Preparation and characterization of chemically deposited \(\text{As}_2\text{S}_3\) thin films

R S Mane, B J Lokhande, M D Uplane & C D Lokhande
Thin Film Physics Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004

Received 8 August 1997; revised 17 February 1998; accepted 7 January 1999

A method for chemical bath deposition of \(\text{As}_2\text{S}_3\) thin films in an aqueous acidic medium is described. \(\text{As}_2\text{O}_3\) was used as \(\text{As}^{3+}\) ion source and thioacetamide as a \(\text{S}_2^2-\) ion source. Sodium salt of ethylene diamine tetracetic acid was used as a complexing agent for \(\text{As}_2\text{O}_3\). The preparative parameters like solution concentration, volume of sulphur ion source etc. have been optimized. X-ray diffraction, SEM, optical absorption, electrical resistivity, etc. are used to characterize the films.

Introduction

Preparation of nanocrystalline metallic and non-metallic thin films become more popular because of their usefulness in many fields, such as solar cells, photoconductors etc. Thin films of \(\text{CdS}, \text{PbSe}, \text{Bi}_2\text{S}_3\) have deposited chemically in nanocrystalline thin film form and their properties have been reported. Thin films of \(\text{As}_2\text{S}_3\) also have important applications in optical imaging, holography recording and optical mass memories. Thin films of \(\text{As}_2\text{S}_3\) are prepared in an aqueous acidic medium by using chemical bath deposition technique, for that \(\text{As}_2\text{O}_3\) was used as a \(\text{As}^{3+}\) ion source and thioacetamide was used as a \(\text{S}_2^2-\) ion source. Sodium salt of ethylene diamine tetracetic acid was used as a complexing agent for \(\text{As}_2\text{O}_3\). Preparative parameters of bath have been optimized. X-ray diffraction, SEM, optical absorption, electrical resistivity of these films have been studied.

2 Experimental Details

Thin films of \(\text{As}_2\text{S}_3\) were obtained onto a plane amorphous glass substrates, which are cleaned carefully by using ultrasonic cleaner. The \(\text{As}_2\text{S}_3\) thin films were prepared at two temperatures 0 and 25°C. First of all \(\text{As}_2\text{O}_3\) was dissolved in concentrated \(\text{HCl}\) and diluted with double distilled water to make 0.1 \(M\) solution. While diluting care was taken that \(p\text{H}\) of the solution should not rise above 2.5, because initially it was noted that, when \(\text{As}_2\text{O}_3\) (0.1 \(M\)) is dissolved in water and TAM (0.1 \(M\)) is added to it (\(p\text{H}=4-5\)), \(\text{As}_2\text{S}_3\) deposition at room temperature or even at high temperature is not possible. 0.1 \(M\) stock solution of thioacetamide (TAM) was used as a \(\text{S}_2^2-\) ion source. The effect of \(\text{S}_2^2-\) ion source concentration on \(\text{As}_2\text{S}_3\) deposition was studied to optimize TAM volume. To achieve this to 10 ml of 0.1 \(M\) \(\text{As}_2\text{S}_3\) solution different volumes of TAM (0.1 \(M\)) stock solution was added. After one hour colourless solution gradually turns yellow and after five hours lemon yellow coloured films were obtained. Thickness of the films were measured by the gravimetric method employing a sensitive microbalance.

Optical absorption of the films on glass substrates was studied in the wavelength range 350-850 nm by using Hitachi -330 spectrometer. Philips PW-1710. X-ray diffractometer, Cu\text{K}_{\alpha} radiation with wavelength 1.542 \(\text{Å}\) was used for XRD studies. SEMs were taken with the help of Cambridge stereoscan 250-MK-3 assembly (10 \(kV\)).

Results and Discussion

Plot of thickness of \(\text{As}_2\text{S}_3\) films versus volume is shown in Fig. 1. It shows that maximum thickness was obtained when volume of TAM was 8 ml, below 8 ml and above, the thickness decreases because when ionic product (IP) of \(\text{As}^{3+}\) and \(\text{S}_2^2-\) exceeds the solubility product (SP) of \(\text{As}_2\text{S}_3\), \(\text{As}_2\text{S}_3\) will form IP/SP defines the degree of supersaturation (S). When S 1, \(\text{As}_2\text{S}_3\) nuclei forms on the substrate in the solution, which grow with time to give the film and precipitate respectively. Once stable nucleation centers of \(\text{As}_2\text{S}_3\) are formed, they act as catalysts for further deposition of \(\text{As}_2\text{S}_3\). As a catalytic surface develops both on substrate and in the solution, the proportion of \(\text{As}_2\text{S}_3\) formed on the substrate is deter-
mined by the ratio of nuclei formed on the substrate and in the solution. The deposition rate is initially higher owing to an abundance of As$^{3+}$ and S$^{2-}$ ions. As more and more As$_2$S$_3$ is formed, the solution becomes deficient in ions giving a lower rate of deposition. After attaining maximum thickness, additional TAM volume decreases the thickness because As$_2$S$_3$ film dissolves in acidic medium. Fig. 2 shows the variation of film thickness with EDTA volumes. When EDTA volume is zero, thickness of As$_2$S$_3$ film is equal to that of previous one. The function of complexing agent is to control the supply of free metal ions (As$^{3+}$) for reduction. Initially thickness of As$_2$S$_3$ increases with volume of EDTA, which could be due to the combined effect of (a) release of As$^{3+}$ ions from complex and (b) As$^{3+}$ ions not taking part (due to deficient EDTA ions) in complex formation.

Both the types of As$^{3+}$ ions react with S$^{2-}$ ions to give a thin film. After 10 ml of EDTA volume, thickness of film decreases due to strong complex formation 2. Dissociation of the As$_2$S$_3$ film, which slow down the reaction rate. XRD studies for the films deposited with optimized bath composition (10 ml As$_2$O$_3$ + 10 ml Na$_2$EDTA + 8 ml TAM) for a period of 14 hours has been carried out for the films deposited with optimum bath composition at 0 and 25 °C show that films were amorphous in nature, however some peaks are observed and it may be the indication of presence of some crystallites. For microstructural studies SEM, are taken with the help of Cambridge stereoscan 250 MK-3 assembly (10 kV). The grain size was found from SEM by using the relation

$$P_L = \frac{n}{2\pi r M}$$

$$L = \frac{1}{P_L}$$

where $P_L$ is number of intercepts of the grain boundary per unit length, $n$ is total number of intercepts, $r$ is radius of reference circle, $M$ is magnification and $L$ is grain size. The average grain size of As$_2$S$_3$ film decreased from 0.2 to 0.04 μm with temperature. It has been found that the grain size decreases with decreasing deposition temperature, because the nucleation and grain growth depends upon the rate of release of As$^{3+}$ ions from the complexant. The rate of release of As$^{3+}$ ions is lower at 0°C than at 25°C, which gives the lower thickness for the film deposited at 0°C. The optical absorption of the films were studied in the wavelength range 350-850 nm. Fig. 3 shows the variation of optical absorption coefficient with the wavelength. Absorption coefficients for the films prepared at 0°C is lower than the films prepared at 25°C. The optical absorption data are further analysed to determine the bandgap energy of the deposited material by plotting the plot of $(h\nu)^2$ Vs $\nu$ as shown in Fig. 3. The bandgap energy for the films prepared at room temperature (25 °C) is 2.48 eV, which is smaller than the band gap of film prepared at 0°C (2.56 eV). The higher bandgap for the films prepared at 0°C may be attributed to the decrease in grain size. Electrical resistivity of the film with different thickness was measured in the temperature range 313-558 K. The resistivity measured at 25 °C is 0.812 × 10$^{-5}$ ohm-cm and for the
film deposited at 0 °C is $1.339 \times 10^5$ ohm-cm. The increase in resistivity at 0 °C can be attributed to the smaller grain size of As$_2$S$_3$.

**Conclusions**

By using chemical bath deposition, As$_2$S$_3$ films have been deposited onto glass substrates. Films were amorphous, continuous and well adherent to the glass substrates. The grain size decreases as bath temperature changes from 25 °C to 0 °C. The band gap energy increases as deposition temperature decreases whereas resistivity increases with decreases in temperature.

**References**