# Synthesis of Nanostructured $As_2S_3$ Thin Films by Chemical Route: Effect of Complexing Agent

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## ABSTRACT
The effect of complexing agent on electrical properties of nanostructured As2S3thin films deposited by chemical bath deposition method is reported. For the deposition, the complex of arsenic was allowed to react with sodium thiosulphate in aqueous medium at room temperature.The effect of various complexing agents like Ethylenediaminetetraacetic acid (EDTA), oxalic acid, tartaric acid and acetic acid on electrical properties are studied. The electrical resistivity and activation energy is found complex dependent.

## Keywords
Chemical synthesis; Semiconducting materials; Nanostructure; Thin films

## 1. INTRODUCTION
Arsenic trisulfide (As2S3) is a scientifically important metal chalcogenide because it has variety of applications in optical imaging, hologram recording, and recently in various electronic devices including electro-optic information storage devices, optical mass memories and for integrated non-linear optical devices due to its electrical, optical and thermal properties [1–6]. Also arsenic chalcogenide is having great importance in the bulk infrared optics due to its good infrared transmission and great glass forming tendency [7-9]. Because of its non-hygroscopic nature, chemical stability, resistance to devitrification and high resistivity arsenic chalcogenide became an attractive material for various applications especially in photoconductors, electronic switching devices and optic devices [10-15].Various physical and chemical methods have been employed to deposit As2S3 thin films.As compared with vacuum thermal evaporation, magnetron sputtering, chemical vapour deposition techniques, etc., the CBD has several advantages.It is the simplest and most economical technique and has many advantages with respect to other methods.The films can be deposited on different kinds, shapes and size of substrates. One of the chief advantages of such a method is that it is possible to deposit films on non-accessible surface. Chemical deposition gives pin-hole free and uniform deposits of films since solution and substrate are in contact during deposition process.

In the present investigation CBD method is utilized to deposit As2S3thin films from complexed and un-complexed baths and studied its effect on electrical properties.

## 2. EXPERIMENTAL
The simple and economic chemical bath deposition method for preparation of thin films nowadays is very important for industrial development of semiconductor technology. Nowadays, the nanotechnology tools for the fabrication of thin films with high robustness should provide higher efficiency in preparation procedures, higher mechanical stability of the thin films and low costs, respectively. The chemical bath deposition method assures the given criteria.

For the deposition of As2S3 thin films, the bath solution was made by vigorous mixing of 30 mL (0.2M) As2O3 solution and 30 mL (0.2 M) complexing agent (EDTA, Tartaric acid, Acetic acid and Oxalic acid) solution in 100 mL beaker. To this, 30 mL (0.2 M) sodium thiosulphate was added to get final bath at room temperature. The pH of these baths was maintained around 3. Cleaned glass slides were positioned vertically using a specially designed substrate holder in the reaction mixture. The solution colour was changed to greenish yellow after about 30 min. After 6 h, the well adherent shining yellow coloured glass slides were retired from the bath. The films deposited on both the sides were rinsed several times with double distilled water, dried naturally and preserved in a desiccator over hydrous calcium chloride.

The electrical resistance measurements were carried out in the temperature range 343–436 K using the two-probe method. A quick drying silver paste was applied to the film for better ohmic contact. To determine type of conductivity, thermo-emf measurements were carried out. The temperature gradient was maintained along the length of the film and the potential difference across the terminals having a separation of 1cm was measured with the help of digital micro-voltmeter. A calibrated thermocouple probe with a digital indicator was used to sense the working temperature difference applied across the sample.

## 3. RESULT AND DISCUSSION
In chemical bath deposition method the film growth is affected by the precipitate formation process in the solution. To achieve auspicious condition for the film growth the ionic product (IP) must exceed the solubility product (SP), (IP>SP) thus the formation of thin film on the substrate takes place by ion-by-ion condensation .If the ion product does not exceed, no solid phase will form, except possibly transiently due to local fluctuations in the solution, and the small solid nuclei will re-dissolve before growing to a stable size. The deposition of metal chalcogenide thin filmoccurs due to substrate maintained in contact with dilute chemicalbath containing metal and chalcogen ions.The complexing agent as a constituent of the bath eliminates spontaneous precipitation by slowing down the release of the metallic ions on dissociation, thereby resulting in slow precipitation of the compound. The metal ions form a metal-complex in aqueous medium and this complexed metal ions and sulfur ions are diffused to-the substrate surface. This dissociation ofNa2S2O3 takes places and bivalent sulfide thin films are formed on the substrates. Nucleation of the precipitate in the solution starts at some local in-homogeneities present in the solution, where the ionic produce exceeds the solubility product. The growth of these nuclei by the addition of more ions from the solution results in the formation of a stable nucleus of a size greater than the critical size. The low

temperature deposition avoids oxidation or corrosion of metallic substrates. In chemical deposition process pinhole free and uniform thin films were obtained as the reaction mixture from which these are deposited for all time remains in touch with the substrates.

In the present work As2S3 films were prepared from un-complexed and complexed bath. The arsenic trioxide is dissolved in distill water with the help of HCL as,

$$As_2O_3 + 6HCl \xrightarrow{95^0C} 2AsCl_3 + 3H_2O \qquad (1)$$

In aqueous solution $Na_2S_2O_3$ dissociates as,

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

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

$$6S_2O_3^{2-} \rightarrow 3S_4O_6^{2-} + 6e^- (3)$$

In acidic medium dissociation of $S_2O_3^{2-}$ takes place as,

$$3S_2O_3^{2-} + 3H^+ \rightarrow 3HSO_3^- + 3S \quad (4)$$

The electrons released in equation (3) react with S as,

$$3S + 6e^- \rightarrow 3S^{2-} \quad (5)$$

(a) Un-complexed bath: $As^{3+}$ ions directly react with $S^{2-}$ ions to produce $As_2S_3$,

$$2As^{3+} + 3S^{2-} \rightarrow As_2S_3 \downarrow \ (6)$$

(b) Complexed bath: The $As^{3+}$ ions complex which decompses very slowely to liberate $As^{3+}$ ions for the film formation as,

$$2[As(complex\ ion)]^{3-} + 3S^{2-} \rightarrow As_2S_3 \downarrow + \text{complex ion} (7)$$

The As2S3 film formation is influenced by the complex used in the deposition process. The films deposited without complex have maximum thickness (383 nm). And it decreases when complex is used (Table1). The addition of complexing agent (acetic acid, EDTA, oxalic acid and tartaric acid) in reaction bath forms complex with metal ions, which then slowly dissociates to release As3+ ions to form As2S3film. The intermediate complex formation and decomposition mechanism avoids direct reaction between free cations and anions that decrease the precipitate formation rate which in turn reduce the wastage of precipitate.The complex decomposition mechanism is based on the formation of solid phase instead of reacting directly with a free anion; it forms an intermediate complex with the anion-forming reagent. The deposited films areyellow in colour however, the film colour changes slightly according to the complex used (fig 1). The films deposited from un-complexed bath and using EDTA are dark yellow in colour, however, they are light yellow for acetic acid, which may be because of variation in thickness.

***Table 1. Variation of $As_2S_3$ film thickness, with complexing agent.***

| S.N. | Complex used | Thickness(nm) |
|---|---|---|
| A | Without complex | 383 |
| B | EDTA | 301 |
| C | Tartaric acid | 287 |
| D | Acetic acid | 217 |
| E | Oxalic acid | 207 |

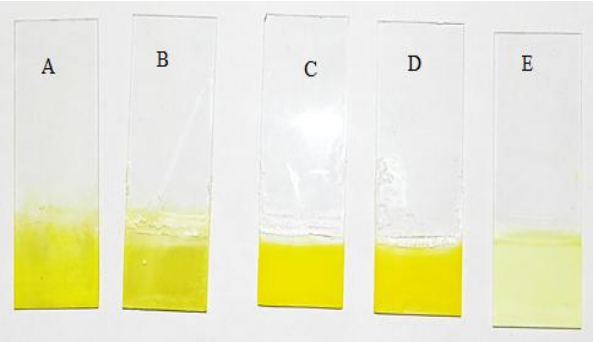


**Fig.1. Photograph of $As_2S_3$thin films deposited using complexing agents: (A) without complexing agent; (B) EDTA; (C) Oxalic acid ;( D) Tartaric acid and (E) Acetic acid.**

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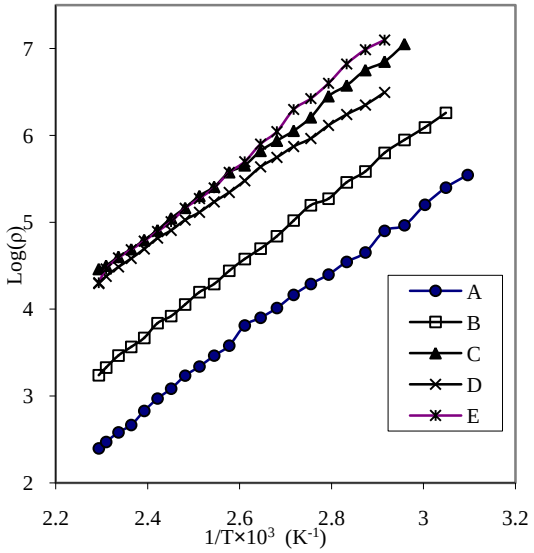


**Fig.2. Variation of log of electrical resistivity with reciprocal of temperature of $As_2S_3$ thin films deposited using complexing agents: (A) without complexing agent; (B) EDTA; (C) Oxalic acid ;( D) Tartaric acid and (E) Acetic acid.**

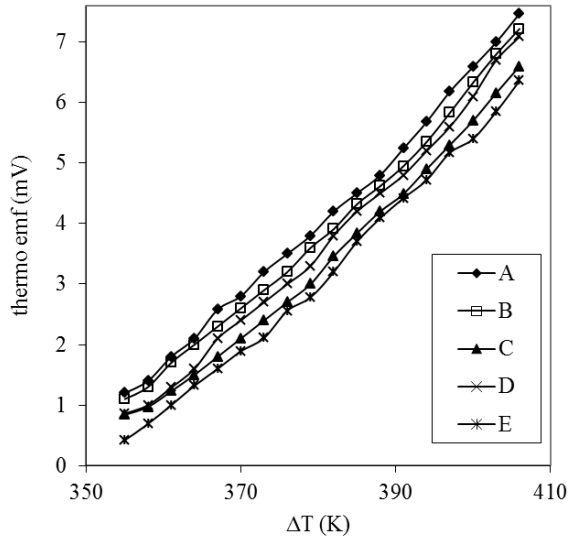


**Fig.3. Variation of thermo-emf with temperature difference of $As_2S_3$ thin films deposited using complexing agents: (A) without complexing agent; (B) EDTA; (C) Oxalic acid;( D) Tartaric acid and (E) Acetic acid.**

The variation of dark electrical resistivity of As2S3 films deposited using various complexing agents was studied in the temperature range 323 to 436 K using dc two-point probe method. The electrical resistivity of As2S3film at 343K temperature was found to be of the order of 9×106 Ω cm for the film deposited using acetic acid and it decreases to 7.9×104 Ω cm for the film deposited from un-complexed bath which may be due to variation in film thickness from 207 to 313 nm. The high value of resistivity may be attributed due to nano crystallinity of the film, grain boundary discontinuities, presence of surface states and small thickness of the film, etc. Fig.2 shows the variation of log of resistivity (log ρ) with reciprocal of temperature (1/T) x 103. It is seen that resistivity decreases with increase in temperature indicating semiconducting nature of films

The thermal activation energy was calculated using the relation,

$$\rho = \rho_0 \exp^{E_0/KT} \quad (8)$$

where, ρ is resistivity at temperature T, ρ0 is a constant, K is Boltzmann constant (8.62 x 10-5 eV/K) and E0 is the activation energy required for conduction. The variation in activation energy from 0.3 to 0.39 eV is observed depending on complex used (Table 1). It may due to variation in crystalline nature of film depending on complex used. The temperature difference applied across a semiconductor thin film causes a transport of carriers from hot to cold end and thus creates an electric field which gives thermal voltage.

## 4. CONCLUSIONS

The As2S3thin films were successfully deposited using CBD method from complexed and un-complexed bath. The influence of complexing agents on electrical properties of As2S3 thin films was studied. The activation energy varies from 0.3 to 0.39 eV depending on complex used.The thermo-emf measurement across a semiconductor As2S3thin film developed due to transport of carriers from hot to cold end confirms its n-type conductivity.

## ACKNOWLEDGEMENT

The authors are thankful to University Grants Commission, WRO, Pune (India), for financial support under the project (No: F.47-1695/10 dated 16/3/2011).

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