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Growth And Characterization Of Znse Thin Film By Spray Pyrolysis Technique For Solar Cell Applications

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Abstract

Zinc selenide (ZnSe) thin films were deposited onto the glass substrates by spray pyrolysis technique. Deposition parameters were optimized. XRD pattern revealed that thin films were uniformly deposited by nanocrystalline grains distributed over the entire glass substrate. Transmission spectra showed high transmission (~ 55%) with direct optical band gap energy equal to 2.71 eV. The I-V characteristic showed good photo response, suitable for solar cell applications.

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I. Introduction

In order to substitute exhausting fossil fuels and moreover to avoid a further increase of environmental pollution for future energy supply the use of renewable energy and in particular conversion of solar radiation is a must. Due to greater surface to volume ratio, nanocrystalline semiconducting thin films have been found to be useful in the fabrication of solar cells. Zinc selenide (ZnSe) is an interesting II-VI, n-type semiconductor material, suitable for applications in wide range of optoelectronic devices. ZnSe has been regarded as material with many attractive properties, such as large bandgap, low resistivity, and remarkable photosensitivity. Consequently, this compound offers an important number of applications such as blue laser diodes [1], white light emitting diodes (LEDs) [2] and optically controlled switches [3]. It has also gained importance as window layer for $CuInSe_2$-based [4], $CuGaSe_2$-based [5] and tandem [6] solar cells. Many efforts are currently directed to a new generation of solar celle, based on wide bandgap compound semiconductors. ZnSe meets this requirement because it has a wide bandgap and is capable of emitting light in the short wavelength region. Variety of methods have been employed in the fabrication of high quality ZnSe thin films such as electrochemical deposition [a], thermal evaporation [b], RF sputtering [c], sol-gel technique [d], spray pyrolysis [e], CBD technique [7–8] has been developed to deposit ZnSe thin films from an aqueous solution.

In the present investigation, we report a simple spray pyrolysis technique for the growth of ZnSe thin films using ammonia free precursors and its characterization for structural and optoelectronic properties.

II. Experimental

Thin film preparation

The substrates used for the deposition of ZnSe thin films were commercial microscope glass slides (size of 75 x 25 x 1.35 mm). Before deposition, the substrates were degreased in HNO_3 solution for 24 h, cleaned by commercial detergent and finally rinsed with de-ionized water and dried in air. Clean surface is essential for formation of nucleation centers. Typically, 0.25 M of 20 mL zinc sulphate solution was taken in a 50 mL glass beaker. Under continuous stirring 30 drops TEA, 4 M of 5 mL NaOH, and 5 drops hydrazine hydrate solutions were added slowly. Initially the solution was milky and turbid due to the formation of Zn(OH)2 suspension. Addition of excess NaOH led to the dissolution of turbidity and made the solution clear and transparent. Then 0.2 M of 5 mL trisodium citrate and 0.25 M of 20 mL freshly obtained sodium selenosulphate solutions were added slowly with constant stirring and the pH of final mixture was adjusted to ~ 13. Sodium selenosulphate was prepared by refluxing 0.25 M selenium powder mixed with 1 M sodium sulphite in de- ionized water, which was heated to 80 °C for 8 h.

The glass substrates were cleaned using nitric acid, methanol, and acetone and immersed in deionized water for every step and were placed in an electric oven at 250 ° C for 1 h to eliminate any impurities from the surface.

During the deposition by spray pyrolysis method, the cleaned substrates were placed on a heating plate fixed at 400 °C temperature. The sprayed nozzle was fixed perpendicular to the substrate at a distance of 30 cm. The nozzle is linked to the air compressor and the spraying solution. The growth time was taken 5 min with a constant flow rate of 0.5 ml/min.

Characterization Techniques

Thickness was measured by weight difference method. Glancing incidence angle X-ray diffraction (GIXRD) pattern of the film was recorded on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20–70o (2) using Cu-K1 radiations with wavelength 1.5405 Å at 0.5° glancing angle. Transmittance and absorbance spectra were recorded in the range 300–1100 nm by means of Jasco V630 spectrophotometer. The photosensitivity property of ZnSe was studied by I-V characteristics in dark and under illumination (visible spectra) with different intensities using lab equipment unit (model no. 2004), over the range ± 3V.

III.Results And Discussions

Structural Studies

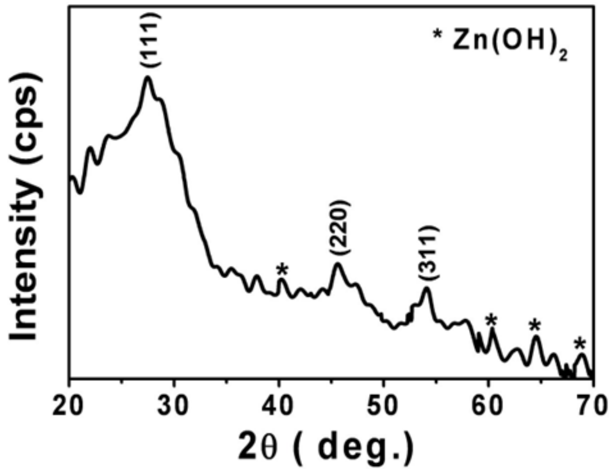

Figure. 1. GI XRD pattern obtained from the as- deposited ZnSe thin film.

Fig.1. shows X-ray diffraction pattern of as-deposited ZnSe thin film. The XRD peaks indicate that the film is nanocrystalline in nature. The 2è peaks at 27.45°, 45.57°, and 54.06° corresponds to reflections from (111), (220), and (311) planes, respectively. The (111) plane is the preferred orientation, and it is the close-packing direction of the zinc- blende structure of cubic ZnSe phase (JCPDS card No 80- 0021). Crystallite size (D) of the film was calculated using Scherrer's formula [9] from the full width at half maximum (β) of the peaks expressed in radians,

$$D = \frac{K\lambda}{\beta Cos\theta} \qquad (1)$$

where 'K' is constant dependent on crystallite shape (0.89), 'λ' is wavelength of CuK$_{\alpha 1}$ radiation, and 'θ' is angle between the incident and scattered X-rays. The average crystallite size (derived from Fig. 2) is found to be < 10 nm.

Optical Studies

Fig. 2 shows transmittance and absorbance spectra obtained from as-deposited ZnSe thin film. The optical transmittance of over 55% is noted in the visible region.The relation between the absorption coefficient and the incident photon energy (h) [10] can be written as,

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

where 'A' is constant, n= ½ for direct allowed transition, 'Eg' is optical band gap of the material.

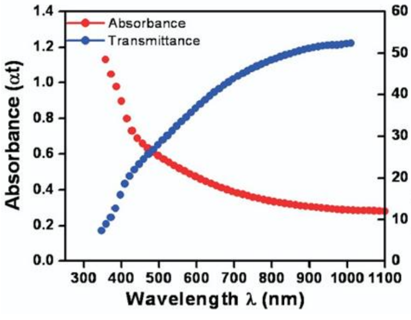

Fig.2. Plot of absorbance and transmittance versus wavelength.

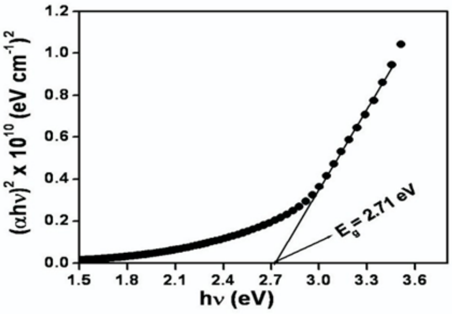

Fig.3 Plot of (αhν)2 versus (hν) obtained from as-deposited ZnSe thin film

Fig. 3 shows the plot of (αhν) ^{2} against (hν) for ZnSe thin film derived from the absorbance spectra. Extrapolating the straight-line portion of the plot of (αhν) ^{2} vs (hν) for zero absorption coefficient value gives the band gap, which is found to be 2.78 eV at room temperature. Compare with the direct ZnSe band gap (2.7 eV), the band gap energy of these ZnSe shifted to higher energies, due to quantum confinement effect [11].

Photosensitivity Studies

Fig. 4 shows I-V characteristics curve obtained from the as-deposited ZnSe thin film for different illumination intensities. The area of ZnSe thin film (1 cm^{2}) on glass substrate was defined. Silver paste was applied (two Ag contacts separated by a distance of 1 cm) to ensure the good neutral electrical contacts to the films. The linearity of the plots suggest the formation of ohmic contact between metal-semiconductor (Ag/ZnSe) junction, indicating that the work function of metal Ag is higher than semiconductor ZnSe film. This aligns the metal Fermi level of Ag with the upper valence band edge. Further resistivity decreases with increase in illumination intensity. This suggests that the incident photon energy breakes some of the covalent bonds in the ZnSe semiconductor. The dark resistivity is found to be 0.3 X 10^{8} Ω cm and it decreases to 0.47 X 10^{7} Ω cm (calculated from fig.4) for light of intensity 15000 Lux/cm^{2} in the visible region

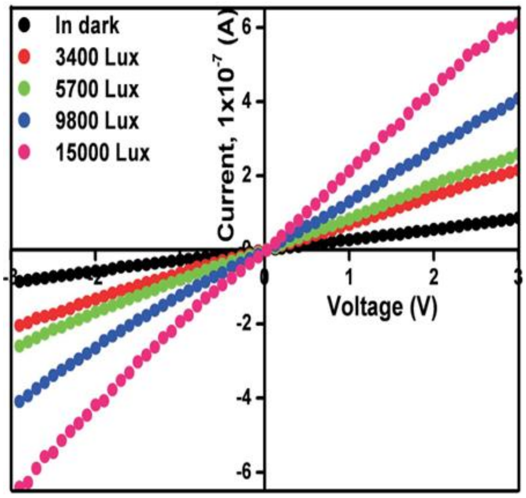

Fig. 4. Current–Voltage (I–V) characteristics curve

IV. Conclusion

Spray pyrolysis, a nove method was used to prepare nanocrystalline ZnSe thin film. The deposition is uncomplicated, environmentally friendly and economical. It increases the utilization efficiency of chemicals, simplifies the experimental process, and reduces cost. The physical, optical and electrical properties study reveal that the nanocrystalline ZnSe thin film can be suitably employed in solar cell applications as a window material.

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