# CHARGE TRANSPORT MECHANISM OF Al/Cd<sub>1-x</sub>Zn<sub>x</sub>S/ITO SCHOTTKY DIODE AND ITS PHOTOSENSING BEHAVIOR

Joydeep Datta<sup>1</sup>, Mrinmay Das<sup>2</sup>, Arka Dey<sup>3</sup>, Sayantan Sil<sup>4</sup>, Rajkumar Jana<sup>5</sup>, Partha Pratim Ray<sup>6</sup>

<sup>1</sup>Department of Physics, Jadavpur University, Kolkata-700032, India <sup>2</sup>Department of Physics, Jadavpur University, Kolkata-700032, India <sup>3</sup>Department of Physics, Jadavpur University, Kolkata-700032, India <sup>4</sup>Department of Physics, Jadavpur University, Kolkata-700032, India <sup>5</sup>Department of Physics, Jadavpur University, Kolkata-700032, India <sup>6</sup>Department of Physics, Jadavpur University, Kolkata-700032, India

#### Abstract

In this study, nanocrystalline  $Cd_{1,x}Zn_xS$  (x=0, 0.4, 0.8) were synthesized by co precipitation method. Material characterization was done by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-Vis absorption spectroscopy. From XRD data, it is noticed that the particle size of CdS is changed due to the doping of Zn. The band gap of CdS is also tuned with the introduction of Zn within the nanocomposite. The synthesized nanomaterials were applied in metal-semiconductor Schottky device and studied at room temperature. Its charge transport mechanism is explained with the help of SCLC (space charge limited current) theory. The outcome of this explanation has inspired us to find out the capability of the nanocomposite in the application of devices like photodetector, photosensor etc.. So, we have derived the photosensitive parameter from the current-voltage (I-V) data under illumination. The conclusions from the electrical characterizations of the Schottky diodes reveal the higher mobility of  $Cd_{0,6}Zn_{0,4}S$  is  $(4.61 \times 10^{-6} \text{ m}^2 \text{V}^1 \text{s}^{-1})$  and better detectivity ability  $(11.336 \times 10^9 \text{ Jones})$  than the other synthesized nanomaterial. So,  $Cd_{0,6}Zn_{0,4}S$  shows the potential as a better candidate in the application of photovoltaic device.

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## **1. INTRODUCTION**

Now a day, II-VI semiconductors have become a significant interest for the researchers due to their low cost, uncomplicated preparation techniques and vast application field. These types of compounds have attracted interest more than the other inorganic semiconductors due to their flexibility in the band gap tuning and ability in the particle size alteration. Cd<sub>1-x</sub>Zn<sub>x</sub>S is a II-VI semiconductor and a promising and wide bandgap window material which has enormous applications in the photovoltaic field such as heterojunction photovoltaic solar cells [1] and various photoconductive devices [2]. The efficiency of solar cell strongly depends on the choice of an appropriate window material.  $Cd_{1-x}Zn_xS$  has a wider bandgap than CdS, so substitution of CdS by Cd<sub>1-x</sub>Zn<sub>x</sub>S could reduce window absorption loss and increase short-circuit current. Moreover, the stability of CdS is not adequate due to its photocorrosion behavior. Because of wide visible-light absorption, ternary Cd<sub>1-x</sub>Zn<sub>x</sub>S shows more stability than CdS under illumination [3]. Furthermore, Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films are promising from the view point of exciton localization to realize the high luminescence efficiency [4].

In this present study, we have investigated optical, structural and electrical properties of synthesized  $Cd_{1-x}Zn_xS$  (x=0, 0.4, 0.8) nanocomposite. The XRD pattern revealed altering of particle size due to doping of Zinc to Cadmium Sulfide. We have obtained the absorbance property of the synthesized material from the UV data. Then, we have fabricated the Schottky device using these materials. Our main objective is to study the charge transport mechanism of the synthesized material in the Schottky device and to check the potential of the device in the photovoltaic field.

## 2. PREPARATION AND DIODE FABRICATION

Cadmium Chloride monohydrate (CdCl<sub>2</sub>, H<sub>2</sub>O), Zinc Chloride (ZnCl<sub>2</sub>) and Sodium Sulfide Nonahydrate (Na<sub>2</sub>S, 9H<sub>2</sub>O) are used as precursor to synthesize Cd<sub>1-x</sub>Zn<sub>x</sub>S (x=0, 0.4, 0.8). These are bought from Merck and used without additional purification. For the synthesis of CdS, we have taken 0.1 N of Cadmium Chloride monohydrate and Sodium Sulfide Nonahydrate water solution. 50 ml of each solution were taken and stirred for 15 min individually. Under stirred condition, 50 ml sodium sulfide nonahydrate solution was poured into Cadmium sulfide solution drop by drop. Then, the total 100 ml solution was stirred for 24 hrs at room temperature. A yellowish orange precipitate was formed after washing. Then the precipitate was dried in vacuum and collected as powder. To synthesize Cd<sub>0.6</sub>Zn<sub>0.4</sub>S, we have taken 25ml water solution of each 0.06N CdCl<sub>2</sub>, H<sub>2</sub>O; 0.04N ZnCl<sub>2</sub> and 50 ml water solution of 0.1N Na<sub>2</sub>S, 9H<sub>2</sub>O. At first the CdCl<sub>2</sub>, H<sub>2</sub>O and ZnCl<sub>2</sub> solutions were mixed and stirred for 15 min. Then, the Na<sub>2</sub>S, 9H<sub>2</sub>O solution was poured into previous solution under stirring. The remaining steps are same as the CdS preparation. In the similar way, Cd<sub>0.2</sub>Zn<sub>0.8</sub>S is prepared by taking the molar concentration of CdCl<sub>2</sub>, H<sub>2</sub>O as 0.02N and 0.08 N for ZnCl<sub>2</sub>.

To fabricate the Schottky device of the synthesized materials, Indium Tin Oxide (ITO) coated glass substrates were cleaned with acetone, ethanol and distilled water accordingly by sonication technique. The samples were dispersed into the ethanol solution to prepare homogeneous medium. These solutions of the synthesized material were spin coated onto the ITO glass at 450 rpm for 30 sec with the help of SCU 2700 spin coating unit in vacuum. The last step was repeated for 3 times. Then, we have measured the film thickness as 10  $\mu$ m by surface profiler. Finally, aluminum (Al) electrodes were deposited onto the film by using a Vacuum Coating Unit (12A4D of HINDHIVAC) at the base pressure of 10<sup>-6</sup> Torr.

We have studied the materials by X-ray diffraction (XRD) technique to identify the structural and phase with the help of Bruker D8 X-Ray Diffractometer with CuK $\alpha$  target (wavelength ~0.154 nm), scanned between 20°-60°. The morphology of the synthesized sulfide was gathered from FEI make field effect scanning electron microscope (FESEM) (Inspect F50). Optical absorbance spectra were obtained from a UV-vis spectrophotometer (Shimadzu, 2401PC UV/Visible PC). The electrical characterization of the diodes was analyzed from current-voltage (I-V) characteristics using the Keithley 2400 sourcemeter interfaced with PC.

#### **3. RESULT AND DISCUSSION**

#### 3.1 Structural and Optical Analysis

Figure 1 shows XRD pattern of  $Cd_{1-x}Zn_xS$  (x=0, 0.4, 0.8) which indicates that the diffraction peak positions are getting shifted to upper 2 $\theta$  values with the increase of Zn presence. The three diffraction peaks for the undoped CdS nanoparticles were 26.5894 (1 1 1), 43.7922 (2 2 0) and

51.9571 (3 1 1). The diffraction lines of cubic phases of Cd<sub>1</sub>.  $_x$ Zn<sub>x</sub>S peaks are confirmed by JCPDS file no. 05-0566 (cubic). For x= 0.4 and 0.8, the synthesized material does not show any trace of individual CdS or ZnS peak which is pinpointing to the pure alloy material. We have estimated the crystallite size of the synthesized material from the XRD data using Debye Scherrer formula [5].

$$\mathbf{D} = \frac{\mathbf{k}\lambda}{\mathbf{\beta}\mathbf{Cos}\theta} \tag{1}$$

where D is crystallite size,  $\lambda$  is the wavelength of X-ray (0.1541nm),  $\beta$  is full width at half maxima (FWHM) in radian, k is shape factor. The value of k = 0.9 is considered as standard. The average crystallite size is derived as 3.3776nm, 2.8564nm and 3.1583nm for CdS, Cd<sub>0.6</sub>Zn<sub>0.4</sub>S and Cd<sub>0.2</sub>Zn<sub>0.8</sub>S respectively. The decrement of crystallite size due to adding of Zn may be due to the increase of micro strain. At more Zn doping, the leading re crystallization mechanism in the poly crystalline and the movement of interstitial zinc atoms from inside the crystallites to its grain may be the cause behind the greater particle size.

FESEM was carried out to study the morphology of  $Cd_{1.x}Zn_xS$  (x=0, 0.4, 0.8). Figure 2 shows spherical shapes of synthesized particles for the synthesized material.



**Fig.1**: XRD spectra of  $Cd_{1-x}Zn_xS$  (x=0, 0.4, 0.8); **Fig.2**: FESEM image of (a) CdS, (b)  $Cd_{0.6}Zn_{0.4}S$ , (c)  $Cd_{0.2}Zn_{0.8}S$ ; **Fig.3**: Tauc's plot to determine the band gap energy.

To investigate the optical property of the  $Cd_{1-x}Zn_xS$  (x=0, 0.4, 0.8) nanoparticle, the absorbance spectra of the thin film were recorded (Inset of Figure 3) and bandgap energy was derived using the Tauc's equation [6].

$$(\boldsymbol{\alpha}\mathbf{h}\mathbf{v})^{n} = \mathbf{c}\left(\mathbf{h}\mathbf{v} - \mathbf{E}_{g}\right)$$
(2)

where  $\alpha$  is the absorption coefficient, hv is photon energy, c is a constant and was considered as 1 for ideal case. The linear nature of the plots at the absorption edge confirms that sample is a semiconductor with a direct bandgap formation. The band gap energies were derived as 2.32 eV, 2.87 eV and 3.05 eV for CdS, Cd<sub>0.6</sub>Zn<sub>0.4</sub>S and Cd<sub>0.2</sub>Zn<sub>0.8</sub>S respectively from the Tauc's plot (Figure 3). We observed that the band gap of CdS is increased due to doping of Zn

from 2.32 eV to 3.05 eV which is an indication of blue shifting.

#### 3.2 Electrical Analysis

We have measured the current-voltage characteristics of the individual Schottky devices under dark and illumination to understand the charge transport mechanism. From Figure 4, it can be easily seen that the current value at the same voltage is higher in illumination than dark condition for every device. Because, under illumination the photon energy is higher than the semiconductor band gap energy and photon directly engages through the metal-semiconductor junction to increase the major charge carrier density. The diode fabricated with  $Cd_{0.6}Zn_{0.4}S$  shows better sensitivity for the applied bias in both conditions.



Fig. 4: I-V characteristics of  $Cd_{1-x}Zn_xS$  (x=0, 0.4, 0.8) Schottky device under dark and illumination.

To move forward, we have derived photosensitivity, responsivity and specific detectivity (Table-1). The photosensitivity ( $P_S$ ) is obtained from the ratio of photocurrent ( $I_{ph}$ =  $I_L$ - $I_D$ ;  $I_L$  is the current under light) to the dark current ( $I_D$ ).

$$\mathbf{P}_{\mathbf{S}} = \frac{\mathbf{I}_{\mathbf{L}} - \mathbf{I}_{\mathbf{D}}}{\mathbf{I}_{\mathbf{D}}} \tag{3}$$

Responsivity and Specific detectivity indicate the photodetector sensitivity to the incident light. Responsivity is defined as the photocurrent generated per unit incident light power on the effective diode area which can be obtained from the following mathematical expression [7].

$$\mathbf{R} = \frac{\mathbf{I}_{\mathbf{ph}}}{\mathbf{PA}} \tag{4}$$

Where P is the illumination power (P=1000W/m<sup>2</sup>), A is the effective diode area. (A=  $7.065 \times 10^{-6}$  m<sup>2</sup>). The mathematical expression of specific detectivity is [7]

$$\mathbf{D}^* = \frac{\mathbf{R}}{\left(2\mathbf{q}\mathbf{I}_{\mathbf{D}}\right)^{1/2}} \tag{5}$$

From the outcome of the photosensing parameters, we have seen that  $Cd_{0.6}Zn_{0.4}S$  fabricated device has greater sensitivity than the other two materials devices and is established as better candidate for photodetector application.

So, we have derived the diode parameter and analyzed the charge transport mechanism with the help of SCLC theory. In order to determine the ideality factor and the barrier height, we have analyzed the I-V characteristics of the diodes using Cheung method [8]. According to the thermionic emission theory of Schottky contacts, the current intensity can be written as

$$\mathbf{I} = \mathbf{I}_{0} \left[ \exp \left( \frac{\mathbf{q} \left( \mathbf{V} - \mathbf{I} \mathbf{R}_{s} \right)}{\mathbf{n} \mathbf{k} \mathbf{T}} \right) - \mathbf{1} \right]$$
(6)

Where,  $R_s$  is the series resistance ( $R_s$ ) of the devices.  $I_0$  is the saturated current. By substituting  $I_0$  (  $I_0 = AA^*T^2exp(-\frac{q\phi_B}{kT})$ ) into Equation (6), one can obtain the following expression:

$$\mathbf{V} = \mathbf{IR}_{\mathbf{S}} + \mathbf{n}\boldsymbol{\varphi}_{\mathbf{B}} + \frac{\mathbf{n}\mathbf{k}\mathbf{T}}{\mathbf{q}}\mathbf{ln}(\frac{\mathbf{I}}{\mathbf{A}\mathbf{A}^{*}\mathbf{T}^{2}})$$
(7)

Where  $\phi_B$  is the barrier height, k is the Boltzmann Constant, A is the effective diode area and A<sup>\*</sup>(A<sup>\*</sup>=4 $\pi$ qm<sub>e</sub>k<sup>2</sup>/h<sup>3</sup>) is the Richardson Constant. By differentiating the equation (7) with respect to lnI, it can be written as:

$$\frac{\mathrm{d}\mathbf{V}}{\mathrm{d}\mathbf{l}\mathbf{n}\mathbf{I}} = \frac{\mathbf{n}\mathbf{k}\mathbf{T}}{\mathbf{q}} + \mathbf{I}\mathbf{R}_{\mathbf{S}} \tag{8}$$



Ideality factor (n) was estimated from the slope of the plot (dV/dlnI vs I) and are presented in Table 1. To determine the barrier height, Cheung et al. defined a function H(I) as

$$\mathbf{H}(\mathbf{I}) = \mathbf{V} - \frac{\mathbf{n}\mathbf{k}\mathbf{T}}{\mathbf{q}}\mathbf{ln}(\frac{\mathbf{I}}{\mathbf{A}\mathbf{A}^{*}\mathbf{T}^{2}}) = \mathbf{n}\boldsymbol{\varphi}_{\mathrm{B}} + \mathbf{I}\mathbf{R}_{\mathrm{S}} \qquad (9)$$

From the slope of the curve (H(I) vs I) (Figure 5),  $\phi_B$  is evaluated. Figure 5 represents the dV/dln(I) and H(I) versus I plot which is a straight line at low bias voltage for both conditions. The values of ideality factor and the barrier height are presented in Table-1. The ideality factor values are deviated from unity for the devices in both conditions. The metal oxide insulating layer at the interface, barrier inhomogeneities, carrier recombination process at the metalsemiconductor interface may be the possible reasons behind such deviation from unity [9]. There is a formation of trapping states in metal-semiconductor interfacing layer which act as localized recombination-generation centers. Here, we have found that the device which has lower barrier height has greater ideality factor. Tung [10] has approached earlier that Schottky barrier is formed with laterally inhomogeneous patches of different barrier heights. These patches with lesser barrier height give a higher ideality factor. To get the better view about the conduction mechanism and mobility, diffusion length, we have analyzed the I-V data with SCLC theory.

In their forbidden gap, the semiconductors include a large number of localized defect states which act as carrier trapping centers and have been charged during the carrier charge emission from electrode. As a consequence, space charge region would be built in the semiconductor film and it is effective in the higher bias region [11]. The I-V (in logarithm scale) (Figure 6(a)) curve provides the current transport mechanism idea and we have observed the whole forward bias dependent current can be divided into three different regions. In these three regions, current follows I~V (Region-I),  $I \sim V^2$  (Region-II) and  $I \sim V^n$  (n>2) (Region-III) due to ohmic, the space charge limited conduction mechanism and the SCLC mechanism characterized by exponential distribution of traps respectively. So, from the SCLC theory, we have derived the mobility, transit time and carrier diffusion length.

From  $I-V^2$  (Figure 6(c)), the effective carrier mobility is evaluated using the Mott-Gurney equation [12],

$$\mathbf{I} = \frac{9\mu_{\rm eff}\varepsilon_0\varepsilon_r \mathbf{A}}{8} \left(\frac{\mathbf{V}^2}{\mathbf{d}^3}\right) \tag{10}$$



Where  $\mu_{eff}$  is the effective mobility, A is the effective diode area (7.065×10<sup>-6</sup> m<sup>2</sup>), d is the film thickness (10µm). The transit time is calculated using the following equation [13].

$$\tau = \frac{9\varepsilon_0 \varepsilon_r A}{8d} \left(\frac{V}{I}\right) \tag{11}$$

The diffusion length of charge carrier is estimated using Einstein-Smoluchowski equation [14].

$$\mathbf{L}_{\mathbf{D}} = \sqrt{2\mathbf{D}\tau} \tag{12}$$

Where, D is the diffusion co-efficient and is calculated from

$$\boldsymbol{\mu}_{\text{eff}} = \frac{\mathbf{q}\mathbf{D}}{\mathbf{k}\mathbf{T}} \tag{13}$$

The values of effective mobility, transit time and diffusion length are listed in Table-1. All these parameters are improved for the devices fabricated with  $Cd_{0.6}Zn_{0.4}S$  in dark. Diffusion length depends on the mobility transit time product. Here, the transit time of Al/  $Cd_{0.6}Zn_{0.4}S$ /ITO decreases but it's the product of mobility-transit time improves for higher mobility. Higher diffusion length of  $Cd_{0.6}Zn_{0.4}S$  signifies that it is a better candidate for the photovoltaic devices.

Device	Device Parameter				SCLC parameter			Photosensing Parameter		
Tabricated by										
	dV/dlnI vs I		H(I) vs I		Mobilit	Transit	Diffusi	Photos	Respon	Sp.
					y ×10 <sup>-6</sup>	time	on	ensitivi	sivity(	Detectivity
					$m^2 V^{-1} s^{-1}$	(sec)×	length	ty	A/W)	(Jones)×
					I	10-7	(nm)			10 <sup>9</sup>
	n	R <sub>S</sub>	$\phi_B$ (in	R <sub>S</sub> (oh						
		(ohm)	eV)	m)						
CdS	3.47	868	0.66	1059	2.61	4.32	242	0.048	0.054	1.07
Cd <sub>0.6</sub> Zn <sub>0.4</sub> S	4.25	219	0.61	263	4.61	2.74	256	0.398	0.73	11.336
Cd <sub>0.2</sub> Zn <sub>0.8</sub> S	3.74	443	0.63	705	3.02	3.91	247	0.224	0.285	5.317

Table-1: I-V characteristics parameter:

We know that the device performance and charge transportation directly depends on Schottky device parameter and SCLC parameter. Al/  $Cd_{0.6}Zn_{0.4}S/ITO$  Schottky device shows better barrier height and lower series resistance which is an indication of better device. Mobility of a material depends on many factors - one of them is nano crystallite size. Generally, greater particle size assists to better charge transportation due to lower grain boundary resistance. But sometimes, lower crystallite size enhances the free carrier wavefunction leakage at the surface of the nanomaterials. As a consequence, it improves the electronic coupling between the element. Here, the crystallite size of  $Cd_{0.6}Zn_{0.4}S$  is lower than ZnS and  $Cd_{0.2}Zn_{0.8}S$ . This lower crystallite size of  $Zn_{0.6}Cd_{0.4}S$  may be the reason behind such

enhancement of mobility and the lowering in effective energy barrier.

#### 4. CONCLUSION

The structural analysis assists us to characterize the crystallite size and the phase. So, we have concluded that  $Cd_{0.6}Zn_{0.4}S$  has lower crystallite size than the other two materials. From the optical characterization, we have observed a band gap change for the doping of Zn into CdS. From the I-V characteristics, we have derived barrier height, series resistance, ideality factor, mobility, diffusion length and transit time. Hence, we are convinced that Al/  $Cd_{0.6}Zn_{0.4}S/ITO$  diode is proficient as a superior Schottky device compared to Al/  $Cd_{0.2}Zn_{0.8}S/ITO$  & Al/ CdS/ITO

device. From the calculated photosensing parameter using the I-V characteristics under illumination, we have concluded that Al/  $Zn_{0.6}Cd_{0.4}S$ /ITO device executes improved sensitivity upon illumination.

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