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Growth of stoichiometric indium sulfide films by thermal evaporation: Influence of vacuum annealing on structural and physical properties

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ABSTRACT

The paper describes studies on the compositional, structural and optical characteristics of indium sulfide films deposited by thermal evaporation of chemically synthesized indium sulfide powders and subsequently annealed in vacuum in 523–773 K temperature range. Rutherford backscattering spectrometry measurements and depth profiling of sulfur by $^{32}S(p, p'\gamma)^{32}S$ nuclear resonance reaction analysis show that the pristine films possess the nominal atomic composition of indium sulfide (In_2S_3) which remains invariant during vacuum annealing. The pristine as well as vacuum annealed films do not possess, as measured by $^{16}O(\alpha, \alpha)^{16}O$ resonant scattering, any detectable oxygen contamination. The pristine films are amorphous but crystallize into β-In_2S_3 (tetragonal) phase on annealing. The pristine films and those annealed at high temperatures (>673 K) exhibit about 65% transmission in visible region. These films are characterized by both indirect and direct band gaps which increase with increase in annealing temperature. The band gaps lie in 1.9–2.2 eV and 2.6–3.3 eV regions respectively. The electrical resistivity of the pristine films is about 5×10^5 Ω.cm which decreases by about an order of magnitude on annealing in vacuum in the 523–623 K region. It, however, increases with subsequent increase in annealing temperature. The structural and the physical properties of the films are explained in terms of the defective spinel structure of β-In_2S_3 and the inclusion of Na (from the glass substrate) into the lattice of In_2S_3 at higher annealing temperatures.

1. Introduction

Indium sulfide (In_2S_3), an n-type III–VI compound semiconductor, has attracted numerous investigations in recent years due to its interesting optical, electronic and structural properties. It possesses a fairly large (2–3 eV) band gap (E_g), exhibits high optical transmission (~70%) in visible region and has a defective structure, amenable to doping by cations as well as anions. As a result, thin films of In_2S_3 are eminently suitable for the fabrication of optoelectronic and photovoltaic devices [1–3]. Furthermore, In is chemically non-toxic which makes In_2S_3 one of the main contenders for the replacement of n-type CdS layer in polycrystalline heterojunction thin film solar cells.

Preparation of homogeneous and stoichiometric films of a material is the first and foremost step for a substantial realization of its potential. Accordingly, films of indium sulfide have been prepared by a number of chemical and physical techniques. Chemical bath deposition (CBD), successive ionic adsorption and reaction and chemical spray pyrolysis are some of the prominent chemical techniques used for their deposition [4–6]. Among physical techniques, thermal evaporation has been used more frequently [7–11]. The simplicity of approach and the possibility of large area deposition are the two main merits of chemical techniques. However, these films often exhibit significant In or S deficiency, contain fairly large concentration of oxygen and possess poor crystallinity. These films also tend to be non-uniform and rough. Physical methods are, in general, techniques of choice for the deposition of good quality films since they offer better control over composition, morphology and impurities. However, there are several instances wherein indium sulfide films prepared by physical methods also possess, albeit to a lesser extent, nonstoichiometric composition, oxygen impurity and secondary phases. For example, the films prepared by Revathi et al. through thermal evaporation of indium sulfide powder were significantly deficient in sulfur [7]. Moreover in another study by the same authors the atomic ratio of S to In (N_S:N_{In}) in the films, depending on thickness that ranged from 1000 Å to 7000 Å, varied from 0.95:1 to 1.46:1 [8]. Interestingly, the indium sulfide powder used for evaporation contained S and In in a 1:1 atomic ratio. Similarly, films prepared by Timoumi et al. through the same technique also exhibited S deficiency (N_S:N_{In} = 1.06:1) [10,11]. The films, in addition, were not well crystallized and contained In_6S_7 as an impurity phase. It is important to note that no specific attempts were made to probe the presence of oxygen in these studies. Sulfur deficiency as well as significant oxygen contamination were also observed in films prepared by solid state reaction among stacked layers of In and S grown alternatively by thermal evaporation [9]. The preparation of stoichiometric films by this method requires a precise control over the deposition parameters in view of the facts that In and S

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have significantly different vapor pressures and the metallic In films grown by thermal evaporation exhibit pronounced roughness. Nonetheless, non-stoichiometry and/or the presence of impurity elements or phases can bring about substantial modifications in the electrical properties of indium sulfide films. For example, cationic and anionic vacancies can serve as acceptors and donors respectively while oxygen, prevailing in grain boundary regions, gives rise to electron trapping surface states.

In this paper we report on the preparation of indium sulfide films that are compositionally stoichiometric, possess good crystallinity and are devoid of oxygen and secondary phases. The films are grown by the thermal evaporation of indium sulfide powders and are subsequently annealed in vacuum to introduce crystallinity. An important aspect of the present study is that the composition of the films has been determined by ion beam analysis (IBA) techniques namely Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA). These techniques not only provide average atomic composition but also the depth distribution of In and S across the films non-destructively. This obviates the uncertainties and compositional variations encountered during depth profiling using sputter etching as a means of layer removal.

2. Experimental details

2.1. Deposition and vacuum annealing of films

The In_2S_3 powder used as the evaporant was synthesized chemically by precipitation method using sodium sulfide ($Na_2S\cdot xH_2O$) as the precipitating agent. As the water of crystallization associated with Na_2S was not known precisely, the salt was first analyzed for its Na(S) content in order to prepare a solution of known sulfide concentration. The precipitation was carried out by adding about 20% excess of sulfide solution to that of metal ion (pH ~ 4) obtained by dissolving In metal in hydrochloric acid. The precipitate was filtered, washed copiously with water and dried at ~ 403 K under the flow of Ar gas. Analysis of the resulting powder by energy dispersive X-ray spectroscopy (EDS) showed that (a) N_S:N_{In} in the powder was ~ 1.5:1, (b) it did not contain any detectable amount of oxygen and (c) about 3 at.% Na, attributable to the precipitating agent, was present as an impurity.

Indium sulfide films were deposited at a rate of ~ 1 Å/s on soda lime glass as well as Si substrates at 1.3×10^{-4} Pa vacuum by resistively-heating In_2S_3 powder held in a Mo-boat in a thermal evaporation unit. The rate of deposition was measured by a quartz crystal monitor. Prior to the depositions, the substrates were initially cleaned ultrasonically in isopropanol, mounted on a platen and subsequently sputter etched in situ in Ar plasma created at about 1000 V in the deposition chamber. The distance from Mo-boat to the platen was about 70 mm. The platen rotated at 25 rpm during depositions. Though the substrates were not intentionally heated, their temperature rose to about 323 K during deposition. Films of two different thicknesses (~ 2900 and 5500 Å) were deposited. The thicknesses of the films were determined by RBS measurements. Several films of a particular thickness were deposited in a run. The variation in the thickness of such films is about 5%. It was ascertained by analyzing a few films selected randomly. It is to be noted that RBS provides the areal densities (atoms/cm^2) of the films. The precise thickness of a film in linear dimensions depends on its density. Presently, the thicknesses were deduced from the measured areal densities by assuming the film density to be 4.9×10^3 kg/m^3. Subsequent to their deposition the films were annealed in vacuum in a quartz tubular furnace in the 523–773 K temperature range for the duration of 2, 4 or 6 h. The vacuum during annealing, created by a turbomolecular pump was better than 6.6×10^{-3} Pa. The pristine and differently processed films were stored in the static vacuum of a rotary pump for their characterization.

2.2. Structural, compositional and optical characterization

2.2.1. Glancing incidence X-ray diffraction measurements

The crystallinity and phase evolution in the films were examined by a Rigaku (Ultima IV) diffractometer in glancing incidence (angle, 0.5°) configuration using Cu K_α radiation ($\lambda = 1.5402$ Å). The lattice parameters a and c for the tetragonal β-In_2S_3 structure were calculated from the recorded diffraction patterns by the relation

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l}{c^2} \tag{1}$$

where d is the interplanar spacing determined using the Bragg's equation and h, k and l are the Miller indices of the lattice planes.

2.2.2. Compositional analysis by ion beam analysis

Two IBA methodologies, backscattering spectrometry (BS) and NRA, were employed to determine the atomic composition of the films. Conventional RBS measurements were carried out to determine N_S:N_{In} in the films. It was performed using 2.0 MeV α-particles. Since the sensitivity of conventional RBS towards oxygen is rather low, $^{16}O(\alpha, \alpha)^{16}O$ resonant scattering that exhibits a resonance at 3.034 MeV was used to ascertain the content of oxygen [12]. The resonance, attributable to nuclear (non-Rutherford) scattering, is strong (~ 730 mb/sr) and sharp (full width at half maximum = 10 keV) and therefore facilitates depth profiling of oxygen with good sensitivity (<1 at.%) and depth resolution (~ 250 Å). The measurement at incident beam energy (E_α) of 3.034 MeV provides the analysis of oxygen in top surface regions while the one at a higher energy (>3.034 MeV), at a depth governed by energy loss-stopping power relationship. Incidentally, these measurements also provide the determination of N_S:N_{In} in the films with the backscattering cross-sections of In and S being Rutherford in nature. Since depth profiling by this technique across the thickness of all the films is tedious, most of the measurements were performed only at 3.039 MeV, though certain films were probed with 3.055 MeV ion beam as well.

In order to assess the overall content of oxygen with greater rapidity, all the films were analyzed by $^{18}O(p, \alpha)^{15}N$ nuclear reaction using 730 keV proton beam [12]. It is to be noted that the excitation function of the reaction exhibits a plateau at 730 keV that can be used to measure the overall content of oxygen in films with a detection sensitivity of 1×10^{16} atoms/cm^2. To avoid any interference from the oxygen of glass substrates, the films deposited on Si were examined by this technique. Meanwhile, nuclear resonance reaction analysis involving $^{32}S(p, p'\gamma)^{32}S$ (resonance energy, $E_r =$ 3.079 MeV) was employed to determine the depth profile of S across the films [13].

The IBA measurements were carried out using the 3 MV Tandetron (HVEE, Europa) at the centre. The vacuum in the scattering chamber during IBA experiments was better than 6.6×10^{-3} Pa. In BS measurements a well collimated beam (~ 10 nA current, 1.5 mm diameter) of He^+ particles of requisite energy (2.0 MeV for RBS, and 3.039 and 3.055 MeV for resonant scattering) bombarded the specimens at normal incidence. The backscattered particles were detected by a Si surface barrier detector (SBD) positioned at backward angle of 170° subtending a solid angle of about 1×10^{-3} sr. In experiments involving $^{18}O(p, \alpha)^{15}N$ nuclear reaction, the films were irradiated with 730 keV proton beam (~ 300 nA current, 2 mm diameter) and the α-ejectiles were detected by a 300 mm^2 SBD located at an angle of 160°. A 10 μm Mylar foil was used as a filter to prevent backscattered protons from entering the detector. The experimental set-up used for depth profiling sulfur by $^{32}S(p, p'\gamma)^{32}S$ reaction are described in detail in reference [14]. Briefly, the experiments involved the irradiation of films with proton beams of energies > 3.079 MeV and 2230 keV γ-rays, characteristic of the reaction, were measured by a high purity germanium detector placed along the direction of the beam.