

Facile synthesis of ZnSe nanostructured thin films by using simple chemical method as a semiconductor for ZnSe/Ag type Schottky diode

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Abstract: The present study investigates the fabrication of Ag/ZnSe/FTO configuration by simple and inexpensive chemical method. The proposed study encompasses a detailed examination of the optical characteristics, structural attributes, surface morphology, and electron kinetic behaviour of the Ag/ZnSe/FTO, focusing on the electrical conductivity, ideality factor (η), barrier height (Φ_b), series resistance, and photoresponsivity for the fabricated device under the dark and illumination condition. The as-deposited ZnSe films shows remarkable absorbance within a visible region at a band gap of 2.81 eV and the XRD studies were reveal the nanocrystalline hexagonal phase. The electrical properties shows the drastic increase in current after light illumination. The fabricated Ag/ZnSe/FTO metal semiconductor Schottky device showed the electrical conductivity of 80.81 Sm^{-1} , ideality factor of 1.14, barrier height of 0.246 eV, series resistance of 165 ohm and photosensitivity of 9 mA W^{-1} .

Keywords: Zinc selenide (ZnSe), CBD, metal-semiconductor junction, Schottky diode, photoresponsivity.

1. INTRODUCTION

The increasing demands of efficient optoelectronics devices, become a challenge to the modern material fabrication techniques. However, some efforts taken by the scientific community to resolve these issues by incorporating the nanostructured material. Owing to favourable and controllable properties of nanostructured materials, they made revolutionary changes in modern device fabrication. Especially, II-VI compounds owing to their unique properties have a significant market share and have helped meet the technological demands in various filed including solar cells and optoelectronics [1], energy conversion applications [2]. ZnSe is one of II-VI group compounds promising material due to its, broad direct band gap of 2.7 eV [3], low resistivity [4], high luminescence efficiency [5], high exciton binding

energy of 21 MeV [6], and remarkable photosensitivity [7] for fabrication of optoelectronic devices [8-12]. Furthermore it was also employed in laser screen, thin transistors [5], white light emitting diodes, optically controlled switches [13], high infrared laser lenses, dielectric mirrors [14]. ZnSe is eco-friendly and less toxic [15] hence it is considered as a substitute material applied as a buffer layer in the development of extremely effective solar cells utilizing Cd-free thin films [16].

In last decades, ZnSe has been synthesized by using different deposition method such as solution growth technique (SGT) [7], thermal evaporation [17], chemical vapour deposition (CVD)[18], pulsed laser deposition[19], atomic layer deposition [20], electrochemical deposition [21], spray pyrolysis[22], electron beam evaporation [23], hydrothermal [24], solvothermal [25], successive ionic layer adsorption and reaction (SILAR)[26], photo-assisted chemical bath deposition(PCBD) [27]. Recently a novel technique called chemical bath deposition (CBD) has been used to deposit ZnSe thin film in an aqueous solution [28-29]. Because it is low-cost, have a need of simple equipment's and works at low temperatures, CBD is a very advantageous technique. Substrates are implanted in an alkalic solution containing the metal ion, the chalcogenide source, an additional base, and a complexing agent in this technique. Through adjustment of the bath's parameters, including temperature, solution pH, stirring speed, and relative concentrations of the solutions in the bath, the rate of deposition can be controlled. [28].

Recent studies have explored ZnSe-based Schottky diodes and heterojunctions for optoelectronic applications. Wongcharoen & Gaewdang [30] fabricated n-ZnSe/p-Si heterojunctions, investigating their electrical properties and identifying a trap level

near the valence band. Sharma & Tripathi [31] analyzed barrier in homogeneities in Al/Al₂O₃/PVA:n-ZnSe metal oxide semiconductor diodes, examining temperature dependent I-V and C-V characteristics. Dey & Ray [32] studied photoresponse and charge transport in ZnSe nanoparticle-based Schottky devices synthesized hydrothermally. These studies contribute to the evolution of ZnSe and related materials for various applications, including solar cells and other optoelectronic devices. Among the literature survey, a very few study is on Ag/ZnSe metal semiconductor Schottky barrier diodes is reported [33, 34] and however, Ag/ZnSe metal semiconductor Schottky barrier diodes synthesized by chemical bath deposition technique not yet been reported.

The present study encompasses a detailed examination of the optical characteristics, structural attributes, surface morphology, and electron kinetic behaviour of the Ag/ZnSe/FTO, focusing on the electrical conductivity, ideality factor (η), barrier height (Φ_b), series resistance, and photoresponsivity for the fabricated device under the dark and irradiation condition. Collectively, these studies underscore the versatility and challenges of Ag-doped semiconductor materials in device applications.

2. EXPERIMENTAL

2.1 Chemicals and materials

Synthesis of the films was carried out by using following chemicals, Zinc sulfate (ZnSO₄) (Merck), liquid ammonia (NH₄OH) (Loba chemie), hydrazine hydrate (N₂H₅OH) (Loba chemie), selenium powder (Se) (Loba chemie) and sodium sulphite (Na₂SO₃) (Merck). All chemicals were used without further additional purification.

2.2 Substrate Cleaning

Fluorine doped Tin Oxide (FTO) conductive glass substrate was used for deposition of ZnSe thin film. The FTO substrates were immaculate by using slandered process reported [35-36], typically process involves, 5 minutes treatment of dilute hydrochloric acid followed by 15 minutes ultrasonication in a soap solutions. Then substrates were rinsed in de-ionized water for 20 minutes. Wet FTO substrates were then treated with isopropyl alcohol for 10 minutes. Then after 15 minutes ultrasonication with de-ionized water substrates were used for film deposition.

2.3 Fabrication of ZnSe thin film

In present investigation, facile chemical route involves a chemical bath deposition (CBD). CBD known for its easiness, simplicity, and affordability for the growth of ZnSe nanostructures [37]. Compared to alternative conventional techniques, CBD has the ability to deposit various materials thin films across a wide range of stoichiometric, large reproducibility, and environmentally friendly with good control over films thickness by simply optimizing CBD deposition conditions [38].

For the preparation of ZnSe thin films, zinc sulfate, selenium powder (Se), sodium sulphite, hydrazine hydrate and liquid ammonia (AR grade) were grab as ingredients. 0.1 M for Zn²⁺ source solution was prepared in distilled water by dissolving Zinc Sulfate (ZnSO₄) powder complexes with hydrazine hydrate. Then liquid ammonia was added drop wise for consisting the pH \approx 11. In another container Se²⁻ ionic solution was prepared by using sodium selenosulfate (Na₂SeSO₃) and following the earlier reported slandered procedure. [37] The pre-cleaned FTO substrates were placed in reaction container and both equivolume precursors' solutions were concurrently added one by one. The FTO substrates were placed in such a way that the conducting side will be facing towards the precursor solutions. Here, hydrazine hydrate and ammonia were acted as chelating agents to attach Zn²⁺ ions and reduce the rate of precipitation. The deposition was allowed to conduct at 65 °C. Following that, the substrates was removed from the bath and rinsed with de-ionized water to eliminate surface contaminants and loosely attached ions or atoms, and then it was allowed to dry naturally. The fabricated film exhibited a yellowish-red colour, demonstrating strong adhesion to the glass substrate and showing a consistent distribution across the entire surface. The Fig. 1 illustrates the schematic of deposition method.

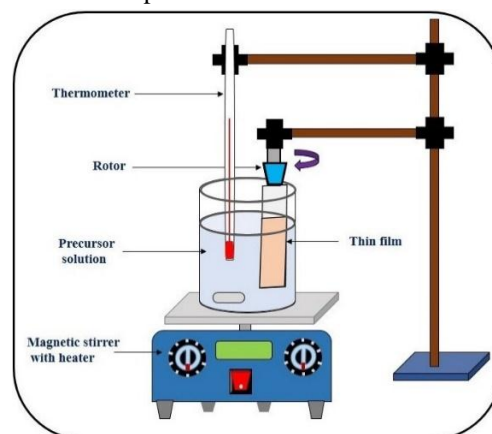


Fig. 1: Schematic depiction of ZnSe synthesized via chemical bath deposition (CBD) method on FTO coated glass substrate.

2.4 Device Fabrication

In order to prepare a metal semiconductor Schottky device, freshly implanted ZnSe thin film on FTO coated conductive glass by CBD is used. The Ag/ZnSe/FTO metal semiconductor Schottky device was created by treating thin layer of pure silver (Ag) on ZnSe thin film by electron beam evaporation technique. An incandescent light bulb is used to illuminate the device with visible light so that electrical properties can be studied. The Fig. 2 shows that measurements of the visible light sensing characteristics were made in ambient conditions and at room temperature.

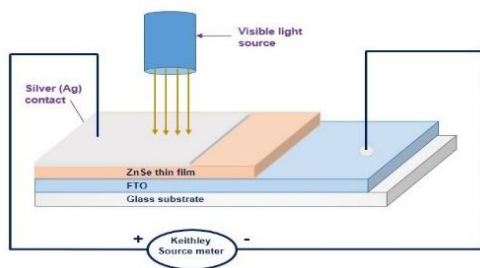


Fig. 2: Schematic depiction of Ag/ZnSe/FTO structure for visible light photodetector.

3. RESULTS AND DISCUSSION

Using an X-ray diffraction pattern (XRD) captured by a Bruker D8-Advanced X-ray diffractometer using a $\text{CuK}\alpha$ radiation ($\lambda=1.54056 \text{ \AA}$), the structural analysis of the suggested heterostructure was examined. To measure optical absorption spectra in the wavelength range of 300 to 800 nm, a Shimadzu Model-1601 UV-Vis spectrophotometer is used. Using the Hitachi S-4800 model Field Emission Scanning Electron Microscopy (FESEM), the surface morphological analysis was demonstrated. Additionally, for compositional analysis, a FESEM unit in conjunction with Energy Dispersive X-ray Spectroscopy (EDS) is used. The photovoltaic evaluation were carried out in simulated sun light of intensity 100 mW/cm^2 utilizing solar simulator (Tektronix, model Keithaly 4200A-SC-PKA high resolution IV).

3.1 Structural studies

Fig. 3 shows the XRD pattern were noted in the 2θ range of $20^\circ - 60^\circ$ for chemical bath deposited ZnSe nanoparticles thin films.

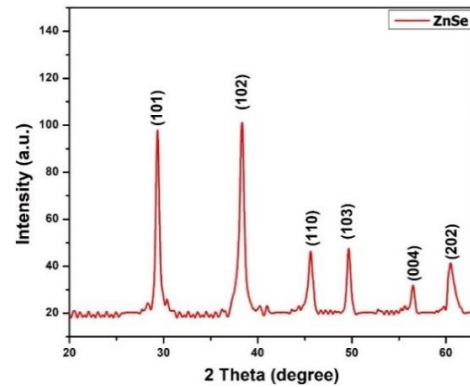


Fig. 3: X-ray diffraction patterns illustrating the crystallographic features of ZnSe.

The most prominent peak was observed at $2\theta = 38.26^\circ$, corresponding to the hexagonal crystal structure of ZnSe with an anatase phase, which is anticipated to be advantageous for photoconversion devices having lattice orientation along the (102) plane [JCPDS card data no.# 80-0008]. Additionally some small peaks appeared at 29.33° , 45.70° , 49.68° , 56.55° and 60.51° are assigned to (101), (110), (103), (004) and (202) planes respectively related with similar crystal structure and phase of ZnSe. The XRD result well support the formation of ZnSe onto FTO coated conductive glass by CBD method.

Herein the Debye-Scherrer's equation is applied at different angle for calculating average crystallite size (D) of ZnSe.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where X-ray wavelength ($\lambda=1.541 \text{ \AA}$), β is the full width at half of the peak maximum in radians, θ is Bragg's angle, and k is the shape factor (0.9). The average crystallite size was established to be nearly 16 nm for chemical bath deposited ZnSe.

3.2 Optical absorption studies

The light sensing ability of Ag/ZnSe was demonstrated by noting optical absorption spectra in the 300 to 800 nm wavelength procedure for incident light. Fig. 4 represent the typical absorption spectra of ZnSe thin films. The observed absorption curve for the Ag/ZnSe thin film showed a significant improvement in light absorption at the smaller wavelength range (UV region) of the ranges of incident light. Its use as a window layer, which is beneficial when building solar conversion devices, was strongly advised by this result.

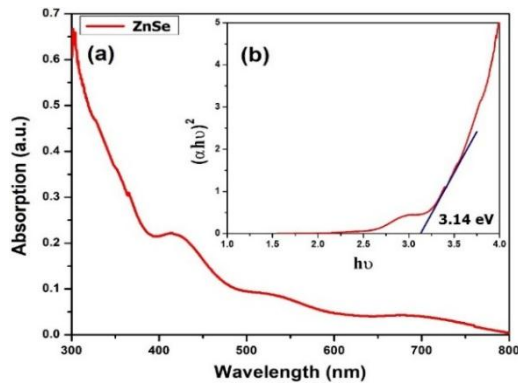


Fig. 4 UV-Vis absorption spectra and plot of $(\alpha h\nu)^2$ versus $h\nu$ for ZnSe photoanode.

Fig. 4 shows Tau plot for Ag/ZnSe metal semiconductor thin film. Here, a linear section of the curve was extrapolated to a zero absorption coefficient in order to estimate the optical band gap. The worth of optical band gap were found to be 3.14 eV for Ag/ZnSe metal semiconductor thin film which shows the clear blue shift of 0.44 eV from the standard band gap of bulk ZnSe (2.7 eV).

The shifting of optical band gap clearly disclosed of formation of Ag/ZnSe metal semiconductor junction to study electrical properties.

3.3 Surface characteristics and compositional evaluation

The surface characteristics texture of nanomaterials had a substantial impact on their physical and chemical properties. Fig. 5 displays the top viewed field emission scanning electron microscope (FESEM) image of a ZnSe nanoparticles thin film, which has been fabricated on a fluorine-doped tin oxide (FTO) coated conductive glass substrate, with a scale bar measuring 250 nm.

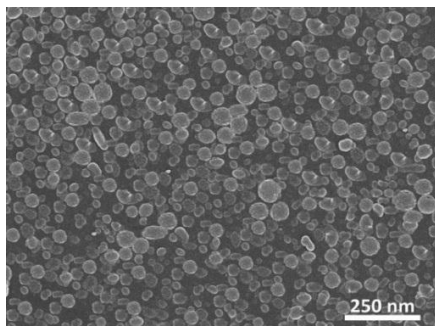


Fig. 5 Field emission scanning electron microscope images of ZnSe.

Fig. 5 depicted sensitized ZnSe nanoparticles uniformly coated on favourable sites on FTO due to favourable nucleation. The surface morphological

analysis is confirmed that ZnSe nanoparticles are successfully assembled on the FTO coated conductive glass substrate via the CBD process at 65 °C temperature.

The compositional analysis was carried out using energy dispersive X-ray spectroscopy (EDX) along with a FESEM unit for the deposited ZnSe film, which operates at 20 KV. The EDX spectrum clearly showed peaks corresponding to Zn and Se, indicating the formation of a nanoparticles thin layer of ZnSe on the FTO surface. Finally EDX analysis strongly support the XRD and again confirms the Ag/ZnSe architecture successfully deposited by the proposed chemical result.

3.4 I-V characteristics of Ag/ZnSe/FTO Schottky contact

We have examined the electrical characteristics through the fabrication of a thin film device based on metal-semiconductor (Ag/ZnSe) junctions under shadowy conditions and when exposed to visible light is examined in fig. 2.

The appropriate visual band gap indicates that the ZnSe nanoparticles we synthesized exhibit characteristics of a semiconducting material. Fig. 6 illustrates the current-voltage (J-V) aspect of the ZnSe-based metal semiconductor Schottky junction diode in both dark and visible light illustration (100 mW cm^{-2}) at ambient temperature has been recorded at relative applied bias voltage in the range ± 1 volt. Under shadowy conditions, the electrical conductivity of devices based on synthesized Ag/ZnSe nanoparticles has been estimated to be 23.03 Sm^{-1} and under photoirradiation, it has been estimated to be 80.81 Sm^{-1} . It is evident that under irradiation conditions, the conductivity of devices based on systemized Ag/ZnSe nanoparticles greatly improves.

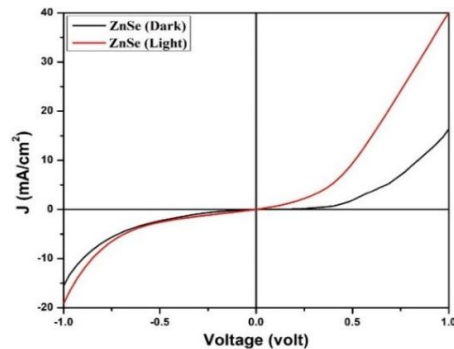


Fig. 6 Schematic representation of photocurrent density (J) versus photovoltage (V) characteristics curves of ZnSe Schottky junction in dark and light.

Furthermore, the J-V properties (Fig. 6) of the Ag/ZnSe interface in both dark and irradiated conditions shows the Schottky diode-like nonlinear rectifying behaviour. Thermionic emission theory has been used to further analyze the J-V characteristic of the systemized Ag/ZnSe nanoparticle-based Schottky diode, and Chewig's method has been used to extract significant diode parameters [39]. In this context, we have examined J-V curves using the standard equations listed below [39, 40].

$$J = J_0 \left[\exp\left(\frac{qV}{\eta KT}\right) - 1 \right] \quad (2)$$

$$J_0 = AA^*T^2 \exp\left(\frac{q\Phi_B}{KT}\right) \quad (3)$$

Where J_0 , A , q , A^* , K , T , V , and η stands for saturation current density, effective diode area, electronic charge, effective Richardson constant, Boltzmann constant, temperature in Kelvin, forward bias voltage and ideality factor respectively.

The devices' effective Richardson constant has been observed to be $32 \text{ AK}^{-2} \text{ cm}^{-2}$, and their effective diode area has been estimated to be 1 cm^2 . The ideality factor, series resistance and barrier potential height have also been ascertained. The devices' ideality factor (η) values under both circumstances deviate from their ideal value (~ 1). This could be because of the existence of interface states, series resistance, and Schottky barrier height in homogeneities at the junction [41, 42]. Interestingly, our manufactured Schottky diodes' ideality factor (η) 1.14 value considerably approaches more ideal (closer to 1) under irradiation conditions. This illustrates the creation of improved homogeneity at the Schottky junction barrier and the recombination of fewer interfacial charge carriers [39]. There is good consistency in the series resistance that was obtained from both processes. The measured series resistance decreases when exposed to light (Table 1), indicating its potential use in optoelectronic devices.

The photoresponsivity (R_λ) of the Ag/ZnSe/FTO metal-semiconductor Schottky junction was evaluated under alternating shadowy and white light exposure (100 mW cm^{-2}) at ambient temperature. The photoresponsivity (R) refers to the photoresponse produced for each unit of light power density incident on the device and given by [43, 44].

$$R_\lambda = \frac{\Delta I}{P_{in} S} \quad (4)$$

Where, $\Delta I = I_{photo} - I_{dark}$ the change in photoresponse due to incident light, P_{in} is the incident

light intensity, and S is the active area of the device. The calculated value of photoresponsivity for the ZnSe-based metal-semiconductor Schottky junction is 9 mA W^{-1} . The obtain values of all the parameters under the shadowy and irradiation conditions for Ag/ZnSe/FTO metal-semiconductor Schottky junction are listed in table 1.

Table 1. Schottky devise parameter of Ag/ZnSe/ FTO metal semiconductor nanoparticles.

Condit ions	σ (S/cm)	Photo sensitivity (mA W^{-1})	Ideality factor	ϕ_B (eV)	Series Resistanc e (Rs)
Dark	23.03	9	1.39	0.282	579
Light	80.81		1.14	0.246	165

4. CONCLUSION

Ag/ZnSe/FTO metal-semiconductor Schottky junction by a soft chemical solution method have been successfully Fabricated. XRD analysis reveal that the fabricated ZnSe film having hexagonal crystalline structure. No any other impurity peak was found confirming formation of pure ZnSe phase. Surface topographical investigation by FESEM images shows uniform distribution of spherical grains. The electrical characterization of Ag/ZnSe/FTO metal-semiconductor Schottky device confirms the rectifier nature of IV curve. The significant variation in the IV curve with dark and illumination conditions reveals photosensitivity of ZnSe material. The computed values of photosensitivity is found to be 9 mA W^{-1} . The measured value of series resistance varies from 579 to 165 ohm. Significant improvement in the diode characteristics was revelled by measured the values of ideality factor for dark ($n=1.39$) and light ($n=1.14$) conditions. This change in ideality factor may be owing to change in the barrier height from 0.282 to 0.246 eV respectively. The present investigation we concluded that, CBD will be the and straightforward, inexpensive method for fabrication of industrial scale Ag/ZnSe/FTO based metal-semiconductor Schottky diode.

5. ACKNOWLEDGEMENTS

The authors are sincerely thankful to Dr. S.V. Desale, Dr. P.N. Patil, Dr. M.S. Sonawane, Dr. K.E. Suryavanshi, Dr. K.A. Isai, V.K. Suryavanshi, Dr. P.V. Baviskar for supporting during the work. The

authors are also thankful to Prof. J. V. Sali, Dr. S. R. Gosavi, Shubham Patil Dr. Devashri Upasani for characterization support and lab facility. The authors are also thankful to RCPIT Shirpur. The author also gratefully acknowledge management members, Principal and faculty members of S.V.S's Dadasaheb Rawal College, Dondaicha for constant encouragement and kind support in the research work.

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