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Electrical and optical properties of solution phase deposited As_2S_3 and As_2Se_3 chalcogenide thin films: A comparative study with thermally deposited films

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ABSTRACT

In this paper, Arsenic sulfide (As_2S_3) and Arsenic selenide (As_2Se_3) chalcogenide thin films are prepared by solution phase spin coating and thermal evaporation technique. Optical properties (band gap and refractive index) and electrical properties (DC conductivity and Activation Energy) of the deposited films are studied. A comparative study of electrical and optical properties of thermally deposited films and spin coated films has been done. The value of electrical conductivity of As_2S_3 and As_2Se_3 solution based thin films increases with annealing temperature and found that beyond 70 °C, its conductivity is higher as compared to the value of thermally deposited thin films at room temperature. The band gap of solution phase spin coated films decrease with annealing temperature whereas refractive index increases and reaches approximately the same value of the thermally deposited thin film at room temperature.

1. Introduction

Chalcogenide glasses, namely the amorphous compounds of sulfur, selenium and tellurium are one of the interesting classes of materials having potential application in phase-change memory, transistors, electronic, semiconductor and optical device fabrication [1–3]. These materials have received a great deal of attention due to their large value of refractive index, high photosensitivity, low phonon energy, infrared transparency and large optical nonlinearities, making them a good candidate for the new generation thin film based optical and electronic devices [4,5]. Traditionally, bulk chalcogenide glasses are prepared by melt quenching, and their thin films are prepared by thermal evaporation, sputtering, chemical vapour deposition etc. [6,7]. These methods require high vacuum and complicated instrumentation to deposit films. Also, to fabricate the complicated structures with different dimensions, these methods are unpractical [8]. Alternatively, thin films of chalcogenides can also be prepared by solution based approach, taking advantage of dissolution of chalcogenides in various organic solvents. Spin-coating and dip coating methods for thin film preparation are gaining much attention these days [9–12]. Solution phase thin film preparation method gives a pathway to incorporate different doping agents such as metal based nanoparticles in to the films, which in turn enhances the optical and electronic properties of prepared thin films [13,14]. Hence, the solution phase deposition methods open a new route to deposit chalcogenide thin films on large areas for various optical and electronic devices fabrication [3,15–17]. Here, we are mainly concentrated on the optical and electrical properties of amorphous As_2S_3 and As_2Se_3 thin films prepared by thermal deposition and spin coating methods. Although, such studies has been done on the optical and electrical properties of thermally deposited films of these chalcogenides [18,19]. However, the study of electrical conductivity of solution driven films of binary As_2S_3 and As_2Se_3 chalcogenides has not been reported so far. Therefore, our focus is, to present the comparative study of optical and electrical properties of these chalcogenides films, made by thermal evaporation and spin coating methods. Since, the change in structure can have an influence on the charge carriers' transport, photo-generation, carrier trapping and other fundamental properties. Hence, the knowledge of optical and electrical properties of these solution driven films are critical for the development of opto-electronics devices.

Here we report, a comparative study of electrical and optical parameters of deposited films such as activation energy (ΔE), DC conductivity (σ_{dc}), optical band gap (E_g) and refractive index (n) of As_2S_3 and As_2Se_3 films prepared by solution of corresponding bulk powder

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samples in ethanol-amine solvent and by thermal deposition technique. Heat treatment is employed to remove the excess amount of solvent present in the film, which results in the change in optical and electrical properties of these films.

2. Experimental

2.1. Bulk sample

Bulk As_2S_3 and As_2Se_3 glasses are prepared by melt quenching technique. For this purpose, corresponding elements (As: Alfa-Aesar 99.999%, Ge: Sigma–Aldrich 99.999%, Se: Alfa-Aesar 99.999% and S: Cerac 99.999%) are weighted according to their atomic percentages and sealed under vacuum of 10^{-5} Torr in quartz ampoules using gas–oxygen torch. Purification of the batch and ampoule are done prior to the sealing. The batched sealed ampoules are loaded into a muffle furnace and temperature is increased gradually to the melting temperature at the rate of 3-4 °C/min to prepare the melt. To achieve a homogeneous melt, these ampoules are frequently rocked for 12 h. Once homogenized, the melt-containing ampoules are cooled air-quenched and samples are taken out by breaking the quartz ampoules. Furthermore, the samples are annealed at 60 °C well below the glass transition temperature for 15 h to remove oxides or oxygen that might come during the breaking of ampoules. Prepared bulks are further characterized for their stoichiometry and phase.

2.2. Thin film preparation

Arsenic Sulfide (As_2S_3) and Arsenic Selenide (As_2Se_3) thin films are prepared by two different methods i.e. spin coating and thermal evaporation.

2.2.1. Solution and spin coated film deposition

The solution of As_2S_3 and As_2Se_3 are prepared using ethanolamine as a solvent. Bulk As_2S_3, As_2Se_3 are ground into fine powder using pre cleaned ceramic mortar and pestle. Fine powders of As_2S_3 and As_2Se_3 then combined with low molecular weight ethanolamine (SRL, purity > 99%) in the ratio of 0.5 g/ml. The solution is continuously agitated using a magnetic stirrer and allowed to dissolve for three days in argon atmosphere inside the glove box (VAC, USA) to avoid oxide formation until a clear orange and light brown solutions of As_2S_3 and As_2Se_3 are formed respectively with no precipitation. The solutions are then centrifuged at 3000 rpm for 5 min to remove any suspended particulates or non-dissolved impurities. The centrifuged solution is filtered using a 5 ml piston which contains a filter of 200 nm on top to remove any precipitates. For electrical measurements the solution is filled in between the indium electrodes using a micropipette. The thickness of the film deposited between electrodes is found to be ~1–2 μm. These electrodes are prepared by thermal evaporation technique. For optical measurements, the solution is deposited onto pre cleaned silicon/glass substrates using spin coater unit (Ducom, India) for further characterization. Deposited films are soft baked at 70 °C for 1 h and hard baked at 150 °C for 2 h to evaporate organic solvent residuals present in prepared thin films, using a hot plate.

2.2.2. Thermally deposited films

For thermal evaporation method of thin film preparation, the glass substrates (2.54 cm × 2 cm) are cleaned properly and washed with deionized water. Before depositing the chalcogenide sample, indium is deposited by thermal deposition method onto the glass substrate which serves as an electrode. An electrode gap of about 0.50 mm is created on the substrate by covering with a wire, while deposition process. Again, films of glassy As_2S_3 and As_2Se_3 are deposited in between these electrodes by covering the electrode properly. The deposition rate of the films was ~10 nm/s and the pressure is maintained about 2×10^{-6} Torr throughout the process. The substrate holder is set to be rotated at frequency 3 Hz during the deposition to produce uniform films. Thickness of the films are measured by using a single crystal thickness monitor and found to be in the range of ~1–2 μm. The amorphous nature of the samples is checked by using Regaku X-ray diffractometer with $\lambda = 1.54$ Å ($CuK\alpha_1$) and structural analysis is done using Raman (WiTec CRM 2000 Raman spectrometer). For electrical measurements, of the films having geometry (length ~2 cm, electrode gaps 0.5 mm and thickness ~1–2 μm) a DC voltage of 1.5 V is applied across the sample and the resulting current measured by a Keithley electrometer (6514). DC conductivity is carried out in a specially designed metallic sample holder with pressure 10^{-3} Torr. The temperature of the film is controlled by mounting a heater below the sample and measured by calibrated copper-constantan thermocouple above the film. The error in conductivity measurements is <1%. For optical measurements, thin films of bulk As_2S_3 and As_2Se_3 are deposited on glass substrate with same deposition parameters as mentioned above and optical parameters of these films are carried out by using UV/Vis spectrophotometer (Model: Camspec M550 double beam) in the spectral wavelength range of 190–1100 nm.

3. Results and discussions

3.1. Structural and compositional analysis

The amorphous nature of prepared bulk/thin film is confirmed by X-Ray diffraction technique. In this set up a copper target is used as an X-ray source of wavelength 1.54 Å ($CuK\alpha1$); 2θ spectrum from 10° to 90° is recorded with a scan speed of 2°/min and chart speed of 1 cm/min. It is evident from Fig. 1(a) and (b) that there are no sharp diffraction peaks in the X-Ray spectrum for both thermally deposited and spin coated films of As_2S_3 and As_2Se_3 films which conforms the amorphous nature of the films.

Fig. 2(a) and (b) represents the micro- Raman spectra of As_2S_3 and As_2Se_3 films respectively. As seen in the Fig. 1(a) there is a clear shift in

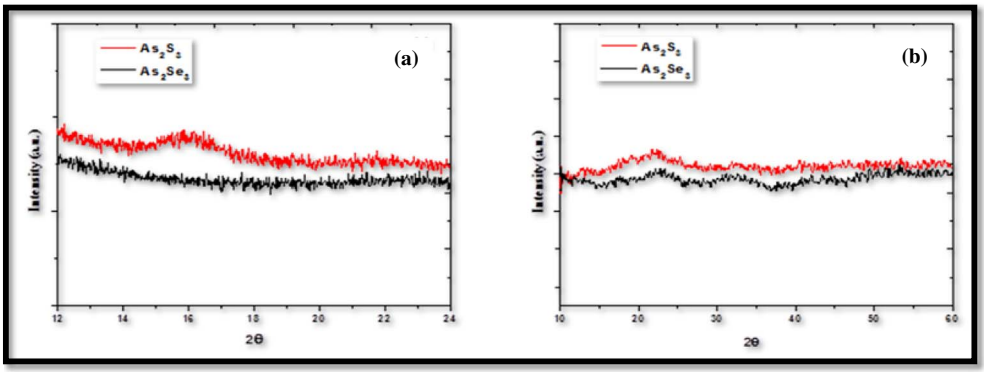

Fig. 1. XRD patterns of As_2S_3 and As_2Se_3 Thin film by (a) Thermally deposited (b) Spin coated.