



Synthesis of Silver Sulphide Nanoparticles by Modified Chemical Route For Solar Cell Applications

Jadhav U.M.¹, Patel S.N.² and Patil R.S.^{1*}

¹PSGVPM'S Arts, Science and Commerce College Shahada, Dist- Nandurbar-425409, MS, INDIA

²SPDM Arts SBB & SHD Commerce and SMA Science College, Shirpur, Dhule-425405, MS, INDIA

Available online at: www.isca.in

Received 22nd June 2013, revised 28th June 2013, accepted 16th July 2013

Abstract

Modified chemical bath deposition technique has been implemented for the deposition of silver sulphide thin (CBD) method onto the glass and fluorine doped tin oxide (FTO) coated glass substrate from an aqueous alkaline bath at room temperature (300K). The deposition bath consists of silver nitrate, thiourea and ammonia. The preparative parameters such as ion concentration, deposition time, pH of solution, were optimized for Ag₂S thin films. The as deposited films on glass substrate were studied for their structural, surface morphological, optical and electrical properties using techniques such as X-ray diffraction, atomic force microscopy (AFM), Scanning electron microscopy (SEM), optical absorption and dc two probe method. The photoelectrochemical (PEC) investigations of Ag₂S films were carried out by using chemical cell configuration n- Ag₂S /IM/NaOH-Na₂S-S/Pt. and the nanocrystalline films were found to be photoactive in polysulphide solution. The dynamic current-voltage (I-V) characteristic was examined at room temperature. The photovoltaic output characteristics were used to calculate the fill factor (FF) and power conversion efficiency (η). The photovoltaic conversion efficiency of the thin film was found to be 0.002% with n-type conductivity.

Keywords: Silver sulphide, chemical synthesis, nanocrystalline thin films, PEC properties. X-ray diffraction, morphological, optical properties and Band gap.

Introduction

Silver sulfide (Ag₂S) is an important inorganic compound which has been studied for its numerous applications. Silver sulphide (Ag₂S) belongs to I-VI compound semiconductor materials with monoclinic crystal structure. Silver sulphide appears to be a promising material for conversion of solar energy into electrical energy as its band gap is in between 1-2 eV. The semiconductor silver sulfide has photoelectric and thermoelectric properties^{1,2}. Silver sulphide (Ag₂S) has been used in IR detectors³, photoconductors, photovoltaic cells, electrochemical storage cells^{4,5}, etc. Various techniques such as chemical bath deposition^{6,7} (CBD), spray pyrolysis deposition⁸ (SPD), successive ionic layer adsorption and reaction (SILAR)⁹, molecular beam epitaxy (MBE)¹⁰, thermal evaporation¹¹, sol-gel and ion implantation techniques¹², gamma irradiation¹³ etc. have been reported for the preparation of silver sulphide thin films. Among these chemical deposition processes are economically effective and has been industrially exploited to large area deposition. Chemical deposition techniques are most important methods for the growth of the films due to their versatility for depositing very large no of elements and compounds at relatively low temperature¹⁴. Chemical methods are chemical bath deposition or modified chemical bath deposition method may be used. In chemical deposition method, thin films are deposited on the substrate from aqueous solution by chemical reaction under appropriate conditions. Among them, chemical bath deposition (CBD) is well known as a low

temperature aqueous technique for depositing large area of semiconductor thin films. Many researchers have deposited Ag₂S thin film by CBD. In CBD method the precipitation and film deposition takes place when ionic product exceeds the solubility product which produces wasteful unavoidable and uncontrollable bulk precipitate¹⁵. To overcome the difficulty, we have used the modified chemical bath deposition method for the synthesis of Ag₂S thin film. Modified chemical bath deposition method (MCBD)^{16,17} is simple, less expensive and useful for large area deposition of any composition, easily controlled film thickness method at atomic level. This method does require sophisticated instruments and conductive substrate. The MCBD method is suitable for growing thin multilayer structure due to low temperature since diffusion of ion is slow. The growth of the film can be easily controlled through various parameters including concentration of bath temperature, immersions time and immersion cycles, etc. Semiconducting nanocrystalline thin films have attracted the attention of the scientists as non-conventional energy resources for solar energy conversion in recent years^{18,19}. Recent investigations are carried out in the field of energy sources to meet the challenges of diminishing fossil fuels. It is necessary to find the easiest way of conversion of solar energy into electrical energy, which is abundant, nonpolluting and inexhaustible source of energy. One of the most efficient solar to electrical energy conversion devices is the photo electrochemical (PEC) cells. Many workers have reported PEC characteristics of silver sulphide semiconducting thin films. Many binary as well as ternary and

quaternary materials applied for solar energy conversion^{20,21}. Properties of nanocrystalline materials are different and often superior to those of conventional coarse-grained materials and also amorphous alloys of the same configuration²⁰⁻²⁵.

In the present investigation, nanocrystalline Ag₂S thin films have been deposited using MCBBD method at room temperature. The MCBBD method for metal chalcogenide thin film preparation is currently attracting considerable attention, as it is relatively less expensive, simple. A variety of substrates such as insulators, semiconductors or metals can be used, since it is a low temperature process, avoids oxidation or corrosion of metallic substrates. The structural, compositional, surface morphological and optical characterizations were carried out for the confirmation of nanocrystalline nature. The nanocrystalline Ag₂S thin films deposited onto FTO substrate were used as photoelectrode in PEC cells. The current voltage (I-V) and photovoltaic power output characteristics of Ag₂S thin films deposited onto FTO substrate were studied.

Material and Methods

Preparation of thin film: Loba analytical reagent grade silver nitrate and thiourea were used for the deposition of nanocrystalline Ag₂S thin films. The Ag₂S films were grown on ultrasonically cleaned corning glass substrate (25mm X 75mm X 1mm) from an alkaline bath. In the synthesis of Ag₂S thin film the cationic precursor was 0.1M silver sulphate solution complexed with ammonia solution at pH=10 for silver ion and anionic precursor was 0.5M thiourea solution for sulphide ion. Direct exchange of cationic and anionic ions was modified by means of rinsing in double distilled water. Each MCBBD cycle consist of i. adsorption of Ag⁺ ions from silver sulphate solution for 20s, ii. rinsing with double distilled water for 10s, iii. reaction with sulphide precursor solution from thiourea solution for 20s and finally iv. rinsing with double distilled water for 10 s. This process was repeated for 30 times to get desired film thickness. The substrates were taken out, washed with distilled water and dried in open air at room temperature. A film obtained was uniform, well adherent and blackish gray in color. The films on the glass substrates were used to study structural, compositional, surface morphological and optical properties. For PEC study, Ag₂S films deposited onto the FTO coated glass substrates were used.

Characterizations of thin film: The as-deposited thin films of Ag₂S were characterized for structural, optical and electrical properties. The Ag₂S film thickness was measured by weight difference method. The structural characterization of films was carried out using a Philips (PW-3710) X-ray diffractometer in the scanning range 20–80°(2θ) using Cu Kα radiations with wavelength 1.5405Å. The semi-quantitative elemental composition was determined by EDAX technique. The surface morphology was studied by scanning electron microscopy (SEM, JOEL-JSM-5600) model. The three dimensional surface morphology of the film was recorded using atomic force

microscopy by Quesant Instrument corporation; Q-Scope 250. The optical absorption spectrum of the film was recorded in the range 350–800 nm by means of Shimadzu UV-3101PC spectrophotometer.

Photo electrochemical characterization of Ag₂S thin film: The photoelectrochemical cell was devised by employing Ag₂S thin film as photoelectrode, platinum as counter electrode and polysulphide (1M NaOH + 1M Na₂S + 1M S) as an electrolyte. The distance between photoelectrode and counter electrode was 0.5 cm. The photocurrent was measured under 35 mW/cm² light intensity. The current-voltage characteristics were determined in dark and under illumination. The fill factor and power conversion efficiency of the cell was calculated from the power output characteristics. The spectral response of the cell was recorded in the voltage range from - 200 mV to + 400 mV under dark and light illumination using standard AM 1.5 conditions with 100 mW/cm² for structure FTO / Ag₂S / Electrolyte / Platinum.

Results and Discussion

Optimisation of preparative parameters: The preparative parameters for silver sulphide thin films deposited using MCBBD were optimized. In the present study, for the concentration of anionic precursor (thiourea) was arbitrarily kept constant as 0.5 M (pH ~ 10) and the concentration of cationic precursor (silver nitrate) was optimized. For cationic precursor, initially 20 ml silver nitrate solution was taken in a 50 ml capacity beaker, and ammonia solution was added to it, which acts as a complexing agent. The pH of the cationic precursor solution was maintained at 10 by adding ammonia solution. Making several trials for different concentration, immersion cycle, and immersion time, preparative conditions for Ag₂S thin films were optimized. Table. 1 shows optimized preparative parameters for Ag₂S thin films on glass substrate. The variation of film thickness against concentration of silver nitrate for 30 deposition cycles is shown in figure 1(a). The Ag₂S film formation was started from concentration 0.025 M of silver nitrate. Initially the film thickness increases with concentration, reaches maximum at concentration 0.1 M. After this Ag₂S film thickness was decreased, this may be due to formation of outer porous layer as film peeled off from the glass substrate²⁶. Figure 1(b) shows variation of Ag₂S film thickness with number of immersion cycles for optimized concentration of silver nitrate (0.1M) and thiourea (0.5M).

The Ag₂S film had a maximum terminal thickness of 135 nm at 30 immersion cycles afterwards, Ag₂S film thickness was decreased due to the peeling off the outer powdery layer.

Film formation reaction mechanism: The reactions for the Ag₂S film formation can be written as follows:

- i. Formation of a complex $\text{AgNO}_3 + 4\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]\text{NO}_3$,
- ii. Dissociation of thiourea in an alkaline medium as $\text{CS}(\text{NH}_2)_2 + \text{OH}^- \rightleftharpoons \text{CH}_2\text{N}_2 + \text{H}_2\text{O} + \text{HS}^-$,

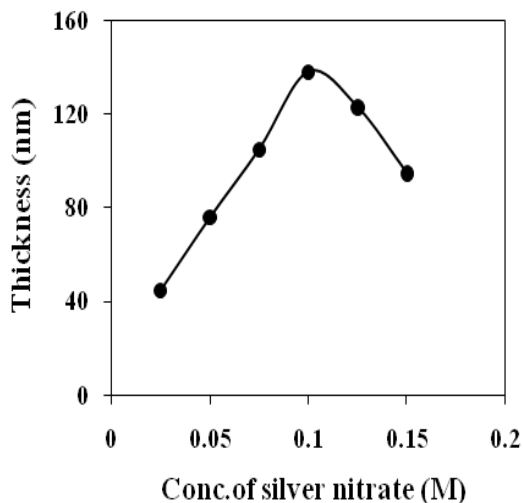
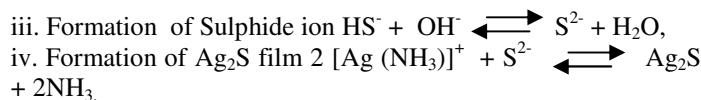


Figure-1a

Variation of Ag_2S thin film thickness with concentration

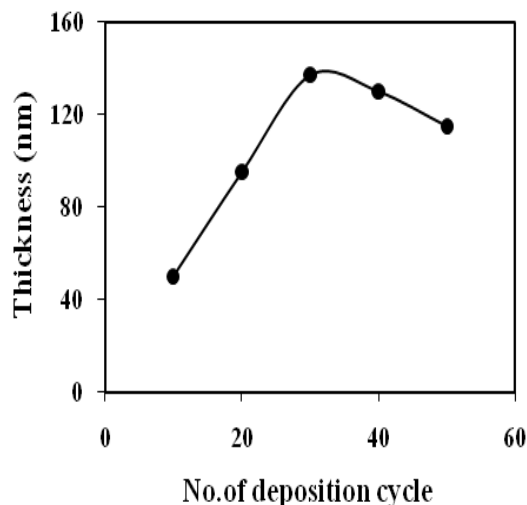


Figure-1b

Variation of Ag_2S thin film thickness with deposition cycle

Table-1

Optimized preparative parameters for Ag_2S thin films deposited on glass substrate

Sr. No.	Parameters	Precursors	
		Silver nitrate	Thiourea
1	Concentration (M)	0.1	0.5
2	Complexing agent	Ammonia	Ammonia
3	pH	5	10
4	Immersion time (sec)	20	20
5	Rinsing time (sec)	10	10
6	Number of deposition cycles	30	30
7	Deposition temperature (K)	300	300

Structural studies: The XRD pattern of Ag_2S thin film onto the glass substrate is shown in Fig. 2. In the diffraction pattern, five dominant peaks at 24.90° , 36.33° , 40.55° , 43.43° and 44.32° corresponding to (110), (120), (031), (200) and (102) planes are seen with polycrystalline monoclinic (acantite) crystal structure. The average crystallite size of was calculated by using well known Debye-Scherrer's formula.

$$D = 0.9\lambda/\beta\cos\theta$$

Where D is the crystallite size, β is the broadening of diffraction line measured at half of its maximum intensity (FWHM) and λ is the X-ray wavelength (1.5406\AA). The plot of $(\alpha h\nu)^2$ versus $h\nu$, which is linear at the absorption edge, confirming that the material has a direct band gap. The calculated average crystallite size was 21 nm.

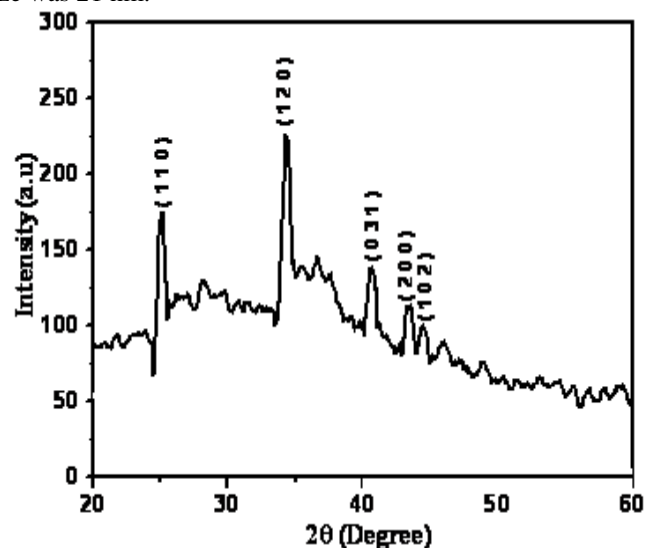


Figure-2

XRD pattern of Ag_2S thin film

The quantitative analysis of Ag_2S film deposited on glass substrate was carried out using EDAX technique at room temperature to study the stoichiometry of the film. The EDAX was recorded in the energy region 0-20 keV. The presence of EDAX peaks for Ag and S are confirmed from analysis and the presence of other elements like Si and O from the glass substrate. A typical EDAX pattern is shown in figure 3.

Surface morphological studies: The SEM micrograph is a convenient method to study the the microstructure of thin film. Figure 4 shows the surface morphology of the Ag_2S thin films deposited by M CBD at magnification 30,000 X. The scale bar length is $0.5\ \mu\text{m}$. Films are found to be nanocrystalline. Ag_2S thin film deposited on to glass substrate with 135 nm thickness was used for study of surface morphology. It is observed from the images that the as-deposited Ag_2S film is homogeneous, well covered the substrate without any voids and cracks. The SEM image shows that surface is smooth and well covered with Ag_2S film. It can be seen that nanoparticles are grouped and form large grain.

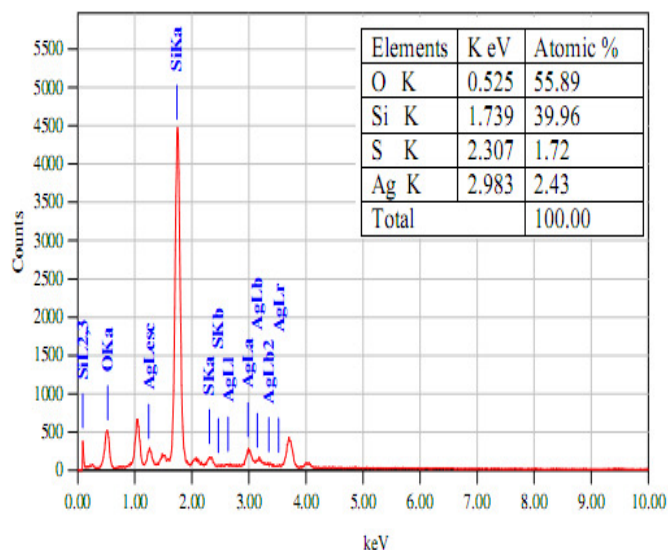


Figure-3
The EDAX spectrum of Ag₂S thin film

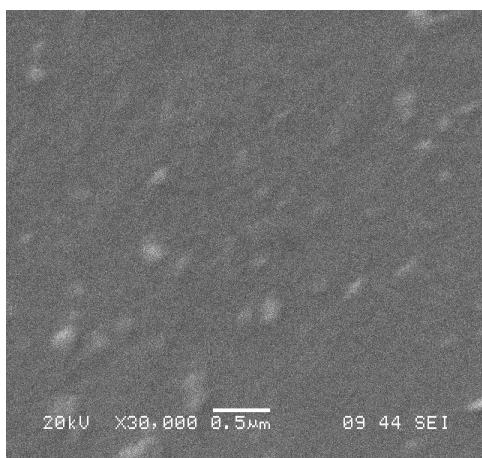


Figure-4
The SEM pattern of Ag₂S thin film

The atomic force microscopy is one of the primary method and foremost tools for imaging, measuring, and manipulating matter at the nanoscale. Fig. 5(a) shows 2D and Fig. 5(b) shows 3D atomic force microscopy images of Ag₂S thin film. The AFM images clearly show the layer like morphology of Ag₂S nanoparticles. The surface roughness of the Ag₂S thin film is 96.35 nm.

Optical studies: The optical absorption spectrum of as-deposited Ag₂S film has been recorded at room temperature without considering losses due to reflection and transmission. The absorption spectra of Ag₂S thin film deposited on glass substrate was studied in the wavelength range 350– 800 nm. This spectrum reveals that film has high absorbance (10⁴ cm⁻¹). Figure 6 shows the optical absorption curves for Ag₂S thin film. The figure shows that absorbance decays exponentially with an increase in wavelength. The long absorption tail confirms the formation of Ag₂S thin film. The absorption coefficient for direct band gap is determined by using the relation,

$$(\alpha h\nu) = A (h\nu - E_g)^{1/2}$$

where, α is the absorption coefficient, $h\nu$ is photon energy, A is constant which is related to the effective masses with the valence and conduction bands, E_g is separation between valence and conduction bands. The band gap were determined from the intersect of straight line portion of $(\alpha h\nu)^2$ versus $h\nu$ graph. The straight line nature of the graph suggests the Ag₂S is direct band gap material²⁷. The as-deposited Ag₂S thin film shows the optical band gap 2.09 eV.

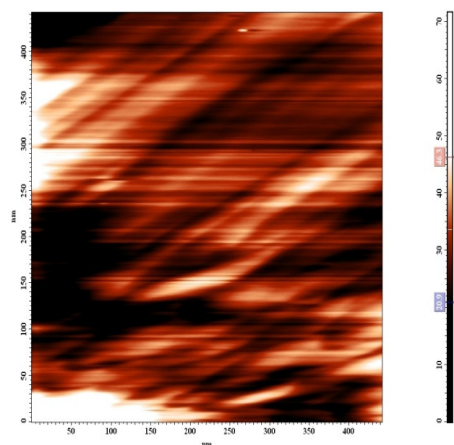


Figure- 5(a)

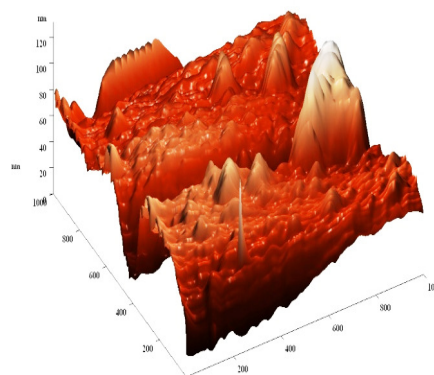


Figure- 5 (b)
The 2D and 3D image of AFM image of Ag₂S thin film respectively

Photoelectrochemical characterization: Type of conductivity: The PEC cell with Ag₂S as photoelectrode can be represented as n-Ag₂S/polysulphide/platinum. The PEC cell gives some dark voltage V_d , and dark current I_d . The polarity of the dark voltage is positive towards the Ag₂S electrode. The origin of this dark voltage is attributed to the difference between two half cell potentials in the PEC cell and can be written as Ag₂S

$$E = E_{\text{platinum}} - E_{\text{Ag}_2\text{S}}$$

Where E_{platinum} and $E_{\text{Ag}_2\text{S}}$ are the half cell potentials when dipped in the polysulphide electrolyte.

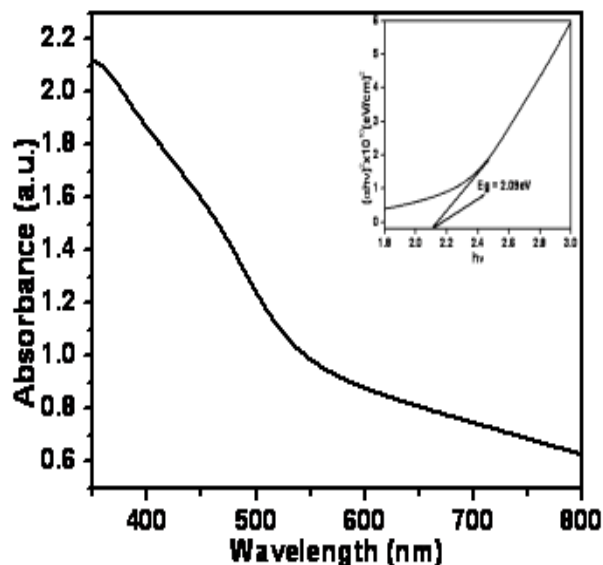


Figure- 6

Absorbance spectra of Ag₂S thin film on glass substrate

PEC Solar Cell Studies: The Ag₂S thin films were deposited onto FTO coated glass substrate using optimized conditions by CBD method. The basic requirements of a good thin film electrode for PEC cells are low resistivity and large crystallite size or grain size. The large crystallite/grain size leads to reduction of grain boundary area of thin film with important consequence for efficient energy conversion. The efficiency of the PEC system is controlled by light intensity, spectral quality, properties of electrolyte, cell configuration etc. The photoelectrode used in the solar cell should satisfy the requirements as, the band gap energy should match with span of solar spectrum, stable throughout the process, should be direct band gap type with high absorption coefficient, charge carrier should have high mobility and life time. The as-deposited Ag₂S thin films were used in the PEC cells as a photoelectrode and their performance as tested by using Ag₂S thin films grown onto FTO coated glass substrate as photoelectrode (anode), the polysulphide as an electrolyte and Platinum (Pt.) as a counter electrode (cathode). The I-V characteristics of the PEC cell formed with Ag₂S thin film electrode in dark and light illumination of 35 mW/cm² are shown in figure 7. The non-symmetric nature of the I-V curve in the forward and reverse bias shows the rectification property of the semiconductor electrolyte junction. After illumination, shifting of the I-V curve in the fourth quadrant of the graph suggests that the electrons are the majority carriers, confirming the n-type conductivity of Ag₂S and act as generator for electricity. Increase in the current under illumination indicated that the Ag₂S film is photoactive.

The power conversion efficiency (η %), fill factor (FF %), short circuit current (I_{sc}), high series resistance R_s and low shunt resistance R_{sh} calculated from I-V Curve are listed in the table 2.

Table- 2
Photovoltaic parameters for Ag₂S thin film

Sr. No	Photovoltaic parameters	Values
1	I_{sc} (mA/cm ²)	0.080
2	FF	0.085
3	V_{oc} (V)	0.325
4	η (%)	0.002
5	R_s (Ω)	291
6	R_{sh} (Ω)	709

The low efficiency in this investigation may be due to high series resistance R_s and low shunt resistance R_{sh} of the cell and interface states, which are responsible for the recombination mechanism.

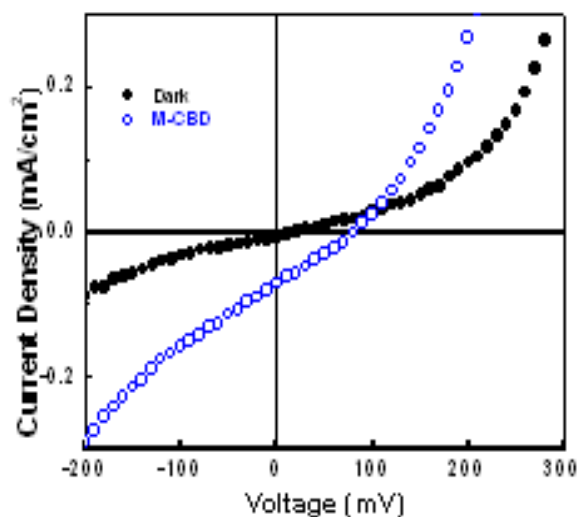


Figure- 7

Current-Voltage (I-V) output characteristic of Ag₂S polysulphide/Pt. PEC cell

Conclusion

In this work the silver sulphide thin film on glass and FTO coated glass substrate have been successfully deposited using, a simple, cost effective, entirely reproducible modified chemical bath deposition (MCBD) method. Good quality Ag₂S thin films were deposited. XRD study showed that the grains are small. The films are nanocrystalline having monoclinic crystal structure. The SEM study reveals that a uniform distribution of particles on substrate. The films are found to have high absorbance. The energy band gap for the deposited films was found to be 2.09 eV. The Ag₂S thin films showed PEC properties in polysulphide electrolyte and the power conversion efficiency was found to be 0.002%. The low efficiency of cell is due to nanocrystalline grain size of Ag₂S films and high series resistance of film. Thus we conclude that modified chemical bath deposition (MCBD) method is prominent low cost method for fabrication of Ag₂S thin film as a device for solar cell application.

References

1. Munoz J.A., C. Gomez, A. Ballester, M.L. Blazquez, F. Gonzalez, M. Figueroa, Electrochemical behavior of chalcopyrites in the presence of silver and sulfobolus bacteria., *J. Appl. Electrochem.* (28), 49 (1998)
2. Brelle M. C., Zhang J .Z., J. Femtostudy of photoinduced electron dynamics in AgI and core shell structured AgI/Ag₂S and AgI/Ag₂S colloidal particles, *Chem. Phys.*, (108), 3119 (1998)
3. Hsu T., Buhay H., Murarka N., Characterisation of Ag₂S thin films in millimeter wavelength region., *SPIE* (259), 38 (1980)
4. Cope R.G., Oldsmid H.J., Thermal switching in silversulphide and some of its alloys, *Bri J Appl Phys*, (16), 1501 (1965)
5. Wanger C., Investigations on silversulphide, *J Chem Phys*, (21), 1819 (1953)
6. Dhumare S.S.and Lokhande., Preparation and characterisation fo chemically deposited Ag₂S thin films, *Sol.Energy Mater.and Sol.Cells*, (28), 159-166 (1992)
7. Dhumure S. S., Lokhande C.D., Studies on PEC storage ceells formed with chemically depositd CdSe and Ag₂S thin films, *Sol. Energy Mater. Sol. Cells*, (29), 183 (1993)
8. Dhumure S. S., Lokhande C.D. Redox storage cells formed with chemically deposited Ag₂S electrodes, *Thin Solid Films*, (240), 1 (1994)
9. Pathan H. M., Salunke P. V., Sankpal B. R. and Lokhande C. D., Photoelectrochemical investgation of Ag₂S thin films deposited by successive ionic layer adsorption and reaction method, *Mater. Chem. and Phys.*, (72), 105-108 (2011)
10. Sankpal B. R., Mane R. S., Lokhande C. D., Preparation and characterisatio of Ag₂S thin films by SILAR process, *Mater. Chem. Phys.*, (63), 226 (2000)
11. Nozaki H., Onoda M., Yukino K., Kurashima K., Kosuda K., Maki H., Hishita S., Epitaxial growth of Ag₂S films on MgO., *J. Sol. State Chem.*, (177), 1165 (2004)
12. El-Nahass M. M., Farag A. A. M., Ibrahim E.M., Abd-El-Rahman S., Structural, optical and electrical properties of thermally evaporated Ag₂S thin films., *Vacuum*, (72), 453-460 (2004)
13. Chen M., Xie Y., Chen H.Y., Qiao Z.P., Qian Y.T., Preparation and characterization of metal sulfides in ethylenediammine under ambient condition through array irradiation route., *J. of Colloid Interf. Sci.*, (237), 47 (2001)
14. Deshmukh L. P., Palve A. B. and Sawant V. S., An arsenic doped solar cells., *Sol. Energy Mater.*(28) 1-10 (1990)
15. Patil R.S., Lokhande C.D., Pathan H.M., Oh-Shimjoo, Sung-Hwan. Han, Successive ionic layer adsorption and reaction (SILAR) trend for nanocrystalline mercury sulfide thin films growth, *Material Science and Eng. B*, 129, 59-63 (2006)
16. Nicolaue Y.F., Solution deposition of thin solid compound films by a successive ionic-layer adsorption and reaction process, *Appl. Surf. Sci.*, (22),1061-1074 (1985)
17. Yashar Azizian Kalandaragh, Murador M. B., Ali Kaodayari, Growth process and investigation of some physical properties of CdS nanocrystals formed in polymer matrix by successive ionic layer adsorption and reaction (SILAR) method, *J. Cryst. Growth*,(305), 175 (2007)
18. Jadhav U.M., Patel S.N. and Patil R.S., Chemical synthesis of nanocrystalline silversulphide thin films for solar cell application, *Inverties J. of Ren. Energy*, (3), 15-25(2013).
19. Patil P.S., Lokhande C.D. and Pawar S.H., Electrodeposition of silver sulphide thin films, *Bulletin of Electrochemistry*, (5) 842-844 (1989)
20. McCandless B.E, Dobson K.D, Processing option for CdTe thin film for solar cells, *Sol. Energy*, (77), 839-856
21. Kaelin M, Rudmann D, Tiwari A. N, Low cost processing of CIGS solar cells, *Sol Energy*, (77), 749-756 (2004)
22. Lokhande C. D, Sankpal B. R, Pathan H. M, Giersig M, Tributch H, Structural studies on successive ionic layer adsorption deposited thin films, *Appl Surf Sci*, (181) 277-282 (2001)
23. Suryanarayan C, Structure and properties of nanocrystalline materials, *Bull Mater Sci*, (17) 307-346 (1994)
24. Henglein A, Silver nanoparticles in organic synthesis, *Chem Rev*, (89),1861-1873 (1989)
25. Fukuka A, Sakamoto Y, Guan S, Ingaki S, Sugimoto N, Fukushima Y, Hirahara K, Lijima S, KIkawa M, *J Amer Chem Soc*, (123), 3373-3374 (2001)
26. Patil R.S., Lokhande C.D., Mane R.S., Pathan H.M., Oh-Shim and Han S. H.Successive ionic layer adsorption and reaction (SILAR) trend for nanocrystlline mercury sulphide thin films growth, *Material Sci. and Eng. B*. (129), 59-63 (2006)
27. Kawar S.S., Chalcogenide thin film having nanometer grain size for photovoltaic applications, *Research journal of chemical sciences*, 1(8), 31-35 (2011)