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Research Paper

The Influence of Substrate Preparation Conditions on the Raman Spectra of In_2S_3 Thin Films Made by Physical Vapor Deposition

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Abstract:

In this paper, we employed Raman spectroscopy to investigate Indium sulfide thin layer films deposited on glass substrates using the PVD method. The results showed that the bandwidth and Raman shift of different In_2S_3 thin films depended on the annealing temperature. In addition, the crystallization stage from tetragonal to cubic occurred at the excessive temperature range of 350-400 °C. The Raman spectroscopy of the In_2S_3 thin films before annealing and at 300 °C indicated the existence of β- In_2S_3 at 70, 166 and 281 cm^{-1} in the active modes of the spectra. New modes that were related to α-In_2S_3 appeared at 126, 244, and 266 cm^{-1} after thermal treatment at 400 °C for 30 and 60 min. Our results are in agreement with the phase transitions observed from the XRD analysis of In_2S_3 thin films. There are few reports about the Raman spectroscopy of In_2S_3 thin layer films deposited using vacuum thermal evaporation. In the present paper, the Raman spectra of In_2S_3 thin films with different thicknesses as well as the effects of temperature on their depositions in vacuum were examined.

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1. INTRODUCTION

World warming and lose of energy are major challenges now. We should use renewable energy instead of fossil fuels. Solar cell technology is one of best solution for this challenges [1]. In_2S_3 thin film layer has been known and used as buffer layer in CIGS solar cells and physical properties of them was studied [2].

Increasing the thickness of the absorber layer of CIGS has a direct relative with increase of amount of current and voltage and cell efficiency [3].

In_2S_3 thin films supply a buffer layer and an active absorption medium in a novel kind of solar cells which are named 'intermediate band solar cells'[4]. Raman scattering is a technique widely used for the analysis of thin film layers. Raman spectroscopy is employed for describing In_2S_3 films made by various techniques including chemical spray pyrolysis, chemical spray pyrolysis (CSP), co-evaporation, electro-chemical deposition, CVD, atomic coating methods, photo chemical deposition, and flash evaporation [5-12]. Studies and experimental results show that band gap energy is related with the annealing temperature [13]. Since Raman spectroscopy is an indicator for determining the crystalline quality of the material as well as the atom location in the crystal lattice, it is very useful for examining the crystalline disorder. On the other hand, the Raman spectra also contain valuable information about the second phase, pulled lattice duplications, and the chemical composition. Raman scattering is a valuable assessment tool to due to its high sensitivity. There are few studies on the Raman spectroscopy of the In_2S_3 thin films deposited with different preparation conditions. Therefore, the study of In_2S_3 crystal using Raman spectroscopy is of practical importance.

2. MATERIALS AND METHODS

In the present study, Raman spectroscopy was employed to investigate the microstructure of In_2S_3 thin films. In_2S_3 has a crystalloid spinel-type structure with three modifications. β-In_2S_3 is a spinel-type structure with a tetragonal phase and is stable at room temperature, α-In_2S_3 has a transition temperature of about 420 °C and is a cubic structure, and γ-In_2S_3 which is stable at the temperatures of above 754 °C and is a trigonal phase [14-16]. In_2S_3 possesses an optical band gap which is often between 2.0 and 2.20 ev. However, it might rise up to 2.95 ev, for instance, when it is doped with sodium or oxygen. In improving In_2S_3 thin films, the preparation conditions and temperature performance are of importance [17-19].

Here, using the vacuum method, the thermal deposition of In_2S_3 thin films was studied to materialize our expectations of solar cells.

Among buffer layer candidates, In_2S_3 has the potential to be used as a suitable buffer layer in CIGS solar cells with high efficiency [20].

Thermal evaporation was employed to deposit In_2S_3 thin films with different thicknesses on glass substrates. The annealing on the films deposited in vacuum was done at 330 °C and 400 °C for 30 and 60 min.

We systematically investigated the quality of the source material with respect to grain size, pollution, stoichiometry, crystallization, and evaporation behavior.

We also examined the effects of stability and the quality of the source material on the growth of In_2S_3 layer and its characteristics using different optical and surface crystallographic techniques. These results are related to the operation of Cu (In, Ga) Se_2 solar cells built using an In_2S_3 buffer layer. These findings include the analysis of quantum efficiencies and JV curves of solar cells built using various CIGS absorbers. The current-voltage curve is one of the most important outputs used for the solar cells [21].

A post thermal treatment step was performed in the air. Afterward, the finest cells obtained a standard efficiency of 15.2% with a considerably high F.F. (75.6%) and an OC voltage (677 mv).

In this paper, the optical properties, the structural dependence, and spectral characteristics of In_2S_3 thin films were examined in various deposition conditions. Moreover, optical absorption and Raman scattering are among the reliable methods for the analysis and non-destructive testing of the framework of thin films. Differently put, these methods are reliable for obtaining information about the characteristics of new thin films which could be used in optoelectronic devices.

3. RESULTS AND DISCUSSION

The tetragonal phase of In_2S_3 is stable at room temperature with a I41/αmd-D194h space group which includes 16 molecules in the unit cell. The group theory analysis provides the subsequent forecasts for the Raman- and infrared-active tetragonal In_2S_3 phases which are at the center of the Brillouin region [22]:

$$\Gamma IR = 10A2u + 16Eu \quad (1)$$

$$\Gamma R = 9A1g + 9B1g + 4B2g + 14E \quad (2)$$

Stable α-In_2S_3 samples can be obtained at standard temperature when a surplus of In atoms is added to the same fabrication method as for β-In_2S_3. It is largely introduced to the structure of cubic spinel cells to determine the number of lattice vibrations. Using the following equation, we can obtain the all number of vibration trends at the center of the Brillouin region which is defined by the clear description of the point group Oh [23]:

$$\Gamma = A1g + Eg + 3F2g + 5F1u + 2A2u + 2Eu + F1g + 2F2u \quad (3)$$

Since the unit cell contains two formula units of the cubic structure, it gives rise to the observed 24 phonon modes - Γ = A1 + 2A2 + 3B1 + 4V2 + 7E. Of these, 21 are optical modes - Γopt = A1 + 2A2 + 3B1 + 3B2 + 6E and three acoustic - Γak = B2 + E, of which only mode E is doubly degenerate. All optical modes, except for two 2A2 modes are Raman active. From these oscillations B2 and E modes are both infrared and active Raman, A1 and B1 only Raman active mode A2 is inactivity. The optical modes with symmetry A1 and A2 are associated with oscillations caused by displacement of the atoms of the anion and modes B1, B2 and E - cations. The most intense in the Raman spectra is In_2S_3 mode A1 due to vibrations of these anion (sulfur) for resting atoms cation (indium) [24, 25].

By employing a spectrometer SPECORD PC 210 UV-VIS at room temperature, the transmission Raman spectra In_2S_3 thin films with the thicknesses of 50, 470, and 1200 nanometer were acquired in the wavelength range of 500-2000 nanometer.

In Fig. 1, the Raman spectra of In_2S_3 thin films with a thickness of 1200 nm are measured before and after annealing in the temperature range of 330 °C up to 400 °C for 30 minutes and 60 minutes. They also demonstrate the low intensive modes related to the tetragonal structure at 95 and 131 cm^{-1} [22]. The Raman active modes at 70, 166, and 281 cm^{-1} showed the existence of a β-In_2S_3 defect spinel structure before and after annealing at 330 °C. The Raman spectra were used to observe some vibrations for β-In_2S_3 dendrites.

New modes appeared at 126, 244, and 266 cm^{-1} after annealing at 400 °C for 30 and 60 min. They belonged to α-In_2S_3. The annealing time and temperature certainly influenced the intensity and shape of the peaks. Table 1 lists the measured Raman modes of β-In_2S_3 and α-In_2S_3 in the wave number range of 0-400 cm^{-1}. Table 1 shows how thermal treatment affects the transition modes from α-In_2S_3 to β-In_2S_3 at temperatures of higher than 330 °C.

In Fig. 2, the Raman spectra of In_2S_3 thin films with a thickness of 50 nm are presented in the energy range of 0 to 500 cm^{-1} before and after thermal treatment. We calculated the temperature dependence of the Raman-active mode frequencies at 330 °C and 400 °C for 30 and 60 min. The Raman modes were broad and had a very low intensity before annealing. This confirmed their nanocrystalline or amorphous nature. The spectra changes were recorded (Fig. 2b) after thermal treatment at 330 °C. The active modes of β-In_2S_3 given at 290, 180, and 102 cm^{-1} verify the framework of the samples [26, 27]. The band at 480 cm^{-1} may belong

to the Raman spectra A1 mode of elemental S. It was observed that the intensity of the vibration substantially depends on the thermal annealing of the films. Low intensity modes at 266, 244, and 126 cm^{-1} belonging to α-In_2S_3 phase were observed at 400 °C [28]. To determine the modes precisely, a Gaussian analysis was employed as demonstrated in the inset of Fig. 2.

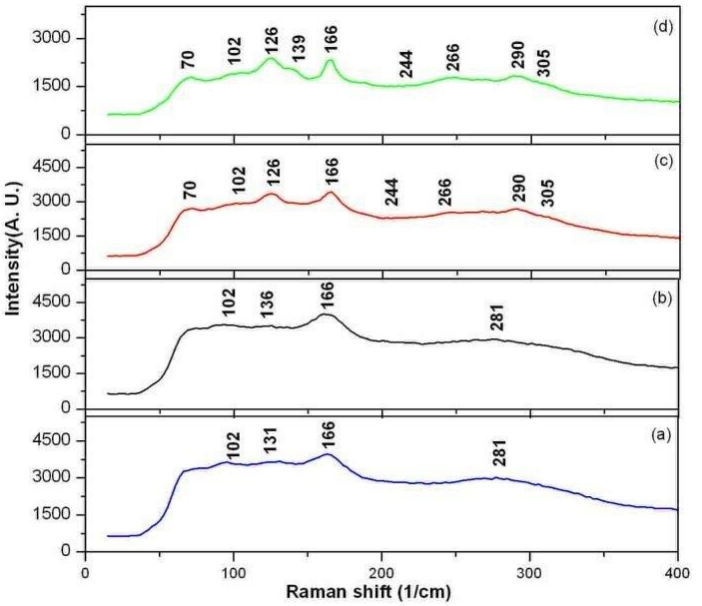

Fig. 1. The Raman spectra of In_2S_3 thin films with a thickness of 1200 (nm) (a) before annealing, (b) annealing at 330 °C for 60 min, (c) annealing at 400 °C for 30 min, and (d) annealing at 400 °C for 60 min

It is important to note that a rise in the sintering temperature increases the desired crystalline orientation of In_2S_3 thin films. It also improves the microstructure in the grain growth both parallel and perpendicular to the substrate.

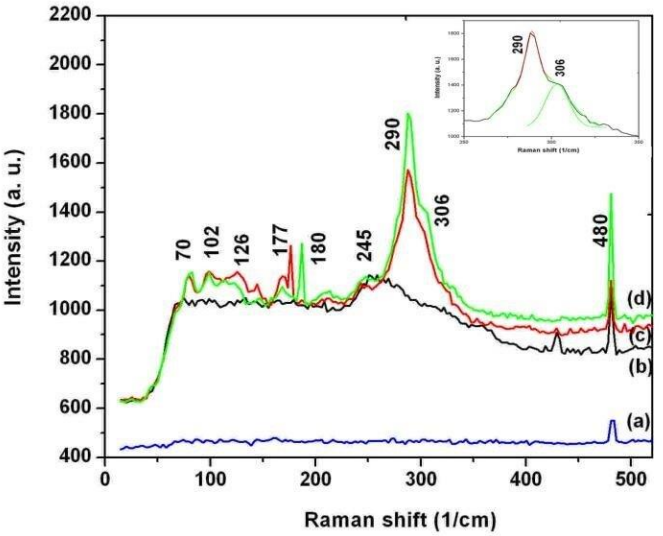

Fig. 2. The Raman spectra of In_2S_3 thin films (d=50 nm) (a) before thermal treatment, (b) annealing at 330 °C for 30 min, (c) annealing at 400 °C for 30 min, and (d) annealing at 400 °C for 60 min. Inset: The typical Gaussian function of the Raman modes (290 and 306 cm^{-1}).

Fig 3. exhibits the Raman spectra of In_2S_3 thin films. They had various thicknesses and were heated at 400 °C for 30 min in the spectral range of 0–500 cm^{-1}. The results of the present study demonstrate that 306, 245, and 126 cm^{-1} modes are symmetric [4]. It is recommended that the 305 cm^{-1} mode could originate from the existence of a β-In_2S_3 phase with A1 symmetry. We see the spectra of other Raman modes at 70, 124, 166, 266, and 305 cm^{-1}, respectively, because In_2S_3 phases are different in their crystalline framework. According to Table 1, we may assume that the intensive peak at 305 cm^{-1} is affected by the possible existence of cubic or tetragonal phases of In_2S_3, whereas the 124 cm^{-1} mode belongs to the α-In_2S_3 phase[27].

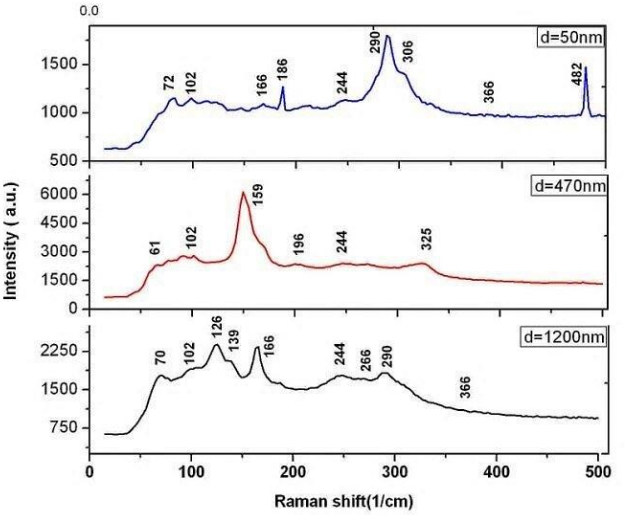

Fig. 3. The Raman spectra of In_2S_3 thin films with various thicknesses and annealed at 400 °C for 30 min.

4. CONCLUSIONS

In this paper, we employed Raman spectroscopy to investigate methodically Indium sulfide thin films deposited on glass substrates using the PVD method. Moreover, we invetisgated the impacts of annealing on the crystalline framework and phase composition of In_2S_3 films with different thicknesses. In this paper, the Raman spectra of In_2S_3 thin films showed all the vibration modes. The vibrational spectra of the studied films only showed the modes similar to the vibrations of a basic In_2S_3 compound. Other types of frequencies due to the existence of phases with various symmetries are unobservable.

The results of the XRD analysis and Raman spectroscopy showed that, at high temperatures, annealing modified the stractural phase from tetragonal to cubic [29,30].

TABLE I

The calculated Raman modes of β-In_2S_3 and α-In_2S_3 in the various wave number range of 0-400 cm^{-1} (with a thickness of 1200 nm) (a) before annealing, (b) annealing at T=330 °C for t=60 min, (c) annealing at T=400 °C for t=30 min, and (d) annealing at T=400 °C for t=60 min

Sample (a)	Sample (b)	Sample (c)	Sample (d)	Spinel $In_{21.33}S_{32}$	Tetragonal In_2S_3	Tetragonal In_2S_3	Cubic In_2S_3
102	70	70	70	179	132	42	245
131	102	102	102	245	159	57	266
166	136	126	126	305	177	61	306
281	166	166	139	358	243	70	325
	252	198	166		263	102	366
	281	244	198		306	113	
	306	266	244		324	137	
	325	290	266		365	180	
		305	290			196	
			305			217	
						244	
						266	
						306	
						326	
						367	

The tetragonal phase of β-In_2S_3 thin films was verified by Raman analysis. This showed that it was possible to control the structure of thin films by adjusting the temperature and time of annealing. The results present a more thorough understanding of the effects of annealing parameters on the morphological properties of the films. They could also help in fitting the preparation parameters based on optical and electrical requirements for solar cell applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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