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This is an **author produced version** of a paper published in:

Thin Solid Films 612 (2016): 202-207

DOI: http://dx.doi.org/10.1016/j.tsf.2016.06.018

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SnS thin films grown by sulfurization of evaporated Sn layers: Effect of sulfurization temperature and pressure

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Abstract

SnS thin films were grown by sulfurization of Sn layers evaporated by electron beam. The effect of sulfurization parameters, such as temperature and pressure, on the properties of tin sulfide layers has been investigated. Ar pressure used during the sulfurization has a strong impact on the development of a proper SnS/Mo back interface. However, the sulfurization temperature is the parameter that regulates the formation of an orthorrombic single phase SnS thin film with the optimum properties to be used as absorber for solar cell devices. Sulfurization temperature of 220º C for 240 minutes led to the formation of single phase tin sulphide layers. Direct band gap energy about 1.2 eV has been determined.

Keywords: SnS; sulfurization; SnS_2 secondary phase; earth abundant; solar cells

1. Introduction

Thin films solar cells have the potential to significatively decrease the cost of photovoltaic technologies. Currently, $Cu(In,Ga)Se_2$ (CIGSe) thin film solar cells have achieved an efficiency of 22.3 % [1]. However, the scarcity of In and Ga compromises the large scale mass production. An attractive alternative has been found in the kesterites, $Cu_2ZnSn(S,Se)_4$ (CZTSSe). It is also important to consider the material deposition processes to transfer to cheaper large-scale industrial processes. In general, the processing of binary systems is likely to be simpler compared to quaternary compounds including CIGSe and kesterite. Tin sulfide (SnS) is a potential candidate material to be used as absorber for low-cost thin film solar cells. SnS consists of non-toxic and earth-abundant elements, has a band gap between 1.1-1.4 eV [2-3], a high absorption coefficient $> 10^4$ cm^{-1} above 1.3 eV [4] and p-type conductivity. Despite all these advantages, single phase thin films are difficult to grow due to the formation of secondary phases such as SnS_2 and Sn_2S_3 [5]. While SnS can be used as absorber material for photovoltaic devices, SnS_2 with n-type conductivity and band gap energy of 2.12-2.44 eV can be used as window layer [6]. This shows the versatility of these Sn_XS_y semiconductor materials. On the other hand, due to the high vapour pressure of SnS, losses of material happen when working at high temperatures. SnS thin films have been deposited by different methods such as thermal evaporation [7-8], co-evaporation [9], spray pyrolisis [10], multilayer-based solid-state reaction [11], RF sputtering [12], sulfurization of Sn sheet [13-14], of Sn evaporated film [14] and of Sn sputtered layer [15-16] between others. The maximum efficiency reported up to date of SnS solar cells is of 4.36 % [17]. This absorber material was grown by atomic layer deposition (ALD). ALD is an expensive fabrication method for growing films of around 1 µm thickness, being a challenge to industrial scale-up.

In this work, SnS thin films have been grown by the sulfurization of evaporated Sn layers at room temperature. First, this method allows us to work at low nominal temperature around 220º C, avoiding the loss of SnS. This growth temperature is beneficial for SnS solar cells deposited on flexible light polyimide substrates, extending the range of applications. Secondly, this deposition process is easily suitable for large-scale industrial implementation. Here, a study of the effect of sulfurization processes on the properties of tin sulfide films is shown. The objective of this work is to find the sulfurization parameters to produce single phase SnS thin films with the proper properties to be used as absorber for photovoltaic devices.

2. Experimental methods

Tin sulfide thin films were fabricated by a two-stage process. In the first stage, Sn thin films with purity of 99.995 % (Good Fellow) were evaporated onto soda-lime glass and Mo/glass by electron beam. The base pressure of the vacuum chamber was of 10^{-6} Torr. The substrates were not heated. In the second stage, Sn layers were sulfurized using S powder as a source under Ar atmosphere. For that purpose, the Sn thin films were placed in a partially closed graphite box, of 56 mm x 70 mm x 20.5 mm with a hole of 1 mm diameter in the lid, and inserted into a quartz tube furnace. The samples size was of 100 mm^2 approximately. In order to have an overpressure of S, 100 mg of elemental sulfur were also placed inside the graphite container next to the substrate. The maximum S overpressure was of 2.05 x 10^3 Pa at 220º C. The heating and cooling rates were 5º C/min and 10º C/min respectively. The sulfurization temperature was measured by a thermocouple located at the bottom side of the graphite box. Parameters such as the maximum temperature and the Ar pressure were varied to obtain the tin sulfide material with the optimum properties.

The composition was measured by Energy Dispersive X-ray spectroscopy (EDX) (Oxford instruments, model INCAx-sight) inside a Hitachi S-3000N scanning electron microscope (SEM). EDX measurements were carried out at 12 kV operating voltage, and the Sn L and S K lines were used for quantification. The composition of the thin films and the details of the sulfurization processes applied are collected in Table 1.

Grazing incidence X-ray diffraction (GIXRD) was performed to investigate the structural properties of the SnS thin films. GIXRD data were collected with a PaNAlytical X´Pert Pro MPD diffractometer, using Cu Kα radiation and a multilayer mirror. Detector scans with incident angle of 4º were carried out.

Scanning electron microscopy was used to study the morphology of the SnS/Mo/glass structure using a Philips XL30S FEG scanning electron microscope at 10 kV operating voltage.

Transmittance and reflectance spectra of tin sulfide layers deposited on glass substrates were measured using a Perkin Elmer Lambda 1050 UV/VIS/NIR spectrophotometer.

3. Results and discussion

First of all, the influence of the evaporation rate of Sn on the composition and structure of the final SnS films was investigated. Three different deposition rates, from 7 to 3 Å/s, were compared using the same sulfurization process at nominal temperature T of 215º C for 120 minutes at 4.9 x10^3 Pa Ar pressure. As shown in Table 1, lower incorporation of S into the Sn layer during the sulfurization takes place when the Sn growth rate was increased. Figure 1 displays the GIXRD spectra of the tin evaporated at 3 and 7 Å/s

after sulfurization. The JCPDS data for orthorrombic SnS (no. 00-039-0354) and metallic Sn (no. 00-004-0673) are also shown. SnS together with Sn metal were identified for the film obtained using the higher tin evaporation rate. The decrease Sn growth rate to 3 Å/s led to the presence of SnS single phase. The evaporation rate has also affected the morphology. As shown in Figure 2.a-2.c., the grain growth of the Sn layer depends on the evaporation rate used. A smaller grain size and less elongated grain shape (Figure 2.a.) is observed for the metallic Sn evaporated at lower rate. Figure 2.d-2.f. show cross-sectional SEM micrographs of SnS/Mo/glass structure by using the Sn film from Figure 2.1.-2.c. respectively and the same sulfurization procedures. A worse quality Mo/absorber interface with the formation of big voids is observed when using 7 Å/s. Steinmann et al. [7] reported an increase in SnS film porosity and surface roughness at high deposition rates. From here only evaporation rates of Sn $\leq$ 4 Å/s were used.

Different sulfurization parameters were studied to determine the conditions to produce SnS thin films with the suitable properties to be used as absorber material for a photovoltaic device. The effect of Ar pressure, P_{Ar}, during the sulfurization process on the compositional, optical and structural properties of tin sulfide thin films was investigated. Using the optical transmittance and reflectance spectra, the band gap energy E_g was estimated. E_g can be determined by the following formula:

$$(\alpha h\nu)^n = A(h\nu - E_g) \tag{1}$$

where A is a constant and n characterizes the transition process, corresponding n = 2 and ½ to direct and indirect band gap respectively. In the literature, direct and indirect band gap energies have been reported for SnS thin films. As mentioned in [12], there is a discrepancy in the literature concerning this point. As an example, Soussa et al [5] observed both behaviors depending on the annealing treatment applied. Robles et al [9] determined direct band gap energies between 1.14-1.20 for SnS thin films deposited by co-evaporation. Figure 3 displays $(\alpha h\nu)^2$ vs hν of samples evaporated onto glass substrate by using Sn growth rates of 3 Å/s and sulfurization processes at 215° C and different P_{Ar}. The straight line with an intercept on the hν axis determines direct E_g between 1.16 and 1.22 eV. These values are in agreement with that of E_g = 1.22 eV for SnS single crystal obtained by spectroscopic ellipsometry [18]. A satisfactory linear fit for indirect band gap estimation cannot be made for any sample by using n = ½ in the equation 1. The fitting of the optical data is complicated by the presence of band tailing. This band-tail absorption may be related to the presence of secondary samples. As shown in Figure 3, no clear dependence of the E_g with the Ar pressure takes place. Nevertheless, higher band gap energy has been obtained for the sample with higher S concentration (see Table 1). The presence of SnS_2 secondary phase could lead to higher E_g values.

Figure 4.a. displays the GIXRD spectra of samples evaporated at 1 Å/s and sulfurized at 225 ºC and different Ar pressures. Albers et al. [19] observed that the lower pressure is helpful for the formation of phases with simple stoichiometry. Sugiyama et al. [13] also observed extra phases such as S and SnS_2 when SnS films were grown at high S vapor pressure. Nevertheless, the composition of the samples sulfurized at higher P_{Ar} is near stoichiometric. The composition shown in Table 1 is the average of five measurements of 1 cm^2 size samples. However, some grains of the films grown at high P_{Ar} have been identified as SnS_2. Sn richer films are now obtained when sulfurization is carried out at much lower pressure, 2.0 x 10^2 Pa and 2.0 Pa. SnS and also SnS_2 secondary phase are identified when higher pressure is used during sulfurization, as shown in Figure 4.a. Not only the 001 Bragg peak of SnS_2 is observed for samples sulfurized at 9.3x 10^4 Pa, but

also the 100 and 110. Much weaker intensity SnS_2 diffraction peaks are observed for the sample sulfurized at 7.1 x 10^4 Pa. Figure 4.b. shows the cross-sectional SEM pictures of SnS films grown at different Ar pressures. Better adhesion of tin sulfide to the Mo back contact is observed for higher P_{Ar}. It seems that the Ar pressure during the sulfurization is a crucial growth parameter to develop a good SnS/Mo interface. Not only is it important the quality of the heterojunction interface for a high performance solar cell, but also the back interface. Therefore, it will be very important the Ar pressure to form the SnS absorber layer to use for photovoltaic applications. Different from the optical properties, the structural properties studied by GIXRD and SEM micrographs show a clear dependence with the Ar pressure used during sulfurization.

Sulfurization processes at different nominal temperatures were carried out to determine the SnS formation. Because of the adhesion problems at the SnS/Mo back interface at lower Ar pressure, a first investigation was performed at 7.1x10^4 Pa. Figure 5.a. shows GIXRD spectra of Sn layers evaporated at 4 Å/s and sulfurized at 195° C, 215°C, 225° C, 260° C and 315° C. Orthorrombic SnS is already formed at 195° C together with some metal Sn. Minemura et al. [14] also detected the presence of SnS + Sn when Sn evaporated layer on glass was sulfurized at 200° C. The increased sulfurization T at 215° C shows SnS as the predominant phase in conjunction with Sn peaks of lower intensity. Almost only SnS single phase was obtained for temperature of 225° C. The higher temperature of 315° C is more favourable for the growth of hexagonal SnS_2 coexisting with SnS. For sulfurization temperature of 225° C, the XRD data indicated the stronger peak that was consistent with {111} reflections from SnS. This peak decreased in intensity as the sulfurization temperature was raised to 315° C. For T = 315° C the Bragg peak with higher intensity is that at $2\theta = 31.9°$ because of the coexistence of SnS_2 and SnS. These results are consistent with the composition shown in Table 1. A narrow range of temperature has been found to produce single phase orthorrombic SnS thin films. Reddy et al. [20] observed the formation of SnS thin films for T = 300°-350° C and the presence of SnS_2 and Sn_2S_3 secondary phases for T = 150°-300° C in vacuum. Our experimental results show a very different behavior with the predominant presence of SnS_2 at 315° C using Ar pressure of 7.1x10^4 Pa. SnS_2 is not only the main phase at this pressure and temperatures around 315° C, but also has been clearly observed for 260 °C and at 325°C at lower pressure of 2 Pa, as shown in Figure 4.a. Cross-sectional SEM images of the samples sulfurized at 225° and 315° C from Figure 5.a. are shown in Figure 5.b. The grain size of samples sulfurized at higher temperature seems to be smaller associated to the SnS_2 secondary phase. The tin sulfide/Mo interface was not affected by the increased sulfurization temperature.

A narrow range of nominal temperature, of 220-230° C, was study in order to elucidate the importance of the sulfurization temperature (see Table 1). Figure 6.a shows the GIXRD spectra of Sn layers evaporated at 1.5 Å/s and sulfurized at 7.1x10^4 Pa Ar pressure in that range of temperature. These spectra confirm that the temperature is the most important parameter to control the formation of tin sulfide layers. According to the Sn-S phase diagram, tin and sulfur can react to form SnS at the temperature of 231.9° C [21]. SnS and a very little contribution of amorphous SnS_2 were detected for sulfurization nominal temperature of 230° C. However, the samples sulfurized at 220° and 225° C present Bragg peaks corresponding to metallic tin. Our experimental results fit quite well with the phase diagram. Noguchi et al. [22] reported that the orientation of evaporated SnS films in vacuum changed from (111) to (040) crystal plane with the increase of susbtrate temperature. A zoom in Figure 6.a. of the GIXRD spectra shows that change when sulfurization temperature reaches 230° C. All these thin films were

carried out by using 120 minutes as sulfurization time. Jiang et al. [15] investigated the sulfurization of tin at 220º C for 15-60 minutes. They observed a higher reaction of Sn atoms with sulfur when the sulfurization time increases. In the present work, Sn layer was also sulfurized at 220º C for 240 minutes. GIXRD spectra of both thin films sulfurized at 220º C are shown in Figure 6.a. No secondary phases are observed, neither Sn nor SnS_2, for the sample sulfurized for longer time at 220º C and $7.1x10^4$ Pa Ar pressure. Orthorrombic SnS is formed following the reaction:

$$Sn + S \rightarrow SnS \text{ at } 220\text{º C for } 240 \text{ min}$$
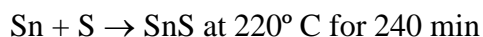
Longer sulfurization time in comparison to the literature is necessary to form single phase SnS thin films. It can be linked to the pressure used in our furnace.

SEM surface morphology of Sn layers before and after sulfurization at $T_{sulf} = 220\text{-}230$º C is displayed in Figure 6.b. A gradual change in the growth of grains is observed with the sulfurization temperature. The sulfurized films exhibit a grain structure uniformly distributed and good coverage of the Mo surface. The layer sulfurized at lower temperature for 120 min show some grains similar to those observed for metallic Sn layer in agreement with GIXRD measurements. A decrease grain size is observed when the temperature increases related to the tin sulfide phase.

4. Conclusions

Polycrystalline SnS thin films with direct band gap energy around 1.2 eV have been grown by a two-stage process. The process involved the evaporation of Sn by electron beam and subsequent sulfurization using S powder in a graphite box inside a quartz tube furnace under Ar atmosphere. The lowest pressure used during the sulfurization, the worse quality of the SnS/Mo back interface. By using an Ar pressure of 7.1×10^4 Pa, sulfurization temperature has been found to be one of the most important parameter for the development of a single phase SnS layer. An increased sulfurization time up to 240 min at nominal temperature of 220º C led to the formation of single phase orthorrombic SnS layers.

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Figure Captions

Figure 1. GIXRD spectra of tin layers evaporated at different rates and sulfurized at 215º C and Ar pressure of 4.9×10^3 Pa. JCPDS references of SnS (no. 00-039-0354) and Sn (no. 00-004-0673) are shown for comparison.

Figure 2. (a), (b) and (c) SEM surface morphology of Sn layers evaporated at 3, 4 and 7 Å/s respectively. (d), (e) and (f) Cross-sectional SEM micrographs of (a), (b) and (c) respectively after sulfurization at 215º C and Ar pressure of 4.9×10^3 Pa.

Figure 3. $(\alpha h\nu)^2$ vs $h\nu$ of Sn evaporated onto glass substrate at 3 Å/s and sulfurized at different P_{Ar}.

Figure 4. (a) GIXRD spectra and (b) cross-sectional SEM micrographs of Sn layers evaporated at 1 Å/s and sulfurized at different Ar pressures and 225º C. In (a), JCPDS of SnS (no. 00-039-0354) and SnS_2 (no. 00-023-0677) are shown for comparison.

Figure 5. (a) GIXRD spectra and (b) cross-sectional SEM of tin sulfide/Mo structure obtained by sulfurization of Sn layers at 7.1×10^4 Pa and different temperatures. Sn layers were evaporated at 4 Å/s. JCPDS references of SnS_2 (no. 00-023-0677), SnS (no. 00-039-0354) and Sn (no. 00-004-0673) are shown for comparison.

Figure 6. (a) GIXRD spectra and (b) SEM surface morphology of tin sulfide thin films sulfurized at 7.1×10^4 Pa and 220º, 225º and 230º C. Sulfurization time of 120 and 240 minutes has been used for the sample treated at 220º C. In (b), all the layers have been sulfurized for 120 minutes and it is also shown the surface morphology of Sn layer evaporated at 1.5 Å/s on Mo/glass substrate. JCPDS references of SnS_2 (no. 00-023-0677), SnS (no. 00-039-0354) and Sn (no. 00-004-0673) are shown for comparison.
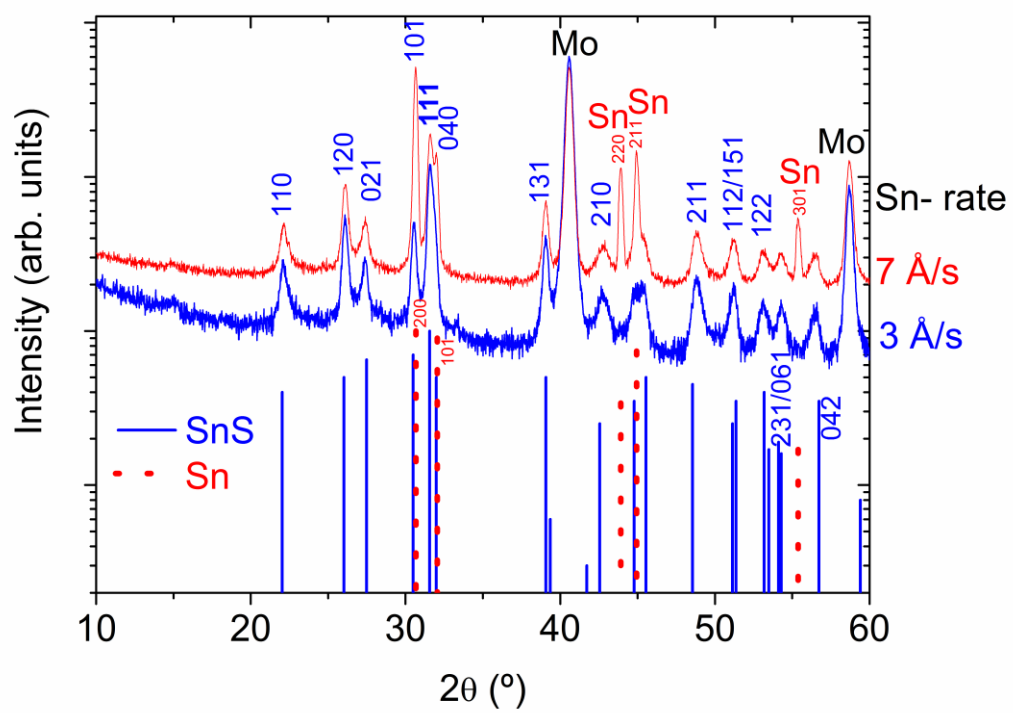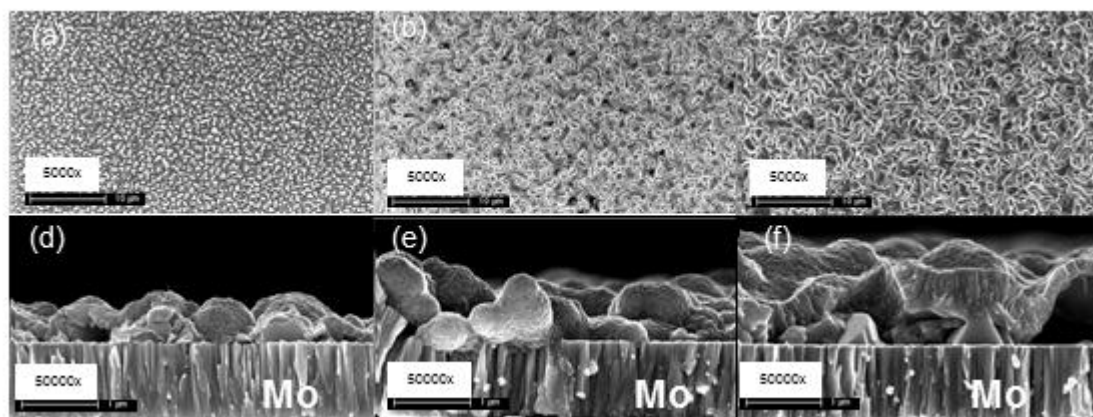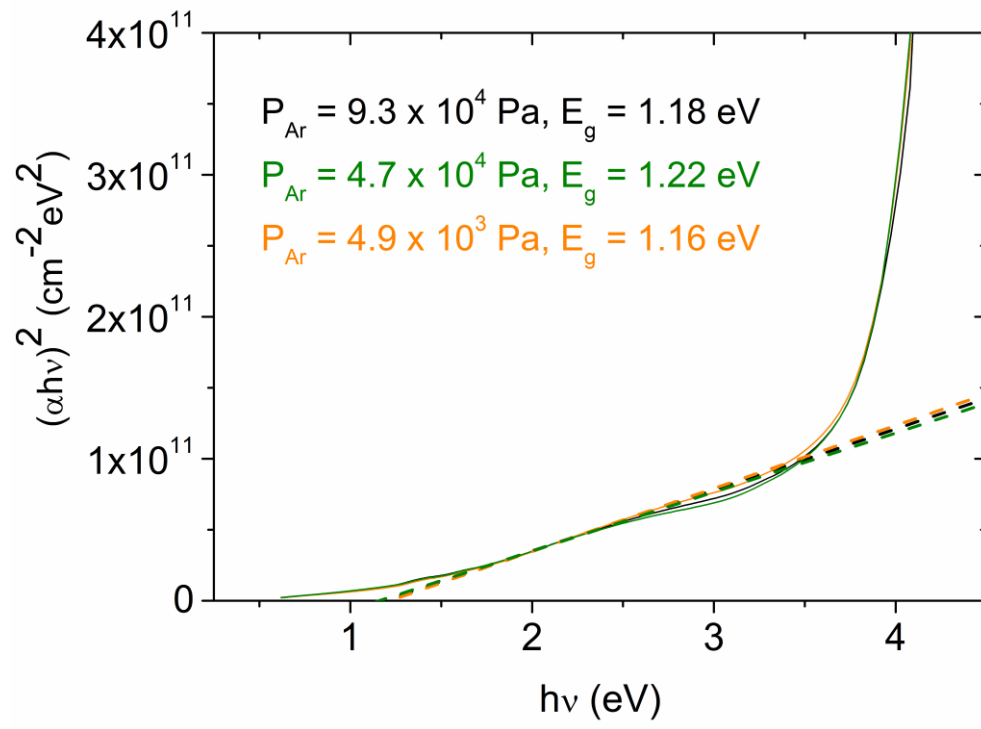
Figure 1

Figure 2

Figure 3

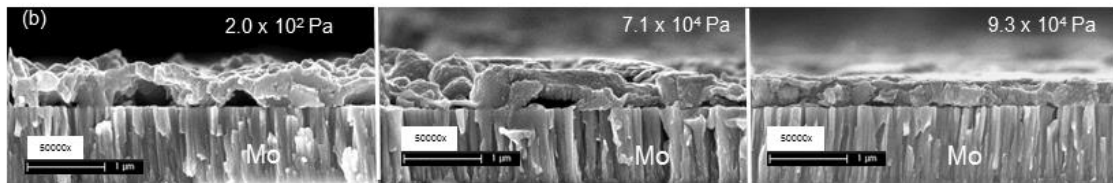P$_{Ar}$ = 9.3 x 10^4 Pa, E$_g$ = 1.18 eV
P$_{Ar}$ = 4.7 x 10^4 Pa, E$_g$ = 1.22 eV
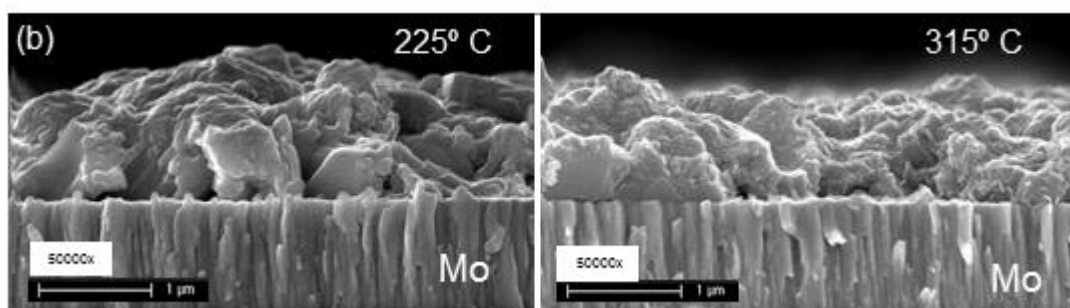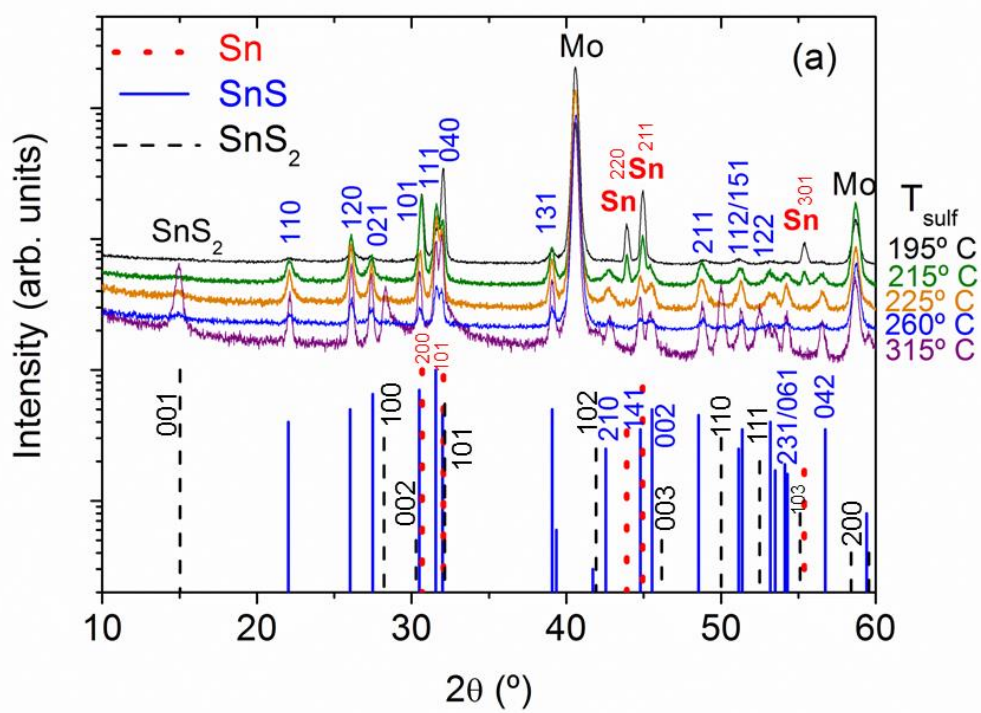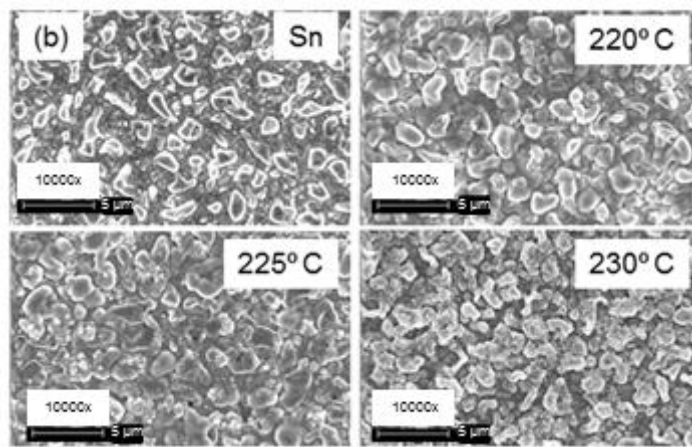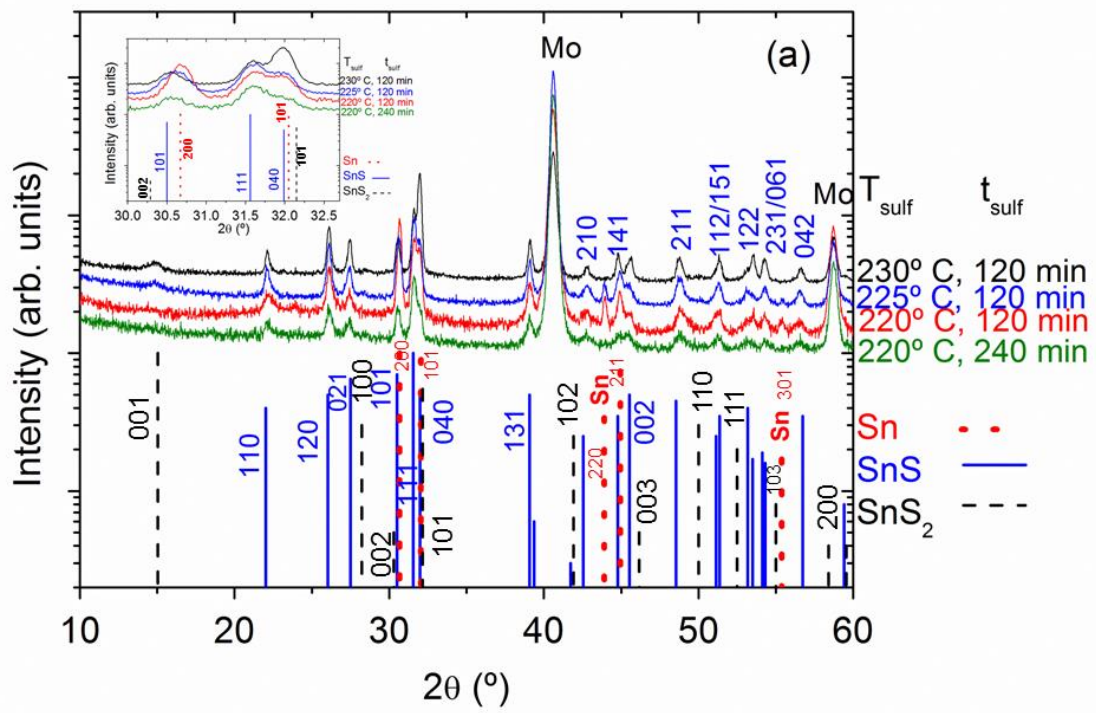P$_{Ar}$ = 4.9 x 10^3 Pa, E$_g$ = 1.16 eV
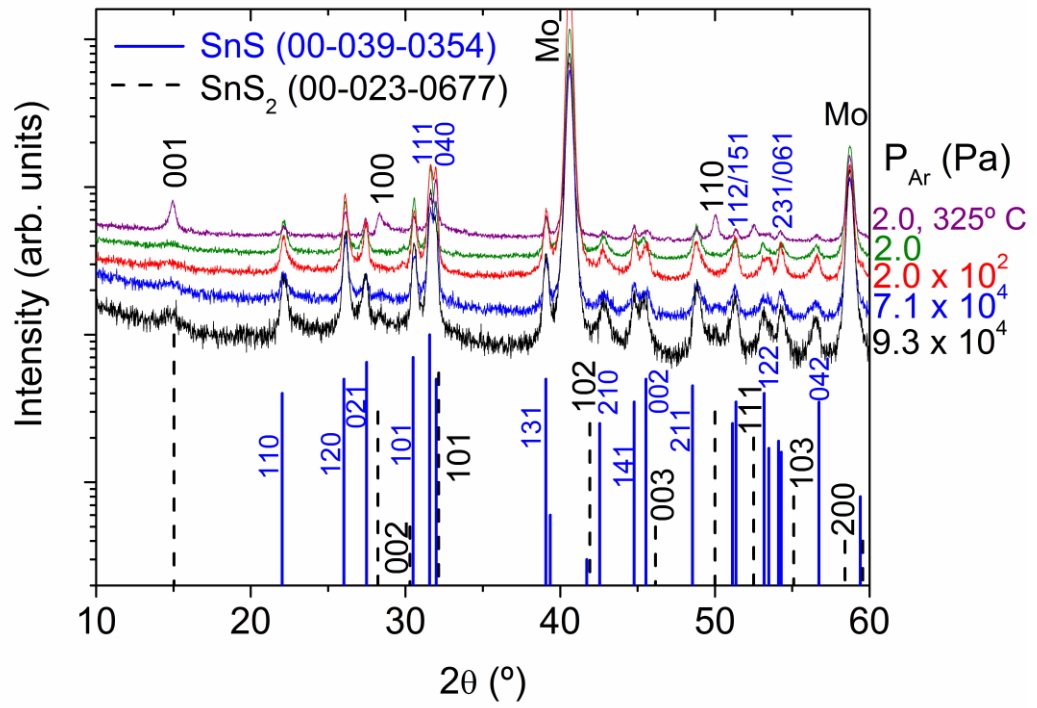
Figure 4

Figure 5

Figure 6

Table 1. Composition of SnS thin films as measured by EDX.

Evaporation rate (Å/s)	Sulfurization process	Sn (at %)	S (at %)
7		55.8 ± 0.6	44.2 ± 0.4
4	215º C, 4.9 x10^3 Pa	54.1 ± 0.5	45.9 ± 0.5
3		49.9 ± 0.5	50.1 ± 0.5
3	215º C, 4.7 x10^4 Pa	48.0 ± 0.5	52.0 ± 0.5
3	215º C, 9.3 x10^4 Pa	49.0 ± 0.5	51.0 ± 0.5
4	195º C, 7.1 x10^4 Pa	72.7 ± 0.7	27.3 ± 0.3
4	215º C, 7.1 x10^4 Pa	55.5 ± 0.6	44.5 ± 0.4
4	225º C, 7.1 x10^4 Pa	49.7 ± 0.5	50.3 ± 0.5
4	260º C, 7.1 x10^4 Pa	48.7 ± 0.5	51.3 ± 0.5
4	315º C, 7.1 x10^4 Pa	38.4 ± 0.4	61.6 ± 0.6
1	325º C, 2.0 Pa, 60 min*	41.6 ± 0.4	58.4 ± 0.6
1	225º C, 2.0 Pa	52.8 ± 0.5	47.2 ± 0.5
1	225º C, 2.0 x10^2 Pa	52.6 ± 0.5	47.4 ± 0.5
1	225º C, 7.1 x10^4 Pa	50.8 ± 0.5	49.2 ± 0.5
1	225º C, 9.3 x10^4 Pa	50.5 ± 0.5	49.5 ± 0.5
1.5	220º C, 7.1 x10^4 Pa	55.7 ± 0.6	42.3 ± 0.4
1.5	220º C, 7.1 x10^4 Pa, 240 min*	50.8 ± 0.5	49.2 ± 0.5
1.5	225º C, 7.1 x10^4 Pa	51.4 ± 0.5	48.6 ± 0.5
1.5	228º C, 7.1 x10^4 Pa	50.5 ± 0.5	49.5 ± 0.5
1.5	230º C, 7.1 x10^4 Pa	49.7 ± 0.5	50.3 ± 0.5

*Note: All the sulfurization processes were at the maximum temperature for 120 minutes with the exception of the two processes indicated in the table.