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Influence of deposition temperature on the structural and optical properties of nanostructured As$_2$S$_3$ thin films prepared by chemical bath deposition technique

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ABSTRACT

This paper reports the growth of As$_2$S$_3$ thin films on amorphous glass substrates by Chemical Bath Deposition (CBD) method at different bath temperatures. The films were deposited over deposition temperature range 283 to 333K .The effect of bath temperature on structural, electrical and optical properties was studied. The X-ray diffraction studies showed that films deposited below 303K are amorphous and becomes polycrystalline with monoclinic structure above. The dependence of growth rate and conductivity on the deposition temperature was studied. A blue shift of 0.4eV is observed in optical band gap energy of As$_2$S$_3$ which supports Quantum size effect that takes place due quantum confinement of electrons with diminishing size of crystallites. Activation energy was found to decrease from 0.23 to 0.11 eV with increase in film thickness from 67 to 265 nm.   © 2013 Trade Science Inc. - INDIA

INTRODUCTION

Nanostructured semiconductor thin films are important in nanotechnology due to their size dependent outstanding electrical optical and structural properties. During the last decade there is considerable inertest in these size dependent properties[1-3]. The size dependent properties are realized when the bulk materials are reduced below a critical size, typically in nanometer range. For semiconductors this transition occurs when particle sizes are comparable to the de Brogile wavelength of the electron[4]. The increase in surface area and surface free energy with decreasing particle size is responsible in changing many properties. Using these aspects the field semiconductor technology is rapidly developing by producing new type of components for electronic and optoelectronic devices such as like catalysis[5], resonant tunneling devices[6] and solar cells[7]. This semiconductor nanostructure physics is one of the frontier areas of research in condensed matter physics. Arsenic trisulphide (As$_2$S$_3$) films have drawn wide attention of the scientific community in the world since last to decades because of various useful properties. It is a technically important binary semiconductor mate-

rial with 2 .2 eV[8] energy gap and good transparency in the 0.7–11-μm wavelength range. It has number of applications in various electronic and optoelectronic devices, optical imaging, and hologram recording[9-11].Several chemical techniques have been used to deposit As_2S_3 thin films including spin-coating[12], solution gas interface technique[13], chemical bath deposition[14-16] and successive ionic layer adsorption and reaction (SILAR) method[17]. The chemical bath deposition method is particularly useful for continuous deposition of thin films. It is a bottom up process in which atoms, ions, molecules even nanoparticles themselves acts as building blocks for the creation of thin film. Uniform and highly oriented surface morphologies of films deposited using disclosed embodiments are clearly improved compared to films deposited by a conventional process. The technique can be used to tailor the composition and morphology of the deposited material depending on various types of substrates and deposition parameters at low temperature. In technology revolution inexpensive and flexible integrated circuits are needed. One simple way of making inexpensive and flexible integrated circuits, is to fabricate semiconductor devices on flexible polymeric (any shape and size) substrates at low temperature. Chemical bath deposition (CBD), is a powerful method with the constituent ions dissolved in a water solution, can be used to deposit epitaxial semiconductor layers at low temperatures. The growth rate in CBD method can be adjusted by varying the concentrations of the ion sources, using appropriate complexing agents, temperature of bath and combinations of such parameters[18]. The film formation takes place when the ionic product exceeds the solubility product (IP >SP). This results in the formation of precipitate in the solution and produces favorable condition for nucleation. The deposition of nanostructured thin films by chemical bath technique from aqueous solution is a simplest and most economical way, as it does not require any sophisticated instruments. Lokhande et al.[14,15] have reported solution growth of As_2S_3 films from acidic and alkaline aqueous baths, and optimized various parameters such as As^{3+} and S^{2-} ion concentration,volume of complexing reagent, deposition time and deposition temperature. The films deposited from EDTA complex alkaline bath were uniform, smooth, and compact, and the film thickness was

between 0.3 and 0.4 mm. The films deposited onto glass substrates from an acidic sodium thiosulphate bath, using EDTA as a complexing reagent were amorphous, with an optical band gap of 2.36 eV and a resistivity of the order of 10^6 Ω-cm. Mane et al.[19] have deposited As_2S_3 thin films in aqueous medium at a low temperature (6°C) by using a chemical bath deposition technique. The aim of this work is to prepare nanostructured As_2S_3 thin films by convenient and economic solution growth method, CBD in the low temperature range 283 to 333K and investigate effect of this deposition temperature on optical, electrical, morphological and structural properties.

EXPERIMENTAL

Growth of As_2S_3 thin films

The As_2S_3 thin films were prepared by chemical bath deposition method. The solutions of 120 ml of 0.1 M arsenic trioxide, 30ml of 0.1M EDTA and 120ml of 0.2 M sodium thiosulphate were prepared in aqueous medium. Before deposition cleaning of glass substrate is a very important step in CBD method. The glass substrates were boiled in chromic acid for two hours and then kept in it for 48 hours. These slides were then cleaned with dilute hydrochloric acid followed by detergent and distilled water and finally dried in AR grade acetone.

To obtain deposition of As_2S_3 thin film, 120 ml of 0.1 M arsenic trioxide solution was taken in a 200 ml capacity glass beaker and to it; 30ml of 0.1M EDTA solution was slowly added with constant stirring. To this mixture, 120 ml of freshly prepared $Na_2S_2O_3$ was added slowly with constant stirring. The pH of final solution was adjusted to 3. The solution was stirred for few seconds and then transferred into another beaker containing cleaned glass substrates kept vertically. The bath colour was changed to pale yellow within five minute. The deposition temperature was varied between 283 and 333 K however 40 min deposition time was kept constant. At every deposition temperature due care was taken that temperature of reacting solutions before and after mixing was same. After film formation, they were taken out of the bath, washed with double distilled water, and preserved in airtight contain

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Characterization

Thickness of the films is one of the most important parameter since it largely affects the properties of the film[20, 21]. The thickness of the film with high accuracy can be measured by obtaining interference due to two optical flat reflecting surfaces, one of them supporting the film and other flat in contact with film surface (Tolansky's method)[22]. The layer on which interference is formed is wedge shaped air gap between two surfaces. The air film is illuminated with a parallel monochromatic beam of light at normal incidence. The two adjacent fringes are displaced at the site of the film step. The film thickness is calculated by using the formula,

$$t = \frac{\Delta L}{L} \times \frac{\lambda}{2} \qquad (1)$$

Where L is the fringe spacing, ΔL is displacement of fringe and λ is the wavelength of monochromatic light.

The structural properties of As_2S_3 thin films have been analyzed by X-ray diffraction (XRD) using CuKα radiation of wavelength 0.154 nm with Phlips 1710 diffractogram. The microstructure of the As_2S_3 thin films on glass substrate was studied by using a Scanning electron microscope JSM 610. The optical absorption was studied by using UV-VIS-NIR Spectrophotometer Hitachi330. The dark electrical resistivity of As_2S_3 film was measured using two-point dc probe method. A silver paste is applied for good ohmic contact to As_2S_3 thin film. The area defined was 0.5 cm^2.
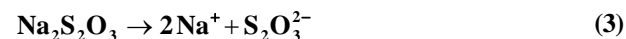
RESULTS AND DISCUSSION

The fundamental principle in CBD process is that in order to precipitate a certain compound from a solution, its ionic product (I.P) must exceed the solubility product (S.P). When this condition is satisfied, the thin film of a specific compound is formed on the substrate surface by the process of atom by- atom, molecule-by-molecule, and ion-by-ion or cluster-by-cluster condensation. The appropriate complexing agent is always added to control the precipitate formation and thereby resulting to deposition of thin films on a particular substrate. As_2S_3 thin films were prepared by decomposition of sodium thiosulphate in an acidic bath containing an arsenic salt and a suitable complexing agent EDTA which allows slow release of soluble species of As^{3+} in

the medium. The deposition process is based on the slow release of As^{3+} and S^{2-} ions in the solution which then condense on the substrates which were suitably mounted in the solution. The deposition of As_2S_3 occurs when the ionic product of As^{3+} and S^{2-} exceeds the solubility product of the As_2S_3. Many workers[19-23, 24] have proposed reaction mechanism for the formation of As_2S_3 thin film by using thioacetamide and sodium thiosulphate in an acidic and alkaline bath. The formation of As_2S_3 in the present case can be described on similar line. In the beginning arsenic trioxide is dissolved in distill water with the help of HCL as,
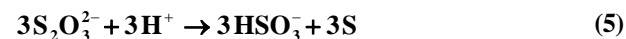
$$As_2O_3 + HCL \xrightarrow{95^0 C} 2AsCl_3 + 3H_2O \qquad (2)$$

In aqueous solution $Na_2S_2O_3$ dissociates as,

$$Na_2S_2O_3 \rightarrow 2Na^+ + S_2O_3^{2-} \qquad (3)$$

$Na_2S_2O_3$ is a reducing agent by virtue of half cell reaction,

$$6S_2O_3^{2-} \rightarrow 3S_4O_6^{2-} + 6e^- \qquad (4)$$
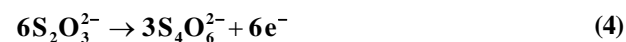
In acidic medium dissociation of $S_2O_3^{2-}$ takes place as,

$$3S_2O_3^{2-} + 3H^+ \rightarrow 3HSO_3^- + 3S \qquad (5)$$

The electrons released in equation 2 react with S as,

$$3S + 6e^- \rightarrow 3S^{2-} \qquad (6)$$

With the addition of Na_2EDTA, As^{3+} forms a complex as

$$As^{3+} + Na_2EDTA \rightarrow As^{3+}(Na_2EDTA) \qquad (7)$$
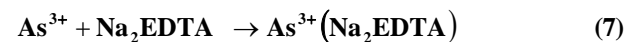
The EDTA complex of As^{3+} from solution reacts to give As_2S_3 thin films as,

$$2As^{3+}(Na_2EDTA) + 3S^{2-} \rightarrow As_2S_3 + 2(Na_2EDTA) \qquad (8)$$
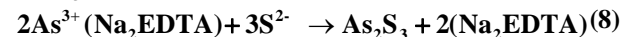
The dependence of growth rate on deposition temperature is shown in the figure 1. The rate of deposition increases with temperature. At 283 K, the rate of film growth is slow (1.67nm/min.) and terminal film thickness of 67nm attained after 40 min. However, at 333K the growth rate is higher (6.63nm/min.) and a terminal film thickness of 265nm is attained after a period of 40nm. At higher temperature the kinetic energy of the ions released is higher which increases the chance of interaction between them and the resulting condensation at the substrate surface[25]. It reveals that deposition rate is lowered at lower temperature. The films deposited at lower growth rate at low temperatures are more adhesive and specularly reflective as that of films

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TABLE 1 : Effect of deposition temperature on different properties of As_2S_3 thin films.

Sr. No.	Sample	Deposition temperature (K)	Film thickness (nm)	Growth rate (nm/min.)	Grain size (nm)	Resistivity x 10^4 (Ω cm)	Activation energy (eV)	Band gap energy(eV)
1	A	283	67	1.67	-	78.1	0.23	2.60
2	B	303	99	2.47	-	31.7	0.2	2.53
3	C	313	142	3.55	3.4	21.3	0.17	2.44
4	D	323	186	4.65	6.2	13.2	0.13	2.26
5	E	333	265	6.63	13.5	7.5	0.11	2.20
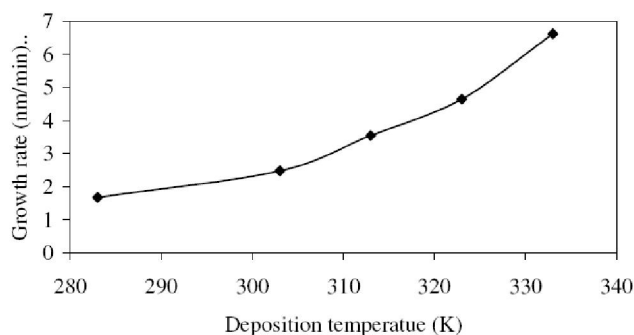
Figure 1 : Variation of growth rate (nm/min.) of As_2S_3 film with deposition temperature (K).
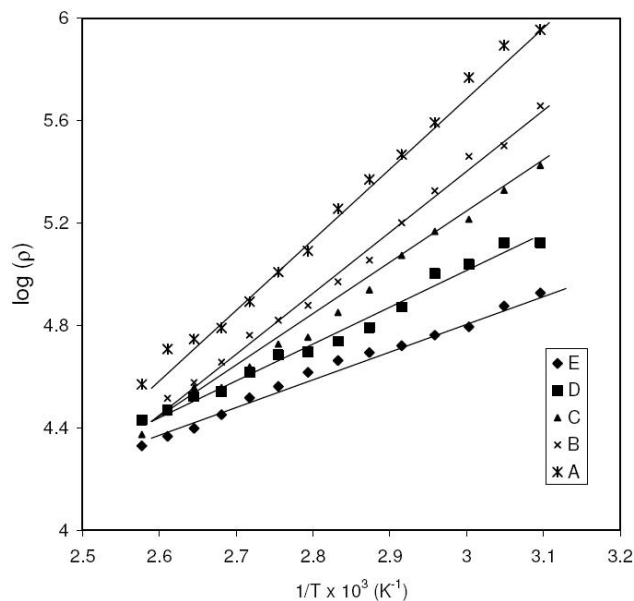
Figure 3 : Variation of log (ρ) vs. 1/T x 10^3 (K^{-1}) for As_2S_3 films with different thickness: 67nm, 283 K; (B) 99nm, 303 K; (C) 142nm, 313 K; (D) 186nm, 323 K; (E) 265nm, 333 K.

deposited at higher temperature. The dissociation of the complex and anion of the compound is highly influenced by the temperature. The dissociation rate is more at higher temperature and gives more number of As^{3+} and S^{2-} ions which enhances the growth rate

Structural identification of As_2S_3 films was carried out with X-ray diffraction in the range of angle 2θ between 10 to 80 ^{0}. Figure 2 shows the XRD patterns of
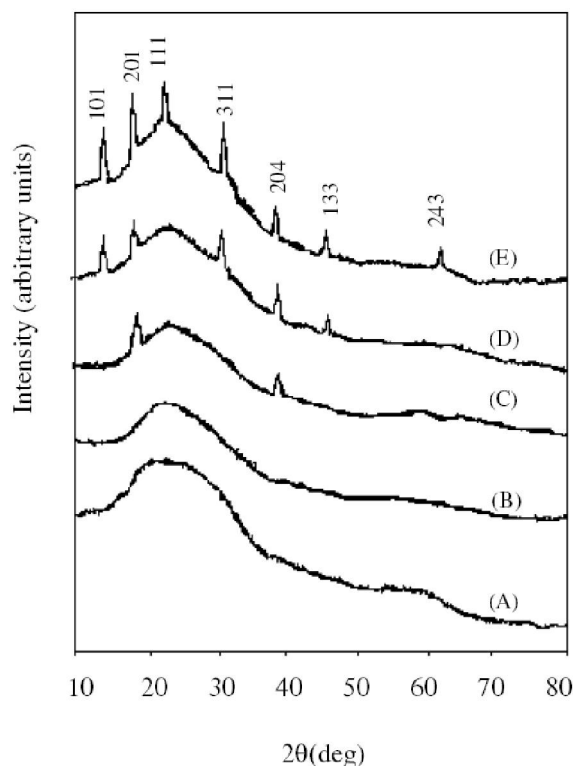
Figure 2 : X-Ray diffraction patterns of As_2S_3 thin films deposited at various deposition temperatures: (A) 67nm, 283 K; (B) 99nm, 303 K; (C) 142nm, 313 K; (D) 186nm, 323 K; (E) 265nm, 333 K.

As_2S_3 thin films deposited at various deposition temperatures. The observed broad hump in XRD pattern is due to amorphous glass substrate. The patterns show that the films deposited above 303 K temperature are nanocrystalline and comparison of the observed d values with standard d values of As_2S_3 shows good agreement, indicating monoclinic structure[26]. However films deposited at lower temperature shows amorphous nature indicating tiny crystallinity. The existence of the characteristic diffraction lines corresponding to the (1 0 1), (2 0 1), (1 1 1), (3 1 1), (2 0 4), (1 3 3) and (2 4 3) planes for As_2S_3 are clearly shown in the figure. The crystallite size of the films were calculated by applying Scherrer's formula[27],
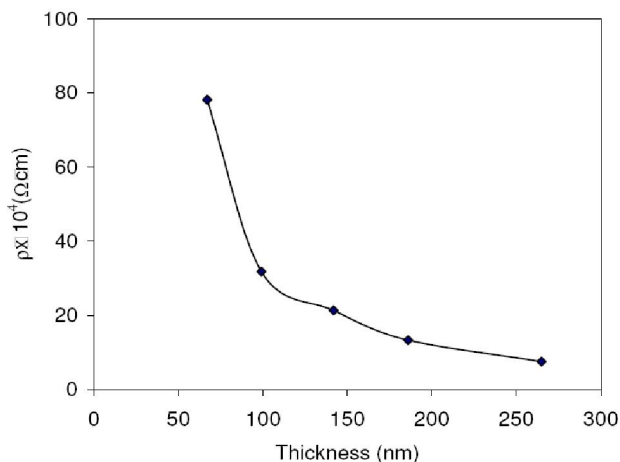
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Figure 4 : Plot of variation of electrical resistivity ($\rho \times 10^4$ Ω cm), with thickness of As$_2$S$_3$ films at temperature 328K
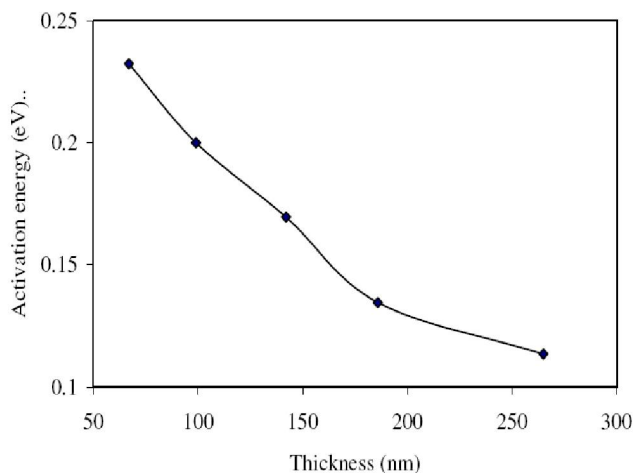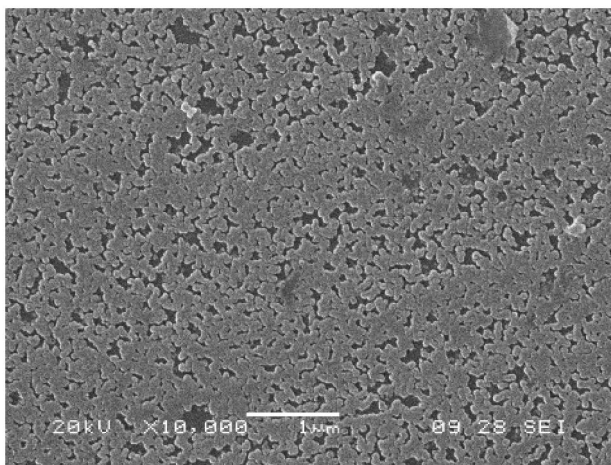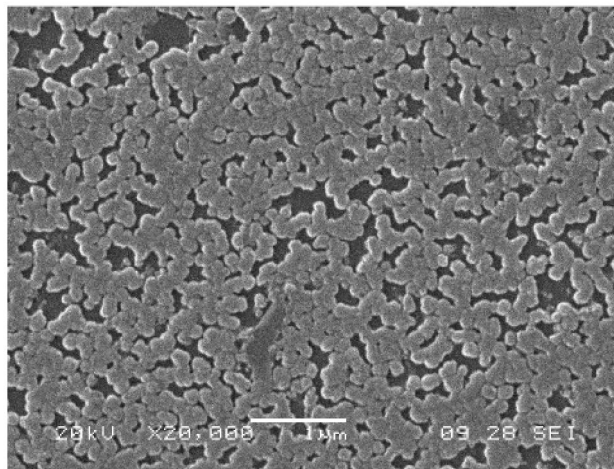
Figure 5 : Variation of activation energy, eV, with film thickness.

(A)

(B)

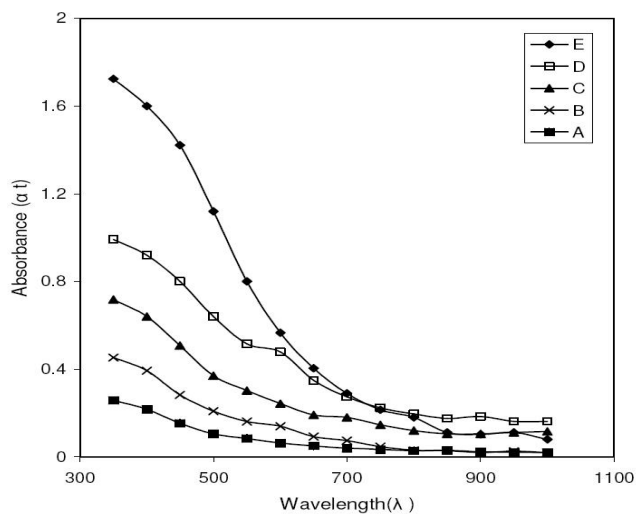**Figure 6 : SEM images of As$_2$S$_3$ film of thickness (A) 99nm, 303 K; (B) 186nm, 323 K**

Figure 7 : Plot of optical absorption (αt) vs. wavelength for As$_2$S$_3$ films with different thickness: (A) 67nm, 283 K; (B) 99nm, 303 K; (C) 142nm, 313 K; (D) 186nm, 323 K; (E) 265nm, 333 K
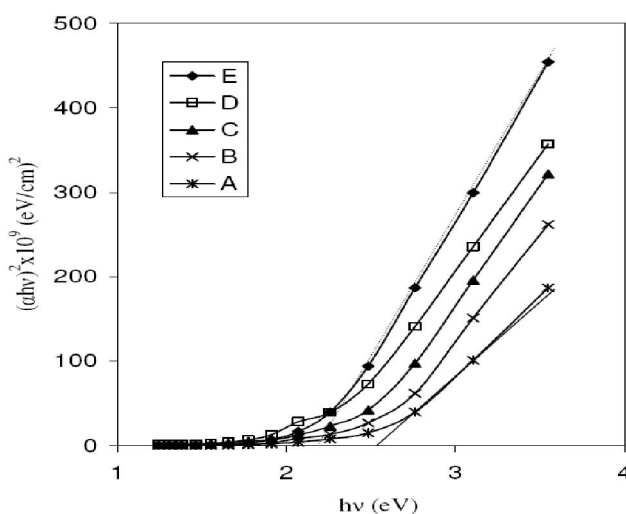
Figure 8 : Plot of ($\alpha h\nu$)^2 vs. hν for As$_2$S$_3$ films with different thickness: (A) 67nm, 283 K; (B) 99nm, 303 K; (C) 142nm, 313 K; (D) 186nm, 323 K; (E) 265nm, 333 K
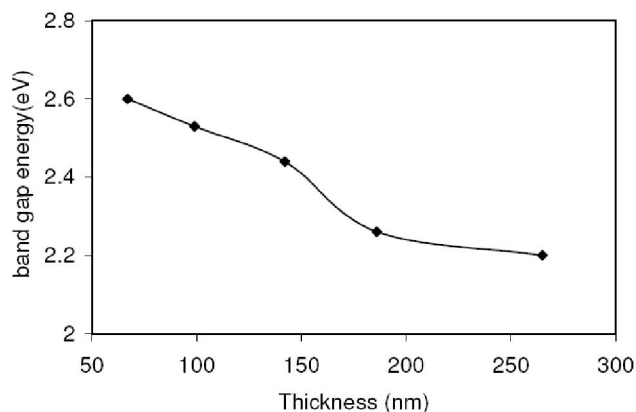
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Figure 9 : Variation of optical band gap energy, Eg, with film thickness.

$$d = \frac{\lambda}{\beta\cos\theta} \qquad (9)$$

Where λ is the wavelength used (0.154 nm); β is the angular line width at half maximum intensity in radians; θ is the Bragg's angle.

The grain size of As_2S_3 thin films increases from 3.4 to 13.5 nm with increase in film thickness from 142 to 256 nm. The substrate temperature influences the crystalline structure of the deposited film. By increasing the substrate temperature the reaction rate in bath is accelerated which enhances crystallization of the film.

The variation of dark electrical resistivity of As_2S_3 films deposited at various bath temperatures was studied in the temperature range 323 to 433 K using dc two-point probe method. Figure 3 shows the variation of log of resistivity (log ρ) with reciprocal of temperature (1/T) x 10^3. It is seen that resistivity decreases with temperature indicating semiconducting nature of films. Figure 4 shows the variation of electrical resistivity, ρ, with film thickness. It was decreased between 78.16×10^4 and $7.50 \times 10^4 \, \Omega$ cm when film thickness was changed from 67 to 265 nm at 328 K (TABLE1). These observations may be due to size effects that are arising because of quantum confinement of charge carriers within the particles. The most important mechanisms limiting electron transport in nanocrystalline As_2S_3 films are grain boundary scattering, scattering due to lattice vibrations and and ionized impurity scattering[28]. The scattering mechanism in film is dependent on film quality and carrier concentration.

The thermal activation energy was calculated using the relation,

$$\rho = \rho_0 \exp (E_0/KT) \qquad (10)$$

where, ρ is resistivity at temperature T, ρ_0 is a constant, K is Boltzmann constant (8.62×10^{-5} eV/K) and E_0 is the activation energy required for conduction. Figure 5 shows variation in activation energy from 0.23 to 0.11 eV as thickness changes from 67 to 265 nm (TABLE 1). It may be due to increase in defect levels in nanosize thin films. Estarde et al.[29, 30] have reported that increase in charge carrier mobility with increase in grain size reduces activation energy.

The microstructure of As_2S_3 thin film deposited at 303 and 323 K temperature were studied by SEM. The surface of the film is quite rough (Figure 6). It was observed from the micrograph study that the shape of the grains in film is not uniform but consisted with the rod like and dumbbell shape grains.

The optical absorption behavior of nanostructured As_2S_3 thin films in the wavelength range 350 to 1000 nm are shown in the Figure 7. All the films show higher absorption on the shorter wavelength side with presence of an absorption edge. The nature of the transition (direct or indirect) is determined by using the relation

$$\alpha = \frac{A(h\upsilon - Eg)^n}{h\upsilon} \qquad (11)$$

where hυ is the photon energy, E_g is the band gap energy, A and n are constants.

For allowed direct transitions n = 1/2 for allowed indirect transitions n = 2. The plots of $(\alpha h\nu)^2$ versus hν were shown in Figure 8 for As_2S_3 films having different thicknesses.. Band gap energy, Eg was determined by extrapolating the straight line portion to the energy axis for zero adsorption coefficient (α). The band gap energy value of the semiconductor films plays a key role on the solar cell fabrication. Figure 9 shows variation in optical band gap energy from 2.2 to 2.6 eV with thickness from 67 to 265 nm deposited in the temperature 283to 333K. The band gap values of the film were always found to be higher compared to the value of bulk As_2S_3. It may be noted that film deposited at 283 K temperature showed the maximum shift in band gap which clearly indicates a blue shift with decreasing crystalline size.

CONCLUSIONS

In summary, a low temperature rout for the growth

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of nanocrystalline As_2S_3 thin films by CBD method is reported. The influence of bath temperature on growth characteristics of As_2S_3 thin films was studied. Electro-optical and structural properties of As_2S_3 thin films were studied. XRD studies reveal that as deposited As_2S_3 films are amorphous at low and exhibit nanocrystalline monoclinic structure comparatively at high deposition temperature. Optical studies shows that the absorption spectrum is due to transition from one band to another and is mainly caused by allowed direct transitions. The optical band gap energy varies from 2.2 to 2.6 eV with thickness variation from 67 to 265 nm. The increase in band gap energy is attributed to small nanocrystallite size as determined by XRD. The electrical resistivity and therefore activation energy are observed to be thickness dependent.

ACKNOWLEDGEMENT

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