn}W_1^2}{2\varepsilon_n} + \frac{qN_{ap}W_2^2}{2\varepsilon_p} \tag{1}$$

where ε_n and ε_p are permittivities, N_{dn} and N_{ap} are the carrier concentrations of CdS and Cu_2S materials, respectively, W_1 and W_2 are widths of the depletion regions, q is the electronic charge, $V_{bi}$is the built-in potential. Here it is assumed that ε_n and ε_p have the same order of magnitude.

Total depletion width shown in Eqn. (2) is equal to:

$$W = W_1 + W_2 = \left\{ \frac{2\varepsilon_n \varepsilon_p (N_{dn} + N_{ap})^2 V_{bi}}{qN_{dn}N_{ap}(\varepsilon_n N_{dn} + \varepsilon_p N_{ap})} \right\}^{1/2} \tag{2}$$

The junction capacitance shown in Eqn. (3) is equal to:

$$C_j = \left\{ \frac{qN_{dn}N_{ap}\varepsilon_n \varepsilon_p}{2(\varepsilon_n N_{dn} + \varepsilon_p N_{ap})(V_{bi} + V)} \right\}^{1/2} \tag{3}$$

where V is the total applied voltage. Since the barrier heights seen by electrons and holes are not the same in case of heterojunction so their current-voltage characteristics are derived on the basis of thermionic emission of carriers over the barrier shown in Eqn. (4):

$$J = A^* T^2 \exp\left(\frac{-\Phi}{kT}\right) \tag{4}$$

where A* is the effective Richardson constant and Φ is the effective barrier height [8, 11, 12].

EXPERIMENTAL

All chemicals used in this study were of 99.99% spectroscopic purity, manufactured by Aldrich.

Cleaning of glass samples

Glass samples were cleaned with trichloroethylene (TCE), acetone and methanol before they were used for deposition.

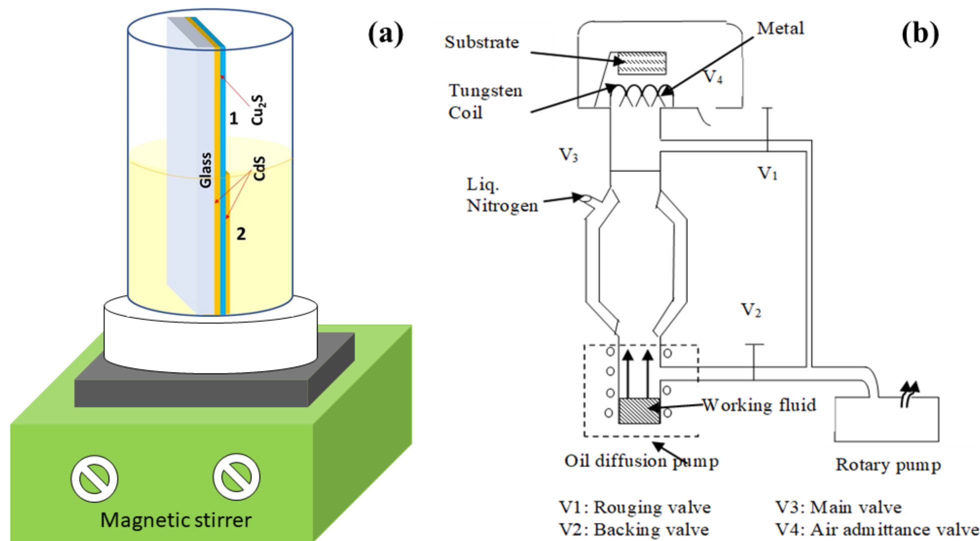
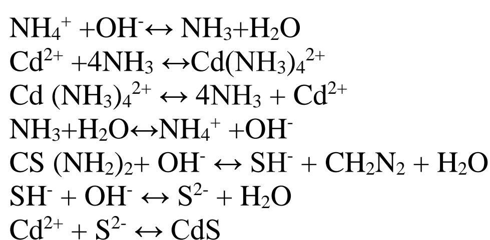


Fig. 2. Schematic illustrations of (a) CBDT setup and (b) vacuum coating unit

Deposition of CdS thin film on glass surface

(a) Synthesis of CdS thin film. A mixture of 0.5 cm^3 of 10^{-3} M $CdCl_2$ solution, 9.5 cm^3 of 0.005M $(NH_2)_2CS$ (thiourea) solution, 0.8 cm^3 of 0.01M NH_4Ac (ammonium acetate) solution, 5.6 cm^3 of 0.25M NH_4OH solution was prepared. The solution was taken in a glass beaker and placed on the pad of a magnetic stirrer. The schematic of the deposition setup is illustrated in Fig. 2(a). The heater was switched on and the temperature was fixed at 75-80°C. The glass samples were immersed in the solution on stirring for 1.5 h until the solution became deep yellow. CdS was formed by the chemical reaction of $CdCl_2$ with $(NH_2)_2CS$ buffered by NH_4OH and NH_4Ac. The chemical reactions for the formation of CdS layer are as follows [13, 14]:



$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$$
$$Cd^{2+} + 4NH_3 \leftrightarrow Cd(NH_3)_4^{2+}$$
$$Cd(NH_3)_4^{2+} \leftrightarrow 4NH_3 + Cd^{2+}$$
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
$$CS(NH_2)_2 + OH^- \leftrightarrow SH^- + CH_2N_2 + H_2O$$
$$SH^- + OH^- \leftrightarrow S^{2-} + H_2O$$
$$Cd^{2+} + S^{2-} \leftrightarrow CdS$$

(b) Deposition of Cu_2S thin film. The Cu_2S film was grown by conversion of the CdS film by chemical reaction with cuprous chloride (Cu_2Cl_2). A Cu_2Cl_2 solution was prepared by mixing Cu_2Cl_2 powder in distilled water. Now by dipping the whole slide in the solution for 2 min the CdS film was converted into Cu_2S film following the reaction shown below [15]:

$$CdS + 2\,CuCl \leftrightarrow Cu_2S + CdC1_2$$

A topotaxial layer of copper sulfide was formed by mutual exchange of two Cu^+ ions for each Cd^{2+} ion from the CdS layer. The excess amount of Cu_2Cl_2 was removed from the samples by rinsing repeatedly with distilled water.

Formation of the CdS-Cu_2S junction

A second layer of CdS was grown on a selected portion of the Cu_2S film for the formation of the CdS-Cu_2S heterojunction. Initially some composite mixture prepared for synthesis of CdS thin film was taken in a glass beaker and a half portion of the sample was immersed in the solution. The beaker was placed on a magnetic stirrer and the solution was stirred in such a way that the solution could not wet the whole slide. In this way CdS thin film could be deposited on the half portion of the slide. This selected deposition step was repeated thrice. At this step proper masking arrangement was made to cover the upper portion of the Cu_2S film. Such an arrangement led to a clean well-defined junction at the half portion of the sample. The samples thus prepared were kept at room temperature for a day for proper drying.

Metallization

To deposit metal dots on the as-prepared samples a vacuum coating system was used. Al metal wire (99.999% pure) was cut into small pieces which were bent according to the shape '^' and a metal mask with circular aperture was used. The mask and the metal wires were ultrasonically cleaned with trichloroethylene, acetone, methanol and distilled water. Air admittance valve (V_4) was opened for loading of samples. Metal pieces were loaded on the heating filament. The mask was loaded on the top of the sample and the chamber was closed. For the deposition of metal dots, the required chamber pressure was of the order of 10^{-6} bar. This was achieved by joining the deposition chamber to the vacuum line consisting of a rotary pump and an oil diffusion pump. In addition to this, as $p = nKT$ (where the terms have their usual significance), in order to achieve the operating pressure, the chamber was covered externally by flowing boiling liquid nitrogen through the outer jacket of the chamber. The whole process of metal dot deposition is conceptually depicted in Fig. 2(b) [16].

Preparation of doping solution

Boron was doped into the CdS-Cu_2S heterojunction with different concentrations by dipping region 2 of the as-prepared diodes (as indicated in Fig. 2(a)) in a solution that was prepared by adding aqueous solutions of H_3BO_3 of different molarity to the $CdCl_2$ solution. During this process, region 1 was masked properly to avoid Cd contamination in this layer. The pH of the resultant solution was measured by using Global digital pH meter of type DpH-500. The pH values of the different solutions were calibrated noting that pH=10.68, 10.58 and 10.56 corresponded to 0 M, 10^{-4} M, and 10^{-2} M H_3BO_3 solution, respectively. Thus, lowering of the pH value of the above-mentioned solution is indicative of constant enhancement in the B^{3+} ion concentration in the solution, and hence, of a higher probability of doping. This process enabled us to dope the CdS layer with boron directly and the Cu_2S layer indirectly through diffusion, thereby forming a boron-doped n-CdS and p-Cu_2S heterojunction diode.

X-ray diffraction (XRD)

The as-prepared diodes were examined by XRD using CuKα radiation. To accomplish this, the two halves of the diodes were exposed to X-rays

separately in a Rigaku made SmartLab SE diffractometer. Before recording the XRD spectra, the instrument was calibrated by using the (422) diffraction peak of a standard silicon sample.

Electrical measurements

The current-voltage characteristics of the fabricated devices were studied using an HP multimeter of microvolt resolution and current sensitivity of ±1% of the actual value. The RS-232 port was used for computer interfacing. The capacitance of the device was measured with the help of an HP LCR meter. In order to apply a bias voltage, a triple output HP power supply was used.

RESULTS AND DISCUSSION

In this work, the crystalline compositions of the two halves of the as-prepared CdS-Cu_2S heterojunction diodes, and their I-V and C-V characteristics, were determined.

Fig. 3 shows the typical XRD spectra recorded corresponding to the portions marked as 1 and 2 in Fig. 2(a) for one of the as-prepared undoped samples.

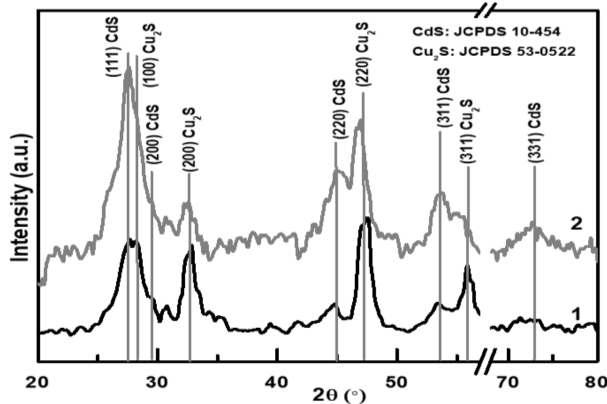


Fig. 3. Typical XRD spectra of the two halves of one of the undoped diodes, as indicated in Fig. 2(a).

Both spectra are found to contain some well-defined peaks signifying the presence of crystalline species within the sample. However, a significant amount of noise, which is characteristic of defects within a sample, is also seen in both spectra. This noise is consistent with the chemical synthesis processes that are quite different from the high-temperature routes. Comparing the XRD spectra of the sample with the standard XRD data, (the JCPDS card numbers are mentioned in Fig. 3), it was found that both portions 1 and 2 of the sample contain mixtures of crystalline CdS and Cu_2S, however with different mass fractions. In the XRD spectrum corresponding to region 1, the (220) peak of Cu_2S is the most intense one. On the other hand, the intensity of the (111) peak corresponding to CdS (the most intense peak for CdS) is higher than that of the (220) peak of Cu_2S. The XRD spectra are thus consistent with the structure of the diode, as is schematically demonstrated in Fig. 2(a). No noticeable changes were detected in the XRD spectra for the doped diodes, possibly because boron did not take part in the formation of the crystallites; rather, it took place in the interstitial sites.

I-V and C-V characteristics were measured for a number of CdS-Cu_2S thin film heterojunction diodes, which were fabricated by repeating the whole experimental procedure (Figs. 4 and 5). The qualitative behavior of the undoped and the doped diodes was almost the same with a quantitative difference. The cut-in voltage (V_γ) was approximately 0.3 V for the undoped case (Fig. 4). For the doped diodes, the value of V_γ was found to vary between 2-3 V (for the diodes doped with 10^{-4}M H_3BO_3 solution), and between 3-4 V (for the diodes doped with 10^{-2} M H_3BO_3 solution). The change in V_γ for different doping cases could be attributed to a change in barrier height or built-in potential. From the expression of current density (J) the following expression (Eqn. 5) can be obtained [11]:

$$\frac{J_1}{J_2} = \frac{(V_{bi})_1}{(V_{bi})_2} \exp(-38\Delta V_{bi}) \quad (5)$$

where ΔV_{bi} is the change in barrier height. This expression shows that a slight change in barrier height drastically changes the current density. The change in barrier height can be explained as follows: CdS is an n-type material and the associated Fermi level is closer towards the conduction band whereas Cu_2S is a p-type material with Fermi level closer to the valence band. Boron is an n-type dopant to CdS and a p-type to Cu_2S. Boron is doped in the form of B^{3+} ions derived from H_3BO_3 which was mixed in the solution that was already prepared for depositing CdS in the second phase. As the Cu_2S thin film was dipped in the doping solution the B^{3+}ions penetrated inside the material and introduced p-type impurity. But as the CdS film was earlier deposited on the whole substrate so the effect of doping on the converted Cu_2S layer will be less as compared to the single CdS layer. Therefore, the doped CdS will create a larger barrier height with the doped or undoped Cu_2S as compared to undoped CdS layer [5]. Slight change of barrier height causes a large change in the values of J and V_γ [11, 17]. The C-V characteristic shows that the forward capacitance increases with voltage for doped and undoped diodes (Fig. 5). Increase in the forward capacitance may be due to charge storage at the semiconductor junction [8, 17]. Charge storage is caused by the charges that cannot follow up the change in signal voltage. All measurements were performed at a frequency of 100 kHz because at this

frequency the energy levels are properly populated and therefore a significant accumulation of charges was obtained. The reverse capacitance changes very slowly with the voltage for the undoped case and remains almost constant for doped diodes (Fig. 5). This result may be due to non-uniform film structures along with other nonidealities such as interface traps, etc. [8, 17].

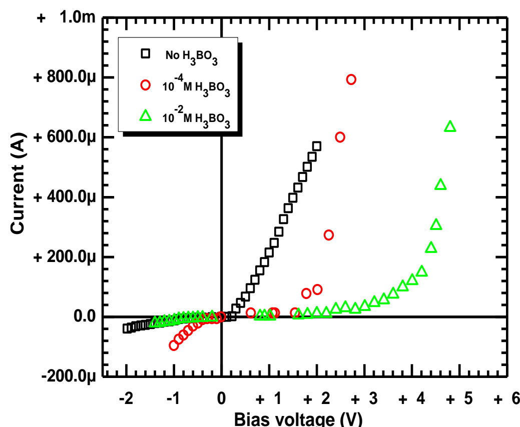


Fig. 4. I-V characteristics of the as-prepared diodes.

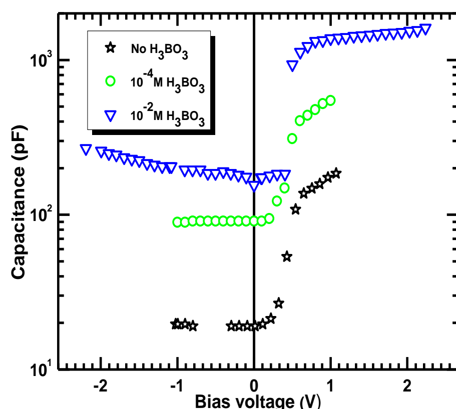


Fig. 5. C-V characteristics of the as-prepared diodes.

CONCLUSIONS

In this paper a low-cost CdS-Cu_2S heterojunction fabrication by using chemical bath deposition technique was discussed. I-V, C-V characteristics of the fabricated heterojunction diode were measured by computer interfacing measurement technique.

I-V characteristics showed that, as the doping concentration changes, the cut-in voltage of the heterojunction diode also changes due to a change in the barrier height. Both the forward and reverse bias currents were also found changing with doping concentration. C-V characteristics showed the known characteristic changes due to the change in doping concentration.

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