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Comprehensive optical studies on SnS layers synthesized by chemical bath deposition

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ABSTRACT

A simple non-vacuum and cost effective wet chemical technique, chemical bath deposition was used to prepare tin sulphide (SnS) layers on glass substrates. The layers were formed by varying bath temperature in the range, 40–80 °C, keeping other deposition parameters as constant. An exhaustive investigation on their optical properties with bath temperature was made using the transmittance and reflectance measurements. The absorption coefficient was evaluated from the optical transmittance data utilizing Lambert's principle and is $>10^4$ cm^{-1} for all the as-prepared layers. The energy band gap of the layers was determined from the differential reflectance spectra that varied from 1.41 eV to 1.30 eV. Consequently, refractive index and extinction coefficient were obtained from Pankov relations and dispersion constants were calculated using Wemple–Didomenico method. In addition, other optical parameters such as the optical conductivity, dielectric constants, dissipation factor, high frequency dielectric constant and relaxation time were also calculated. Finally electrical parameters such as resistivity, carrier mobility and carrier density of as-prepared layers were estimated using optical data. A detailed analysis of the dependence of all above mentioned parameters on bath temperature is reported and discussed for a clean understanding of electronic characteristics of SnS layers.

1. Introduction

Metal chalcogenides have great importance in the field of electronic contrivances, especially for sizably voluminous scale engenderment of inexpensive photovoltaic arrays. In metal chalcogenide family, tin sulphide (SnS) is a non-toxic, simple binary compound and contains earth abundant elements with easily controllable chemical stoichiometry and high chemical, environmental stability compared to Cu_2ZnSnS_4 and Cu_3SnS_4. It preferentially crystallizes in the layered orthorhombic structure, where each layer of S and Sn atoms are bonded by weak van der Waals forces, with the space group D_{16}^{2h} Pnma [1]. It has direct optical energy band gap, which varied in the range, 1.2–1.5 eV with an absorption coefficient $>10^4$ cm^{-1} [2]. It shows p-type electrical conductivity [3] with hole concentration in the range of 10^{15}–10^{18} cm^{-3} with controllable electrical conductivity using appropriate doping. Owing to its optimum characteristics, SnS is treated as a potentially important absorber for heterojunction solar cells.

Many papers have been published in literature on the deposition of SnS layers by several physical methods, followed by characterization to study the various properties [4–9]. However, the utilization of complicated instrumentation, material wastage and high cost per surface area of deposition are the main disadvantages of physical methods. So there is a considerable interest in the deposition of films by wet chemical methods, specifically chemical bath deposition (CBD) which involves relatively low capital expense and is technically undemanding on the experimental side. So it is particularly important in the production of large area devices at low cost particularly for wider public acceptability of solar cells [10]. Furthermore, the consummate optical analyzation of such films is indispensable for more preponderant designing of heterojunction solar cells because only the optical properties give the information to understand of their electronic properties and band structures. Many researchers studied the optical properties of SnS films, however they analyzed only the transmittance, reflectance and absorbance properties including the determination of energy band gap value. This analyzation was extended to finding of refractive index, extinction coefficient, dielectric constants and other optical

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parameters by El-Nahass et al. [11], Ahmed [12], Koteeswara Reddy et al. [13], Nwofe et al. [14], Shama et al. [15], Hashem et al. [16], Selim et al. [17], Mariappan et al. [18] and Patel et al. [19] in case of thermally evaporated, electrodeposited and sprayed SnS films with respect to the deposition conditions. In case of chemical bath deposition, optical properties and other related parameters were demonstrated by Turan et al. [20] and Akkari et al. [21]. To our knowledge, the previous reports were not able to systematically and comprehensively analyze the optical characteristics of chemically deposited SnS layers to estimate dispersion constants, optical conductivity, dissipation factor, high frequency dielectric constant and relaxation time in addition to the electrical parameters such as resistivity, carrier mobility and density using optical data. It is therefore recognized that such a detailed study on the optical properties and estimation of opto-electrical constants of chemically deposited SnS layers are very much essential for finding the suitability of these layers for solar cell fabrication.

Hence, in the present investigation, SnS layers were grown on Corning 7059 glass substrates using CBD by varying the bath temperature (T_b). The layers were prepared using environmental friendly complexing agent 'tartaric acid' instead of other commonly used reagents for the first time. Optical characteristics including the opto-electrical constants of as-prepared layers were analyzed using transmittance and reflectance measurements and discussed in relation to bath temperature.

2. Experimental

2.1. Reagents

Analytical grade stannous chloride ($SnCl_2{\cdot}2H_2O$) and thioacetimide (C_2H_5NS) were used as source materials for Sn and S ions respectively and tartaric acid ($C_4H_6O_6$) as the complexing agent for the formation of SnS layers.

2.2. Formation of SnS layers

At first, 20 ml of stannous chloride and thioacetimide were prepared discretely using distilled water as a solvent such that precursor ratio of S/Sn was maintained as 6. The bath used for the layer deposition is a mixture of 20 ml of stannous chloride, 20 ml of thioacetamide and 1M of tartaric acid followed by sufficient quantity of double distilled water to make up total volume of the bath as 100 ml in a glass beaker. The pH of the total solution was maintained as 1.5. The total bath set up was kept on the magnetic stirrer, which has a facility to control the bath temperature. Ultrasonically cleaned corning 7059 glass substrates were immersed vertically into the reaction bath. In the initial stage, the color of solution was light brown that turned into dark brown at the final stage of layer deposition. The deposition carried out for 50 min and the bath temperature (T_b) varied in the range, 40–80 °C, keeping the other parameters constant. The deposited layers were cleaned using distilled water and dried in a hot air oven. The grown layers were uniform, pinhole free, well adherent and appear tenebrous brown in colour.

2.3. Growth mechanism in the formation of SnS layers

The physical properties of the grown layers on the substrate were affected by the chemistry of the solution bath. Particularly nucleation and growth of the layers changed due to the degree of supersaturation, interfacial energy and the strength of coordination bonds of the complexing agents. So it is highly essential to know the actual mechanism taking place in the solution to control the characteristics of the deposited layers. In the present work, SnS layers can be obtained from an aqueous bath containing Sn, S salts and a suitable complexing agent (tartaric acid), which allows to control the Sn^{2+} concentration and to have a soluble species of Sn^{2+} in aqueous medium. The deposition process is based on the slow release of Sn^{2+} and S^{2-} ions in the solution, which then condense on an ion-by-ion basis on the substrates that are suitably mounted in the solution. The deposition of SnS occurs when the ionic product of Sn^{2+} and S^{2-} exceeds the solubility product of SnS. The possible growth mechanism of the layers is discussed below using the stability of metal complexes and classical nucleation theory.

In an aqueous acid solution bath, thioacetamide undergoes the following reaction [22],

$$CH_3CSNH_2 + H_2O \leftrightarrow CH_3CONH_2 + H_2S \quad (1)$$

When the reaction undergoes equilibrium condition [23],

$$H_2S + H_2O \leftrightarrow H_3O^+ + HS^- \quad (K_0 = 10^{-7}) \quad (2)$$

$$HS^- + H_2O \leftrightarrow H_3O^+ + S^{-2} \quad (K_1 = 10^{-17}) \quad (3)$$

It is clear from the former reaction sequence and their equilibrium constants that the predominant species in the solution will be the HS^- ions, while the S^{2-} ion concentration will be kept low. The concentration of S^{2-} species can be increased by addition of excessive hydroxide ion to facilitate the forward reaction.

With the addition of tartaric acid (TA), Sn^{2+} ion in the Sn-salt can be complexed as,

$$SnCl_2 + TA \leftrightarrow [Sn(TA)]^{2+} + Cl^{2-} \quad (4)$$

The complex ions slowly release free Sn^{2+} ions in a controlled way. These Sn^{2+} ions react with S^{2-} arising out of hydrolysis of thioacetamide forming SnS. The reaction is given by,

$$[Sn(TA)]^{2+} + S^{2-} \rightarrow SnS + TA \quad (5)$$

The reaction represented in Eq. (5) is the growth condition for formation of SnS layers.

3. Results and discussion

The optical transmittance (T) and reflectance (R) quantifications of SnS layers grown at different bath temperatures varying in the range, 40–80 °C were carried out using UV–Vis–NIR spectrophotometer in the wavelength range, 300–2500 nm. The measurements revealed that all the grown layers had a direct optical transition and showed an average optical transmittance of approximately 60–70% and a reflectance of <20% above the fundamental absorption edge. Using these T and R measurements, the entire optical nature of as-prepared layers was analyzed and given below.

3.1. Optical absorption coefficient (α)

The dependence of absorption coefficient, 'α' on the photon energy, '$h\nu$' gives the information regarding the type of optical transition occurred between the valence band and conduction band of the sample. When the envelope method is not valid as the region was interference free then α in the strong absorption region was evaluated from the optical transmittance data using Lambert's principle [24],

$$\alpha = \frac{-\ln(T)}{t} \quad (6)$$

where t = thickness of the layer. Fig. 1 shows the plots of absorption coefficient versus photon energy. The plots showed that the absorption edge was found to shift towards the longer wavelength side as the bath temperature increased from 40 °C to 70 °C and with further increase of bath temperature to 80 °C, it showed a small blue shift.