Analysis of Photoresponse and Charge Transport Properties of Hydrothermally Synthesized ZnSe Nanoparticle Based Schottky Device

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ABSTRACT: In the present study, ZnSe nanoparticles (NPs) have been successfully synthesized via a hydrothermal process. Sample characterization has been done using Powder X-ray diffraction, UV–Vis spectroscopy, and Field emission scanning electron microscopy. ZnSe NPs show significant optical absorption in the visible light range and the direct optical energy bandgap has been measured as 3.22 eV, which shows the clear blue shift of 0.5 eV from the standard bandgap for bulk ZnSe ($E_g = 2.7 \text{ eV}$). Hence, Al/ZnSe metal-semiconductor (MS) junctions have been fabricated to study the electrical properties. The obtained current density-voltage (*J-V*) characteristics revealed that the thin film devices have non-linear behaviour like Schottky diode (SD). The thermionic emission is the main phenomenon for current transport across these barriers. Here I have measured series resistance (R_s), ideality factor (η), barrier height (Φ_b) and photosensitivity for the fabricated devices under dark and irradiation conditions and also compared those accordingly. The photosensitivity of the Al/ZnSe SD has been found to be 2.85. For the better realization of charge transport phenomena through the MS junction, space charge limited current (SCLC) theory has been employed. The effective mobility of the carrier has been evaluated in dark and light condition as 3.01 x 10⁻³ and 8.58 x 10⁻³ m²V⁻¹s⁻¹, respectively. It has been observed that all the electrical properties improved under illumination condition shows its probable application in photosensitive devices.

KEYWORDS: ZnSe nanoparticles, hydrothermal, metal-semiconductor junction, Schottky diode.

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1.INTRODUCTION

Due to quantum confinement, the semiconductor nanocrystals (NCs) exhibit unique size-dependent electronic and optical properties. These properties made them popular for extensive studies in various applications [1]. Continuous absorption bands, intensive and narrow emission spectra, high chemical, surface functionality and photo bleaching stability are among the most attractive properties of these materials. These are the explicit properties from either bulk materials or isolated atoms. Due to the size-dependent properties, the wide bandgap semiconductor materials have attracted considerable attention for various technological applications throughout the past decades [2]. Zinc selenide (ZnSe), from II-VI semiconductors family, is a wide bandgap semiconductor. Due to quantum confinement affect it shows luminescence properties in the blue to the ultraviolet range. This made ZnSe a widely popular material for studied in various application such as nonlinear optical devices [3], displays [4], sensors [5] and infrared windows [6] etc. For suitable optoelectronic and luminescent applications, the controlled size and morphological depended synthesis of materials is always potentially important. For nanostructured materials, the size and dimensions are the key characteristics to determine the physical and chemical properties [7]. Among the conventional methods to prepare ZnSe

NPs, it is believed that the most straightforward way to synthesize ZnSe is a direct combination of element zinc and selenium at high temperature. The advantage of the hydrothermal processes is that they required relatively low temperatures and pressures. The crystal sizes of a material get minimized due to the low temperature, high concentration, and short time reaction during synthesis.

In this study, a simple hydrothermal route has been introduced to the synthesis of ZnSe NPs. The physical properties have been characterized by powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FESEM) and UV-Vis spectroscopy. We believe the analysis of metalsemiconductor (MS) barriers on the predominantly ionic wide band-gap material ZnSe are of wide interest. Hence, the aim of this work is to put forward experimental information on photophysical and photoelectrical properties such as the mechanism of the charge transport and carrier trapping in Al/ZnSe Schottky diode via the study of space charge limited currents (SCLC).

2. EXPERIMENTAL 2.1 Materials and Method

Prior to the synthesis of ZnSe, Zinc Nitrate Heptahydrate ($Zn(NO_3)_2.7H_2O$), and Sodium Selenite (Na_2SeO_3) of AR grade were purchased from Merck.

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Zinc Nitrate Heptahydrate and Sodium Selenite were used as sources for zinc and selenium. The preparation of ZnSe NPs was performed by a one-pot approach. In a typical synthesis, 14 mmol of NaOH was dissolved in 14 mL of distilled water and then 0.35 mmol of $Zn(NO_3)_2$ ·7H₂O and 3 mmol of Ethylene Diamine Tetraacetic Acid (EDTA) were added successively into the above solution by maintaining the pH value at \sim 7. The resulting mixture was sonicated until a clear solution was obtained. Afterwards, $0.34\ mmol\ of\ Na_2SeO_3$ and 7mL of Hydrazine Hydrate (N₂H₄.H₂O) (80%) were sequentially added into this reaction. After stirring the mixture for 1 hour by magnetic stirring, the final solution was transferred into a Teflon-lined autoclave. The sealed autoclave was maintained at 180° C for 24 hours in a vacuum oven and allowed to cool to room temperature naturally. By centrifuge technique, the resultant products were washed with absolute ethanol and distilled water sequentially and repeatedly to remove possible impurities. After drying (@80° C for 3 hours) and grinding in a mortar the final product of the synthesized material was collected.

2.1 Device Fabrication

perform electrical То the analysis, ITO/synthesized ZnSe/Al sandwich structured metal-semiconductor (MS) junction multiple devices were fabricated. Using an ultrasonic bath, the ITO coated glass substrate was cleaned with soap solution, acetone, ethanol and distilled water sequentially to fabricate the active device. In this regard, well dispersion of the synthesized ZnSe NPs was made in CHCl₃ (Chloroform) by mixing and sonicated the right proportion (25 mg/ml) of synthesized NPs. With the help of SCU 2700 spin coating unit, that freshly prepared stable dispersion of our synthesized ZnSe NPs was deposited by spun firstly @ 600 rpm for 5 min and thereafter @ 900 rpm for another 5 min on the top of the ITO coated glass substrate. To evaporate the solvent part fully, all the as-deposited thin films were dried afterward in a vacuum oven (at a base pressure of 5 \times 10⁻³ Torr) @60 °C for several minutes. The thicknesses of the developed films were measured by surface profiler as $\sim 1 \mu m$. The aluminium were deposited as electrodes under base pressure (10⁻⁶ Torr) by maintaining the effective area as $7.065 \times 10^{-2} \text{ cm}^{-2}$ with shadow mask in the Vacuum Coating Unit 12A4D of HINDHIVAC.

3. PHYSICAL MEASUREMENTS

The structural characterizations of the synthesized material were performed by the Powder X-ray Diffraction (PXRD) and Field Emission Scanning Electron Microscopy (FESEM) technique. The field emission scanning electron microscopy (FESEM) image was performed with an FEI make Inspect F-50 electron microscope. The optical scanning characterization was performed bv UV-vis spectrophotometer made by Perkin Elmer (model no: Lambda 365). The capacitance was recorded as a

function of frequency over a wide range (200 Hz–2 MHz) by the computer controlled Agilent make precision E4980 LCR meter at room temperature. For electrical characterization of the devices, the current density-voltage (J-V) characteristic was measured under both dark and AM 1.5G radiation condition and recorded with the help of a Keithley 2635B Source meter by two-probe technique. All the device preparations and measurements were performed at room temperature and under ambient conditions.

4. RESULTS AND DISCUSSIONS 4.1. XRD Analysis

Using Powder-XRD, the phase composition and crystal structure of the sample were investigated. Fig. 1(A) represents the P-XRD pattern of the assynthesized material. The responsible diffraction peaks are appeared at Bragg's angle 27.34, 45.22, 53.73, 66.09 and 72.81 degree, corresponding to the Bragg's plane (111), (220), (311), (400) and (331). All the obtained diffraction peaks matched with the known zinc blend (cubic) ZnSe with lattice constants a = 5.668 Å, in agreement with data in the literature (JCPDS card, no. 37-1463). No other impurities of source materials are detected from the obtained characteristic peaks. The sharp shape and narrow widths of the peaks indicate that synthesized ZnSe has high crystallinity.

4.2 FE-SEM Analysis

The detailed characterization of morphology and composition of the as-prepared ZnSe were performed using FESEM. A high-magnification SEM image, Fig. 1(B), reveals that nearly all of the ZnSe products consist of a large number of monodisperse nanocrystals. This micrograph indicates the presence of spherical agglomerates consisting of individual NPs which are composed of regular shape particles.

4.3 Optical Analysis

The optical characterization of synthesized ZnSe NPs has been performed based on the UV-vis spectrum. As the synthesized ZnSe NPs produce stable dispersion in Chloroform, thin films on normal glass substrate were prepared for solid-state UV-vis spectroscopy. The optical spectra of synthesized ZnSe NPs (inset Fig. 1(C)) have been measured in the range 300–800 nm. The optical band gap for each of the films has been estimated from UV-vis spectrum using Tauc's equation (eqn. 1) [8].

$$(\alpha h\nu) = A(hn - E_g)^n \qquad (1)$$

where, α , E_g , h and v stand for absorption coefficient, band gap, Planck's constant and frequency of light. The exponent 'n' is the electron transition processes dependent constant. 'A' is a constant which is considered as 1 for ideal case. In equation 1, we have consider the $n = \frac{1}{2}$ to calculate the direct optical band gap [8]. From plot $(\alpha hv)^2 vs. hv$ [Fig.1(C)], the values of direct optical band gap (E_g) of the synthesized ZnSe NPs have been calculated as 3.22 eV.

4.4 Electrical Characterization

The suitable optical band gap suggests that our synthesized ZnSe NPs are semiconducting material. Hence, we have studied the electrical properties by fabricating metal (Al)-semiconductor (synthesized ZnSe NPs) (MS) junction thin film device. In this current density-Voltage regard, the (I-V)characteristics of synthesized ZnSe NPs based multiple devices has been recorded with a Source meter made by Keithley (Model no: 2635B) under dark and AM 1.5G condition at corresponding applied bias voltage sequentially within the limit ±2 V.

The electrical conductivity of synthesized ZnSe NPs based devices under dark condition has been estimated as 1.24×10^{-3} S.m⁻¹, typical of a semiconductor. However, after exposed under

photoirradiation, the conductivity has been estimated as 2.42×10^{-3} S.m⁻¹ for the same devices. It is clear that the conductivity of synthesized ZnSe NPs based devices improves significantly under irradiation conditions from the non-irradiated conditions. Moreover, the representative J-V characteristics (Fig. 2(A)) of the Al/ZnSe interface under both conditions (dark and irradiation) represents the nonlinear rectifying behaviour, analogous to the Schottky diode (SD). The rectification ratio (I_{on}/I_{off}) of the SDs at ±2 V has been obtained as 14.61 and 60.52 for our devices under dark and photo illumination condition, respectively. At the presences of light the drawing of greater amount current depicts the photo responsivity of the devices, which has been found to be 2.85 for synthesized ZnSe NPs based SDs.



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Fig. 1 (A) Powder X-Ray diffraction spectra, (B) FESEM image and (C) UV–vis absorption spectra (inset) and Tauc's plots of Synthesized ZnSe



Fig. 2(A) *J–V* characteristics curve for ITO/synthesized ZnSe NPs /Al structured thin film devices under dark and photo illumination condition and (B) Capacitance *vs.* frequency graph for determination of dielectric constant

The J-V characteristic of the synthesized ZnSe NPs based SDs have been further analyzed by thermionic emission theory and Cheung's method has been employed to extract important diode parameters [8]. In this regard, we have analysed J-V curves by considering the following standard equations: [8, 9]

$$J = J_0 \left[exp\left(\frac{qv}{\eta KT}\right) - 1 \right]$$
(2)
$$J_0 = AA^*T^2 exp\left(\frac{-q\varphi_B}{KT}\right)$$
(3)

where J_0 , k, T, V, A, η and A^* stands for saturation current density, electronic charge, Boltzmann

constant, temperature in Kelvin, forward bias voltage, effective diode area, ideality factor and effective Richardson constant, respectively. The effective diode area has been estimated as 7.065×10^{-2} cm² and the effective Richardson constant has been considered as 32 AK⁻² cm⁻² for all the devices.

We have also determined the series resistance, ideality factor and barrier potential height by using equations (4)–(6), which has been extracted from Cheung's idea [10, 11],

$$\frac{dV}{dlnJ} = \left(\frac{\eta KT}{q}\right) + JR \tag{4}$$

$$H(J) = V - \frac{nKT}{q} ln(\frac{J}{AA^*T^2})$$
(5)

$$H(J) = JR_S + n\phi_B \tag{6}$$

The intercept of dV/dlnJ vs. J plot (Fig. 3(A)) gives the value of the ideality factor (η), whereas the slope of same plot denotes the series resistance (R_s) of the devices under both conditions. In Table 1, the obtained value of η for the devices under both conditions (dark and irradiation) has been listed. The values of η of the devices under both the conditions represent a deviation from its ideal value (~1). This may be may be due to the presence of inhomogeneities of Schottky barrier height and existence of interface states and series resistance at the junction [12, 13]. The interesting observation is that under irradiation condition, the value of η of our fabricated SDs significantly approaches more ideal (closer to 1). This depicts the recombination of a fewer number of interfacial charge carriers and generation of better homogeneity at the barrier of Schottky junctions [8].

From the intercept of H(J) vs. J plot (Fig. 3(B)) and using the just calculated ideality factor (η) value, the value of barrier height (\emptyset_B) has been determined [eqn. (6)].



Fig. 3 (A) *dV/dlnJ vs. J* and (B) *H vs. J* curve for the synthesized ZnSe NPs based thin film devices under dark, and photoillumination condition.

Condition	On/Off	Conductivity (S.m ⁻¹)	Photo sensitivity	Ideality factor	Barrier height (eV)	R _s From dV/dlnI vs. I (Ω)	R _s From H vs. I (Ω)
Dark	14.61	1.24 × 10 ⁻³	2.05	1.79	0.40	254.77	247.70
Light	60.52	2.42 × 10 ⁻³	2.85	1.22	0.32	202.40	198.16

Table 1. Schottky device parameters of synthesized ZnSe NPs based SDs



Fig. 4 (A) *LnJ vs. LnV* and (B) *J vs.V*² curves for the synthesized ZnSe NPs based thin film devices under dark and irradiation condition.

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Table 2 Charge conducting parameters of the synthesized ZnSe NPs based SDs								
Condition	Er	μ _{eff} (m ² V ⁻¹ s ⁻¹)	τ (sec)	$\mu_{eff} au$	D	L _D (m)		
Dark	6.31 × 10 ⁻²	3.01× 10-3	1.43 × 10 ⁻⁵	4.30 × 10 ⁻⁸	7.52 × 10 ⁻⁵	4.64×10^{-5}		
Light		8.58 × 10 ⁻³	7.04 × 10 ⁻⁶	6.04 × 10 ⁻⁸	2.14 × 10-4	5.49 × 10 ⁻⁵		

The significant observation is that the barrier potential height of the devices is reduced under irradiation condition. This may be occurring due to the generation of lightinduced charge carriers and their accumulation near the conduction band. The slope of H(J) vs. J plot also gives the values of series resistance (R_s). Obtained all the parameters under both condition (dark and illumination) for the metal (Al)–semiconductor (synthesized ZnSe NPs) (MS) junctions are listed in Table 1. The series resistance obtained from both processes shows good consistency. The obtained series resistance is found to decrease upon light illumination (Table 1), which signifies its applicability in the field of optoelectronic devices.

We have further scrutinized the J-V curves in details for better understanding the charge transport phenomena at MS junction. The characteristic J-V curves under both conditions in the logarithmic scale reveal that it can be differentiated in two slopes (Fig. 4(A)), which has been marked as region-I and region-II.

In the first region, when the value of the slope is ~1, current follows the relation $J \propto V$, which refers to the Ohmic regime. In the second region, the value of the slope is about 2, where current is proportional to V^2 (Fig. 4(A)). This is the characteristic of a trap free space charge limited current (SCLC) regime [8, 14]. If the injected carriers are more than the background carriers, the injected carriers spread and generate a space charge field. The currents are controlled by this space charge field and are known as SCLC [8, 14]. In this study, we have followed this SCLC theory to evaluate the device performance.

Following this model, the effective carrier mobility was estimated by Mott-Gurney equation [8, 11, 14]:

$$J = \frac{9\varepsilon_0\varepsilon_r A V^2 \mu_{eff}}{8d^3} \quad (7)$$

where, *J*, ε_{θ} , ε_{r} and μ_{eff} is the current density, the permittivity of free space, relative dielectric constant and effective dielectric constant of the synthesized material.

To measure the relative dielectric constant, we have drawn the capacitance against the frequency of synthesized material in film format at constant bias potential (Fig. 2(B)).From the saturated values of capacitance at the higher frequency regime (Fig. 2(B)) the dielectric permittivity of the ZnSe NPs has been calculated using the following equation [8]:

$$\varepsilon_r = \frac{1}{\varepsilon_0} \cdot \frac{CD}{A} \tag{8}$$

Where *C*, *D*, and *A* is the capacitance (at saturation), thickness of the film (considered as ~ 1

μm) and effective area. Utilizing the above formula the relative dielectric constant of ZnSe has been estimated as 6.31 × 10⁻². Few more important parameters like Transit time (τ) and diffusion length (*L*_{*D*}) have also been estimated. For this purpose, using eqn. (9) τ has been evaluated from the slope of the SCLC region (region-II) of Fig. 4(A) [8].

$$\tau = \frac{9\varepsilon_0\varepsilon_r}{8d} \left(\frac{V}{I}\right) \qquad (9)$$
$$\mu_{eff} = \frac{qD}{kT} \qquad (10)$$
$$L_D = \sqrt{2D\tau} \qquad (11)$$

where, *D* is the diffusion coefficient and has been determined using the Einstein–Smoluchowski equation (eqn. 10) [9].

When a MS junction is formed, L_D of charge carriers plays a significant role in device performance. L_D has been extracted from the eqn. 11. All the parameters estimated in the SCLC region demonstrate that the charge transport properties of the synthesized ZnSe NPs based SDs improve under irradiation condition (Table 2). The higher mobility implied higher transport rate under irradiation. In a parallel manner, the number of charge carriers also increased under the same condition. The increased value of *L*_D under illumination reveals that the charge carriers got to travel more length before being recombined. This phenomenon led to the eventual increase in current displayed by the device under the light. The diode parameters of the synthesized ZnSe NPs based SDs indicate that it is of superior performance and much-enhanced charge transfer kinetics after light soaking. So, these kinds of material can pave the way for a very promising future in device application.

5. CONCLUSION

In summary, by approaching facile co-precipitation hydrothermal reduction we have synthesized our desired ZnSe nanomaterials. Its semiconductor behaviour was confirmed by measuring the optical band gap energy (3.22 eV). So we have applied this synthesized material (ZnSe) in ITO/ZnSe/Al sandwich structure to form metal-semiconductor Schottky diode. The effects of light on the charge transport network and the current-transport mechanism have been scrutinized. A detailed comparison of device parameters such as On/Off current ratio, ideality factor, barrier potential and series resistance both in dark and light irradiance condition have analyzed. The results illustrate a

current-transport mechanism exhibiting two different regimes. Some deep-level parameters, namely, the mobility of carriers, diffusion length and the lifetime were all calculated. The analyzed results reveal that any change of the above mentioned characteristic parameters due to illumination are perceptible. These results confirm that the synthesized ZnSe can be a promising candidate in fabrication of efficient light sensing Schottky diode as well as electronic devices.

REFERENCES

- Pradhan, N.,Peng, X., 2007, Efficient and Color-Tunable Mn-Doped ZnSe Nanocrystal Emitters: Control of Optical Performance via Greener Synthetic Chemistry, J. American Chem. S. 129: 3339-47.
- [2]. Peng, Q., Dong, Y., Li, Y., 2003, ZnSe semiconductor hollow microspheres, Angewandte Chemie. 42(26): 3027–30.
- [3]. Malik, M. A., Revaprasadu, N., O'Brien P., 2001, Air-stable single-source precursors for the synthesis of chalcogenide semiconductor nanoparticles, Chem Mater. 13(3): 913–20.
- [4]. Jun, Y. W., Koo, J. E., Cheon, J., 2000, One-step synthesis of size tuned zinc selenide quantum dots via a temperature controlled molecular precursor approach, Chem Commun. 20(14): 1243–44.
- [5]. Hines, M. A., Sionnest, P. G., 1998, Bright UVblue luminescent colloidal ZnSe nanocrystals, J Phys Chem B. 102(19): 3655–57.
- [6]. Quinlan, F. T., Kuther, J., Tremel, W., Knoll, W., Risbud, S., Stroeve, P., 2000, Reverse micelle synthesis and characterization of ZnSe nanoparticles, Langmuir. 16: 4049–51.

- [7]. Shi, L., Xu, Y., Li, Q., 2008,Synthesis of ZnSe nanodonuts via a surfactant-assisted process, Solid State Commun. 146: 384-86.
- [8]. Dey, A., Middya, S., Jana, R., Das, M., Datta, J., Layek, A., Ray, P. P., 2016, Light-induced charge transport property analysis of nanostructured ZnS based Schottky diode, J. Mater. Sci. Mater. Electron.27:6325–35.
- [9]. Rhoderick, E. H. Metal-Semiconductor Contacts, Oxford University, Press, London, 1978.
- [10]. Cheung, S. K., Cheung, N. W., 1986, Extraction of Schottky diode parameters from forward current-voltage characteristics, Appl. Phys. Lett. 49: 85–87.
- [11]. Dey, A., Layek, A.,Roychowdhury, A.,Das, M., Datta, J., Middya, S.,Das, D.,Ray, P. P., 2015,Investigation of charge transport properties in less defective nanostructured ZnO based Schottky diode, RSC Adv. 5: 36560– 67.
- [12]. Gupta, R. K.,Yakuphanoglu, F.,2012, Photoconductive Schottky diode based on Al/p-Si/SnS2/Ag for optical sensor applications, Sol. Energy. 86:1539–45.
- [13]. Miao, X., Tongay, S., Petterson, M. K., Berke, K., Rinzler, A. G., Appleton, B. R., Hebard, A. F., 2012, High-Efficiency Graphene Solar Cells by Chemical Doping, Nano Lett. 12:2745–50.
- [14]. Blom, P. W. M.,de Jong, M. J. M.,Munster, van, M. G., 1997, Electric-field and temperature dependence of the hole mobility in poly(pphenylene vinylene), Phys. Rev. B. 55:R656-59.

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