

Highly transparent ZnS buffer layer prepared by ultrasonic spray pyrolysis for photovoltaic applications



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ABSTRACT

Zinc sulfide thin films are deposited by ultrasonic spray pyrolysis. The substrate temperature and sulfur concentrations are varied to attain suitable property for the application as window layer in solar cells. Films prepared at lower temperature have traces of ZnO phase together with the dominant cubic ZnS phase. At 400 °C with Zn/S ratio of 1/1.5, sample exhibited higher transmittance (~86%) consistently in the visible region. With an increase in the sulfur concentration transmittance reduced to ~50%. Band gap varied from 3.5 to 3.8 eV in the films. The existence of single phase ZnS is confirmed through XPS analysis of the optimized sample. 0.5% efficiency is obtained for AgInS₂/ZnS solar cells with the optimized ZnS film.

1. Introduction

Zinc sulfide (ZnS) finds application in versatile fields such as solar cells, electroluminescent devices, light emitting diodes, flat panel display, sensors, photodetectors, infrared windows and biodevices. ZnS appears in two different structures such as cubic zinc blende and hexagonal wurtzite structure [1]. Cubic structure has a band gap of 3.72 eV and for hexagonal structure it is slightly higher, 3.77 eV. ZnS is non-toxic and the constituent elements are abundant in earth. Nowadays it is extensively used as buffer layer in solar cells. The wider band gap of ZnS results in higher transmission in the blue wavelength region thereby increasing the short circuit current in solar cells [2]. It has high refractive index of 2.35 and effectively acts as anti-reflection coating for solar cells [3]. Moreover it has high lattice matching with I-III-VI₂ semiconductors used as absorber layer in solar cells [4].

ZnS thin films are widely deposited by methods such as thermal evaporation, sputtering, pulsed laser deposition, electrodeposition, chemical spray pyrolysis, chemical bath deposition and successive ionic layer adsorption and reaction [5–13]. Among this, chemical spray pyrolysis is one of the widely used cost-effective techniques for large area deposition. There are three types of spray pyrolysis viz, pneumatic, electrostatic and ultrasonic spray pyrolysis which uses air blast, electric field and ultrasonic frequency respectively for atomizing the solution [14]. In addition to the thin film solar cells, currently this method is used in the fabrication of commercial polymer solar cells, dye sensitized and quantum dot sensitized solar cells [15].

There are many reports of ZnS deposition using chemical spray pyrolysis (pneumatic) [16–20]. Zing et al., prepared ZnS with low

temperature spray pyrolysis (~310 °C). Thioacetamide was used as the sulfur source which led to the formation of wurtzite structure at low temperature. Kucukomeroglu et al., studied the influence of fluorine doping in the ZnS. Transmittance of these films was ~75%. The resistivity of the film reduced with fluorine doping. Nasrallah et al., carried out heat treatment in sulfur atmosphere to remove ZnS phase. Lopez et al., studied the effect of Zinc precursors (Zn(O₂CCH₃)₂(H₂O)₂ and ZnCl₂) on the properties of ZnS films. It was found that films prepared using Zn(O₂CCH₃)₂(H₂O)₂ had higher grain size, smoother surface and higher transmittance (80%). Conversion efficiencies such as 18.6%, 18% and 14.18% have been achieved using ZnS as buffer layer in Cu(In,Ga)Se₂ based solar cells [21–23]. 7.8% efficiency was achieved for CuInS₂/ZnS/ZnO and 8.4% for Cu₂ZnSnS₄/ZnS structures [24,25].

Here ZnS films are grown using ultrasonic spray pyrolysis. In ultrasonic spray pyrolysis, the precursor solution is atomized using an ultrasonic frequency nebulizer and spray comes out as a fine vapor mist. The droplet size in the spray jet is inversely proportional to the frequency of the nebulizer which allows to have a control on the droplet size by varying the frequency if required. The main advantage of ultrasonic spray over the popular pneumatic spray is the lower consumption of precursor materials. Also it helps in the formation of very thin layers since the spray is in the form of a mist. We have fabricated an automated spray pyrolysis system to deposit thin films for solar cell applications and the details are given elsewhere [26]. ZnS thin films are grown using this set up and optimized for solar cell application..

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2. Materials and methods

2.1. Deposition of ZnS

0.01 M ZnCl_2 and 0.015 M $\text{SC}(\text{NH}_2)_2$ purchased from sigma-aldrich are used as precursors for the growth of ZnS films and a total volume of 50 ml is prepared in deionized water. An ultrasonic nebulizer (Omron) having a frequency of 1.7 MHz is used in the experiment and rate of the spray is maintained at 2.5 ml/minute. Distance from the nozzle to substrate is maintained at 3 cm. The X-Y movement is controlled by NEMA 17 stepper motor through G2T belt and pulley. The spray is performed in raster movement over an area of $4 \times 4 \text{ cm}^2$. The step size of movement in the Y direction is fixed at 2 mm and the spray jet covers an area of 5 mm^2 . Soda lime glass is used as the substrate and the temperature is varied from 300 to 450 °C in steps of 50. Samples are named as S300, S350, S400 and S450 respectively. Based on the film characterization, the substrate temperature is fixed at 400 °C and the concentration of thiourea is varied from 0.015 to 0.035 M (samples S15, S20, S25, S30 and S35).

2.2. Fabrication of $\text{AgInS}_2/\text{ZnS}$ heterojunction

Solar cell is fabricated on Fluorine doped Tin Oxide (sigma Aldrich) glass having a sheet resistance of $10 \Omega/\text{square}$. AgInS_2 absorber layer is deposited using the same system with 0.005 M $\text{AgC}_2\text{H}_3\text{O}_2$, 0.006 M InCl_3 and 0.06 M $\text{SC}(\text{NH}_2)_2$ (sigma-aldrich make) are used as precursors. The details of optimization of this layer is given elsewhere [27,28]. Ag electrodes of area 0.03 cm^2 are deposited on top of the ZnS layer by thermal evaporation at a pressure of 10^{-5} mbar. Schematic of the cell structure is given in Fig. 1.

2.3. Characterization studies

X-ray diffraction (XRD) patterns of ZnS films are taken using Bruker D8 operated at 40 kV and 40 mA. Cu K α line of wavelength 1.5405 \AA is used as the radiation source. Absorption and transmission spectra are recorded using UV–vis spectrophotometer (SPECORD S600 UV–VIS). Scanning electron microscopy (SEM) images are taken under an acceleration voltage of 5 kV and energy dispersive X-ray analysis (EDX) under 15 kV. The measurements are carried out using Ultra55 FE-SEM Karl Zeiss EDS. Hall Effect measurements are carried out under a magnetic field of 0.5 T using Ecopia HMS5000. Silver paste is used to make electrical contacts. Thickness of the films are measured using Bruker Dektak XT surface profiler. X-ray photoelectron spectroscopy (XPS) analysis is carried out using Kratos-Axis DLD photoelectron spectrometer at a pressure of 2.6×10^{-7} Pa. 1.486 keV. Monochromatic Al K α line is used as the X-ray source at operation conditions of 15 kV and 10 mA. Sample is etched using Ar $^+$ ions for in-depth analysis. The solar cell is characterized using Oriol sol3 A™ solar simulator under AM1.5 condition.

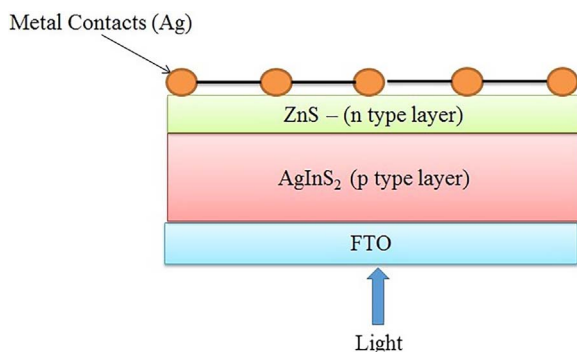


Fig. 1. Schematic diagram of $\text{AgInS}_2/\text{ZnS}$ solar cell.

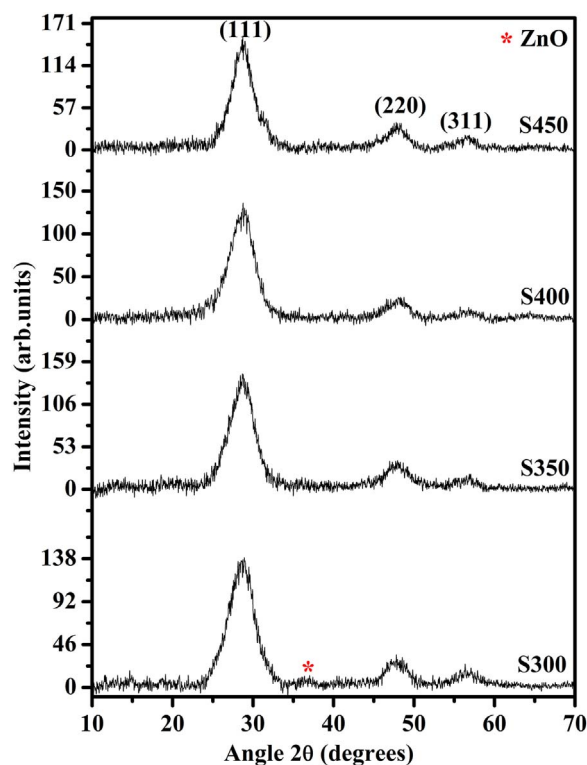


Fig. 2. XRD pattern of ZnS films with variation in substrate temperature.

3. Results and discussions

X-ray diffraction pattern (Fig. 2) reveals the cubic zinc blende structure of the ZnS films. All the films show preferential orientation along (111) plane. Peaks are also observed at (220) and (311) planes of cubic ZnS (JCPDS 005-0566). Films deposited at 300 °C shows the presence of ZnO phase at 36.5° in addition to the prominent ZnS phase. Crystallinity increases slightly with increase in the substrate temperature. The broad peaks may be due to the small particle size of the ZnS film. Composition of the films is determined using EDX as depicted in Table 1. With increase in the substrate temperature the sulfur percentage decreases from 46% to 35% due to the volatile nature of sulfur.

The transmittance spectra of the ZnS films are shown in Fig. 3. S300 shows transmittance varying from 50 to 80% in the visible region. Transmittance increases with increase in the substrate temperature and highest transmittance is achieved by S400. The sample has a transmittance around 86–89%. The transmittance reduces with further increase in the substrate temperature. The higher concentration of Zn may be the reason for this decrease in transmittance. Zinc rich film has higher reflectance which reduces the transmission of light [29].

Band gap of ZnS film is determined using absorption spectra. Extrapolating linear region in the $(\alpha h\nu)^2$ vs $h\nu$ plot the band gap is determined. Band gap increased from 3.5 to 3.8 eV with increase in substrate temperature from 300 to 350 °C. With further increase in substrate temperature, the band gap started decreasing. SEM images of the films are shown in Fig. 4. The grains are having spherical shape with size varying from ~ 150 to 250 nm. S300 and S350 showed cracks on the surface which may be due to the low temperature deposition. S300 has the lowest grain size of 158 nm. S400 and S450 are free of cracks and displayed better distribution of grains. Thickness of the ZnS films prepared at different substrate temperature is ~ 50 nm. There was not any significant variation in the thickness for the films S300 to S450. Electrical characteristics of the films are determined using Hall Effect measurement and the resistivity values are displayed in Table 1. All the samples showed *n*-type conductivity and resistivity varied from 10^6 to $10^3 \Omega \text{ cm}$. The resistivity depends on the concentration of Zn in

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