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Structural and electrial properties of Cu_2S/CdS thin film heterostructure

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Abstract: The fabrication of thin films Cu_2S/CdS by cost affecting spray pyrolysis technique is demonstrated. Thin films of CdS were deposited onto antimony doped tin-oxide (ATO) substrate later Cu_2S film was formed by dipping the alloy films in a heated solution of CuCl. The structural and morphological properties of these thin films were studied by recording X-ray diffraction patterns and atomic force microscope images. The X-ray diffraction pattern of Cu_2S/CdS reveals the peaks due to both Cu_2S and CdS materials and leads to the confirmation of Cu_2S/CdS thin film formation over the ATO substrate. Further, the Cu_2S/CdS thin film-based device was fabricated by forming top contact through complete metallization of the Cu_2S with tin paste. The current-voltage *(I-V)* characteristics of Cu_2S/CdS device reveals diode behavior under applying bias voltage across. Furthermore, the various diode parameters such as ideality factor, saturation current, barrier height, and series resistance were also estimated using different diode equations. The Cu_2S/CdS device exhibits slightly Ohmic characteristics and attributed the presence of defect states at the Cu_2S/CdS interface. Thus, this study may emerges out to be very fascinating for further fabrication of solar cells based on Cu_2S/CdS thin films.

Keywords: Spray pyrolysis, CdS, Cu_2S, XRD, *I-V* characteristics

1.INTRODUCTION

In last three decades thin film technology played a vital role in developing various electronic and optoelectronic devices. Thin film technology has vast potential to overcome many worst problems which the world is suffering today *i.e*., energy demand, pollution, global warming[1]. The energy demand of the world is increasing day by day at an alarming rate. The main source of energy is fossil fuel and to a small extent- the nuclear energy. But fossil fuel is limited and cannot provide us enough energy and is causes pollution. Nuclear energy has its own limitation from security point of view and the problems caused due to the radioactive waste associated with nuclear power stations. A solution of abovementioned problems is to explore the renewable energy sources. Solar energy, among the renewable energy sources is of great importance because of its clean and its free abundance. In last 2-3 decades large number of efforts has been done to develop a device which can overcome the growing demand of energy worldwide and can efficiently convert solar energy to electricity.

In last few decades much more effort has been performed for the development of thin films. Mostly, thin film research is concentrated around II-VI group semiconductors junction thin film[2]. One of the most promising thin films are Cu_2S/CdS due to high percentage of conversion of solar energy into electrical energy more than 10%[3]. Due to large band gap of CdS, it has been used as a window material along with several other semiconductors like $CdS/CuInSe_2$[3] and CdS/Cu_2S[4]. There are many techniques of deposition the thin films such as Spray pyrolysis[5], vacuum evaporation[6], screen printing with sintering[7], and chemical bath deposition[8]. Among all of them Spray pyrolysis process (SPP) is relatively low-cost and simple technique for depositing thin films. Significant research has been demonstrated on deposition and characterization of CdS semiconducting films because of their wide applications in electronic and optoelectronic devices due to their intermediate band gap[9,10]. Besides, Cu_2S has also been regarded as a promising solar energy conversion material because of its favourable visible light absorption and earth abundance. The Cu_2S is available in various distinct crystalline phases and stoichiometries of copper sulfide such as chalcocite (Cu_2S), djurleite ($Cu_{1.96}S$), digenite ($Cu_{1.8}S$), anilite ($Cu_{1.75}S$), and covellite (CuS)[11,12]. However, only Cu_2S can generate free carriers at temperatures below 90 °C, as the excess copper deficiency in other compounds will lead to very high hole concentrations, resulting in a degenerate semiconductor unsuitable for conventional PV[13,14]. Therefore, controlling the stoichiometry to achieve the accurate Cu_2S phase is highly important for solar energy application. It has been broadly investigated for photovoltaics (PV) since the 1960s. Having a direct band gap of 1.8 eV and an indirect band gap of 1.2 eV, it can theoretically provide a power

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conversion efficiency of 30% as a single-junction PV cell[14]. The Cu_2S/CdS heterojunction PV devices exhibits a solar-to-electricity conversion efficiency of 10%[3].
In this work, we have successfully prepared Cu_2S/CdS thin films using spray pyrolysis method. The structural and morphological properties of prepared Cu_2S/CdS thin films have been investigated by measuring X-ray diffraction pattern and atomic force microscopy (AFM) images. Further the electrical measurements on Cu_2S/CdS thin films have carried out after fabrication of Cu_2S/CdS device by depositing metal electrodes. The current-voltage (*I-V*) characteristics of the device shows diode like behavior and the various parameters of the diode such as ideality factor, saturation current, barrier height, and series resistance have also been calculated. Thus, this study may lead to a very important investigation for the development of Cu_2S/CdS thin film based devices for a variety of electronic and optoelrctronic applications.

2.EXPERIMENTAL DETAILS

The Cu_2S/CdS thin films were prepared onto antimony doped tin-oxide (ATO) substrate by cost affecting spray pyrolysis technique. First the CdS film was deposited at temperature of 320 °C and later Cu_2S film was formed by dipping the alloy films in a heated solution of CuCl. Prior to Cu_2S/CdS thin films deposition, the tin oxide and antimony doped tin oxide films on glass substrate were prepared by spray pyrolysis in which an aqueous solution of stannic chloride (1M) mixed with alcohol was sprayed over heated clean glass substrate for the undoped tin oxide films. The sprayed droplets undergo an endothermic reaction on the surface of the substrate. The heat of the substrate initiates the chemical reaction, by providing the necessary thermal energy for decomposition of reacting materials into its constituents and recombination of these constituents form desired oxide films. The other volatile products formed during this process escape out. The reaction involved is given as:

$$SnCl_4 + 2H_2O = SnO_2 + 4HCl \quad (1)$$

However, the reaction does not proceed towards completion, thus forming oxygen deficient SnO_2 films. The alcohol acts as a reducing agent and also deeds as carrier solution and dispersive medium. A transparent layer of antimony doped tin oxide (ATO) which acts as the bottom electrode to the CdS layer, was achieved by adding antimony chloride ($SbCl_2$) dissolved in concentrated hydrochloric acid. This procedure was repeated for different concentrations of antimony chloride. The deposition was carried out at 320 °C for 10 minutes. Thus, we obtain conducting glass. To deposit a film of CdS onto ATO substrate, the solution of cadmium chloride ($CdCl_2$) and thiourea (NH_2CSNH_2) was spread over ATO at 320 °C for 10 minutes. The reaction involved was given as:

$$CdCl_2 + NH_2CSNH_2 + 2H_2O = CdS + 2NH_4Cl + CO_2 \quad (2)$$
$$NH_4Cl = NH_3 + HCl \quad (3)$$

the volatile products formed during this process escapes out to the ambient atmosphere. Now the films were annealed for 10 minutes in vacuum to decrease the resistivity of the alloy films by removal of acceptor like oxygen levels. Thus, Cu_2S film was Is by dipping the alloy films in a heated solution of CuCl for two minutes. The reaction involve was given as

$$2CuCl + CdS = Cu_2S + CdCl_2 \quad (4)$$

After washing away the $CdCl_2$, the Cu_2S/CdS films were inserted for vacuum heat treatment in vacuum 10^{-4} torr. The temperature and duration of the treatment was decided by the composition of the film. Finally, the Cu_2S/CdS device was developed over ATO substrate by fabricating the top contact through complete metallization of Cu_2S film with tin paste. The prepared Cu_2S/CdS thin films were characterized for their structural properties by recording X-ray diffraction pattern using glancing angle X-ray diffractometer (GAXRD) using a setup Bruker D8 diffractometer having Cu-Kα X-ray (λ-1.5418 Å) for 2θ range from 7-50^{o} with a scan rate of 0.2^{o}/m .The surface morphology of Cu_2S/CdS thin films were recording by atomic force microscopy (AFM) image in tapping mode using AFM setup . The electrical measurements on the fabricated Cu_2S/CdS was performed by measuring its current-voltage (*I-V*) characteristics under dark condition using a source meter-2400 at an applying bias voltage of -15 to +15 V.

3.RESULTS AND DISCUSSION

3.1Structural properties of Cu_2S/CdS thin films

Figure 1 (a) shows the X-ray diffraction pattern of the prepared Cu_2S/CdS thin film onto antimony doped tin oxide (ATO) substrate. The diffraction of Cu_2S/CdS thin film exhibits the peaks due to both CdS and Cu_2S. The peaks at 2θ of 24.7°, 43.8°, and 51.6° are well matched with the hexagonal CdS pattern JCPDS# 75-1545[15]. The peaks at 2θ of 37.5°, 46°, and 48.9° confirms the peaks due to hexagonal Cu_2S pattern and matches with JCPDS# 84-0209[15]. These peaks appeared and indicating the transformation of CdS into Cu_2S during ion exchange process. The CdS film exhibits a slightly flat surface including small crystalline grains. The XRD pattern gives the ion exchange method can been successfully used for the preparation of Cu_2S/CdS layered thin films.

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3.2 Surface morphological of Cu_2S/CdS thin films

The importance of surface morphology of Cu_2S/CdS thin film and based electronic heterostucture devices have been accentuated due to charge carriers transport through a device is often strongly affected vai the surface morphology. Therefore, the atomic force microscopy image (AFM) of prepared Cu_2S/CdS thin film onto antimony doped tin oxide (ATO) substrate was recorded in tapping mode and shown in Figure 1 (b). The thin film shows the smooth surface and is ascribed to the good formation of Cu_2S/CdS heterostructure which leads to the further improvement to the charge carrier conduction towards the respective electrodes. The formation of a steady system association between the CdS and Cu_2S may take up the high performance of Cu_2S/CdS thin films based device. In addition, Cu_2S/CdS thin films based heterostructure also provides an active path for the movement of hole and electrons to their respcetive electrodes and assists the separation of the charge carriers at the interface. Furhtermore, the thickness of the Cu_2S/CdS thin films was also estimated and found around 281 nm as shown in the right scale bar of the Figure 1 (b).

3.3 Electrical characterization of Cu_2S/CdS heterostructure device

Figure. 2 (a) shows linear current-voltage (*I–V)* characteristics of Cu_2S/CdS thin film heterostructure device under dark condition at an applying ± 15 V bias voltage. Inset in Figure 2 (a) shows schematic of fabricated Cu_2S/CdS device. While Figure 2 (b) shows the *I-V* characteristics in semi-log scale for better clarity purposes. The *I-V* characteristics of the Cu_2S/CdS device exhibits slightly Ohmic diode like behavior and can be attributed due to the formation of defects and interfacial states at Cu_2S/CdS heterostucture interface during the fabrication process of the device. The diode *I-V* characteristics were further analyzed for investigate the various diode parameters such as ideality factor, barrier height, saturation current, and series resistance and to discuss the carrier transport at applying forward voltage. The *I-V* characteristics of a Cu_2S/CdS diode under applied forward bias can be described by the following well known Schottky diode equations[16]:

$$I = I_s \left[exp\left(\frac{qV}{\eta K_B T}\right) - 1\right] \qquad (5)$$

where I_s is known as saturation current and in case of ideal diode, I_s contains every information associated to charge carrier recombination at the heterostucture interface of the active materials used. q, V and η can be known as the electronic charge, applied bias voltage, and the ideality factor, respectively. K_B is the Boltzmann constant, T is temperature.

The saturation current can be related to interface barrier height (Φ_B) denoted as:

$$I_s = A^* T^2 exp\left[-\frac{q\,\phi_B}{K_B T}\right] \qquad (6)$$

Here, A* represents the Richardson constant and η can be determined from the slope (S) of the linear region of semi-logarithmic plot of forward current vs bias voltage characteristics as shown in Figure 2 (c) and can be written as[17].

$$\ln (I) = \ln (I_s) + \frac{q}{\eta\, K_B T} V \qquad (7)$$

The value of I_s is estimated through extrapolating liner region of the ln *I–V* plot curve to zero bias voltage (Figure 2 (c)), and the value obtained around ~1.25×10^{-6} Ampere. The value of Φ_B at zero bias, can be determined using given relation and found to be ~ 0.75 eV.

$$\Phi_B = \frac{KT}{q} \ln\left(\frac{A^* T^2}{I_s}\right) \qquad (8)$$

Generally, a slightly deviation from linearity in the forward *I-V* characteristics of Cu_2S/CdS diode appeared due to the effect of series resistance (R_s), which occurs because of the presence of interfacial and defects states and interface of the devices. The R_s acts a crucial parameter in the current path at Cu_2S/CdS heterostructure and gives a leakage pathway to minority charge carriers in the device. Besides, the R_s value is estimated using Cheung relation[18] as given below:

$$\frac{dV}{d\ln(I)} = IAR_s + \frac{\eta .\, K_B T}{q} \qquad (9)$$

Here, the term IAR_s shows the voltage drop across the series resistance of Cu_2S/CdS heterostructure diode. Hence, the plot of *dV/d (lnI)* vs *I,* shown in the Figure 2 (d), will be straight line for the data of the downward curvature regime of the forward bias, whose slope (AR_s) will provide R_s value and the intercept ($\eta.K_BT/q$) of the plot gives the value of η. The value of R_s and η are observed to be 2.9 kΩ and 4.2, respectively. These observed values are comparatively high to an ideal diode and attributed to formation of large number of interfacial and defects state at the interface of Cu_2S/CdS heterostructure. Figure 3 shows the energy band diagram of developed Cu_2S/CdS heterostructure. The ATO on the glass substrate and Sn contact on Cu_2S/CdS layers are utilized for collecting the generated and injected charge carriers. The Cu_2S/CdS interface may contribute significantly in the injection of electron-hole pairs, because depletion width at ATO-Cu_2S/CdS and Sn- Cu_2S/CdS interface may assumed to be very narrow and gives the conduction path to electrons that can easily overcome the barrier. The Cu_2S/CdS heterostructure device is beneficial to develop large-area, low cost and high quality various electronic and optoelectronic devices such as solar cells, photodetector, LEDs, etc. The significant development of Cu_2S/CdS solar cell is under progress and will be published in next study.

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4. CONCLUSIONS

In summary, a Cu_2S/CdS thin films were prepared on ATO/glass substrate using spray pyrolysis methods. The films were characterized for their structural, morphological, and electrical properties. The structural properties were measured by recording X-ray diffraction pattern of Cu_2S/CdS film and shows the peaks due to both Cu_2S and CdS materials and leads to the confirmation of Cu_2S/CdS thin film formation. The morphology of Cu_2S/CdS thin films were measured by recoding atomic force microscopy (AFM) image and reveals the smooth Surface morphology and is ascribed to the good formation of Cu_2S/CdS heterostructure which leads to the further improvement to the charge carrier conduction in the film. Furthermore, the electrical properties were observed by developing Cu_2S/CdS heterostructure device and later measuring its dark *I-V* characteristics. The *I-V* characteristics reveal that the devices shows diode like behavior and the various parameters of the were estimated using diode different equations and show quite good response. Thus, the obtained results show that Cu_2S/CdS devices are beneficial to develop large-area, low cost and high quality diode and photovoltaic devices for advanced future technology.

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Figure captions:

Figure 1: (a) The X-ray diffraction (XRD) pattern and **(b)** Atomic force microscopy (AFM) image of CdS/Cu_2S thin film.

Figure 2: (a) Linear current-voltage (*I-V*) characteristics of fabricated CdS/Cu_2S device under dark condition by applying voltage of ± 15 V (Inset shows the schematic of developed device). (b) The logarithm *I-V* characteristics of CdS/Cu_2S device for better clarity purpose. **(c)** The estimation of ideality factor by linear region in lower bias voltage range. **(d)** Calculation of the value of series resistance using Cheung relation.

Figure 3: The developed schematic energy band diagram of CdS/Cu_2S device.

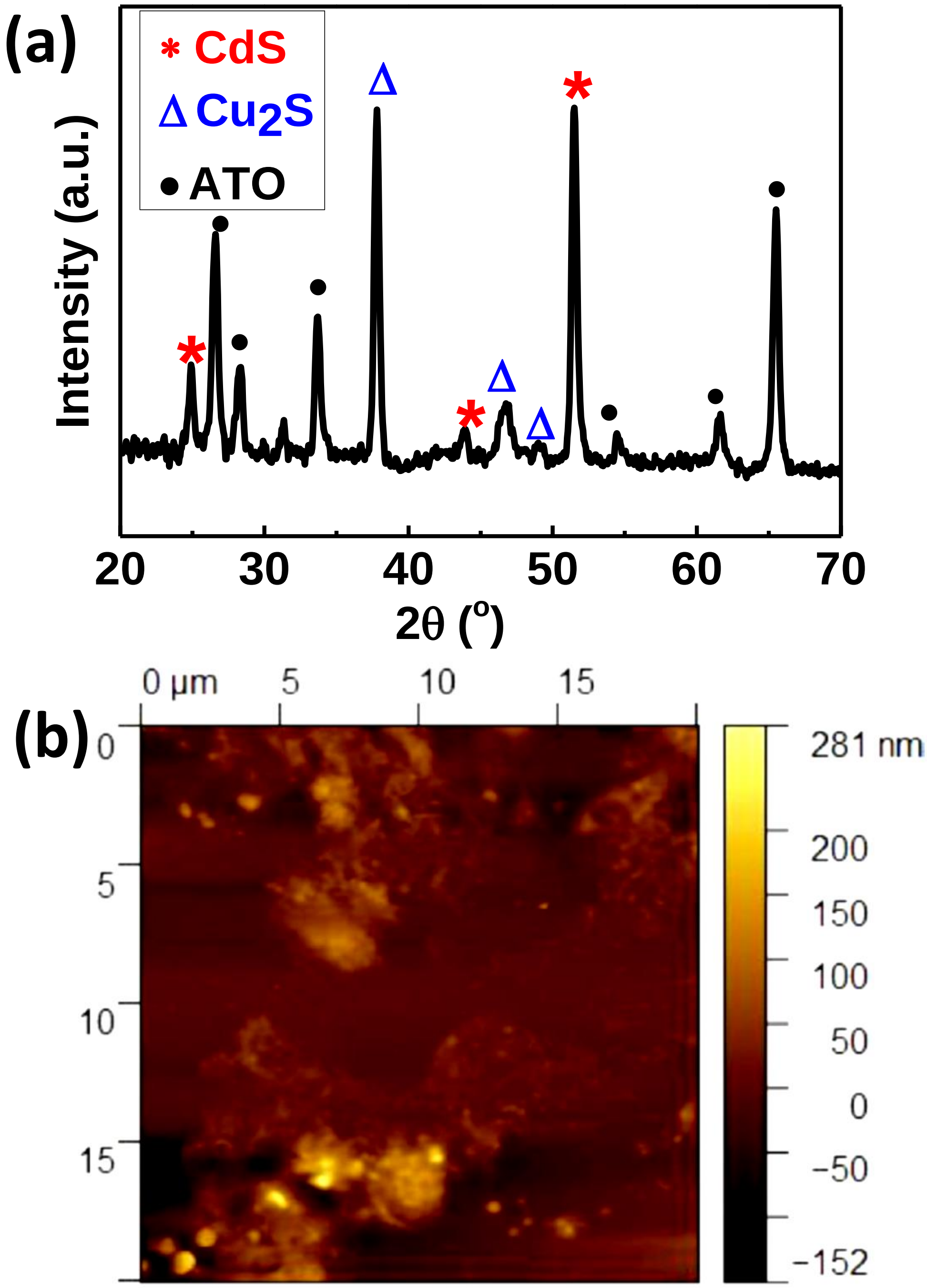

Figure 1

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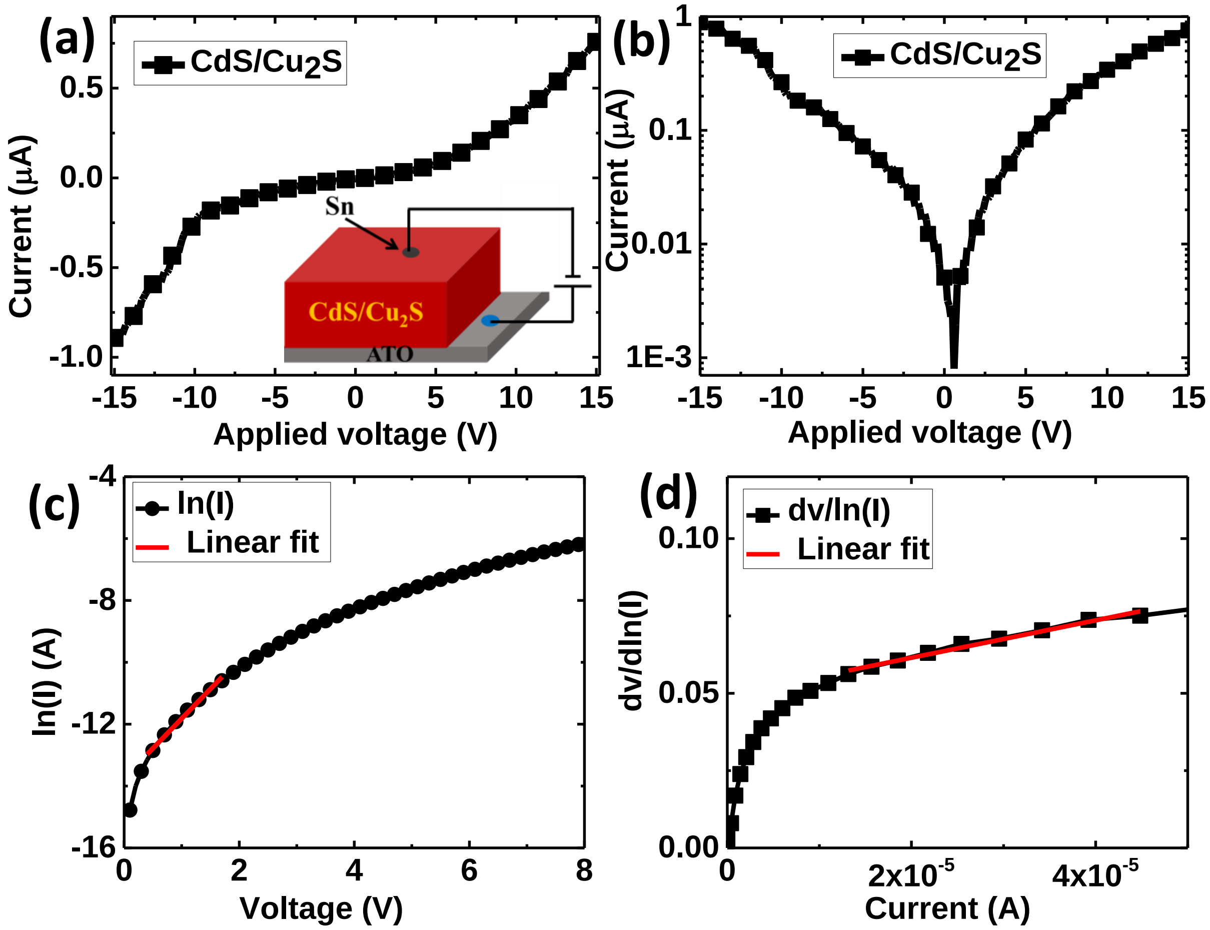

Figure 2

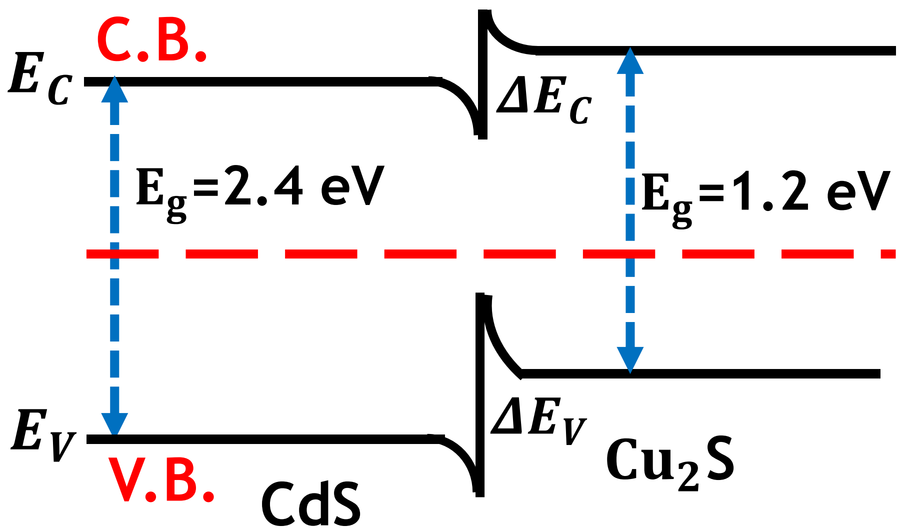

Figure 3