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Thin Solid Films 480–481 (2005) 133–137

thin solid films

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Optoelectronical properties of indium sulfide thin films prepared by spray pyrolysis for photovoltaic applications

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Available online 8 March 2005

Abstract

Indium sulfide (In_2S_3) thin films have been prepared by the spray pyrolysis (SP) technique using indium acetate and *N-N* dimethyl thiourea as precursor compounds. Samples prepared at different temperatures and atomic ratio of In to S in the starting solution, $(In/S)_{sol}$, have been characterized using several techniques. X-ray diffraction studies have shown that the preparation temperature (T_p) affects the crystallinity of the deposited materials as well as the optoelectronic properties. For $(In/S)_{sol}$=1/8, the optical band gap (E_g) increases from 2.2 up to 2.67 eV when T_p increases from 250 up to 450 °C. For $(In/S)_{sol}$=1 and T_p=450 °C, the deposited material shows *n*-type electrical conductivity with a dark value of 1 $(\Omega cm)^{-1}$, and E_g=2.04 eV. The In_2S_3 thin films prepared under these conditions have a big potential use as a window material for photovoltaic heterojunction devices.

Keywords: Indium sulfide; Spray pyrolysis; Solar cell

1. Introduction

It is well known that the actual technology for solar cells based on a single crystal Si has reached a mature state. However, in some cases, the involved costs for getting higher efficiencies are too high to use the devices for terrestrial applications. Thus, it is commonly accepted that a high-efficient thin film solar cell, prepared with a simple technology and in large-scale mass-production, could be an alternative to reduce the involved costs in the fabrication process. These ideas support the fact that thin film research is an essential matter in photovoltaic development.

There are a number of techniques that can be used to prepare thin film materials [1,2]. Among of them, spray pyrolysis (SP) is a technique that meets the requirements looking for technologies involved in the manufacturing process for solar cells devices. Many materials have been deposited by this technique, including insulators and semiconductors [3].

Some of the metal chalcogenide materials have optoelectronic properties that suggest its use in photovoltaic structures [4]. A great number of research works have been done on these kinds of materials, especially those that can be prepared by "soft" techniques like SP [2] and chemical bath deposition [5]. Among them, the compounds based on the binary system In–S can be cited. They have received a lot of attention for their potential in optoelectronic device applications, especially in solar cells, which is the case of In_2S_3. With optimal physical properties, the semiconductor material In_2S_3 can meet the requirements to be used as a window material or buffer layer for photovoltaic structures [6].

Indium sulfide (In_2S_3) is a crystalline compound that exists in four allotropic forms, depending on temperature and pressure: ϵ, α, β, and γ [7]. The beta phase (β-In_2S_3), with a tetragonal structure, has shown to be stable up to 693 K. The In_2S_3 thin films have been prepared by several techniques (see for instance the description presented in

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0040-6090/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.tsf.2004.11.046

short by L. Bhira et al. [8] and the recent description done by T.T. John et al. [9]). Among them, SP has been chosen by several authors due to its simplicity and versatility to prepare semiconductor materials. It has been found that In_2S_3 thin films prepared by the SP technique show optoelectronic properties whose values depend on the deposition parameters. By controlling the deposition parameters, In_2S_3 thin films could be produced with optimized optoelectronic properties.

Most of the research work on In_2S_3 prepared by SP has been carried out by using $InCl_3$ and thiourea as starting materials. However, Cl from the In precursor could unintentionally dope the material being deposited, thus affecting its electrical properties. For this reason, we have chosen indium acetate as the source compound to grow In_2S_3 thin films by the SP technique. This work deals with the deposition and characterization of In_2S_3 thin films prepared from indium acetate and *N*-*N* dimethyl thiourea as precursor compounds using different preparation temperatures (T_p) and atomic ratio of In to S in the starting solution, $(In/S)_{sol}$.

2. Experimental details

Indium acetate [In $(CH_3CO_2)_2$] and *N*-*N* dimethyl thiourea ($CH_3NHCSNHCH_3$) were used as precursor materials to grow In−S-based compounds. A mixture of ethyl alcohol and osmosis inverse-treated water at a 3:1 ratio was chosen as the solvent to dilute the precursor compounds. After a careful screening, it was found that the maximum allowed molar concentrations for both starting materials were 0.025 and 0.5 for indium acetate and *N*-*N* dimethyl thiourea, respectively, if they are to be dissolved in the same solvent. With these values, the $(In/S)_{sol}$ was selected and varied using the molar concentrations of indium acetate to *N*-*N* dimethyl thiourea ratio. Regardless of the $(In/S)_{sol}$ selected, acetic acid in a 1/10 ratio was added to the starting solution in order to avoid the formation of precipitate compounds, mainly indium hydroxide. Borosilicate microscope glass slides from Corning, with dimensions of 1.25 cm×2.5 cm, were used as substrates. The substrates were cleaned using standard procedures.

The spray pyrolysis setup is described in Ref. [10]. Air at a pressure of 4 Pa was used as carrier gas. The gas and solution flow rate were kept constant at 10 l/min and 5 ml/min, respectively, in all the cases. The substrate-to-nozzle distance was 30 cm.

The substrates were heated using a tin bath. The temperature was measured by having a thermocouple in contact with the bottom face of the substrate and regulated. The temperature of the bath, called the preparation temperature, T_p, was varied from 250 to 450 °C in steps of 50 °C.

In order to determine the dependence of the deposition rate for each $(In/S)_{sol}$ selected from T_p, film depositions up to 10 min were made. Knowing the thin film deposition rate, a thickness of ≈0.1 μm was selected for characterization purposes and to understand the role of $(In/S)_{sol}$ and T_p.

The thickness of the deposited thin films was measured with an Alpha Step model 100 profilometer from Tencor Instruments. The structural properties were determined by X-ray diffraction (XRD) measurements using a Siemens D-500 diffractometer with Cu Kα1 radiation (λ=1.5406 Å). The average dimension of the crystallites was determined by the well-known Scherrer method. The surface morphology was studied by scanning electron microscopy (SEM) using a Cambrigde–Leica Stereoscan 440 SEM equipment. The film composition was determined by energy dispersive spectroscopy (EDS) using an Oxford system detector attached to the scanning electron microscope.

The optical transmittance at normal incidence, $T(\lambda)$, and specular reflectance, $R(\lambda)$, of the deposited thin films were measured with a double-beam spectrophotometer Shimadzu model 3101PC in the UV-VIS-NIR region. From these data, the absorption coefficient (α) was calculated, and from its dependence on the photon energy ($h\nu$), the optical band gap (E_g) was determined.

For the electrical measurements, four indium strips (each one 1.25-cm long and 0.1-cm wide, with a separation of 0.1 cm between them) were deposited by thermal evaporation. Electrical contacts were made to these strips to measure the current–voltage (*IV*) characteristics at room temperature. The ohmicity between the evaporated metal contacts and the deposited material was tested in the range of ±1 V at room temperature. In all cases, the In–In_2S_3 contact was found to be of the Ohmic nature. The electrical conductivity in the dark, σ_D, was measured using the well-known Van der Pauw technique [11]. The electrical conductivity of the samples under light, σ_L, was measured by the DC two-point probe method, using a 70 mW/cm^2 white light tungsten–halogen lamp. The electrical conductivity type was determined using the "hot point probe" technique [11].

3. Results and discussion

In order to know the effect of T_p on the physical properties of the deposited material, a solution containing 0.00625M of indium acetate and 0.05M of *N*-*N* dimethyl thiourea, resulting in $(In/S)_{sol}$=1/8, was selected. The deposited thin films were found to be uniform for all T_p investigated. Under these conditions, the growth rate, crystal structure, optical characteristics, and σ_D were studied as a function of T_p.

The results from EDS analysis carried out on the deposited material are shown in Table 1. According to these results, the composition of the as-deposited thin films corresponds to those of the compound In_2S_3.

Fig. 1 shows the XRD patterns for typical thin films with similar thicknesses (≈0.1 μm) deposited under the selected