Assessment of the potential of tin sulphide thin films prepared by sulphurization of metallic precursors as cell absorbers

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Abstract:

In this work, Sn_xS_y (TS) thin films have been grown on soda-lime glass substrates by sulphurization of metallic precursors in a N_2+S_2 atmosphere. Different sulphurization temperatures were tested, ranging from 300ºC to 520ºC. The resulting phases were structurally investigated by XRD and Raman spectroscopy. Composition was studied using EDS being then correlated with the sulphurization temperature. Optical measurements were performed to obtain transmittance and reflectance spectra, from which the energy band gap, were estimated. The values obtained were 1.16 eV for the indirect transition and for direct transition the values varied from 1.26 eV to 1.46 eV. Electrical characterization using Hot Point Probe determined that all samples were p-type semiconductors. Solar cells were built using the structure: SLG/Mo/Sn_xS_y/CdS/ZnO:Ga and the best result for solar cell efficiency was 0.17%.

Keywords: Tin sulphide, sulphurization, thin film, solar cell

1. Introduction

The replacement of the $CuIn_{1-x}Ga_xSe_2$ (CIGS) as solar cell absorber by one that overcomes some of the difficulties has attracted the attention of several research groups in the last decade. The binary tin sulphide compound, SnS, is a promising candidate which gathers two important advantages: it is relatively cheap and non toxic when compared with CIGS. The maximum efficiency attained so far for SnS based solar cells is 1.3 % [1] which is a low value if compared with CIGS, 19.9 % [2]. Due to the increasing number of research group studying this compound it is expectable that this efficiency will increase further in the near future. Despite these advantages the SnS seem to be difficult to grow from raw materials due to the formation of spurious phase, such as SnS_2 and Sn_2S_3, during the sulphurization process. This difficulty is increased, especially for vacuum growth method, because SnS has a high vapour pressure which means that losses of material will happen for low processing pressures and temperatures.

Several methods have already been developed for the growth of Sn_xS_y. Conventional thermal evaporation and electron beam evaporation were tested by E. Ogah *et al* [3] and A. Tanusevski *et al* [4], respectively. K.T. Ramakrishna Reddy *et al* [5] were successful in growing SnS using dc magnetron sputtering of elemental Sn and post sulphurization process. Non vacuum methods have also been developed, namely chemical bath deposition technique by E Turan *et al* [6], spray-pyrolysis by K.T. Ramakrishna Reddy *et al* [1] and electro-deposition process by Shuying Cheng *et al* [7].

The aim of this work is to assess the potential of the binary tin sulphide compounds, Sn_xS_y, to be used as solar cell absorbers. Here we report the results of the growth and characterization of those compounds obtained by sulphurization of dc-magnetron sputtered elemental Sn precursor. Compositional and structural analyses were performed to identify and characterize the compounds that are grown. The influence of the maximum sulphurization temperature on the crystallization process is also investigated. The optical properties relevant for this study are the absorption coefficient (not shown) and band gap energy. The semiconductor conductivity type of the samples was analysed by Hot Point Probe. Solar cells were prepared with the structure SLG/Mo/Sn_xS_y/CdS/ZnO:Ga and characterized through I-V measurements.

2. Experimental Details

2.1. Sample Preparation

The method used in this work to grow the absorber layer can be divided in two stages [8]. First, an elemental Sn precursor layer is deposited by dc magnetron sputtering. The second stage is the formation of the Sn_xS_y layer by sulphurization of the precursor in a programmable tubular furnace.

The 3x3 cm^2 soda lime glass (SLG) substrates are cleaned in successive ultrasound baths of acetone/alcohol/deionised water and later dried with a N_2 flow. Next, the deposition of Mo back contact was performed by dc magnetron sputtering from a Mo target with purity 3 N. In order to be able to perform transmission characterization, a mask was used to avoid the deposition of the Mo back contact in half the samples. Then, the metallic Sn precursor was deposited using dc magnetron sputtering. All depositions were done under an Ar atmosphere, at an operating pressure of 2×10^{-3} mbar and power densities of 0.11 Wcm^{-2}. The purity of the Sn target was 4 N. Initial thickness estimation was done based on the element molecular weight and bulk density. *In situ* monitoring was performed with a quartz crystal monitor.

The CZTS formation was performed in a tubular furnace in a N_2 + S_2 vapour atmosphere at a constant working pressure of 5.0 mbar and a N_2 flow rate of 40 ml/min. Sulphur pellets with purity 5 N, were evaporated at 130 ºC in a temperature-controlled quartz tube source. The furnace temperature was ramped up at 10 ºC/min to the maximum temperature. Different maximum sulphurization temperature were tested, 300 ºC, 340 ºC, 430 ºC and 520 ºC. These temperatures were kept constant for 10 min and then the system was cooled down naturally.

For the solar cell preparation a CdS layer 50 nm thick was deposited on top of the Sn_xS_y absorber by a chemical bath method. Finally a ZnO:Ga window layer 200 nm thick was deposited by RF sputtering.

2.2. Characterization

During the metallic precursor deposition *in situ* thickness measurement was done using a quartz crystal monitor. A Dektak 150 step profiler was used to measure the thickness of individual metallic precursors and the final Sn_xS_y layer thicknesses. X-ray diffraction analysis was performed with a PHILIPS PW 3710 system equipped with a Cu-Kα source (wavelength $\lambda = 1.54060$ Å) and the generator settings were 50 mA, 40 kV. A Hitachi S4100 SEM and a Rontec EDS with setting parameters of 25 kV and 10 μA were used for compositional analysis. Raman scattering measurements have been performed at room temperature in the backscattering configuration and the excitation laser line used was 488 nm. The Jobin-Yvon T64000 Raman spectrometer was equipped with an Olympus microscope with a 100× magnification lens. Optical measurements were done using a Shimadzu UV3600 spectrophotometer equipped with an integrating sphere. The majority carrier type was identified using a hot point probe system. The solar cell parameters have been estimated from the I-V curves measured with a home assembled I-V system under simulated standard illumination conditions. The sample naming scheme is according to the maximum sulphurization temperature.

3. Results and Discussion

Table 1 shows the results of the compositional analysis and the thicknesses for studied samples. This table shows a drop in Sn content of the sample with increasing sulphurization temperature from a near stoichiometric SnS at 300 ºC to composition ratios close to 0.6 at 430 ºC. This value approaches the stoichiometric SnS_2 composition. For higher temperature the results seem to stabilize at composition ratios of 0.7. Analyzing the thicknesses, it is clear that for sulphurization temperatures of 430 ºC and 520 ºC considerable material losses are observed, which is in accordance with the work published by P. A. Fernandes *et al* [9].

The figure 1 shows the XRD spectra for the samples sulphurized at 300 ºC, a), and at 340 ºC, b). For the lowest tested temperature, according to the International Centre for Diffraction Data (ICDD) [10], two compounds are identified: Herzenbergite SnS and SnS_2. According to XRD analysis presented in figure 2 b), increasing the temperature to 340 ºC, promotes the formation of a new compound, Sn_2S_3.

The XRD results of the samples sulphurized at 430 ºC and 520 ºC are shown in figure 2 a) and b), respectively. The spectrum for S430 shows that the sample is formed by a solid mixture of SnS_2 and Sn_2S_3. Unexpectedly no SnS phases were detected in this sample. The figure 2 b) shows that for

520 ºC the sample is formed by SnS and SnS_2 phases. Comparing the XRD spectra of sample S300 and S520 it can be observed an improvement in the cristallinity of the compounds. In sample S520, the peaks seem to be sharper than for S300. In S300 the SnS phase appears to dominate over SnS_2 while in S520 the opposite occurs.

Figure 3 shows the Raman scattering spectra of the samples sulphurized at 300ºC a), 340 ºC b), 430 ºC c) and 520 ºC d). All these results confirmed the presence of SnS_2 with a peak at 316 cm^{-1} [11]. Raman analysis detected SnS phases for samples S300, S340 and S520 with vibration modes located at 162 cm^{-1}, 193 cm^{-1} and 223 cm^{-1} [11]. The spectrum of sample S430, figure 3 c), show peaks at 237 cm^{-1} and 254 cm^{-1} which are assigned to Sn_2S_3 [11]. Note that this compound also has a strong peak at 307 cm^{-1} [11], but for this sample it must be hidden by the SnS_2 peak at 316 cm^{-1}.

In figure 4 it is presented the results of the energy band gap estimation. These graphs show the values for direct allowed and indirect allowed transitions. It can be seen that for indirect transitions the value was independent of the sulphurization temperature and in the range to 1.16 eV - 1.17 eV for all the samples. The estimation for direct transitions presents a decreasing value from 1.45 eV, for the lowest tested sulphurization temperature, 300 ºC, to 1.26 eV, for temperatures of 520 ºC. This behaviour is due to the improvement in the cristallinity of the phases. Note that these values for both indirect and direct transitions refer to SnS phases, [4, 7]. No influence of SnS_2 phases were detected, which present an energy band gap above 2.0 eV [13]. This result is due to the fact that in a solid mixture the optical behaviour of the material is ruled by the one with lower band gap energy. As a consequence, for the samples S340 and S430, a lower band gap value was expectable because of the presence of Sn_2S_3 phases which have band gap close to 1.0 eV [13]. Despite that no traces of Sn_2S_3 phases were found in this analysis.

Hot point probe analysis was performed for majority carrier identification and all the samples showed a p-type semiconductor nature.

In figure 5 the I-V characteristic of the best solar cell, sample S340, is presented. The cell performance parameters measured under simulated AM1.5 illumination were: open circuit voltage, V_{oc}, 183 mV, short circuit current density, j_{sc}, 2.7 mA/cm^2, fill factor, FF, 34 % and conversion efficiency, η, of 0.17 %,. The active area of the cell was 0.16 cm^2. The other samples showed a much weaker photovoltaic effect.

4. Conclusions

This work describes a method to grow Sn_xS_y compounds, using the sulphurization of an elemental Sn precursor, to be used as solar cell absorber. For all the growth conditions tested solid mixtures of SnS, SnS_2 and Sn_2S_3 were obtained. Despite that, optical and electrical measurements showed that the influence of SnS_2 and Sn_2S_3 phases is small compared with the SnS phase. The band gap and majority carrier type is defined mostly by the latter phase. Adjustments in the growth conditions must be performed, namely in the sulphurization pressure and maximum temperature, in order to have a better control of the final composition of the films.

Preliminary solar cell work showed that the best results were obtained for the Sn_xS_y films sulphurized at 340 ºC. The best cell efficiency was 0.17 %. Generally the cell parameters are low probably due to high recombination promoted by the presence of several phases and large density of grain boundaries. Furthermore in the preparation of the cells' window layer no i-ZnO was deposited which may have contributed to the observed low V_{oc}.

5. Acknowledgements:

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6. List of table captions

Table 1: Composition ratios for the various samples. The thickness of the metallic precursor layers and the sulphurized samples.

7. List of figure captions

Figure 1: XRD spectra of the sample a) S300 and b) S340. Peak assignment is made using data reported in reference [10].

Figure 2: XRD spectra of the sample a) S430 and b) S520. Peak assignment is made using data reported in reference [10].

Figure 3: Raman scattering spectra of the absorber layer: a) sample S300; b) sample S340; c) sample S430 and d) sample S520.

Figure 4: Band gap energy estimation of the Sn_xS_y samples S300, S340, S430 and S520.

Figure 5: I - V characteristics of the best solar cell, sample S340.

Tables (if any)

Sample	$\frac{[Sn]}{[S]}$	Sn thick. (nm)	Sn_xS_y thick.(nm)
S300	0.98	1050	1580
S340	0.78	925	1580
S430	0.63	830	1280
S520	0.71	1400	750

Table 1

Figures (if any)

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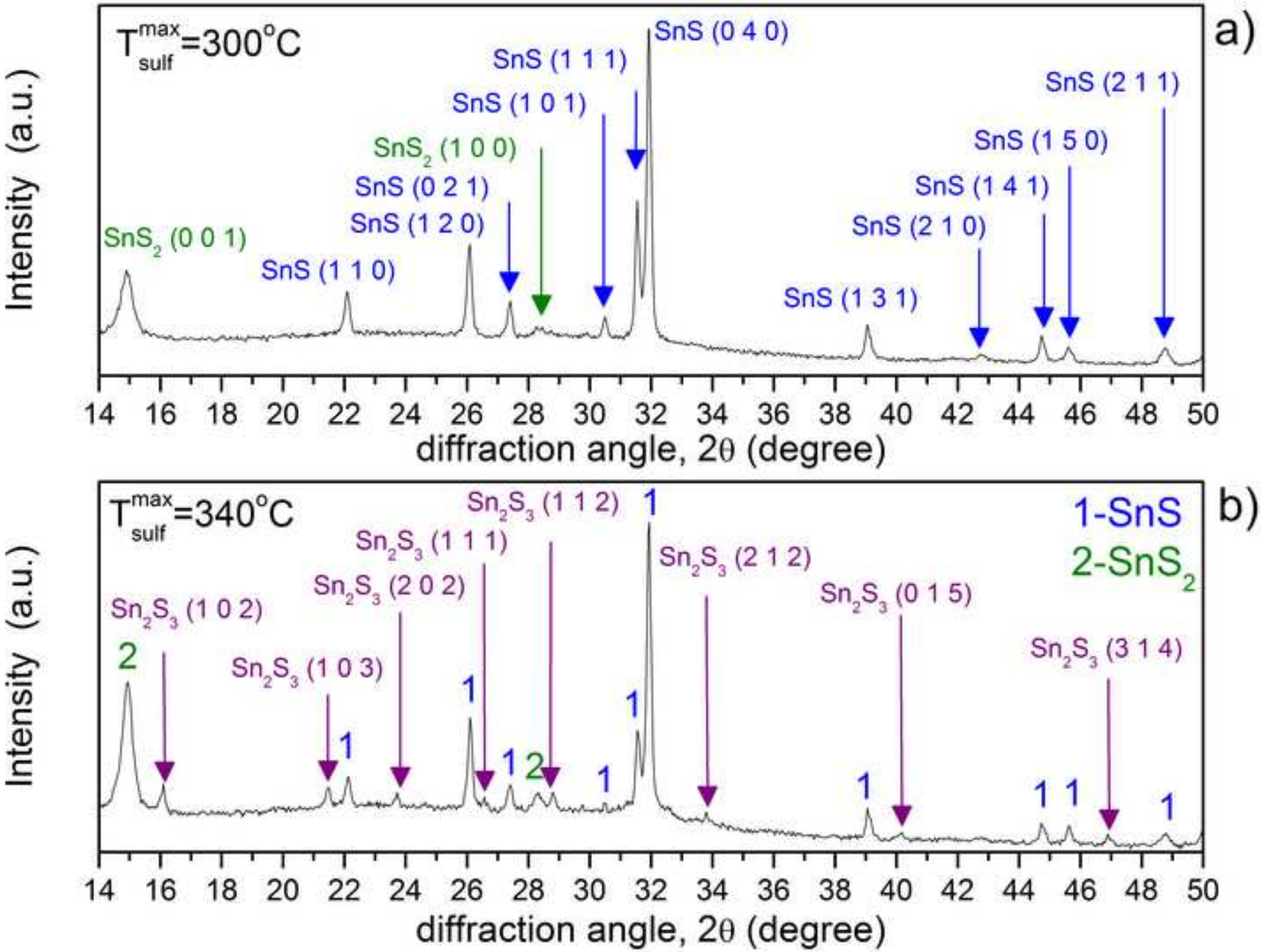

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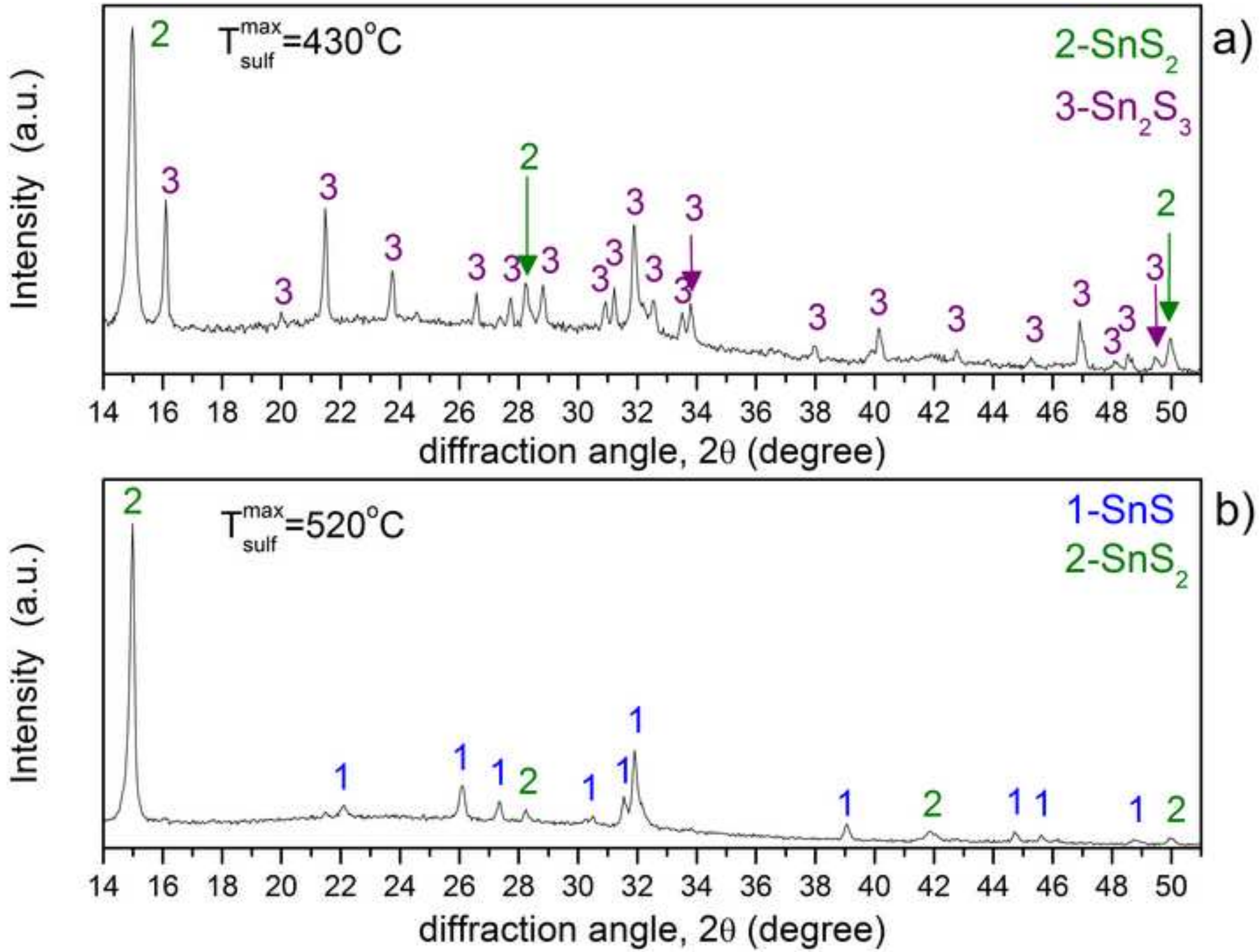
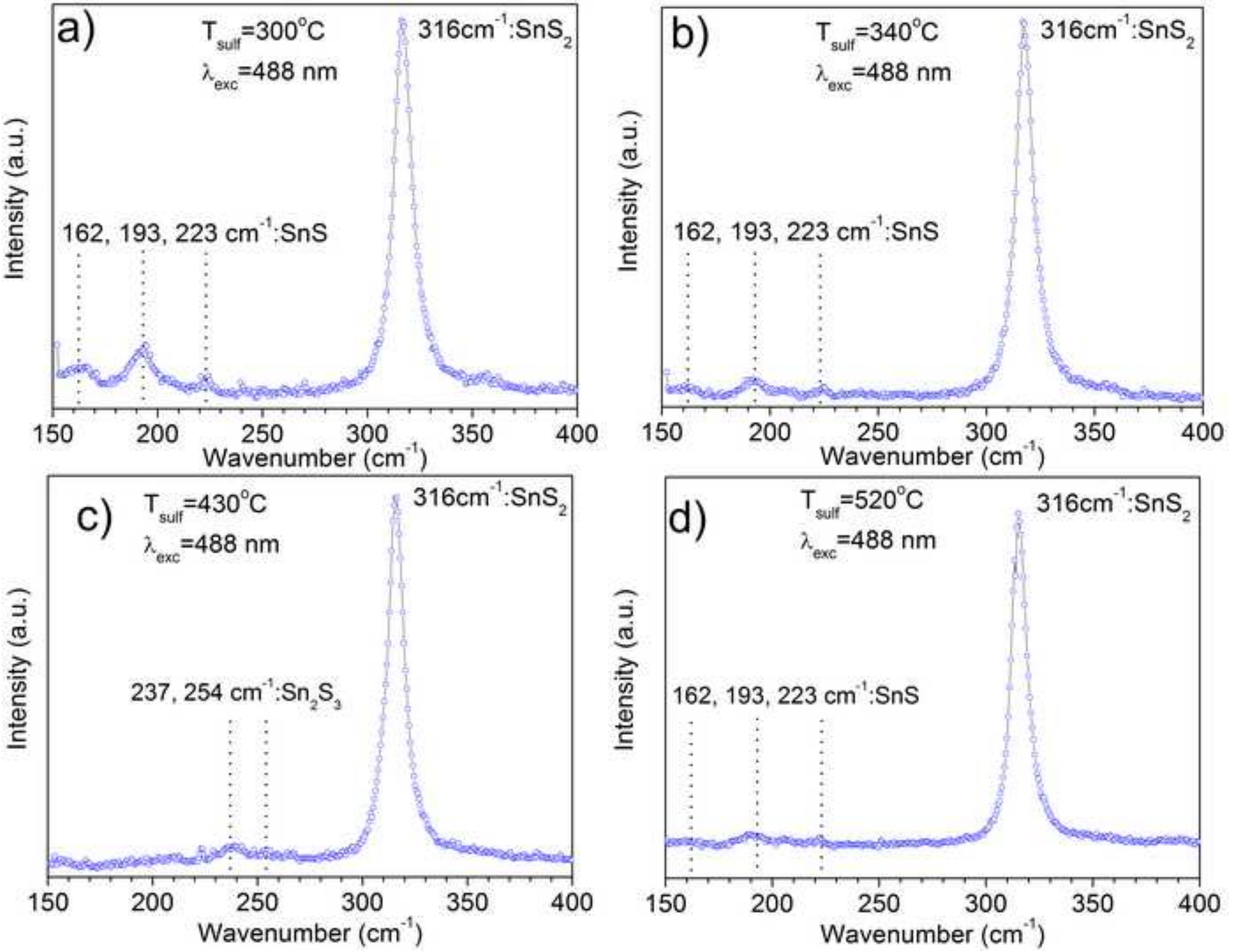
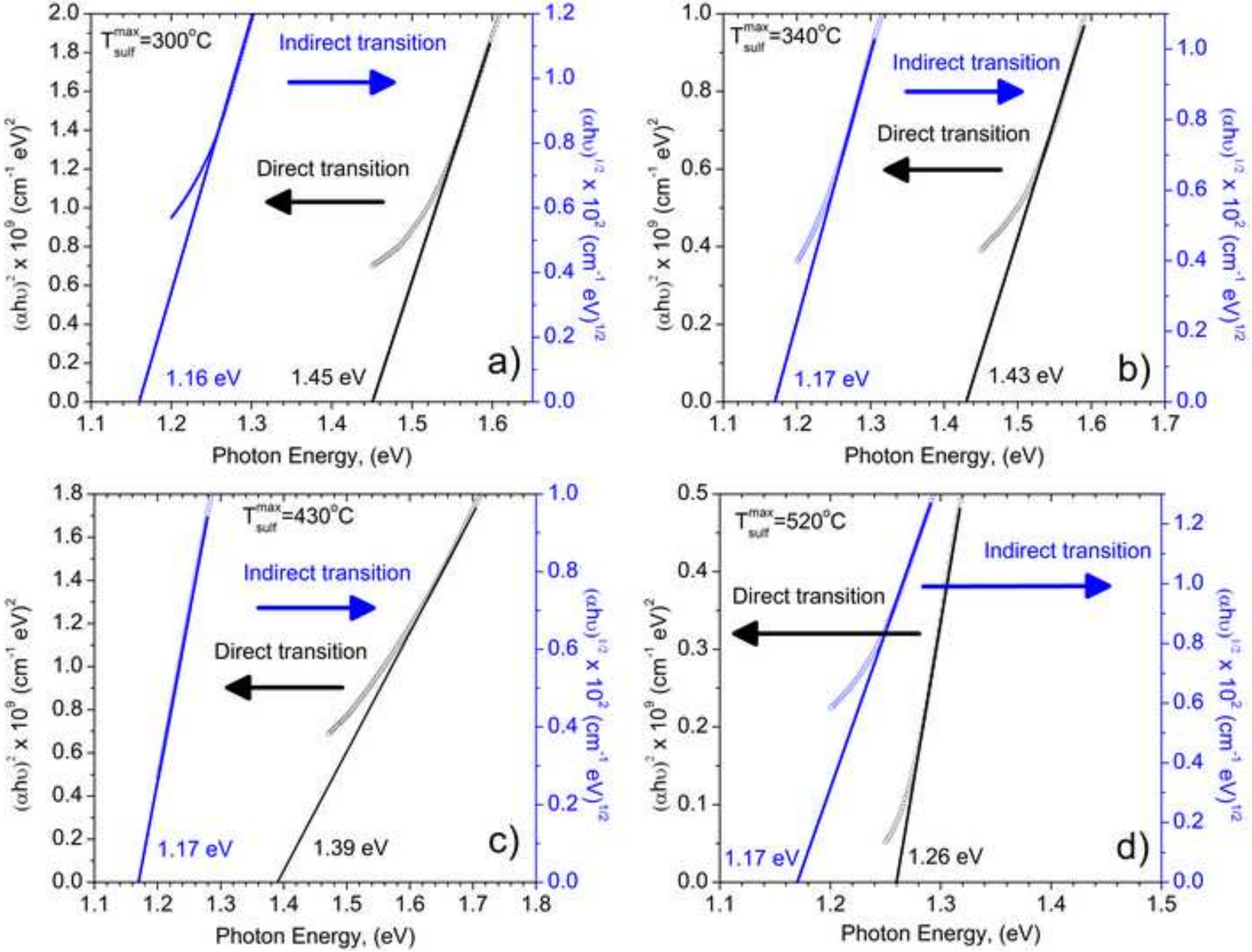
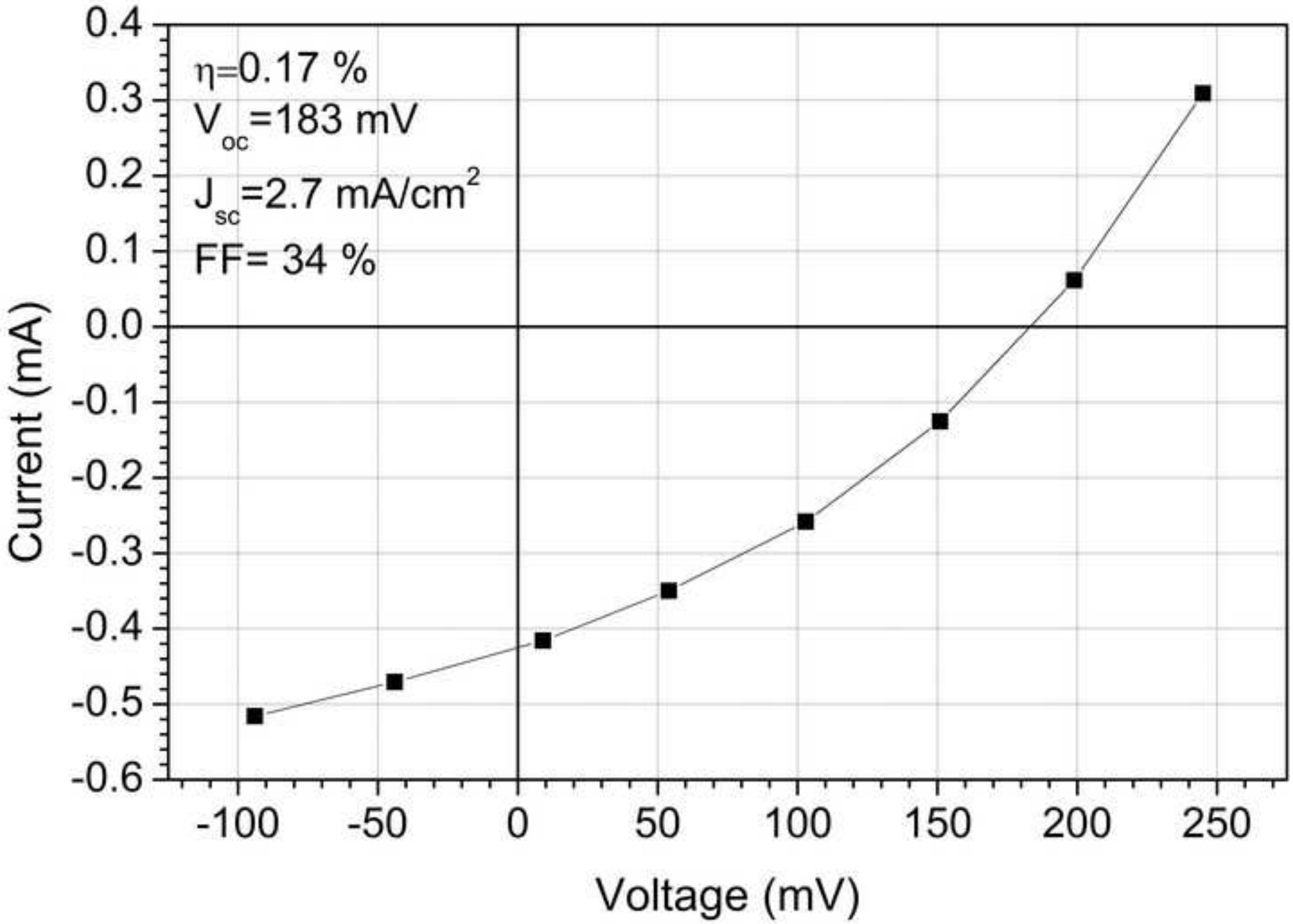



a)
T_sulf=300°C
λ_exc=488 nm
316cm⁻¹:SnS₂
162, 193, 223 cm⁻¹:SnS
Intensity (a.u.)
150
200
250
300
350
400
Wavenumber (cm⁻¹)
b)
T_sulf=340°C
λ_exc=488 nm
316cm⁻¹:SnS₂
162, 193, 223 cm⁻¹:SnS
Intensity (a.u.)
150
200
250
300
350
400
Wavenumber (cm⁻¹)
c)
T_sulf=430°C
λ_exc=488 nm
316cm⁻¹:SnS₂
237, 254 cm⁻¹:Sn₂S₃
Intensity (a.u.)
150
200
250
300
350
400
Wavenumber (cm⁻¹)
d)
T_sulf=520°C
λ_exc=488 nm
316cm⁻¹:SnS₂
162, 193, 223 cm⁻¹:SnS
Intensity (a.u.)
150
200
250
300
350
400
Wavenumber (cm⁻¹)


T_{sulf}^{max}=300°C
Indirect transition
Direct transition
1.16 eV
1.45 eV
a)
T_{sulf}^{max}=340°C
Indirect transition
Direct transition
1.17 eV
1.43 eV
b)
T_{sulf}^{max}=430°C
Indirect transition
Direct transition
1.17 eV
1.39 eV
c)
T_{sulf}^{max}=520°C
Indirect transition
Direct transition
1.17 eV
1.26 eV
d)
$(\alpha h\upsilon)^2 \times 10^9$ (cm^{-1} eV)^2
$(\alpha h\upsilon)^{1/2} \times 10^2$ (cm^{-1} eV)$^{1/2}$
Photon Energy, (eV)


η=0.17 %
V_{oc}=183 mV
J_{sc}=2.7 mA/cm^2
FF= 34 %
Current (mA)
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-100
-50
0
50
100
150
200
250
Voltage (mV)