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DEPARTMENT OF PHYSICS

Growth, Characterization and Solar Cell Potential of $\text{Cu}_2\text{ZnSnS}_4$ Thin Films

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**In partial fulfillment of the requirements
for the Degree of Doctor of Philosophy**

**HATAY
December 2013**

TEZ BİLDİRİMİ

Tez içindeki bütün bilgilerin etik davranış ve akademik kurallar çerçevesinde elde edilerek sunulduğunu, tez yazım kurallarına uygun olarak hazırlanan bu çalışmada bana ait olmayan her türlü ifade ve bilginin kaynağına eksiksiz atıf yapıldığını ve tez üzerinde Yükseköğretim Kurulu tarafından hiçbir değişiklik yapılamayacağı için tezin bilgisayar ekranında görüntülendiğinde asıl nüsha ile aynı olması sorumluluğunun tarafıma ait olduğunu beyan ederim.

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CONTENTS

	Page
ABSTRACT	V
ÖZET	VI
SYMBOLS AND ABBREVIATIONS	VII
LIST OF TABLES	VIII
LIST OF FIGURES	IX
1. INTRODUCTION	1
2. PREVIOUS STUDIES.....	3
3. MATERIAL AND METHOD	16
3.1. Material	16
3.1.1. Photo-voltaic materials	16
3.1.2. Crystal structure, defects, composition and phase diagram of CZTS.....	20
3.2. Method.....	25
3.2.1. Successive Ionic Layer Adsorption and Reaction Method	25
3.2.2. Sol-gel Spin Coating Method	29
3.2.3. Scanning Electron Microscopy	30
3.2.4. Energy Dispersive X-ray Spectrometry	31
3.2.5. X-ray Diffraction	32
3.2.6. Incident photon to current efficiency method.....	34
3.2.7. The growth of CZTS films by using SILAR method	39
3.2.7.1. Selection and cleaning procedure of the substrates	39
3.2.7.2. One-stage film growth	40
3.2.7.3. One-stage modified film growth.....	41
3.2.7.4. Two-stage film growth for different molar ratios.....	42
3.2.7.5. Two-stage film growth for different deposition cycles	44
3.2.8. The growth of CZTS films by using sol-gel method	45
3.2.8.1. Effects of stabilizer content	45
3.2.8.2. Effects of sulfur pressure	47
3.2.8.3. Effects of sulfurization temperature	47

3.3. Characterizations	48
4. RESULTS AND DISCUSSIONS	50
4.1. Morphological and compositional characterization of the CZTS films	50
4.1.1. SILAR grown films	50
4.1.1.1. One-stage SILAR grown films	50
4.1.1.2. Modified one-stage SILAR grown films	55
4.1.1.3. Two-stage SILAR grown films for different molar ratios	57
4.1.1.4. Two-stage SILAR grown films for different deposition cycles	60
4.1.2. Sol-gel grown CZTS films.....	65
4.1.2.1. Effects of stabilizer content	65
4.1.2.2. Effects of sulfur pressure	83
4.1.2.3. Effects of sulfurization temperature	93
4.2. Structural characterization.....	97
4.2.1. SILAR grown films	97
4.2.1.1. One-stage SILAR grown films	97
4.2.1.2. Modified one-stage SILAR grown films	100
4.2.1.3. Two-stage SILAR grown films for different molar ratios	105
4.2.1.4. Two-stage SILAR grown films for different deposition cycles	107
4.2.1.5. Two-stage SILAR grown films for different sulfurization temperatures	110
4.2.2. Sol-gel grown CZTS films.....	112
4.2.2.1. Effects of stabilizer content	112
4.2.2.2. Effects of sulfur pressure	115
4.2.2.3. Effects of sulfurization temperature	116
4.3. Photo-conversion efficiency studies of the CZTS films	119
4.3.1. Sol-gel grown CZTS films.....	119
4.4. Optical studies of the CZTS films	129
4.4.1. SILAR grown films	129
4.4.1.1. One-stage SILAR grown films	129
4.4.1.2. Two-stage SILAR grown films for different deposition cycles	131
4.4.2. Sol-gel grown CZTS films.....	134
4.4.2.1. Effects of stabilizer content	134
4.4.2.2. Effects of sulfurization temperature	136

5. CONCLUSIONS.....	138
REFERENCES.....	141
ACKNOWLEDGEMENTS	153
VITA	154

ABSTRACT**GROWTH, CHARACTERIZATION AND SOLAR CELL POTENTIAL OF
Cu₂ZnSnS₄ THIN FILMS**

In this study Cu₂ZnSnS₄ thin film solar absorbers were obtained via successive ionic layer adsorption-reaction (SILAR) and sol-gel spin coating methods. In SILAR method, deposition conditions such as Cu/Sn initial ratio, number of deposition cycles and the role of sulfurization temperature were optimized. The effects of stabilizer content, sulfur pressure and sulfurization temperature were investigated in sol-gel method.

The characterizations proved the formation Cu₂ZnSnS₄-type phase in all samples. Copper molarity in the precursor solutions significantly affected morphology and crystallinity of the films. The copper molarity below the stoichiometric value decreased the crystallinity while the higher molarity caused formation of Cu_{2-x}S secondary phase.

Moreover, as a stabilizer, diethanolamine concentration in the growth solution has been found to be crucial to obtain void/crack-free films. The grain size of about 2 micron was achieved when the DEA concentration was 1.3 in precursor solution and sulfurization pressure of 1.4 atm. The photo-conversion efficiency of the films changed from 0.1 to 12%.

As a conclusion, deposition conditions of CZTS absorber thin films in SILAR and sol-gel spin coating method were optimized. A contribution to the literature was made for marketable CZTS based solar cells with high efficiency.

2013, 154 pages

Keywords: Solar cell, CZTS, SILAR, sol-gel spin coating, thin film, photovoltaic

ÖZET **$\text{Cu}_2\text{ZnSnS}_4$ İNCE FİLMLERİN BÜYÜTÜLMESİ, KARAKTERİZASYONU VE GÜNEŞ PİLİ POTANSİYELİ**

Bu çalışmada $\text{Cu}_2\text{ZnSnS}_4$ ince filmleri aşamalı iyonik tabaka adsorpsiyon-reaksiyon (SILAR) ve sol-jel spin kaplama yöntemleri ile üretildi. Cu/Sn başlangıç molarite oranları, depolama döngü sayıları, stabilizer konsantrasyonu, sülfür basıncı ve sülfürizasyon sıcaklığı parametreler optimize edilmeye çalışıldı.

Yapılan karakterizasyonlar neticesinde CZTS fazının elde edildiği ispatlanarak başlangıç çözeltilerdeki bakır molaritesinin filmlerin kristal yapısını ve morfolojisini ciddi oranda etkilediği belirlendi. Başlangıç bakır molarite değeri stokiometrik değerin altında olduğu durumlarda filmlerin kristal yapılarının bozulmaya başladığı, aksi durumda film yapısı içerisinde Cu_{2-x}S ikincil fazının oluştuğu tespit edildi.

Ayrıca büyütme çözeltisindeki stabilizer konsantrasyonunun sürekli bir film elde etmede önemli rolü olduğu tespit edildi. Sol-jel yöntemiyle elde edilen filmlerde, dietanolamin molaritesi 1.3, sülfürizasyon basıncı 1.4 atm olduğu durumda yaklaşık 2 μm büyüklükte tanelere sahip filmler elde edildi. Filmlerin foto-verimlilik değerleri %0.1-12 aralığında tespit edildi.

Sonuç olarak çevreci ve ucuz bir güneş pili soğurucu katmanı olarak CZTS ince filmlerinin SILAR ve sol-jel ince film büyütme yöntemleri ile büyütülme şartları optimize edilmiş, yüksek verimli, ticarileştirilebilir düzeyde CZTS tabanlı güneş pilleri üretilmesi konusunda literatür altyapısı oluşturulmuştur.

2013, 154 sayfa

Anahtar Kelimeler: Güneş pili, CZTS, SILAR, sol-jel spin kaplama, ince film, fotovoltaiik

SYMBOLS AND ABBREVIATIONS

XRD	X-ray diffraction
EDS	Energy dispersive x-ray spectroscopy
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
SILAR	Successive ionic layer adsorption and reaction
CBD	Chemical bath deposition
PEC	Photo electro chemistry
IPCE	Incident photon to current efficiency
DSSC	Dye-sensitized solar cell
QDSC	Quantum dot-sensitized solar cell
CZTS	$\text{Cu}_2\text{ZnSnS}_4$
CZTSe	$\text{Cu}_2\text{ZnSnSe}_4$
CIS	CuInSe_2
CIGS	$\text{CuInGa}(\text{S},\text{Se})_2$
NC	Nanocrystal
AM	Air mass
ITO	Indium-doped tin oxide
FTO	Flourine-doped tin oxide
c-Si	Crystalline silicon
a-Si	Amorphous silicon
EQE	External quantum efficiency
IQE	Internal quantum efficiency

LIST OF TABLES

	Page
Table 3.1. Main drawbacks of current photovoltaic materials.....	18
Table 3.2. Expected secondary phases related to the compositional regions in the CZTS ternary phase diagram (adapted from Biswas et al. (2010)).....	22
Table 3.3. Vapor pressure values of the constitutive elements of CZTS at various temperatures.....	23
Table 3.4. Band gaps of the most likely secondary phases in Cu-Zn-Sn-(S,Se) systems (Siebentritt, 2013).....	25
Table 3.5. The initial parameters of one-stage SILAR process.....	40
Table 3.6. The initial experimental conditions of modified one-stage SILAR process.....	41
Table 3.7. The initial experimental molarities of two-stage SILAR process (different molar ratios).....	44
Table 3.8. The initial experimental conditions of SILAR grown ZnS, Cu ₂ SnS ₃ and SnS samples for comparison.....	44
Table 3.9. The initial experimental conditions of two-stage SILAR process (different deposition cycles).....	45
Table 3.10. The experimental parameters for preparing sol-gel grown CZTS film.....	46
Table 4.1. The relative elemental composition of the samples obtained through semi-quantitative, energy-dispersive x-ray spectroscopy (EDS) analysis.....	62
Table 4.2. Semi-quantitative energy-dispersive X-ray spectroscopy analysis of sol-gel grown CZTS films sulfurized at different temperatures.....	95
Table 4.3. Calculated structural parameters of the one-stage SILAR grown samples (obtained by using 0.01M SnCl ₂ and 0.05M Na ₂ S in 50 cycles).....i.....	98
Table 4.4. Derived IPCE or EQE values from the samples used as a photo-cathode in a photo-electro chemical cell.....	120

LIST OF FIGURES

	Page
Figure 3.1. Some device structures of the main TF solar cell approaches: (a) CdTe, (b) a-Si/l-Si, (c) CIGS/CZTS, (d) OPV, and (e) DSSC. (Abermann, 2013).....	17
Figure 3.2. The crystal structure of CZTS which is derived from the sphalerite structure by duplicating the unit cell. Yellow: S, blue: Cu, orange; Zn, red: Sn (Schorr, 2011).....	19
Figure 3.3. Schematic illustration of chalcopyrite, kesterite and stannite structures. The unit cell boundaries are denoted with dashed lines (Mitzi et al., 2011).....	21
Figure 3.4. (a) Ternary CZTS phase diagram including the possible secondary phases at 400 °C, (b) ternary CZTS phase diagram (Chen et al. (2010)).....	22
Figure 3.5. The schematic description of one cycle for the deposition of CZTS film.....	26
Figure 3.6. The image of SILAR setup used in the experiments.....	27
Figure 3.7. Schematic illustrations of sol-gel spin coating method (Adopted from Anonymous, 2013b).....	30
Figure 3.8. Scattering of monochromatic X-rays from the atomic layers of the specimen.....	33
Figure 3.9. Schematic diagram of an IPCE system.....	35
Figure 3.10. Diagram of a photoelectrochemical cell.....	36
Figure 3.11. Principle operation of a LDLS light source (Anonymous, 2013e).....	39
Figure 3.12. The image (a) and (b) schematic diagram of the sulfurization setup.....	43
Figure 3.13. The photograph of the solutions containing different amount of DEA changing from 0.3 to 2.0.....	47
Figure 3.14. Schematic illustration of the IPCE system.....	49

Figure 4.1.	SEM images and EDS results (c) of the SILAR grown sample obtained in one-stage by using 0.01 M CuCl_2 , 0.01 M ZnCl_2 , 0.01 M SnCl_2 , 0.05 M Na_2S in 50 cycles (each duration in the beakers was 5 s).....	51
Figure 4.2.	SEM images (a,b) and EDS results (c) of the SILAR grown sample obtained in one-stage by using 0.01 M CuCl_2 , 0.01 M ZnCl_2 , 0.01 M SnCl_2 , 0.05 M Na_2S in 50 cycles (each duration in the beakers was 15 s)....	52
Figure 4.3.	SEM images (a,b) and EDS results (c) of the SILAR grown sample obtained in one-stage by using 0.005 M CuCl_2 , 0.01 M ZnCl_2 , 0.01 M SnCl_2 , 0.05 M Na_2S in 50 cycles (each duration in the beakers was 15 s).....	53
Figure 4.4.	SEM images (a,b) and EDS results (c) of the SILAR grown sample obtained in one-stage by using 0.01 M CuCl_2 , 0.005 M ZnCl_2 , 0.01 M SnCl_2 , 0.05 M Na_2S in 50 cycles (each duration in the beakers was 15 s)....	54
Figure 4.5.	Images of the sulfurized samples obtained in (a) 15 and (b) 30 cycles.....	55
Figure 4.6.	SEM images of the modified one-stage SILAR grown samples. $M_{\text{Cu}}/M_{\text{Sn}}$: (a) 1.4 b) 1.2 (c) 1.0 (d) 0.8 (e, f) 0.6.....	56
Figure 4.7.	SEM image and EDS result of the two-stage SILAR grown CZTS film via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers. M_{Cu}/M is (a) 1/4 (b) 1/8.....	58
Figure 4.8.	SEM image and EDS result of the two-stage SILAR grown CZTS film via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers. $M_{\text{Cu}}/M_{\text{Sn}}$ is (a) 1/12 (b) 1/16	59
Figure 4.9.	The SEM image and EDS result of the two-stage SILAR grown CZTS films. The number of cycles for the $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers (a) 60/40 (b) 60/20.....	63
Figure 4.10.	The SEM images of the two-stage SILAR grown CZTS films. The number of cycles for the $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers (a) 30/40 (b) 30/20.....	64
Figure 4.11.	(a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 2.5 M DEA (Sulfur pressure: 20 atm).....	68
Figure 4.12.	(a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 2.0 M DEA (Sulfur pressure: 20 atm).....	69

Figure 4.13.	SEM images and EDS result of the sol-gel grown sample prepared from solution containing 1.5 M DEA (Sulfur pressure: 20 atm).....	70
Figure 4.14.	SEM images and EDS result of the sol-gel grown sample prepared from solution containing 1.0 M DEA (Sulfur pressure: 20 atm).....	71
Figure 4.15.	Plain view and cross-section SEM images of the sol-gel grown sample prepared from solution containing 1.0 M DEA (Sulfur pressure: 20 atm)...	72
Figure 4.16.	(a) EDS results and cross-section SEM image of the sol-gel grown sample prepared from solution containing 0,8 M DEA (Sulfur pressure: 20 atm)...	73
Figure 4.17.	SEM image and EDS result of the sol-gel grown sample prepared from solution containing 0.4 M DEA (Sulfur pressure: 20 atm).....	74
Figure 4.18.	SEM image and EDS result of the sol-gel grown sample prepared from solution containing 0.3 M DEA (Sulfur pressure: 20 atm).....	75
Figure 4.19.	(a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 0.9 M DEA (Sulfur pressure: 2.5 atm).....	76
Figure 4.20.	(a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 1.1 M DEA (Sulfur pressure: 2.5 atm).....	77
Figure 4.21.	EDS result of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 2.5 atm).....	78
Figure 4.22.	(a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 1.5 M DEA (Sulfur pressure: 2.5 atm).....	79
Figure 4.23.	(a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 1.7 M DEA (Sulfur pressure: 2.5 atm).....	80
Figure 4.24.	. (a) SEM images (b) EDS result of the sol-gel grown sample prepared from solution containing 1.9 M DEA (Sulfur pressure: 2.5 atm).....	81
Figure 4.25.	(a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 2.1 M DEA (Sulfur pressure: 2.5 atm).....	82
Figure 4.26.	SEM images of the sol-gel grown sample prepared from solution containing 1.5 M DEA (Sulfur pressure: 1.0 atm).....	83

Figure 4.27.	SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA under sulfur pressure of (a) 0.5 atm (b) 0.9 atm and (c) 1.4 atm.....	85
Figure 4.28.	Cross section SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA under sulfur pressure of (a) 0.5 atm (b) 0.9 atm and (c) 1.4 atm.....	86
Figure 4.29.	SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 0.5 atm).....	87
Figure 4.30.	EDS result of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 0.5 atm).....	88
Figure 4.31.	SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 0.9 atm).....	89
Figure 4.32.	EDS result of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 0.9 atm).....	90
Figure 4.33.	Figure 4.33. SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 1.4 atm).....	91
Figure 4.34.	EDS result of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 1.4 atm).....	92
Figure 4.35.	SEM images of the sol-gel grown CZTS films sulfurized at (a,b) 200 °C (c,d) 300 °C (e,f) 400 °C (g,h) 500 °C and (i) 700 °C.....	94
Figure 4.36.	SEM images of sol-gel grown CZTS sample sulfurized at (a) 200 oC and (b) 300 °C for 2 h under 20 atm. sulfur pressure ($M_{DEA}=1$).....	95
Figure 4.37.	SEM images of sol-gel grown CZTS sample sulfurized at (a) 400 (b) 500 and (c) 700 °C for 2 h under 20 atm. sulfur pressure ($M_{DEA}=1$).....	96
Figure 4.38.	The XRD patterns of the one-stage SILAR grown thin film samples prepared by using solutions containing different concentration of metal sources.....	99

Figure 4.39.	The XRD patterns of the modified one-stage SILAR grown films. The peaks (1), (7), (8) and (9) can be assigned to the (112), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(6) can be assigned to Cu_{2-x}S ; 00-024-0060.....	101
Figure 4.40.	The XRD patterns of the modified one-stage SILAR grown films. The peaks (1), (7), (8) and (9) can be assigned to the (112), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(6) can be assigned to Cu_{2-x}S ; 00-024-0060.....	102
Figure 4.41.	The XRD patterns of the modified one-stage SILAR grown films. The peaks (1), (5) and (7)-(9) can be assigned to the (112), (220), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(4) and (6) can be assigned to Cu_{2-x}S ; 00-024-0060.....	103
Figure 4.42.	The XRD patterns of the modified one-stage SILAR grown films. The peaks (1), (5) and (7)-(9) can be assigned to the (112), (220), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(4) and (6) can be assigned to Cu_{2-x}S ; 00-024-0060.....	104
Figure 4.43.	The XRD patterns of two-stage SILAR grown CZTS film via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers deposited with different MCu/MSn ratios.....	106
Figure 4.44.	The XRD patterns of the two-stage SILAR grown CZTS films via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ layers	108
Figure 4.45.	The XRD patterns of the Cu_2SnS_3 and ZnS precursor layers.....	109
Figure 4.46.	The Raman spectroscopy analyses of the samples over the range of 200 to 500cm^{-1}	109
Figure 4.47.	The XRD patterns of the two-stage SILAR grown CZTS films via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ layers.....	111
Figure 4.48.	The Raman spectroscopy analyses of the sample sulfurized at different temperatures. The sample prepared via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers. Number of deposition cycle ratio of the layers: 30/40.....	111
Figure 4.49.	XRD patterns of the CZTS films prepared by using different stabilizer amounts.....	113

Figure 4.50.	XRD patterns of the CZTS films prepared by using different stabilizer amounts.....	114
Figure 4.51.	XRD patterns of the CZTS films sulfurized at different sulfur pressures....	115
Figure 4.52.	The XRD patterns of sol-gel grown CZTS films sulfurized at 200, 300, 400 and 500 °C.....	117
Figure 4.53.	The XRD patterns of sol-gel grown CZTS films sulfurized at 700 °C.....	118
Figure 4.54.	The Raman spectra of the sol-gel grown CZTS films sulfurized at different temperatures.....	118
Figure 4.55.	Obtained IPCE results of the samples prepared under different sulfurization conditions.....	121
Figure 4.56.	Obtained IPCE results of the samples prepared by using 0.9 M DEA and sulfurized under sulfur pressure of 0.5 atm (Inset: Raman spectra).....	121
Figure 4.57.	Obtained IPCE result of the sample prepared by using 0.9 M DEA and sulfurized under sulfur pressure of (a) 0.9 and (b) 1.4 atm (Insets: Raman spectra).....	122
Figure 4.58.	Obtained IPCE results of the samples prepared by using 1.1 M DEA and sulfurized under sulfur pressure of 0.5, 0.9 and 1.4 atm.....	123
Figure 4.59.	Obtained IPCE results of the samples prepared by using 1.1 M DEA and sulfurized under sulfur pressure of 0.5 atm (Inset: Raman spectra).....	123
Figure 4.60.	Obtained IPCE result of the sample prepared by using 1.1 M DEA and sulfurized under sulfur pressure of (a) 0.9 and (b) 1.4 atm (Insets: Raman spectra).....	124
Figure 4.61.	Obtained (a) IPCE result, (b) SEM image and (c) Raman spectra of the sample prepared by using 1.3 M DEA and sulfurized under sulfur pressure of 0.5 atm.....	125
Figure 4.62.	Obtained (a) IPCE result, (b) SEM image and (c) Raman spectra of the sample prepared by using 1.3 M DEA and sulfurized under sulfur pressure of 0.9 atm.....	126

Figure 4.63.	Obtained (a) IPCE result, (b) SEM image and (c) Raman spectra of the sample prepared by using 1.3 M DEA and sulfurized under sulfur pressure of 1.4 atm.....	127
Figure 4.64.	Variation of (a) the IPCE and (b) band gap values sol-gel grown CZTS films with respect to pressure and DEA molarity.....	128
Figure 4.65.	Transmittance and reflectance spectra of the samples (a) $M_{Cu} = 0.005$ (b) $M_{Cu} = 0.01$	130
Figure 4.66.	Band gap energy estimations of the samples (a) $M_{Cu} = 0.005$ (b) $M_{Cu} = 0.01$	130
Figure 4.67.	Band gap energy estimations of the samples.....	133
Figure 4.68.	Band gap energy estimations of the samples of the sol-gel grown samples obtained by using (a) 1.0 M (b) 1.5 M (c) 2.0 M (d) 2.5 M DEA.....	135
Figure 4.69.	Band gap energy estimations of the sol-gel grown samples prepared by using 1.0 M DEA sulfurized at (a) 200 (b) 300 (c) 400 (d) 500 (e) 700 °C..	137

1. INTRODUCTION

As an alternative to carbon-based fuels, the development of green energy resources has become one of the most important tasks of researchers in recent decades. Among the diverse renewable energy resources, solar energy is probably the best to supply the energy consumption of the modern society (Anonymous, 2012). In recent years, due to a rapid increase in the demand for renewable energy sources, the production of solar cells has increased significantly. However, to make photovoltaic devices more widespread, it is required to develop promising, cheaper, more efficient and greener solar cells (Pawar et al., 2010).

Silicon is the most popular material for commercial solar cells. Approximately 80% of the market for photovoltaic devices is based on silicon. To produce silicon solar cells with high efficiency, it is necessary to use mono-crystal silicon wafers. But this necessity increases the production costs. Furthermore, silicon is an indirect-band-gap semiconductor and its absorption coefficient is relatively low, requiring the absorption layer be at least 100 μm thick so as to absorb a significant fraction of the incoming solar spectrum. Owing to those types of problems, the cost of the electricity produced by these solar cells is still higher compared to that produced by fossil fuels (Pawar et al., 2010; Sarswat et al., 2012).

Thin-film chalcogen materials, especially CuInSe_2 (CIS), $\text{CuInGa}(\text{S},\text{Se})_2$ (CIGS) and CdTe are currently used in the production of large-scale commercial photovoltaic devices. However, the shortage of indium and tellurium in the earth's crust limits the future of CIGS- and CdTe -based solar cells. In addition, due to the widespread use of indium in current display technologies and opto-electronic devices, the price of In and related solar cell production costs will increase in the near future. Another problem in CdTe -based solar cells is that cadmium (Cd) is very toxic both to health and the environment. This problem has lead researchers to look for more abundant and greener materials.

Because of its similar properties to the CIGS compound, the $\text{I}_2\text{-II-IV-VI}_4$ group as the basis for a new generation of absorber materials has attracted more attention. For example, the $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) compound is a good candidate in photovoltaic applications as an absorber layer (Ito et al., 1988; Katagiri et al., 2001; 2008; Ennaoui et al., 2009).

To date, physical vapor deposition (Sarswat et al., 2012; Katagiri et al., 2001; 2008; Seol et al., 2003; Katagiri, 2005; Araki et al., 2008; Yamaguchi et al., 2009; Wang et al., 2010; Fernandes et al., 2009; 2011a; 2011b; Schubert et al., 2011), electro-chemical deposition (Scragg et al., 2008; 2010; Zhang et al., 2009b; Pawar et al., 2010), sol-gel spin coating (Tanaka et al., 2007; 2009; 2011; Yeh et al., 2009; Moritake et al., 2009; Sarswat and Free, 2009; Fischereder et al., 2010; Maeda et al., 2011; Park et al., 2012; Chaudhurin and Tiwari, 2012) and successive ionic layer adsorption-reaction methods (Shin et al., 2011; Prabhakar and Jampana, 2011; Mali et al., 2012a; Su et al., 2012; Mali et al., 2012) have been used to produce CZTS thin films.

Although it is a promising absorber material, the studies on CZTS-based solar cells are still at an elementary stage (Sarswat et al., 2012). Nevertheless, 9.6%-efficient CZTS-based solar cells have been reported under laboratory conditions (Todorov et al., 2010). However in view of the fact that its potential theoretical efficiency is as high as 32.2% (Shockley, 1961), it is necessary to make more studies in order to increase the efficiency, to commercialize the material and to produce it through greener methods (Katagiri et al., 2009).

The main problem encountered in the production of CZTS thin films is the difficulty of obtaining high phase purity CZTS compound. This problem also affects the photo-conversion efficiency of the films, negatively. It has been mostly reported in the literature that many CZTS films have secondary phases like copper sulfides (Cu_xS), tin sulfides (SnS_x) or Cu-Sn-S compounds. To overcome this problem, several approaches have been suggested such as using non-stoichiometric precursor solutions, etching the final film with potassium cyanide, depositing copper, zinc and tin metals successively and sulfurizing them. However, in the solution of the aforementioned problem, the initial molar ratios of the constituting elements, stabilization of the precursor solution, sulfurization temperature and sulfur pressure are very crucial.

In this study, therefore, we aimed to optimize deposition conditions for CZTS thin films by changing initial Cu/Sn molar ratio, stabilizer amount in the precursor solution, sulfurization temperature and sulfur pressure.

2. PREVIOUS STUDIES

Ito and Nakazawa (1988) reported the first photovoltaic effect in CZTS-based hetero-junction diode. They deposited CZTS films by using sputtering of a stoichiometric target. They found that the film was (112) oriented and had a p-type conductivity. The films showed an absorption coefficient of 10^4 cm^{-1} in the visible range of the spectrum. The direct optical band gap of the film was estimated as 1.45 eV.

Katagiri et al. (1997) prepared CZTS films by sulfurization of evaporated precursors. They estimated the optical band gap energy and optical absorption coefficient as 1.45 eV and in the order of 10^4 cm^{-1} , respectively. Fabricated solar cells showed an open-circuit voltage up to 400 mV and the conversion efficiency was 0.66%.

Katagiri et al. (2001) formed CZTS films by vapor-phase sulfurization of precursors on Mo-coated SLG substrate. By fabricating Al/ZnO:Al/CdS/CZTS/Mo-SLG solar cell structure, the conversion efficiency of 2.62% and open-circuit voltage of 735 mV were achieved. Those results were the best reported values so far.

Katagiri et al. (2005) produced CZTS thin films by sequential vacuum evaporation of Cu, Sn, and ZnS. They used three different stacking orders: (1) Cu/Sn/ZnS, (2) Sn/Cu/ZnS, and (3) Cu/SnS₂/ZnS. The best conversion efficiency with the heterojunction of ZnO:Al/CdS and CZTS was 4.53%.

Katagiri et al. (2008) achieved an efficiency over 6.7% with co-sputtered CZTS thin film based solar cell for the first time by soaking deionized water which eliminated selectively metal oxide particles.

Tanaka et al. (2007) prepared CZTS thin films by sulfurizing sol-gel deposited precursors. They used copper (II) acetate monohydrate, zinc (II) acetate dihydrate and tin (II) chloride dihydrate as starting material, and 2-methoxyethanol and MEA as solvent and stabilizer, respectively. The chemical composition was almost stoichiometric and the band gap was estimated to be 1.49 eV.

Tanaka et al. (2009) prepared Al/ZnO:Al/CdS/CZTS/Mo/SLG solar cell structure with sol-gel grown CZTS film. Their best solar cell had an open-circuit voltage of 390 mV, a short-circuit current density of 7.8 mA/cm^2 , a fill factor of 0.33 and efficiency of 1.01% under AM 1.5 illumination and 100 mW/cm^2 .

Moritake et al. (2009) fabricated sol-gel grown CZTS based solar cells. They determined an optimum condition for CdS buffer layer deposition. The metal ion ratio was Cu-poor and Zinc-rich, $\text{Cu}/(\text{Zn}+\text{Sn})=0.87$ and $\text{Zn}/\text{Sn}=1.15$, to improve conversion efficiency. They used two types of solutions, 0.35 M and 1.75 M of metal ions. They spin-coated first monoethanolamine (MEA)-free 0.35 M solution to prevent the deterioration of the Mo by MEA. The best solar cell showed 1.61% efficiency which was thus far the highest one for CZTS solar cell prepared under non-vacuum conditions.

Tanaka et al. (2011) investigated the properties of sol-gel grown CZTS films as a function of chemical composition of the sol-gel solution. They changed the $\text{Cu}/(\text{Zn}+\text{Sn})$ chemical composition ratio from 0.73 to 1.00 and kept the Zn/Sn ratio constant as 1.15. The cell with the CZTS layer which was prepared by using the solution with $\text{Cu}/(\text{Zn}+\text{Sn})=0.80$ exhibited the best conversion efficiency of 2.03%.

Tanaka et al. (2013) fabricated three dimensional structured CZTS based solar cells. The short-circuit current density was improved after annealing with a CZTS covering layer, resulting from the reduction of cracks on the CZTS surface. They achieved an efficiency of 1.12% which was thus far the highest value for a 3D-CZTS solar cell.

Araki et al. (2008) fabricated stacked precursors of Cu, Sn and Zn by electron beam evaporation. Six different stacking sequences were prepared. The CZTS based solar cell using a sulfurized Mo/Zn/Cu/Sn precursors exhibited a conversion efficiency of 1.79% with an open-circuit voltage of 478 mV, a short-circuit current of 9.78 mA and a fill factor of 0.38.

Araki et al. (2009) prepared CZTS thin films by sulfurization of electrodeposited Cu-Zn-Sn precursors in one-step process followed by a sulfurization at 580 °C and 600 °C in an N_2 atmosphere. The best photovoltaic cell performance of 3.16% with an open circuit voltage of 540 mV was achieved with Zn-rich samples.

Fernandes et al. (2009) reported CZTS films prepared by sulfurization of sputtered Cu/Zn/Sn precursor layers. They investigated the effects of sulfurization temperature. Some traces of sulfide compounds like Sn_2S_3 , Cu_{2-x}S , ZnS were detected through Raman analysis. They eliminated Cu_{2-x}S phases by controlling the precursor compositions and/or KCN etching treatment.

Fernandes et al. (2010a) sulfurized dc magnetron sputtered Zn/Sn/Cu metallic layers to obtain CZTS based solar cells. They detected MoS₂ layer formed during sulfurization process. Their solar cell had the structure of SLG/Mo/CZTS/CdS/i-Zno/ZnO:Al/Al grid. The best solar cell showed an efficiency of 0.68% under AM 1.5 illumination.

Fernandes et al. (2011) prepared CZTS films by sulfurizing constituent metallic layers. They used different excitation wavelengths of 488, 512, 633 and 785 nm in Raman scattering analysis to detect secondary phases in dept. They showed that preparing single phase CZTS film is not a simple task and thus an in-depth study about the impact of the secondary compounds on cell performance should be performed.

Fernandes et al. (2013) investigated time intervals of sulfurization of dc-sputtered metallic precursor in CZTS solar cells. They detected an increase in electrical activation energy from 10 meV to 54 meV with increasing sulfurization time from 10 min to 60 min. They also found that the average acceptor doping density and built-in voltage decreased from $2.0 \times 10^{17} \text{ cm}^{-3}$ to $6.5 \times 10^{15} \text{ cm}^{-3}$ and from 0.71 V to 0.51 V, respectively.

Ennaoui et al. (2009) fabricated CZTS based thin film solar cells by solid state reaction in H₂S atmosphere of electrodeposited Cu-Zn-Sn precursors. They obtained the best solar cell efficiency with Cu-poor samples. The band gap of the films was estimated as 1.54 eV. A total area (0.5 cm²) efficiency of 3.4% was achieved.

Guo et al. (2009) synthesized slightly poly-dispersed CZTS NCs by hot injection of a solution of sulfur in oleylamine into oleylamine solution containing copper, zinc and tin precursors at 225 °C. The average composition of the CZTS NCs was determined as Cu_{2.12}Zn_{0.84}Sn_{1.06}S₄. By drop-casting the nano particles onto Mo (500 nm) coated glass substrates, they fabricated nano-crystal-ink based solar cells. The prepared cells exhibited 0.74% efficiency under AM 1.5 illumination.

Guo et al. (2010) fabricated CZTSSe solar cells by selenization of CZTS NCs prepared by hot injection method. They achieved a total area efficiency as high as 7.2% under AM 1.5 illumination and light soaking by tuning the composition of the CZTS NCs and developing a robust film coating method. The band gap of the CZTSSe films was estimated to be 1.05 eV which was lower than that of CZTS (~1.5 eV). Interestingly, the CZTSSe solar cells showed serendipitous stability over time. The efficiency was improved

to 6.89% after sitting in standard laboratory conditions for three months. After light soaking for 15 min under one sun illumination, the efficiency was further improved to 7.2%. However the improvement was temporary and the efficiency went back down to its starting point after the light was turned off.

Guo et al. (2012) synthesized $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) by electrodeposition of metal stack precursors followed by selenization. They achieved 7.0% efficiency and compared with a CZTS device of the same power conversion efficiency. They attributed the lower performance of the electrodeposited CZTS or CZTSe solar cells with respect to a solar cell fabricated by evaporation to a higher concentration of oxygen in the electrodeposited absorber. They measured the longest minority lifetime of 18 ns among all the reported kesterite devices.

Riha et al. (2009) reported for the first time the synthesis of homogeneous, nearly monodisperse CZTS nano crystals prepared by using hot-injection solution method. The results indicated that the films of those nano particles exhibit clear photo response. They estimated the band gap of the nano crystals to be 1.5 eV through UV-Vis data.

Riha et al. (2011a) fabricated CZTS thin films on FTO substrates by dip-casting CZTS nano crystals synthesized by a hot injection method. They found that the minority carrier diffusion recombination at back contact is the main loss mechanisms in the cell. They also found that low-temperature (at 350 °C for 1.5 h) annealing resulted in significant increases in the photo-response for films both Zn-rich and stoichiometric CZTS nano crystals.

Riha et al. (2011b) synthesized stoichiometric and Cu-poor/Zn-rich CZTS NCs by a hot injection solution method and fabricated them into films by dip-casting onto fluorine doped tin oxide (FTO) substrates. They investigated the effects of stoichiometry, film thickness and low temperature annealing on the photo-currents. They reported that low temperature annealing resulted in significant increases in the photocurrents for the films made from both Zn-rich and stoichiometric CZTS NCs.

Scragg et al. (2008) studied the feasibility of a new fabrication route for CZTS films, consisting of electrodeposition of metallic precursors. They found that the produced films are p-type with doping densities in the range $(0.5-5) \times 10^{16} \text{ cm}^{-3}$ and the band gaps of

1.49 eV. The study showed that a somewhat Cu-poor composition favors good optoelectronic properties.

Scragg et al. (2009) studied an electrodeposition-annealing route using layered metallic precursors. They investigated the dependence of device performance on composition and found that Cu-deficiency is desirable to produce effective material. They also demonstrated that H₂S annealing enhances films crystallinity.

Scragg et al. (2010) prepared CZTS thin films through annealing of metallic precursor stack in the order Cu/Sn/Cu/Zn in the atmosphere containing sulfur at 575 °C for 2 h. Prior to photoelectrochemical characterization they etched the films in aqueous potassium cyanide (KCN) to remove any copper sulfide phases from the surface. An efficiency of 3.2% was achieved with the best sample.

Scragg et al. (2011) investigated the problem of CZTS surface decomposition during annealing and thermodynamic origins of instability in CZTS. They figured out that to achieve stable CZTS surfaces the sulfur partial pressure should be greater than $(2.3 \pm 0.7) \times 10^{-4}$ mbar, and the product of partial pressures $p_{\text{SnS}} (p_{\text{S}_2})^{1/2}$ should be greater than $(3.8 \pm 1.2) \times 10^{-5}$.

Todorov et al. (2009) deposited Cu₂ZnSnS₄ films by the use of a printing technique. In order to minimize contamination with oxide and hydroxide species they developed a non-aqueous synthesis route. They allowed metal salts to react directly with elemental sulfur in ethylene glycol to obtain homogeneous and dispersible nanoparticles. They found that the addition of polymeric binder improved the film uniformity but impeded crystalline growth. Band gap values of the films were estimated to be between 1.32 and 1.85 eV.

Todorov et al. (2010) demonstrated a hybrid hydrazine processed solution-particle approach, using Cu₂ZnSn(S,Se)₄ system which ensured power conversion efficiency of 9.6%. The prepared solutions were spin-coated as five successive layers. They observed remarkably high photocurrents (36.4 mA cm⁻²) in the Se-rich device, while higher voltages (516 mV) and the best efficiency (9.66%) were measured in mixed sulfo-selenide device.

Todorov et al. (2013) reported hydrazine-processed CZTSSe devices with power conversion efficiency above 10.1% and the highest certified efficiency at the 11.1% level. They spin coated multiple layers of the solution containing constituent elements onto Mo-

coated substrates. Then the precursor films were heat treated at temperatures in excess of 500 °C. They optimized the sulfur concentration in the atmosphere during annealing. They completed the cells with CBD grown CdS buffer, sputtered ZnO and ITO window layers. A Ni-Al collection grid and 110 nm thick MgF_2 anti-reflective layer were deposited on the top of cell by e-beam evaporation. The final structure was glass/Mo/CZTSSe/CdS/ZnO/ITO/Ni-Al.

Schurr et al. (2009) reported the results of in-situ x-ray diffraction (XRD) experiments during crystallization of kesterite thin films from electrochemically co-deposited metal films. They performed angle-dispersive time-resolved XRD measurements. The measurements showed two different reaction paths depending on the metal ratios in the as-deposited films. They found Cu_3Sn and CuZn in copper-rich metal films whereas Cu_6Sn_5 and Sn phases in copper-poor or nearly stoichiometric precursors.

Zhang et al. (2009b) deposited CZTS compound semiconductor on polycrystalline Ag substrates by electrochemical epitaxial method with a sequence of S/Sn/S/Cu/S/Zn/S/Cu. It was proven that the deposits had a strong (112) preferred orientation. They found the stoichiometric ratio to be about 2:1:1:4 from x-ray photoelectron spectroscopy (XPS) and Energy dispersive x-ray spectroscopy (EDS) studies.

Weber et al. (2010) investigated the Sn loss from thin films of the material system Cu-Zn-Sn-S and subsystems Cu-Sn-S and Sn-S in high vacuum. They found that the evaporation rates from different phases decreased according to the order SnS, Cu_2SnS_3 , Cu_4SnS_4 , $\text{Cu}_2\text{ZnSnS}_4$. The SnS phase was assigned as the evaporating compound. It was found that a SnS loss with significant rates occurred at temperatures of 550 °C and above for CZTS films.

Wang et al. (2010) fabricated 6.8% efficient CZTS based solar cells by thermal evaporation of constituent elements. After a detailed electrical analysis they found that the performance of device is limited by high series resistance, a "double diode" behavior of the current voltage characteristics, and an open-circuit voltage which is limited by a carrier recombination process with an activation energy below the band gap of the material.

Pawar et al. (2010) electrodeposited CZTS thin films onto the Mo coated and indium doped tin oxide (ITO) glass substrates at room temperature. The deposition

mechanism was studied through cyclic voltammetry. They investigated the effects of post-annealing treatment. After annealing at 550 °C in Argon atmosphere for 1h, they obtained kesterite nearly stoichiometric CZTS thin films with band gap of 1.50 eV.

Sarswat and Free (2011) deposited CZTS films on FTO substrates by using sol-gel spin coating method for use in semitransparent solar cell applications. They found that the photocurrent response exhibited during the rear illumination was comparable to that obtained from the front illumination.

Sarswat et al. (2012a) examined CZTS films in $\text{Eu}^{3+}/\text{Eu}^{2+}$ electrolyte to evaluate various analytical expressions for photo-current response as a function of applied voltage. They proposed a modified theoretical model to explain J-V characteristics for CZTS-electrolyte solution. They also put forward that the photo-electrochemical transfer of electron at CZTS-solution interface is mainly due to a transition to acceptor states in solution through interfacial barriers.

Sarswat et al. (2012b) fabricated single phase CZTS films on fluorine doped tin oxide (FTO) substrates using a specially designed 3-stage electrochemical system. Sequential electrodeposited tri-layer stacks (Zn/Cu/Sn) were annealed in sulfur environment. All characterizations indicated that the films are single phase with a band gap of 1.5 eV.

Sarswat and Free (2013) reported a microwave assisted synthesis of CZTS NCs. They kept a tube containing constituent precursors in oleylamine for the time period of ~15-20 min. Their results suggested that formation of CZTS phase starts after ~8 min. A shift of $\sim 4 \text{ cm}^{-1}$ for strong peak in Raman spectra was attributed to two different CZTS crystal structure.

Bär et al. (2011) investigated the impact of KCN etching on the chemical and electronic surface structure of Cu-poor and Cu-rich CZTS thin-films via direct and inverse photoemission. After KCN etching they found remarkably changed surface compositions, leading a broadening of the surface band gap.

Maeda et al. (2011) investigated CZTS thin films prepared by a sol-gel spin coating method with respect to H_2S concentration in the annealing atmosphere. The most efficient

solar cell was prepared with an H_2S concentration of 3% and a conversion efficiency of 2.23% was achieved.

Shin et al. (2011) deposited CZTS thin films by sputtering on glass substrates using different stacked precursors. They found that CZTS thin film using a stacking order $\text{Cu/SnS}_2/\text{ZnS/glass}$ had a pure CZTS phase without any secondary phase whereas stacking orders $\text{ZnS/Cu/SnS}_2/\text{glass}$ and $\text{SnS}_2/\text{ZnS/Cu/glass}$ had secondary phases such as Cu_{2-x}S , SnS_2 and SnS .

Shin et al. (2012) synthesized single phase CZTS NCs using a two-step process. They obtained precursor powders by using microwave irradiation of solution containing copper, zinc, tin and sulfur elements at 700 W for 10 min which was followed by sulfurization in H_2S (5%) + N_2 (95%) atmosphere at 550 °C for 1 h. They didn't detect any secondary phases. A weight loss at about 840 °C and endothermic peak at same temperature as CZTS nature was detected through thermal-gravimetric analysis (TGA) and differential thermal analysis (DTA), was detected.

Shin et al. (2013) fabricated CZTS solar cells with 8.4% efficiency. Their optimal composition was Cu-poor and Zn-rich, which was consistent with the literature. They also obtained a reasonably good short-circuit current despite a very thin absorber thickness (~600 nm).

Xin et al. (2011) prepared CZTS NCs with diameter of 15 ± 6 nm by employing a solution based synthesis approach. They spin coated or drop-casted them onto the FTO glass and sintered them at 540 °C for 1 h in selenium vapor. They investigated the electrocatalytic activity of CZTS for use in DSSCs. They presented that CZTS can be exploited as an effective counter electrode (CE) material to replace expensive Pt. They achieved a power conversion efficiency (PCE) of 7.37% by a simple process of spin coating CZTS followed by selenization.

Yakuphanoglu (2011) prepared a hetero-junction diode through depositing CZTS film onto n-type silicon wafer via sol-gel method. He investigated the electrical characteristics of the diode and calculated the ideality factor, barrier height and interface state density as 2.84, 0.738 eV and $3.63 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$, respectively.

Schubert et al. (2011) fabricated solar cells based on Cu-rich CZTS film prepared by evaporation using ZnS, Sn, Cu and S sources. The determined compositional ratios were Cu/(Zn+Sn): 1.0 and Zn/Sn: 1.0. They obtained an efficiency of 4.1% and open-circuit voltage of 541 mV.

Mali et al. (2012a) reported the deposition of CZTS thin films by a SILAR method. Combining XRD and FT-Raman studies, they revealed that the films exhibit preferential orientation along [112] direction and have small Cu_{2-x}S phase. They found that the total conversion efficiency of the CZTS cell was 1.85% under 30 mW/cm^2 illumination through PEC study of the films.

Mali et al. (2012b) reported the SILAR grown CZTS based PEC cells with the power conversion efficiency of 0.396% under 30 mW/cm^2 illumination. But it is spectacular that the prepared films may not be pure CZTS phase. In SILAR method, it is very hard to deposit Zn in one beaker containing Cu. So Zn layer should be grown separately. Moreover they didn't do Raman study to support their assumptions.

Shinde et al. (2012a) reported preparation of CZTS films by a SILAR method. They investigated the effects of vacuum annealing. They characterized the precursor films by using SEM, XRD, UV-Vis, electrical and PEC techniques. They found the optical band gap as 1.55 eV. They claimed that XRD studies revealed the kesterite formation. However, it is well known that XRD patterns of $\text{Cu}_2\text{ZnSnS}_4$, ZnS, Cu_{2-x}S and Cu_2SnS_3 overlap. Thus, it can be said that the results reported in that paper are speculative because additional structural studies like Raman must be carried out to prove phase purity.

Su et al. (2012) fabricated CZTS thin films by sulfurizing stacked precursor thin films via successive ionic layer adsorption and reaction (SILAR) method. They used a stacked structure of glass/ Cu_2SnS_x /ZnS to prevent the migration of Cu to the surface of CZTS to form Cu_{2-x}S phase which can deteriorate the performance of solar cell device. They used $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ as a sulfur source. They proved the phase purity and composition through Raman and EDS spectroscopy, respectively. They reported that the films have kesterite structure and p-type conductivity with a carrier concentration in the order of 10^{18} cm^{-3} and optical band gap of 1.5 eV.

Walsh et al. (2012) reported the theoretical insights on the CZTS' structural, electronic and defect properties and found that the stable kesterite crystal structure of CZTS is gained from the ternary chalcopyrite structure and the stable chemical potential region required to form the stoichiometric compound is very narrow. They also suggested that CZTS should be grown under Cu poor/Zn rich condition for efficient solar cell which can be possible if the precipitation of ZnS is avoided.

Yang et al. (2012) spin coated hydrazine processed CZTS precursor solutions on Mo-coated SLG substrates. They annealed the films under different atmospheres: pure selenium vapor, pure sulfur vapor and combined selenium and sulfur vapors. The most efficient cell produced a short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor, and power conversion efficiency of 32.3 mA/cm², 409 mV, 61.0%, and 8.08% respectively.

Barkhouse et al. (2012) achieved a power conversion efficiency record of 10.1% using a Cu₂ZnSn(S,Se)₄ thin film solar cell made by hydrazine-based solution processing. They found that the performance of the produced record device was limited by interface recombination, minority carrier lifetime and series resistance.

Chaudhuri et al. (2012) deposited pure CZTS films from a methanolic solution of metal-thiourea complex. The precursor films were thermolysed at 200 °C in air for 10 min. The grain sizes were about 100-200 nm and rms roughness was 1-2 nm. The energy band gap of the films was determined as 1.4 eV. They found that a precursor solution of Cu, Zn and Sn salts with thiourea in methanol produce shiny and smooth pure kesterite CZTS films.

Grossberg et al. (2012) synthesized CZTS polycrystalline powder from metallic precursor powders in a quartz ampoule at 1000 °C for 50 h. Cu₂S and S were added to initial CZTS powder. The powder was again inserted into an ampoule and kept at 550 °C for 170 h. They detected two PL bands at 1.27 eV and 1.35 eV at 10 K. Similar behavior with the temperature and the excitation power was found for both PL bands and attributed to the BI-recombination.

Hsu et al. (2012) examined the phase evolution, grain morphology and device performance in Cu-rich, Zn-rich and close-to-stoichiometric growth. They investigated the

film growth starting from a Cu-rich composition and Zn-rich composition. Each growth mechanism was analyzed by examining films obtained from a number of interrupted depositions. They achieved an efficiency of 9.1% with a Zn-rich growth.

Shinde et al. (2012b) deposited CZTS thin films by chemical bath deposition method. They investigated the effects of post-annealing treatment. As-deposited amorphous films were converted to polycrystalline CZTS after annealing at 673 K. The optical band gap was estimated to be 1.5 eV. They found electrical activation energies as 0.62 and 0.67 eV for as-deposited and annealed films.

Shinde et al. (2013) studied the deposition of CZTS thin films by a SILAR method. They investigated the effects of air annealing in the temperature range between 573-773 K for 4 h in order to remove possible hydroxide and to improve the crystallinity. They used 0.1 M Cu, 0.05 M Zn, 0.05 M Sn and 0.2 M S sources. In this study, however, they didn't perform compositional study like EDS or XPS and structural study like Raman to prove CZTS formation. In this respect, it can be said that the results reported in that paper are speculative.

Ananthoju et al. (2013) fabricated CZTS films with densely packed micron size grains using a single bath electrodeposition process followed by sulfurization. They estimated the band gaps of the films to be 1.5 eV through UV-Vis absorption spectra and photoluminescence (PL) measurements.

Ericson et al. (2013) studied how the film properties were affected by substrate heating and composition. They found that substrate temperature during deposition had a significant effect on the solar cell performance. The best solar cell which was prepared onto the substrate heated to 300 °C showed an efficiency of 4.5%.

Huang et al. (2013) fabricated CZTS films by ultrasonic spray pyrolysis on FTO substrates and investigated the substrate temperature. The samples at 400 and 450 °C showed higher photocurrent than the samples at 350 and 500 °C. They measured the band positions of CZTS for the first time. The conduction band position of CZTS was found as 0.26 eV higher than that of CdS buffer. They explained the low open-circuit voltage of CZTS-based solar cells with this phenomenon.

Kang et al. (2013), synthesized CZTS nanocrystals (NCs) through one-pot aqueous chemical method which was carried out at 95 °C for 24 h. The obtained NCs showed enhanced conductivity under illumination of light, exhibited a band gap of 1.43 eV.

Kheraj et al. (2013) reported CZTS powder synthesized in an evacuated quartz ampoule at 1030 K for 24 h. They used 20%, 30% and 40% excess sulfur in the raw mixture. They got a good atomic stoichiometry in the sample prepared with 30% and 40% excess sulfur in the raw mixture. The band gap of the sample was calculated as 1.45 eV for the sample prepared with 40% excess sulfur.

Liu et al. (2013) used a facile hydrothermal method for synthesizing CZTS NCs with an average size of 5-6 nm at temperature as low as 180 °C using Cu(II), Zn(II), Sn(II) inorganic salt and thiourea as precursor. The band gap energy was determined as 1.47 eV.

Mkawi et al. (2013) fabricated CZTS films via sequential electrodeposition method by using a flexible copper plate as substrate. They investigated the effects of copper salt concentration in the precursors. They showed that the chemical homogeneity of the precursors greatly affects the quality of the crystal growth and crystallite size of the particles and they detected small traces of copper sulfide peaks in XRD patterns.

Park et al. (2013) fabricated CZTS thin films without sulfurization step. They prepared precursor solutions with CuCl₂, Zn(ac)₂, SnCl₂, thiourea, and 2-methoxyethanol and annealed them under N₂ atmosphere at 540 °C. The grain size was about 1 μm and Cu/(Zn+Sn) and Zn/Sn ratios were 0.93 and 1.07, respectively.

Patel et al. (2013) synthesized CZTS powder from stoichiometric elemental precursors sealed in an evacuated quartz ampoule. They heated the ampoule at 1030 K for 24 h. They studied the effects of annealing. They detected secondary phases such as SnS and SnS₂ in the as-grown sample and reported that the sample annealed at 1073 K exhibited better stoichiometry than the sample annealed at 773 K.

Platzer-Björkman et al. (2013) made CZTS thin films by using sulfurization of co-sputtered metallic (using Cu:Sn and Zn targets) and sulfur-containing (using Cu:Sn and ZnS targets) precursor films. They used two different sputtering targets: Cu:Sn (60:40) and Zn or ZnS. For several samples with Cu-poor/Sn-rich composition the SnS₂ phase and a tin-rich bottom layer were observed. The highest efficiency of solar cell devices was seen

in two compositional regions: Zn-rich and Cu-poor while stoichiometric material gave poor performance.

Ricardo et al. (2013) obtained $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$ powders through using high energy ball milling method. They optimized the production process as well as the recrystallization thermal treatment leading to fully kesterite samples with different levels of iron contamination from milling vials. No traces of metallic iron were found in the final semiconductor phase. A lower limit in the iron content was found as about 0.5 atomic ratio.

Sun et al. (2013) synthesized CZTS thin films by a dip coating process using CuCl_2 , ZnCl_2 , SnCl_2 and thioacetamide (TAA). They sulfurized or selenized the precursor films at 500 °C for 30 min. They investigated the effects of replacement of S by Se on the CZTS films. They estimated the optical band gap values as 1.48 and 1.35 eV for sulfurized and selenized films, respectively.

Malerba et al. (2014) prepared CZTS kesterite thin films by sulfurization of e-beam evaporated multilayered precursors of ZnS, Cu and Sn, changing the relative amounts to obtain different compositions. They aimed to investigate how the material composition changes the band gap energy. It was found that band gap is strongly influenced by the tin content, in particular, by the $[\text{Cu}]/[\text{Sn}]$ ratio and increased from 1.48 to 1.63 eV with increasing $[\text{Cu}]/[\text{Sn}]$ ratio.

3. MATERIAL AND METHOD

3.1. Material

3.1.1. Photo-voltaic materials

The development of green-energy resources as an alternative to carbon-based fuels has become one of the most important targets assigned to researchers in recent years. Among the diverse forms of renewable energy sources, solar energy is the best option because it can meet the energy demands of modern society (Anonymous, 2012). Lately, the production of solar cells has significantly increased due to a rapid increase in demand for renewable energy sources. In order to make photovoltaic devices more widespread, cheaper, more efficient, green solar cells have to be developed (Pawar et al. 2010). Silicon is the most commonly used material in commercial solar cells, and, about 80% of the photovoltaic market is silicon-based devices. The production of highly efficient silicon solar cells requires the use of mono-crystal silicon wafers, which dramatically increases the production costs. Moreover, silicon is an indirect-band-gap semiconductor and its absorption coefficient is relatively low, requiring the absorption layer to be at least 100 μm thick in order to absorb a significant fraction of the incoming solar spectrum. As a result of these problems, the electricity produced by solar cells is still expensive compared to that produced by fossil fuels (Pawar et al. 2010; Sarswat et al. 2012b).

Thin-film chalcogen materials, especially CuInSe_2 (CIS), $\text{CuInGa}(\text{S},\text{Se})_2$ (CIGS) and CdTe , are currently used in the production of large-scale, commercial and photovoltaic devices. To date thin film solar cells based on the ternary chalcopyrite structure CuInSe_2 (CIS) have emerged as one of the most successful ones, progressing from first proof-of-concepts to high-efficiency record devices of over 20% for laboratory scaled CIGS devices and over 15% for modules that are presently manufactured in the hundreds of MW to GW range (Abermann, 2013). Basic device structures of the main thin film solar cell approaches are shown in Figure 3.1.

However, the scarcity of indium and tellurium in the earth's crust limits the future of CIGS- and CdTe -based solar cells. In addition, the price of In and relatedly solar-cell production costs will increase in the near future due to the extensive use of indium in

display technologies and opto-electronic devices. Another problem with CdTe-based solar cells is that the cadmium is very toxic to health and the environment. Main drawbacks of current photovoltaic materials are summarized in Table 3.1. These drawbacks and the problems discussed above led researchers to search for more abundant and greener materials. The $I_2-II-IV-VI_4$ group has been receiving more attention as a new-generation absorber materials because of its similar properties to the CIGS compound. Copper-zinc-tinsulfide/selenide ($Cu_2ZnSnS_4(Se_4)$, CZTS or CZTS(e)) entered the spotlight of researchers all over the world. CZTS is the $I_2-II-IV-VI_4$ quaternary compound semiconductor obtained by replacing one half of the indium atoms in $CuInSe_2$ with zinc (group II) and the other half with tin (group IV). All components of CZTS are abundant in the earth's crust (Cu: 50-70 ppm, Zn: 75-80 ppm, Sn: 2.2 ppm, S: 260 ppm) and they possess extremely low toxicity (Abermann, 2013). The Cu_2ZnSnS_4 (CZTS) compound is a good candidate for photovoltaic applications as an absorber layer (Ito and Nakazawa, 1988; Katagiri et al. 2008; Ennaoui et al., 2009; Katagiri et al. 2001).

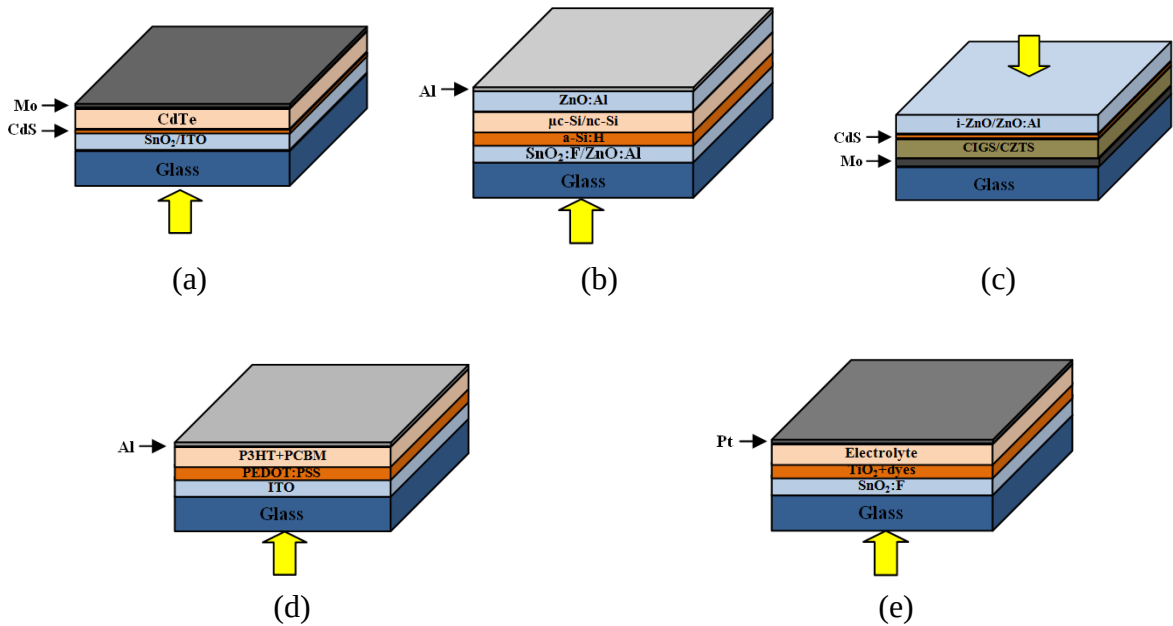


Figure 3.1. Some device structures of the main TF solar cell approaches: (a) CdTe, (b) a-Si/l-Si, (c) CIGS/CZTS, (d) OPV, and (e) DSSC. (Abermann, 2013)

CZTS has a direct band gap ranging from 1.4 to 1.6 eV which is close to the optimum value required for a single junction solar cell's absorber layer, a high absorption coefficient in the visible solar spectrum wavelengths and a p-type conductivity resulting from intrinsic point defects.(Kahraman et al., 2013; Delbos, 2012).

As mentioned above, CZTS is gained from the CIGS structure by the isoelectronic substitution of two In (or Ga, respectively) atoms by one Zn and one Sn atom. Thus the properties of CZTS are similar to those of CIGS. One of main advantages is that the standard device structure of the solar cells can be easily adopted. Moreover, it allows starting directly without spending much time in searching for a working device structure (Flammersberger, 2010).

The crystal structure of CZTS is shown in Figure 3.2. It is referred to as kesterite and can be derived from the sphalerite structure by duplicating the unit cell. The kesterite structure is the most stable phase of CZTS (Maeda et al., 2009). The lattice constants for CZTS are $a=0.54$ nm and $c=1.09$ nm (Hall et al., 1978). The density of CZTS is ~ 4.6 g/cm³ which can be calculated with the atomic masses of Cu, Zn, Sn and S (Lide, 1998).

However, even though it is a promising absorber material, the studies on CZTS-based solar cells are at an early stage (Sarswat et al., 2012b). Contrary to 32.2% theoretical efficiency for quaternaries (Shockley, 1961), an efficiency of 9.6% has been reported for CZTS-based solar cells in laboratory conditions (Todorov et al., 2010).

Table 3.1. Main drawbacks of current photovoltaic materials

Main drawbacks of current PV materials	
c-Si	Requires thick layers which increases production cost
a-Si	Low mobility, stability problems
GaAs	Arsenic toxicity, substrate cost
CIGS	Indium scarcity/cost
CdTe	Cadmium scarcity, tellurium/cost

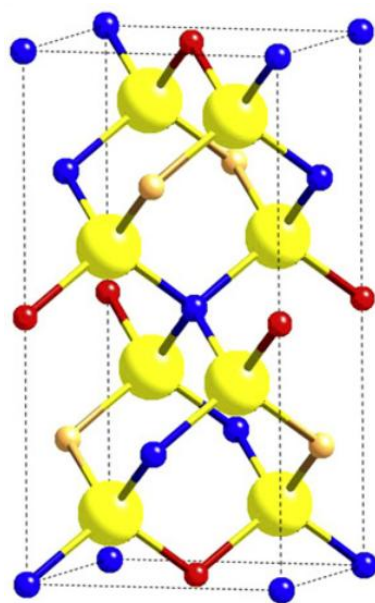


Figure 3.2. The crystal structure of CZTS which is derived from the sphalerite structure by duplicating the unit cell. Yellow: S, blue: Cu, orange; Zn, red: Sn (Schorr, 2011).

This result suggests that more studies are needed to increase the efficiency and to develop green and repeatable production methods, which would ensure successful commercialization (Anonymous, 2010). The most important routes to produce CZTS films are (i) solution-based precursor fabrication followed by a short annealing, (ii) annealing of nano-crystalline precursors, (iii) low-temperature co-evaporation followed by a short annealing, (iv) sputter deposition followed by long annealing in H_2S , and (v) fast co-evaporation (Redinger et al., 2011; Riha et al., 2009).

Generally known as aqueous solution deposition methods have several advantages: Among them, solution-based precursor fabrication is one of the important ones through which a variety of thin films can be grown at low temperatures using cheap manufacturing equipment. The sol-gel method is a very simple and low-cost process based on hydrolysis and poly-condensation reactions. Sulfide films can be directly obtained by sulfurizing oxyhydrate precursors. So far, several research groups have reported CZTS thin films produced via the sol-gel method. To the best of our knowledge, the first sol-gel-grown CZTS film was reported by Tanaka et al., (2007). They prepared CZTS films by annealing oxyhydrate precursors in a $\text{N}_2 + \text{H}_2\text{S}$ toxic gas atmosphere. Yeh et al. (2009) prepared

CZTS films by using metal chlorides with thiourea and investigated the effects of annealing between 160 and 320 °C in air. Fischereder et al. (2010) deposited CZTS films on ITO-coated glass substrates by using thioacetamide (TAA) as a source of sulfur. They studied the influence of vacuum annealing temperature (180-450 °C) and the concentration of TAA in precursor solutions. Park et al., (2013) fabricated CZTS thin films via the sol-gel method and then annealed the samples at temperatures above 500 °C in a N₂ atmosphere without any sulfur source. However, the main roles of the stabilizer in precursor solution, sulfur pressure and sulfurization temperature have not been investigated in detail. Those deposition parameters must be optimized to produce high quality CZTS films. Thus, it is still necessary to improve the quality of sol-gel-processed CZTS films and to find non-toxic ways to tolerate sulfur loss during annealing.

3.1.2. Crystal structure, defects, composition and phase diagram of CZTS

Schematic illustration of chalcopyrite, kesterite and stannite structures are given in Figure 3.3. Although it was not clear whether the crystal structure of Cu₂ZnSn(S,Se)₄ is a kesterite (Hall et al., 1978) or a stannite phase (Bernardini et al., 2000), these two phases only differ in that order of Cu and Zn atoms. Through neutron diffraction study of various Cu₂ZnSn(S,Se)₄ compounds, it was shown that Cu₂ZnSnS₄ and Cu₂ZnSnSe₄ occur in the kesterite structure but not in the stannite structure (Siebentritt and Schorr, 2012; Schorr, 2011).

Similar to the case of CIGS materials, the doping and relatedly the band bending in CZTS are supposed to be resulted from the defects (Delbos, 2012; Siebentritt and Schorr, 2012). Some observed defects are (1) the defect with the lowest formation energy is the acceptor Cu_{Zn} defect, (2) low energy formation acceptors which are Cu_{Sn} and V_{Cu} (Chen et al., 2010a; Chen et al., 2010b), (3) donor defect levels such as V_S or Zn_{Cu} which show higher formation energies in general, in combination with the low energy of Cu_{Zn}. These defects explain that why Cu₂ZnSnS₄ and Cu₂ZnSnSe₄ have intrinsically p-type conductivity (Abermann, 2013). Figure 3.4 shows the experimentally derived phase diagrams for

$\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ compounds. It can be seen that both phase diagrams suggest a narrow region of kesterite with single phase.

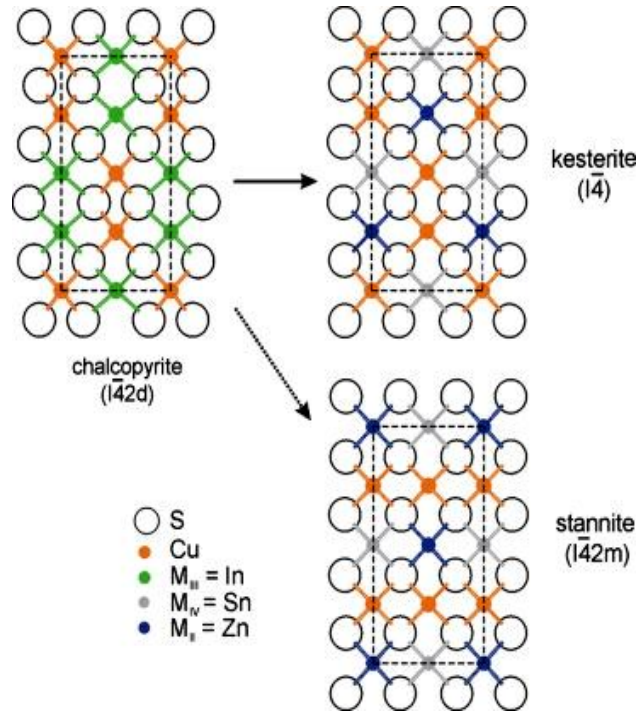


Figure 3.3. Schematic illustration of chalcopyrite, kesterite and stannite structures. The unit cell boundaries are denoted with dashed lines (Mitzi et al., 2011).

Owing to its structural complexity, many secondary phases may exist in CZTS. Expected secondary phases related to the compositional regions are summarized in Table 3.2. As can be seen in Figure 3.4 that there are eleven regions seen in the phase diagram. Each region describes the presence of one or two additional secondary phases. The 11th region approximately in the middle means that only CZTS form is supposed to exist. ZnS is the main expected secondary phase formed by the excess Zn, in the Zn-rich region. The Zn-poor region covers several regions with various possible secondary phases all of which contain sulfur. It can be supposed that no metallic phases form but only sulfides if sufficient amount of sulfur is supplied during sulfurization (Flammersberger, 2010). In the Cu-rich,

Sn-poor and Zn-poor regions, copper sulfides can be found. The main disadvantage of Cu_2S is that it shunts the junction, so that the current cannot be used for an external load.

Another possible binary phase in CZTS systems is SnS_2 which is an n-type semiconductor with a band gap of 2.2 eV (Shibata, 1990). This phase could work as an insulator. If it exists in larger amounts, it may form a second diode with opposite polarity to CZTS, which would act as a barrier to carrier collection and reduce the fill factor (Flammersberger, 2010).

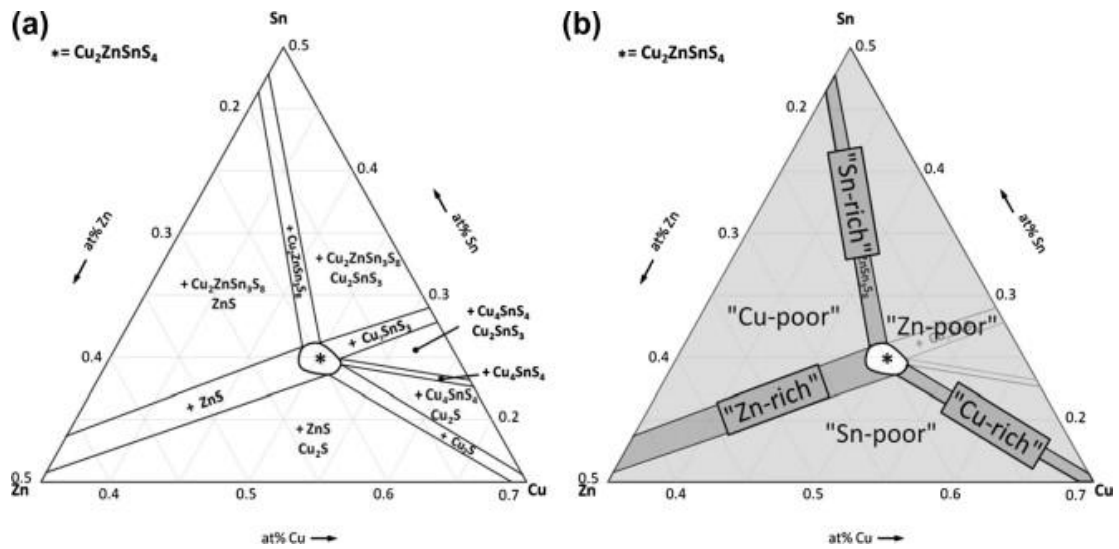


Figure 3.4. (a) Ternary CZTS phase diagram including the possible secondary phases at 400 °C, (b) ternary CZTS phase diagram (Chen et al. (2010))

Table 3.2. Expected secondary phases related to the compositional regions in the CZTS ternary phase diagram (adapted from Biswas et al. (2010)).

Possible secondary phases	Compositional region
$\text{Cu}_2\text{ZnSn}_3\text{S}_8 + \text{ZnS}$	Cu-poor
$\text{Cu}_2\text{ZnSn}_3\text{S}_8$	Sn-rich
$\text{Cu-Sn-S} + \text{Cu}_2\text{ZnSn}_3\text{S}_8/\text{Cu}_2\text{S}$	Zn-poor
Cu_2S	Cu-rich
$\text{Cu}_2\text{S}, \text{ZnS}$	Sn-poor
ZnS	Zn-rich

ZnS is the most encountered secondary phase in the Sn-poor, Cu-poor and Zn-rich regions (Redinger et al., 2011; Wibowo et al., 2013). This material could be assumed as an insulator due to the high band gap (~ 3.7 eV). This implies that the presence of zinc sulfide can both restrain the current conduction and reduce the active area in the absorber. ZnS may be responsible for the observed high series resistance in CZTS solar cells (Mitzi et al., 2011). Its crystal structure is very similar to that of CZTS. CZTS, as the compound CTS (Cu_2SnS_3), is a superlattice to sphalerite. This results in a serious problem concerning XRD measurements, which are one of the analyzing methods used in this thesis. In fact, it is not possible to distinguish ZnS, CTS and CZTS phases by performing only XRD study. CTS is a secondary phase that appear in Zn-poor region of the phase diagram of CZTS. CTS shows metallic properties (Wu et al., 2007), which makes it a very detrimental secondary phase like copper sulfides. It is only possible to assume that CTS can be prevented by producing films which have not a Zn deficiency (Flammersberger, 2010).

It is required to get the temperatures between 500 and 600 °C to obtain quaternary structure (Washio et al., 2011). Before the formation of the quaternary phase, successive reactions form some binaries and ternaries such as CuZn, Cu_3Sn or Cu_5Zn_8 . ZnS reacts with $\text{Cu}_2\text{SnS(e)}_3$ to form $\text{Cu}_2\text{SnZnS(e)}_4$ at temperature between 550 and 580 °C (Washio et al., 2011; Volobujeva et al., 2009; Schurr et al., 2009; Ganchev et al., 2011). It is important to control temperature ramps and intervals to be able to control the reactions in the annealing or sulfo-selenization step and to get large grains (Ge et al., 2012; Maeda et al., 2011).

Table 3.3. Vapor pressure values of the constitutive elements of CZTS at various temperatures

		Vapor pressure (Pa)					
		10^0	10^1	10^2	10^3	10^4	10^5
Cu	Temperature (°C)	1782	1934	2123	2362	2677	3107
Zn		883	943	1023	1125	1263	1452
Sn		1770	1930	2128	2380	2711	3166
S		648	681	722	781	864	990

The formation of $\text{Cu}_{2-x}\text{S(e)}$ has to be suppressed because the presence of $\text{Cu}_{2-x}\text{S(e)}$ leads to an increased layer resistance, reduce in efficiency, and to some voids/defects during cyanide etching after deposition (Delbos, 2012; Muska et al., 2011). Additionally, SnS sublimes at 350 and Zn at 430 °C (Redinger and Siebentritt, 2010; Teeter et al., 2010). As a conclusion it is necessary to prevent CZTS decomposition and binary losses during annealing which can be achieved through (i) controlling the atmosphere during the thermal treatment, or (ii) annealing time and heating/cooling rates. SnS(e) losses can be prevented/deduced by introducing gaseous SnS(e) (Redinger et al., 2011), increasing partial pressure of chalcogen (Fella et al., 2011), or performing the chalcogenation in a closed box (Biccari et al., 2011),

A two-stage annealing sequence where CZTS formation is done during a short (a few minutes) step, followed by a longer (up to a few hours) step for the grain growth can be performed to prevent decomposition. Vapor pressure values of constitutive elements of CZTS at various temperatures are given in Table 3.3.

The band gap of the possible secondary phases may give a first idea to see how detrimental a secondary phase affects solar cell efficiency. The band gaps of the most likely secondary phases are given in Table 3.4. If the band gap of a secondary phase is lower than that of actual absorber, the open-circuit voltage of the solar cell is limited. According to Siebentritt, (2013), the presence of a material with a band gap lower by only 100 meV can reduces the maximum achievable conversion efficiency by 8%. Although secondary phases with higher band gaps are less detrimental, they can block the transport when present in large amounts (Watjen et al. 2012) or increase the series resistance (Redinger et al., 2013).

Table 3.4. Band gaps of the most likely secondary phases in Cu-Zn-Sn-(S,Se) systems (Siebentritt, 2013).

Compound	Band gap (eV)	Reference
Cu ₂ ZnSnS ₄	1.5	Ito and Nakazava, 1988
ZnS	3.7	Yu and Cardona, 2003
SnS ₂	~2.5	Lin et al., 2009
Cu ₂ SnS ₃	1.0	Fernandes et al., 2010b
Cu ₂ S	1.2	Liu et al., 2003
SnS	1.0 indirect, 1.3 direct	Vidal et al., 2012; Sinsermsuksakul et al., 2011
Cu ₂ ZnSnSe ₄	1.0	Siebentritt and Schorr, 2012
ZnSe	2.7	Yu and Cardona, 2003
SnSe ₂	1.0-1.6	Sava et al., 2006
Cu ₂ SnSe ₃	0.8	Marcano et al., 2001
Cu ₂ Se	1.2	Kashida et al., 2003
SnSe	1.3	Franzman et al., 2010

3.2. Method

3.2.1. Successive Ionic Layer Adsorption and Reaction Method

Aqueous solution deposition methods have several advantages. For instance, a variety of thin films can be grown at low temperatures using cheap manufacturing equipment. As a non-vacuum, cheap, precise and controllable technique, successive ionic layer adsorption and reaction (SILAR) method (namely Layer-by-Layer Electrostatic Self-Assembly) can be used to manufacture various thin film compounds without special restrictions. Firstly proposed by Nicolaou in 1985, SILAR method combines the features of atomic layer epitaxy with chemical methods, and is a promising, simple and effective technique (Guan et al., 2012) which allows the uniform formation of multilayers of nanometric thickness. This is because it is not necessary to feed power to the conductive substrates as in electrochemical deposition, or to carry out the process in pressure vessels, as in hydrothermal synthesis.

In the process of SILAR, the substrate is immersed into separate cation and anion precursor solutions (which contain anionic and cationic materials such as polymeric

complexes, particles and metallic oxides, fullerenes, proteins, enzymes and other biomolecules) for adsorption and reaction then rinsed with deionized water after each immersion to remove excess reagents and to avoid homogeneous precipitation. Thus, a single SILAR deposition cycle includes adsorption of cations, rinsing with deionized water, then adsorption and reaction of anions and finally rinsing with deionized water again. By repeating the cycle described above, thin films with desired thickness and suitable compositions can be precisely obtained by adjusting the cycles and the concentration ratio of precursor solutions. It allows the conformal deposition of extremely thin sulfide layers with a control of the thickness even in the order of 1 nm (Oja et al., 2006). Figure 3.5 schematically describes one cycle of SILAR method for the deposition of CZTS. To do each immersion cycle precisely, we produced a micro-processor controlled setup (Figure 3.6). By using this setup, the number of cycles, dipping durations and waiting durations between the beakers and cycles can be controlled. The design of these individual precursor molecules and the control of the order at the molecular level of the multi-layers along the film thickness allow the control of the macroscopic properties (such as electrical, optical, magnetical, thermal, mechanical, etc.) which are important for the development of the new applications (Anonymous, 2013a).

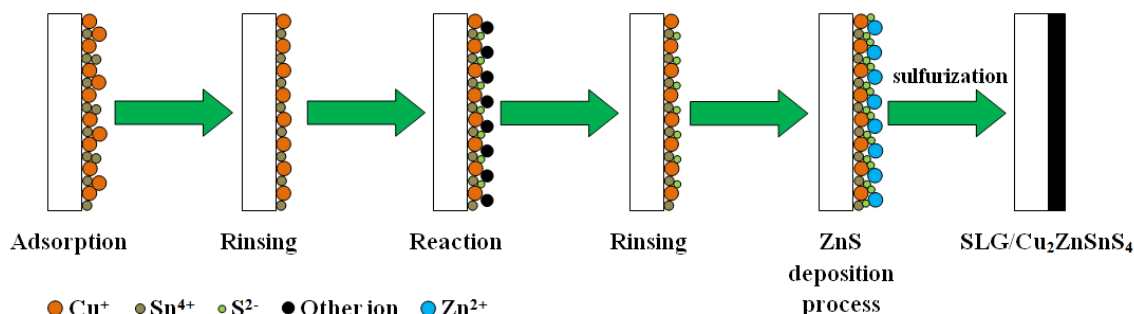
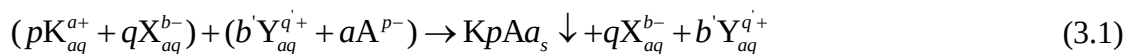


Figure 3.5. The schematic description of one cycle for the deposition of CZTS film.

The SILAR process is intended to grow thin films of water insoluble ionic or ion covalent compounds of the type KpAa by heterogeneous chemical reaction at the solid

solution interface between adsorbed cations, pK_a^+ and anion, aA_p^- , following the reaction (Pathan and Lokhande, 2004);



where, $ap = bq = b'q'$, K represents cation (Cd^{2+} , Zn^{2+} , Fe^{3+} , Cu^+ , etc), p represents the number of cations, a represents the numerical value of charge on cation, X is a ion in cationic precursors having negative charge ($X=SO_4^{2-}, Cl^-, NO_3^-$ etc), q represents the number of X in cationic precursors and b the numerical value of charges on X , b' the number of Y in the anionic solutions, q' the numerical value of charge on Y , Y the ion which is attached to the chalcogen ion, A represents the anion (O, S, Se and Te), a' the number of anions (Pathan and Lokhande, 2004).



Figure 3.6. The image of SILAR setup used in the experiments.

In the presence of complexing agent, above-mentioned reaction can be written as



where C is complexing agent.

In the adsorption step of SILAR process, the cations in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer which is composed of two different layers: the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative one forms the counter ions of the cations. Excess adsorbed ions, pK^{a+} and aA^{p-} are rinsed away from the diffusion layer in the rinsing step in which saturated electrical double layer is formed. In the case of reaction step, the anions are introduced to the system. Due to the low stability of the material, $KpAa$, a solid substance is formed on the interface. This process involves the reaction of pK^{a+} surface species with the anionic precursor, aA^{p-} (Pathan and Lokhande, 2004).

In the last step, the excess and unreacted species aA^{p-} , X, Y, and the reaction byproduct from the diffusion layer are removed away. A thin layer of material, $KpAa$, can be grown by repeating these cycles. Following the above-mentioned steps the maximum achievable film thickness per one reaction cycle is theoretically one monolayer. This results in a solid layer of the compound $KpAa$. The growth rate can be determined by dividing the measured final film thickness by the number of reaction cycles. This gives a numerical value for growth rate under the given conditions. If the measured growth rate exceeded the lattice constant of the material, a homogeneous precipitation in the solution could have taken place (Pathan and Lokhande, 2004).

In practice, however, the increase in thickness is typically less or greater than a monolayer. Thus, the process involves an alternate immersion of the substrate in a solution containing a soluble salt of the cation of the compound to be grown. The substrate supporting the growing film is rinsed in highly purified deionized water after each immersion. The facts affecting the growth phenomena are the quality of the precursor solutions, their pH values, concentrations, counter ions, individual rinsing and dipping times (Pathan and Lokhande, 2004).

In addition, complexing agent and pretreatment of the substrate have been shown to affect the SILAR growth. The growth mechanism involves three important steps: (i) specific adsorption of the most strongly adsorbed ions of the compound to be grown, by the substrate immersion in one solution of its cationic precursors, (ii) water rinsing of the excess solution still adhering to the substrate, and (iii) chemical reaction between the most strongly adsorbed specific cations and the less strongly adsorbed anions by the subsequent substrate immersion in the solution (Pathan and Lokhande, 2004).

3.2.2. Sol-gel Spin Coating Method

Sol-gel based spin coating technique is based on hydrolysis and poly-condensation reactions and very simple, low cost technique for the preparation of various semiconductor thin films. This technique involves two steps for the preparation of thin films: preparing sol-gel solution of precursor and spin coating of precursor solution onto substrate to obtain desired thin films. Figure 3.7 shows the deposition steps for utilizing sol-gel spin coating method. Such type of direct liquid deposition approach including solution, particle and mixed particle-solution precursors is of great interest for large area manufacturing, which is well developed in industry (Suryanwanshi et al., 2013).

Sulfide films can be directly obtained by sulfurizing oxyhydrate precursors. Several groups have reported the CZTS thin films produced via the sol-gel method, so far. To the best of our knowledge, the first sol-gel-grown CZTS films were reported by Tanaka et al., (2007). They prepared CZTS films by annealing oxyhydrate precursors in a $N_2 + H_2S$ toxic gas atmosphere. Yeh et al. (2009) prepared CZTS films by using metal chlorides with thiourea and investigated the effects of annealing between 160 and 320°C in the air. Fischereder et al. (2010) deposited CZTS films on ITO-coated glass substrates by using thioacetamide (TAA) as a source of sulfur. They studied the influence of vacuum annealing temperatures (180-450 °C) and the concentration of TAA in precursor solutions. Park et al. (2013) fabricated CZTS thin films via the sol-gel method and then annealed the samples at temperatures above 500 °C in a N_2 atmosphere without any sulfur source.

In order to utilize the sol-gel technique for obtaining crack-free, uniform, transparent and strongly adherent films, sol stabilization is one of the essential steps in the

film formation (Kaminski et al., 2005). To stabilize the sol and to reduce the rates of hydrolysis and poly-condensation reactions by forming complex intermediates (Djaoued et al., 2002; Zhang et al., 2009a), various stabilization or chelating or complexing agents have been used. Diethanolamine (DEA), diethylenetriamine, monoethanolamine, acetylacetone, acetic acid and polyethylene glycol have widely been used for this purpose (Murugan et al., 2011; Chen et al., 2007; Djaoude et al., 2008; Yu et al., 2006; Jung et al., 2003; Sanchez et al., 1988, Takahashi et al., 2000). DEA is frequently used as a stabilizer in various sol–gel systems (Takahashi and Matsuoka, 1988; Takahashi and Yamaguchi, 1990; Ohya et al., 1994).

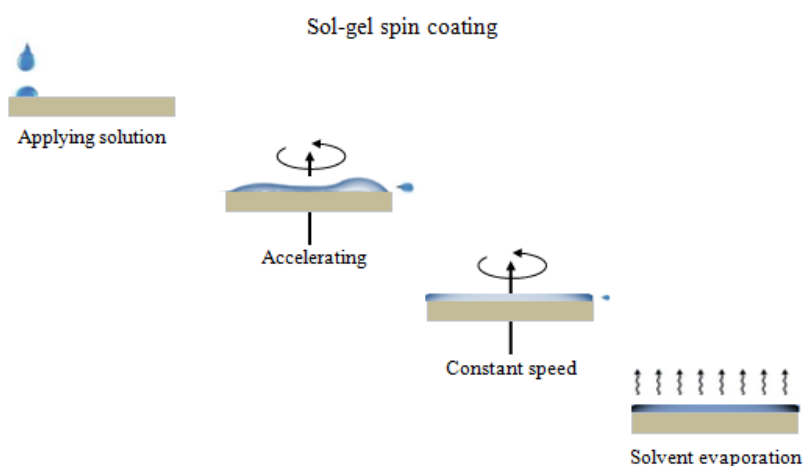


Figure 3.7. Schematic illustrations of sol-gel spin coating method (Adopted from Anonymous, 2013b).

3.2.3. Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with

the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum and (in environmental SEM) in wet conditions.

The most common mode of detection is performed by detecting secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons is a function of the angle between the surface and the beam. On a flat surface, the plume of secondary electrons is mostly contained by the sample whereas, on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the tilt of the surface is created.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to approximately 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, the emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors (Anonymous, 2013c).

3.2.4. Energy Dispersive X-ray Spectrometry

As an analytical technique, Energy-dispersive x-ray spectroscopy is used for the elemental analysis or chemical characterization of a sample. In principle, elements from atomic number 4 (Beryllium) to 92 (Uranium) can be detected. It relies on the investigation

of an interaction of some source of x-ray excitation and a sample under investigation. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its x-ray spectrum. A high-energy beam of charged particles (such as electrons or protons), or a beam of x-rays, is sent into the sample to stimulate the emission of characteristic x-rays from a specimen. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an x-ray. The number and energy of the x-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the x-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. By scanning the beam in a television-like raster and displaying the intensity of a selected x-ray line, element distribution images or 'maps' can be produced. Moreover, the images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected. The scanning electron microscope (SEM) is designed primarily for producing electron images, but can also be used for element mapping, and even point analysis if an x-ray spectrometer is added. Thus, there is a considerable overlap in the functions of these instruments (Goldstein, 2003).

3.2.5. X-ray Diffraction

In 1913, physicists W.H. Bragg and his son W.L. Bragg developed a relationship to explain why the cleavage faces of crystals appear to reflect x-ray beams at certain angles of incidence (θ).

$$n\lambda = 2d \sin \theta \quad (3.3)$$

The variable d is the distance between adjacent atomic layers in a crystal, and the variable λ is the wavelength of the incident x-ray beam; n is an integer. This observation was an example of x-ray wave interference, commonly known as x-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries.

The Nobel Prize in Physics 1915 was awarded jointly to Sir William Henry Bragg and William Lawrence Bragg for their services in the analysis of crystal structure by means of x-rays. Although Bragg's law was used to explain the interference pattern of x-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest (Anonymous, 2013f).

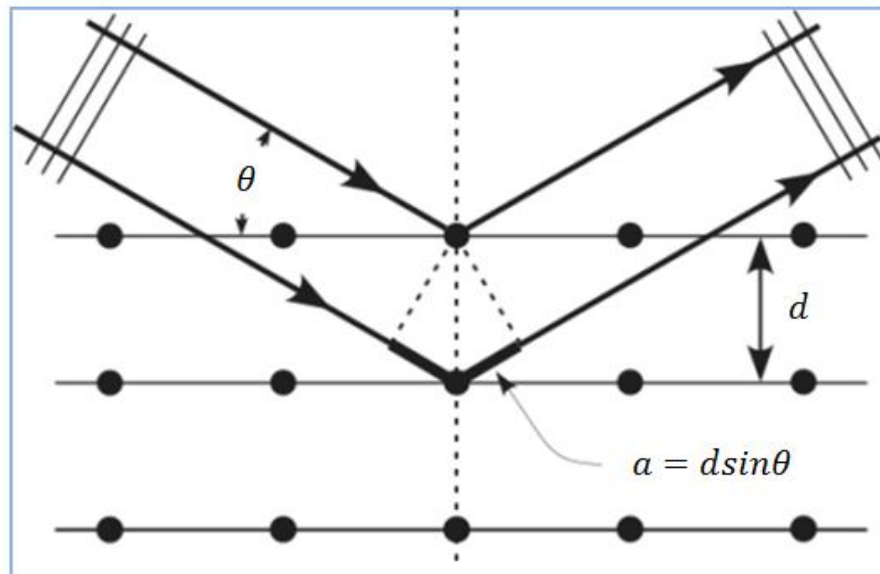


Figure 3.8. Scattering of monochromatic x-rays from the atomic layers of the specimen

3.2.6. Incident photon to current efficiency method

One technique for the analysis of solar cells is incident photon to current efficiency (IPCE) measurement which is also known as External Quantum Efficiency (EQE) measurement. It provides conclusions about the losses in the film, the effectiveness of charge separation and the absorption, or the charge generation. The IPCE value corresponds to the number of electrons generated by monochromatic light in the external circuit, divided by the number of incident photons. Measuring photovoltaic response of a photo-active material to monochromatic light supplies detailed information about how efficiently the material converts photons of a given wavelength into electrons. If all incoming photons result in electron-hole pairs, this means a quantum efficiency of 100% or 1. Theoretically a QE higher than 1 is possible if photons have an energy higher than the double band gap.

The monochromatic light is split by a chopper to produce a reference signal to measure the desired photocurrent referring the measured signal to incoming monochromatic light in an IPCE system. The QE curves allow concluding the absorption and recombination losses in a given material. A schematic diagram of an IPCE system is shown in Figure 3.9. If the absorption spectrum of the solar cell is known, the fraction of absorbed photons can be used to calculate the internal quantum efficiency (IQE). This value gives the percentage of photons absorbed by the cell that are converted into electrons as a function of wavelength.

An IPCE monochromator provides light with very narrow bandwidth and a measurement of the power at each wavelength that can be used to calculate the number of photons generated. If such a light is directed on a solar cell, the output current of the solar cell (with zero bias voltage) can be used to calculate the number of generated electrons. An IPCE measurement does not indicate the total power efficiency of the cell, unlike an AM 1.5 power conversion efficiency. This is because the total output power of the solar cell depends on the operating voltage of the cell and IPCE values are measured with the cell in short circuit conditions. However, a simple calculation can be done to check for the consistency of data obtained from IPCE and AM 1.5 measurements.

The short circuit current of a cell measured under AM 1.5 conditions can be compared to a value calculated from the IPCE data.

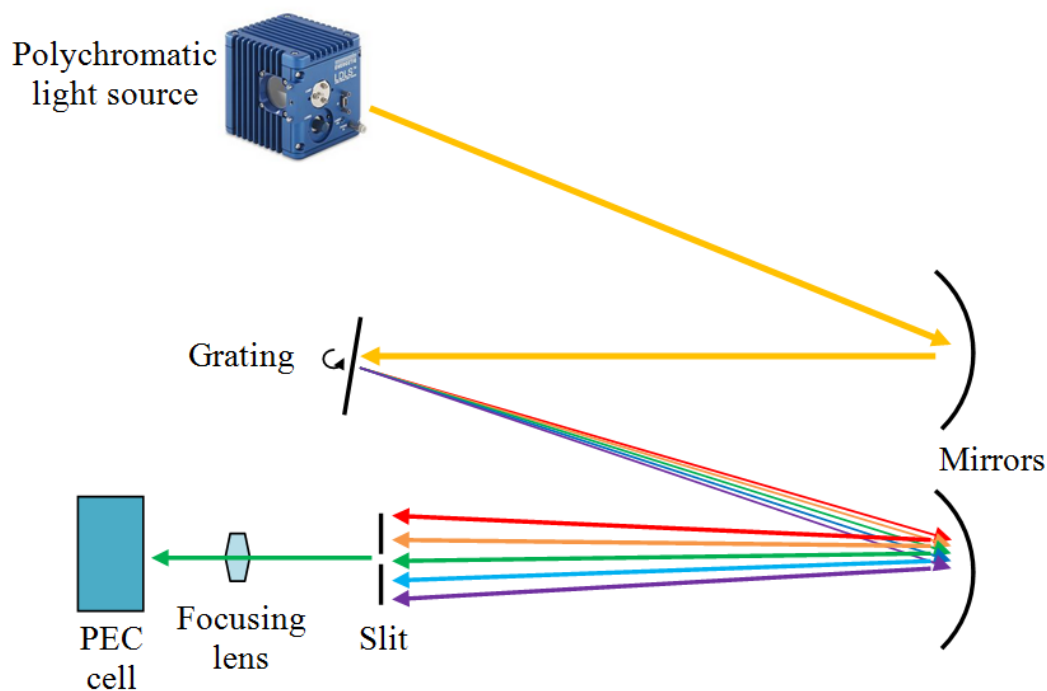


Figure 3.9. Schematic diagram of an IPCE system

Photo-electrochemistry (PEC) is a multidisciplinary field involving surface science, electrochemistry, solid-state physics and optics. The basic concept of a photo-electrochemical cell is shown in Figure 3.10. When light is absorbed by the semiconductor electrode (left), electrons are excited to a higher energy level. These electrons (and their associated absence, the “hole”) are capable of carrying out redox reactions at the semiconductor/liquid interface. In this case, holes oxidize “A” anion at the semiconductor/liquid junction to create “A” molecule. At the counter electrode a reduction reaction occurs, showing the reduction of “B” molecule to “B” anion. This is similar to a standard electrochemical cell except that light is explicitly involved in providing energy to cause the redox reactions to proceed. Two types of photoelectrodes can be discussed according to the whether they cause oxidation or reduction reactions: photoanodes and photocathodes. Also there are two classes of photo-electrochemical systems according to whether they do or do not cause a net change in the solution composition: Photosynthetic/photocatalytic or regenerative.

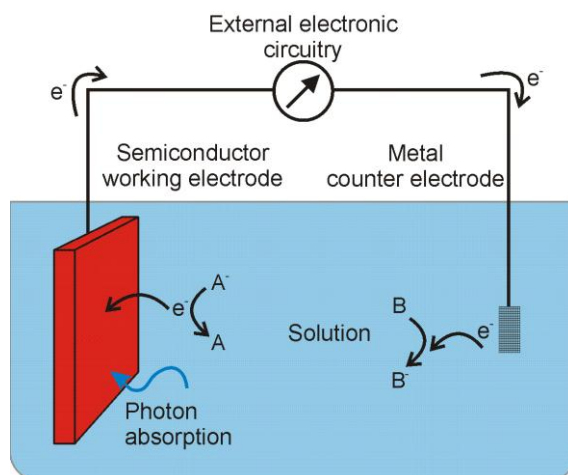


Figure 3.10. Diagram of a photoelectrochemical cell (Strandwitz et al., 2011).

Both types of photo-electrochemical systems are capable of converting solar energy into useful energy, but only photosynthetic cells are capable of directly forming a stored fuel (for example, hydrogen).

One of the initial discoveries that led to the field of photo-electrochemistry was made by Becquerel, (1839) who observed a photocurrent, that is, a flow of electrons upon illumination with light, between two electrodes immersed in solution. In the 1950's researchers at Bell Labs began to study the high purity crystals of germanium and silicon semiconductors by developing models for their electronic behavior. In the 1970's Professor Heinz Gerischer began systematic studies of the behavior of semiconductors immersed in liquid solutions. High efficiency regenerative (electricity producing) photo-electrochemical cells were developed in aqueous and non-aqueous solvents in the 1980's by Lewis et al. A record energy conversion efficiency for a water-splitting photo-electrochemical device was reported by Turner and Khaselev at the National Renewable Energy Lab in 1998. This particular device was unstable over periods of hours, but displayed a conversion efficiency of 12.4% (from light energy to chemical energy). Efficient photo-electrochemical cells based on dye sensitization were first reported by Gratzel and O'Regan in 1991. Those so-called dye sensitized solar cells (DSSCs) convert light energy into electricity and are thus regenerative photo-electrochemical cells.

Semiconductors generally have electrical conductivities between those of metals (for example, gold) and insulators (for example, silicon oxide). Semiconductors have an energy level gap where no electronic states exist. This energy gap separates the valence and conduction bands, which have electronic states. The energetic difference between these two bands is defined as the semiconductor band gap. This band gap, in large part, dictates the optical absorption properties of the semiconductor. For example, a semiconductor with a large band gap (for example, titanium dioxide, or titania) is white in appearance and only absorbs high energy (ultraviolet) light. Conversely, semiconductors with smaller band gaps (for example, silicon) appear black or dark in color, and absorb visible light. Semiconductors can be doped to control the number of mobile charge carriers in each band. Doping involves the addition of small amounts of an impurity (for example, phosphorus in a silicon lattice) resulting in free charge carriers that can move in the crystal. The types of charge carriers are the electrons in the conduction band and the holes in the valence band. Holes are not real particles and are simply the absence of an electron in the valence band. However, they are usually treated like particles because this simplifies the analysis. Through doping, the number of mobile charges is increased, thus increasing the conductivity of the semiconductor. Materials that are doped with electrons in the conduction band are termed “n-type” because their conductivity is described by the movement of negatively charged particles (electrons). Materials doped with holes in the valence band are termed “p-type” because their conductivity is described by the movement of positively charged particles (holes). The control of the electronic properties through doping is an important feature of semiconductors.

When an n-type semiconductor is immersed in a solution that contains a supporting electrolyte (for example, a salt) and a redox couple, the charge (electrons) can move to and from the solid semiconductor to the liquid. For specification, we will consider the properties of a liquid junction with an n-type semiconductor. Due to the excess of electrons in the n-type material, electrons will generally flow from the semiconductor to the liquid. Because electrons are removed from the semiconductor, a region near its surface is formed with a net positive charge. This fixed positive charge creates an electric field within the semiconductor and is responsible for the photo-activity of the

semiconductor photo-electrochemical system. When a light quanta with an energy greater than the semiconductor band gap is sent to the semiconductor, an excess electron and an excess hole will be created within the solid. Because of the electric field near the interface with the solution, the electron is driven away from the interface and the hole is driven toward the interface. When the hole reaches the interface, the hole can oxidize a species in solution. The electron is collected at the electrode's metal contact, which is connected to external electronics (for example, a potentiostat) or a load (for example, a light bulb) and ultimately to a counter electrode, where a reduction reaction occurs. The semiconductor working electrode is also connected to the metal counter electrode through the solution completing the circuit. The opposite argument holds for a p-type semiconductor, in which case electrons are driven to the semiconductor surface causing reduction reactions (Strandwitz et al., 2011).

Researchers using light in a variety of applications, need light sources capable of providing high brightness across a broad wavelength range. Traditionally, multiple lamps (Tungsten/Halogen, Xenon-arc, Deuterium) have been used to cover this broad spectral range. However, combining multiple lamps is costly and optically inefficient, and the use of electrodes within these lamps limits their ability to achieve the high brightness or power needed for the most demanding applications. Furthermore, traditional electrode-driven light sources have short life, need to be changed frequently, and during their life the lamp output declines constantly. To address this problem, a single-light source technology called the Laser-driven light source (LDLS) has been developed. It enables high brightness over a broad spectral range (from 170 nm through visible and beyond) combined with lifetimes an order of magnitude longer than traditional lamps. Principle operation of a LDLS light source is given in Figure 3.11. This technology uses a continuous-wave laser to directly heat a Xenon plasma to the high temperatures necessary for efficient deep ultraviolet production. In traditional approaches such as arc and deuterium lamps, the brightness, UV power, and lamp lifetime are limited by the use of electrodes to couple power to the plasma. The electrodeless LDLS technology creates small, high brightness plasma that allows efficient light collection, broad spectral range from the deepest UV through visible and beyond, and long lamp life.

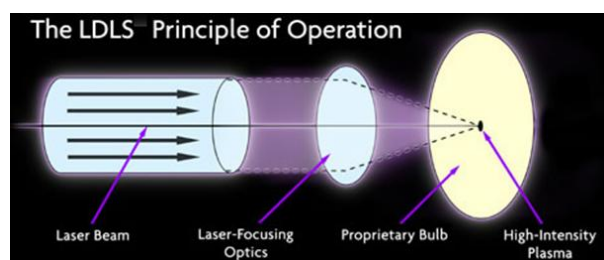


Figure 3.11. Principle operation of a LDLS light source (Anonymous, 2013e)

3.2.7. The growth of CZTS films by using SILAR method

3.2.7.1. Selection and cleaning procedure of the substrates

Soda-lime glass (SLG), also called soda-lime-silica glass, is the most prevalent type of glass used for window panes and glass containers (bottles and jars) for beverages, food, and also some commodity items. Soda-lime glass is relatively inexpensive, chemically stable, reasonably hard, and extremely workable. Chemical composition (wt%) of a conventional SLG is 74% SiO_2 , 13% Na_2O , 10.5% CaO , 1.3% Al_2O_3 and 1.2% other oxides. (Anonymous, 2013d). As can be seen that SLG contains sodium element which is a small alkali metal. It can diffuse easily into the host lattice. Nakada et al., (1997) investigated the effect of Na diffusion on the properties of CIGS based solar cells, and found that the hole concentration of absorber layer increased dramatically. Moreover, it is known that sodium diffusion from the SLG substrate improves the efficiency of CIGS based solar cells (Rudman et al., 2004). Thus Na diffusion from a substrate is an essential factor in the achievement of high efficiency CIGS thin film solar cells (Yuna et al., 2007). Therefore we preferred to use SLG substrates throughout the experiments.

Molybdenum coated soda lime glass (SLG) slides were used as substrates which were ultrasonically cleaned in turn with 10% sulfuric acid, acetone, deionized water and ethanol for 10 min. Sulfuric acid was used to remove natural oxide from surface since acetone and ethanol were used to clean organic contaminations. Another function of ethanol is to make the substrate surface hydrophilic. Ethanol forms hydrogen bonds with water because it has an OH^- group which makes it polar.

3.2.7.2. One-stage film growth

The first SILAR grown CZTS films were reported by Mali et al., (2012a); (2012b). In those studies, they produced CZTS films on fluorine-doped tin oxide (FTO) coated glass substrates by using two different solutions. The first beaker contained Cu^+ , Zn^{2+} and Sn^{4+} cations while the other one contained Na_2S which gives sulfide ions (S^{2-}). They investigated the photo-electrochemical conversion (PEC) efficiency of the films. Shinde et al., (2012a), deposited CZTS thin films using different concentrations of single cationic and anionic precursors. They investigated the effects of vacuum annealing on the structural, morphological, electrical and optical properties. For the deposition of $\text{Cu}_2\text{ZnSnS}_4$ thin films in one stage, two different solutions were prepared by using CuCl_2 , ZnCl_2 , SnCl_2 and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. The first one contained Zn, Sn and Cu ions while the other one had S ions. The initial parameters are shown in Table 3.5.

Various adsorption, reaction and rinsing durations were tried in preliminary studies. But we found that film growth rate was very low when the durations shorter than 15 s while the film quality decreased in case of longer durations. Therefore we chose 15 s for each adsorption, reaction and rinsing time. After the deposition process, dense and black colored films were subjected to an annealing procedure at 550°C for 2 hours. Due to the high vapor pressure of sulfur, 10 g of elemental sulfur was put into the tube to tolerate the possible sulfur loss during annealing. The heating rate was kept as $5^\circ\text{C}/\text{min}$ to prevent rapid evaporation of sulfur and deterioration of the films. After the annealing process, the samples were allowed to cool down naturally to room temperature.

Table 3.5. The initial parameters of one-stage SILAR process

M_{Cu}	M_{Zn}	M_{Sn}	M_{S}	Number of cycle
0.010	0.010	0.010	0.050	100*
0.005	0.010	0.010		
0.010	0.005	0.010		
0.010	0.010	0.005		

* Optimized value to get about one micron thick CZTS film.

3.2.7.3. One-stage modified film growth

There are few studies which report CZTS growth in one cationic solution in the literature (Mali et al., 2012a; 2012b, Shinde et al., 2012a). After the study performed in the previous section, we found that it is unlikely to obtain CZTS compounds in a single cation solution using the SILAR method. Using EDS analysis we were not able to detect Zn in the samples (Kahraman et al., 2014). Due to the competitive adsorption between different metal ions (blocking of zinc deposition by copper ions), it is extremely difficult to deposit a quaternary Cu-Zn-Sn-S thin film to a desired stoichiometric composition in a single cation solution using the SILAR method. To overcome this problem, we tried to modify deposition parameters. Unlike 'one-stage film growth', we dissolved 10 times more zinc source than the stoichiometric value and added 0.5 cc hydrochloric acid into the first and third beakers.

Cu/Sn molarity ratio in the precursor solutions was also investigated. For this purpose the ratio was changed from 2 (stoichiometric ratio) to 0.6. The initial molarities of the experiments are shown in Table 3.6. We preferred to repeat deposition cycles 30 times in this section because peeling effect was observed after 30 cycles,

Table 3.6. The initial experimental conditions of modified one-stage SILAR process

M_{Cu}	M_{Cu}/M_{Sn}	M_{Zn}	M_{Sn}	M_S	Number of cycle
0.020	2.0	0.10	0.010	0.050	30
0.018	1.8				
0.016	1.6				
0.014	1.4				
0.012	1.2				
0.010	1.0				
0.008	0.8				
0.006	0.6				

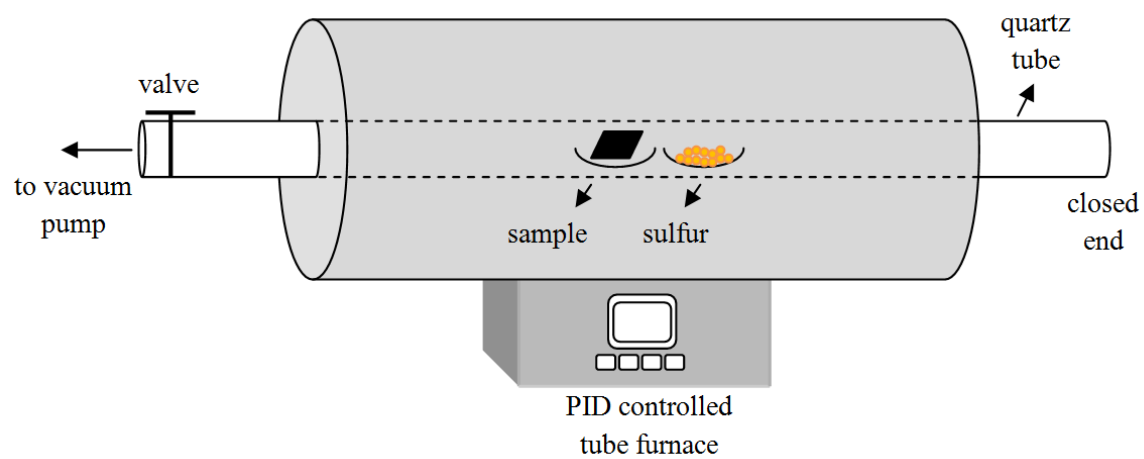
3.2.7.4. Two-stage film growth for different molar ratios

Due to the competitive adsorption between different metal ions, it is extremely difficult to deposit a quaternary Cu-Zn-Sn-S thin film to a desired stoichiometric composition in a single cation solution using the SILAR method. To overcome this problem, Su et al., (2012) suggested a procedure in which two stacked precursor sulfide layers ($\text{Cu}_2\text{SnS}_3/\text{ZnS}$) are grown successively. In that work, they investigated effects of the stacking order of the layers and reported that high-quality and closely stoichiometric CZTS films can be grown using this procedure.

In this study, therefore, the CZTS thin films were obtained by sulfurizing $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacked sulfide layers. For the deposition of the Cu_2SnS_3 layer the cation solution was composed of 0.005 M CuCl_2 , 0.01 M SnCl_2 . Triethanolamin was used to adjust the pH value of the solution. For the deposition of the ZnS layer on the Cu_2SnS_3 layer, the cation solution contained 0.1 M ZnCl_2 while diluted sulfuric acid was used to adjust pH value of the ZnCl_2 solution. Both anion solutions were prepared with 0.05 M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ as a source of sulfur. Five different samples were produced by changing the molar ratio of copper to tin. For comparison, Cu_2SnS_3 , ZnS and SnS single layers were grown separately on bare glass substrates. The preparation conditions of the samples are given Table 3.7 and Table 3.8. Before the annealing, the tube furnace was evacuated to 5×10^{-4} mbar. After the deposition process, the samples were annealed at 500 °C for 2 hours in a setup schematically described in Figure 3.12. Due to the high vapor pressure of sulfur at the annealing temperature, 10 g of elemental sulfur in an alumina crucible was put into the tube underneath the samples to compensate for any possible sulfur loss during the annealing. The heating rate was 5°C/min. After the annealing process, the samples were allowed to cool naturally to room temperature.



(a)



(b)

Figure 3.12. The image (a) and (b) schematic diagram of the sulfurization setup

3.2.7.5. Two-stage film growth for different deposition cycles

In this study, four different samples were produced by changing the number of deposition cycles of each Cu_2SnS_3 and ZnS layers. The preparation conditions of the samples are given in Table 3.9. Rinsing durations were determined according to the reaction rates. Before the annealing, the tube furnace was evacuated to 5×10^{-4} mbar. After the deposition process, the samples were subjected to an annealing procedure at 500°C for 2 hours. Due to the high vapor pressure of sulfur at the annealing temperature, 10 g of elemental sulfur in an alumina crucible was put into the tube underneath the samples to compensate for any possible sulfur loss during the annealing. The heating rate was $5^\circ\text{C}/\text{min}$. After the annealing process, the samples were allowed to cool down naturally to room temperature.

Table 3.7. The initial experimental molarities of two-stage SILAR process (different molar ratios)

$M_{\text{Cu}} / M_{\text{Sn}}$	M_{S}	Number of cycle
1/2	0.050	100
1/4		
1/8		
1/12		
1/16		

Table 3.8. The initial experimental conditions of SILAR grown ZnS , Cu_2SnS_3 and SnS samples.

	M_{Cu}	M_{Zn}	M_{Sn}	M_{S}	Number of cycle
ZnS	---	0.010	---	0.050	30
Cu_2SnS_3	0.050	---	0.010		
Sn_xS_y	---	---	0.010		

Table 3.9. The initial experimental conditions of two-stage SILAR process (different deposition cycles)

M_{Cu}		M_{Zn}	M_{Sn}	M_S	Number of cycle
					Cu_2SnS_3/ZnS
0.005		0.020	0.010	0.050	60/40
					60/20
					30/40
					30/20
	Number of cycle		Adsorption time (s)	Reaction time (s)	Rinsing Time (s)
Cu_2SnS_3 (1 st layer)	60		20	20	10
	60				
	30				
	30				
ZnS (2 nd layer)	40		20	20	100
	20				
	40				
	20				

3.2.8. The growth of CZTS films by using sol-gel method

3.2.8.1. Effects of stabilizer content

In order to utilize the sol–gel technique for obtaining crack-free, uniform, transparent and strongly adherent films, sol stabilization is one of the essential steps in the film formation (Kaminski et al., 2005). To stabilize the sol and to reduce the rates of hydrolysis and poly-condensation reactions by forming complex intermediates (Djaoued et al., 2002; Zhang et al., 2009), various stabilizer, chelating or complexing agents have been used.

Diethanolamine (DEA), diethylenetriamine, monoethanolamine, acetylacetone, acetic acid and polyethylene glycol have widely been used for this purpose (Murugan et al., 2011; Chen et al., 2007; Djaoude et al, 2008; Yu et al., 2006; Jung et al., 2003; Sanchez et

al., 1988, Takahashi et al., 2000). DEA is frequently used one among them as a stabilizer in various sol–gel systems (Takahashi and Matsuoka, 1988; Takahashi and Yamaguchi, 1990; Ohya et al., 1994). The effect of stabilizer agent content has not been investigated so far. In addition, initial molar ratios of the precursor solutions, sulfur pressure and sulfurization temperature have not been investigated in detail. Hence, we investigated the effects of different stabilizer content and sulfurization temperature on the properties of CZTS films.

The CZTS precursor solutions were prepared by dissolving copper (II) acetate monohydrate (0.5 M), zinc (II) acetate dihydrate (0.3 M), tin (II) chloride (0.3 M) and thiourea (1.2 M) into 2-methoxyethanol (20 ml). The final solutions were stirred at 850 rpm (at which the solution stirred vigorously without splash) for 1 h at 45 °C to dissolve the metal compounds completely. During stirring, a certain amount of diethanolamine (DEA) was dropped slowly into each solution as a stabilizer. The molarity of DEA was changed from 2.0 to 0.3 with 0.1 steps. The images of the solutions are given in Figure 3.13. After 24 hours of aging, it was observed that the prepared solutions were stable. To produce the CZTS films, the prepared solutions were spin-coated onto substrates at 3000 rpm for 30 s followed by solvent-drying at 175 °C for 10 min on a hot plate. The spin-coating and solvent-drying processes were repeated 10 times to obtain the desired thickness of the films. Finally, the samples were annealed in a vacuum furnace for 2 h at 550 °C in a quartz tube containing certain amount of elemental sulfur. The heating rate was 5 °C/min. After the annealing process, the samples were allowed to cool down naturally to room temperature (Tanaka et al., 2007; Yeh et al., 2009; Sarswat and Free, 2011; Park et al., 2013). The experimental parameters are shown in Table 3.10.

Table 3.10. The experimental parameters for preparing sol-gel grown CZTS film

Experimental conditions				
M_{Cu}	M_{Zn}	M_{Sn}	M_{S}	M_{DEA}
0.5	0.3	0.3	1.2	2.0 to 0.3 with 0.1 increment

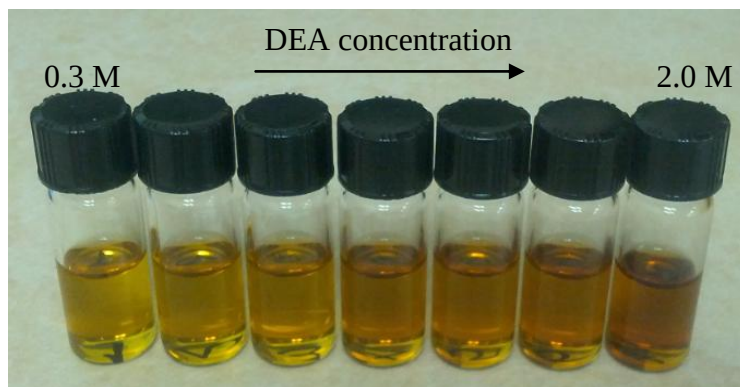


Figure 3.13. The photograph of the solutions containing different amount of DEA changing from 0.3 to 2.0

3.2.8.2. Effects of sulfur pressure

The CZTS precursor solution was prepared by dissolving copper (II) acetate monohydrate (0.5 M), zinc (II) acetate dihydrate (0.3 M), tin (II) chloride (0.3 M) from Sigma Aldrich and thiourea (1.2 M) into 2-methoxyethanol (20 ml). The final solution was stirred at 45 °C, 850 rpm for 1 h to dissolve the metal compounds completely. The optimum DEA molarity was determined as 1.3 M in the previous section. During stirring, thus, 1.3 M DEA was slowly dropped into the solution as a stabilizer. To produce the CZTS film, the prepared solution was spin-coated onto a glass substrate at 3000 rpm for 30 s followed by solvent-drying at 175 °C for 10 min on a hot plate. The spin-coating and solvent-drying processes were repeated 10 times to obtain the desired thickness of the film. The sample was cut into eight (8) pieces for the investigation of the effects of the sulfur pressure. Finally, the samples were subjected to an annealing process in different sulfur pressures in a range of 0.5-20 atm for 2 h at 550 °C in a vacuumed tube. The heating rate was 5 °C/min. After the annealing process, the samples were allowed to cool naturally down to room temperature.

3.2.8.3. Effects of sulfurization temperature

In this section, the effects of sulfurization temperature on the properties of sol-gel grown CZTS films were investigated. To prepare CTZS precursor solution, 0.5 M copper

(II) acetate monohydrate, 0.3 M zinc (II) acetate dihydrate, 0.3 M tin (II) chloride and 1.2 M thiourea were dissolved in 20 ml of 2-methoxyethanol. The final solution was stirred at 45 °C, 850 rpm for 1 h to dissolve the metal compounds completely. 1.3 M diethanolamine (DEA) was slowly dropped into the solution as a stabilizer during stirring. The prepared solution was spin-coated onto a glass substrate at 3000 rpm for 30 s followed by solvent-drying at 175 °C for 10 min on a hot plate. The spin-coating and solvent-drying processes were repeated 10 times to obtain the desired thickness of the film. The sample was cut into five (5) pieces for the investigation of the effects of the sulfurization temperature. The samples were sulfurized at 200, 300, 400, 500 and 700 °C for 2 h, respectively.

3.3. Characterizations

The surface morphology, chemical composition, crystal structure, optical and photo-conversion properties of the samples were examined by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), Raman microscopy, absorbance spectroscopy and incident photon to current measurement (IPCE) methods.

Plain view and cross-section images and elemental composition of the samples were obtained by using JEOL JSM 5800 scanning electron microscope coupled with an Oxford Instruments ISIS 300 energy dispersive x-ray spectroscopy unit working under 20 keV accelerating voltage and 30 mA current .

X-ray diffraction patterns of the samples were obtained by using PANalytical X'Pert PRO MPD x-ray diffractometer with a wavelength of 1.5418 Å Cu K α radiation at 40 keV operating voltage and 35 mA current. The step size and the scan step time were 0.0330° and 1 sec., respectively.

As for proving phase purity of the samples, Raman spectroscopy analysis of the samples were done by using SnR Instruments, Sierra IM-52 Raman microscope, over the range of 200 to 500 cm⁻¹.

In order to evaluate band gap values of the growth samples, absorbance spectroscopy measurements have been done through Lambda 950 spectrometer with 150

mm integrating sphere. An incident photon to current measurement system (IPCE) with laser driven light source (PEC cell with three electrodes) was used in order to evaluate photo-conversion efficiency of the samples. Photo-electrochemical measurements were carried out in a 3-arm electrochemical cell with a Ag/AgCl reference electrode and a platinum basket auxiliary electrode, using a CH Instruments potentiostat. The electrolyte was a 0.1 M KCl/0.1 M $\text{Eu}(\text{NO}_3)_3$ aqueous solution. IPCE data was collected at the wavelength range of 500-900 nm under illumination from filtered (450 nm cut-off filter) and collimated light from a continuous wave laser driven light source (Energetiq, LDLS EQ-99) passed through a grating monochromator, with an applied bias of -350 mV vs Ag/AgCl.

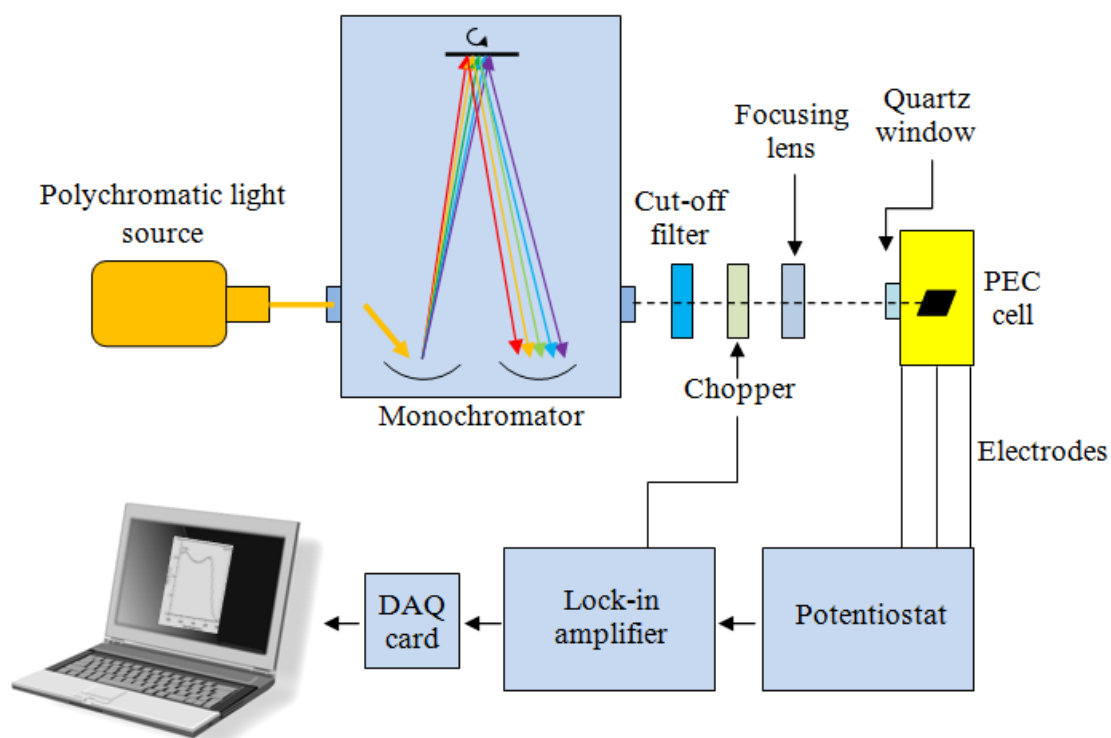


Figure 3.14. Schematic illustration of the IPCE system

4. RESULTS AND DISCUSSIONS

4.1. Morphological and compositional characterization of the CZTS films

4.1.1. SILAR grown films

4.1.1.1. One-stage SILAR grown films

Plain view SEM images and EDS results of the one-stage SILAR grown samples are given in Figure 4.1-4.4. According to the figures, it can be said that the films are continuous and composed of homogeneously distributed large grains. As seen in the images a, b, c, the diameters of the structures change with respect to Cu content. Average diameters of the structures were calculated as ~200 and ~250 nm using an image analyzer programme. The increasing grain size in the samples can be attributed to the increased Cu molarity in the precursor solution. A similar trend in crystallite size of the samples was determined via Debye-Scherrer's equation and will be given in section 4.2.2.1. As can be seen from all composition results, the prepared samples were found to not contain zinc. Due to the competitive adsorption between different metal ions, it is extremely difficult to deposit a quaternary Cu-Zn-Sn-S thin film to a desired stoichiometric composition in a single cation solution using the SILAR method. To overcome this problem, Su *et al.*, 2012 suggested a procedure in which two stacked precursor sulfide layers ($\text{Cu}_2\text{SnS}_x/\text{ZnS}$) are grown successively. Therefore, as will be given in next section, we prepared $\text{Cu}_2\text{SnS}_x/\text{ZnS}$ stacking layers and sulfurized them to produce CZTS films. Moreover, the percentage of Sn is under stoichiometric value in all the composition results. This may be due to the high volatility of Sn and/or high vapor pressure of sulfur. During sulfurization process, some Sn, mainly in the form of SnS, may move away from the structure (Fernandes et al., 2010b).

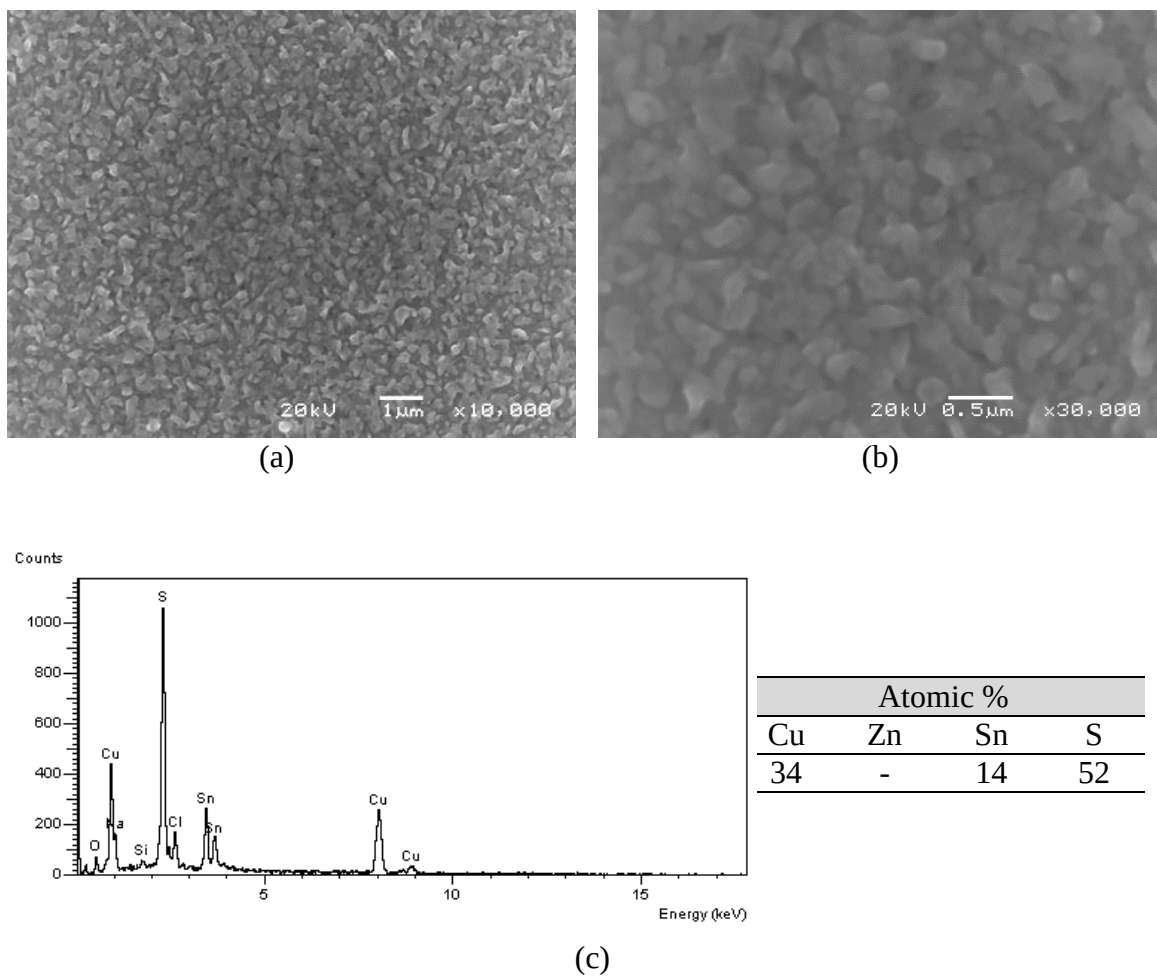


Figure 4.1. SEM images and EDS results (c) of the SILAR grown sample obtained in one-stage by using 0.01 M CuCl_2 , 0.01 M ZnCl_2 , 0.01 M SnCl_2 , 0.05 M Na_2S in 50 cycles (each duration in the beakers was 5 s).

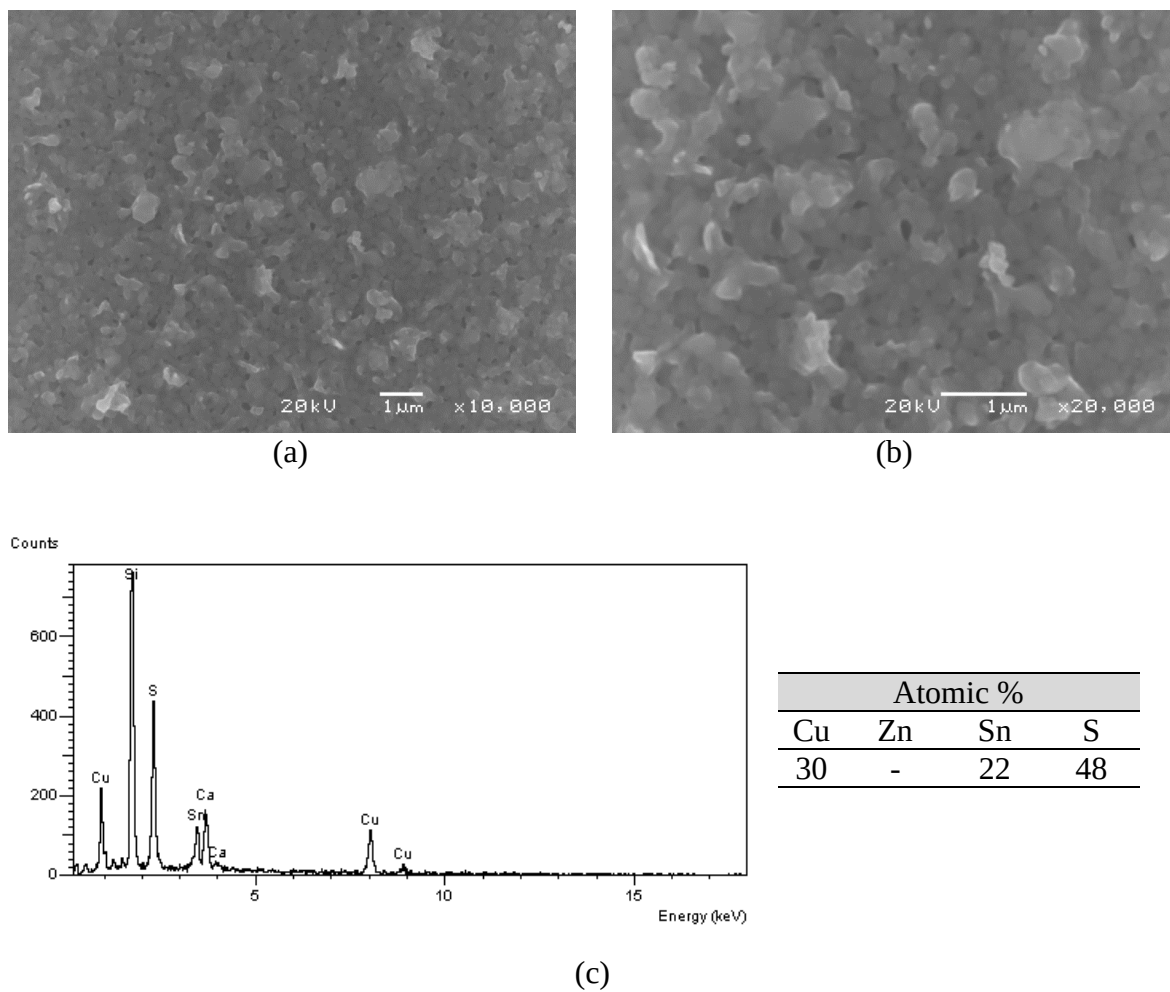


Figure 4.2. SEM images (a,b) and EDS results (c) of the SILAR grown sample obtained in one-stage by using 0.01 M CuCl_2 , 0.01 M ZnCl_2 , 0.01 M SnCl_2 , 0.05 M Na_2S in 50 cycles (each duration in the beakers was 15 s).

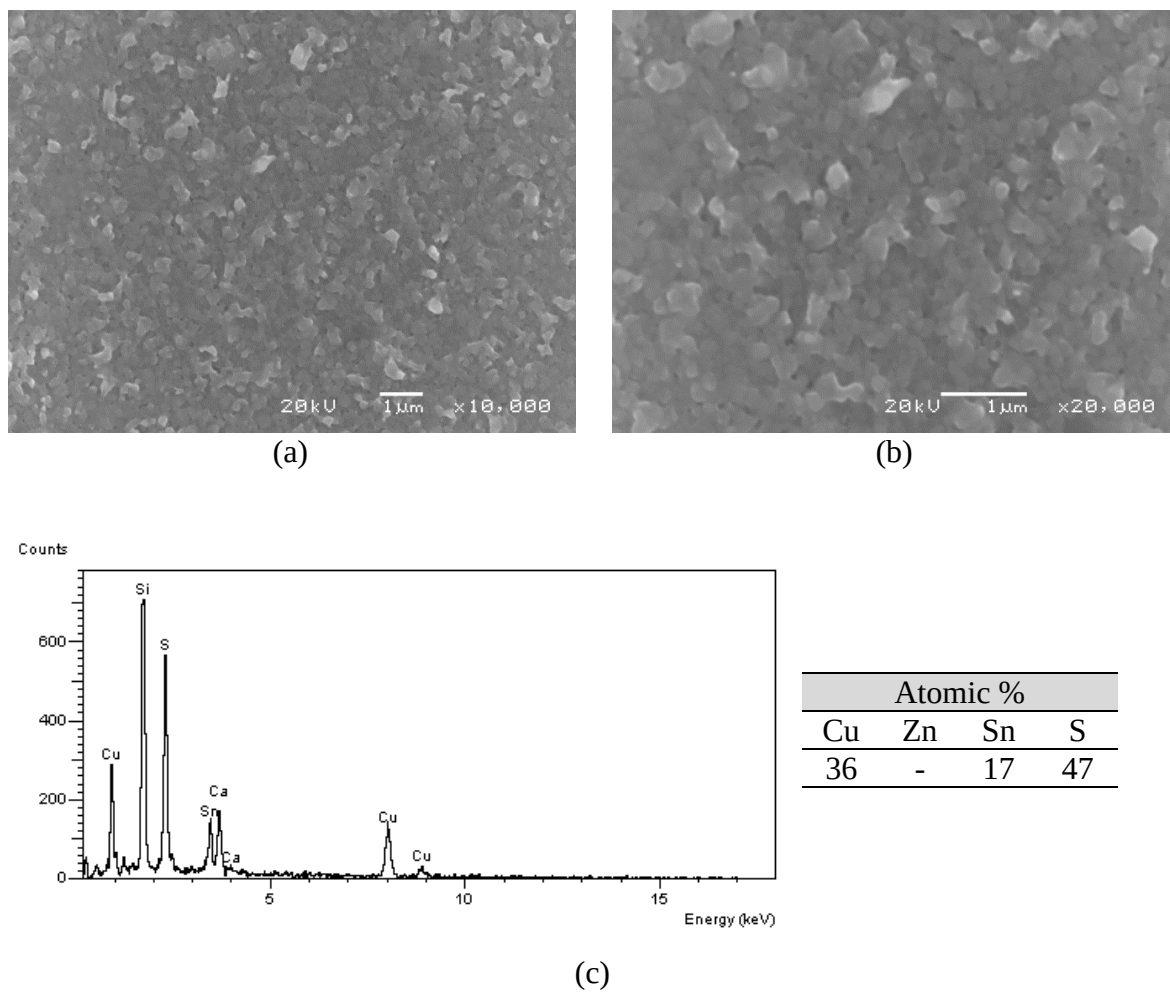


Figure 4.3. SEM images (a,b) and EDS results (c) of the SILAR grown sample obtained in one-stage by using 0.005 M CuCl_2 , 0.01 M ZnCl_2 , 0.01 M SnCl_2 , 0.05 M Na_2S in 50 cycles (each duration in the beakers was 15 s).

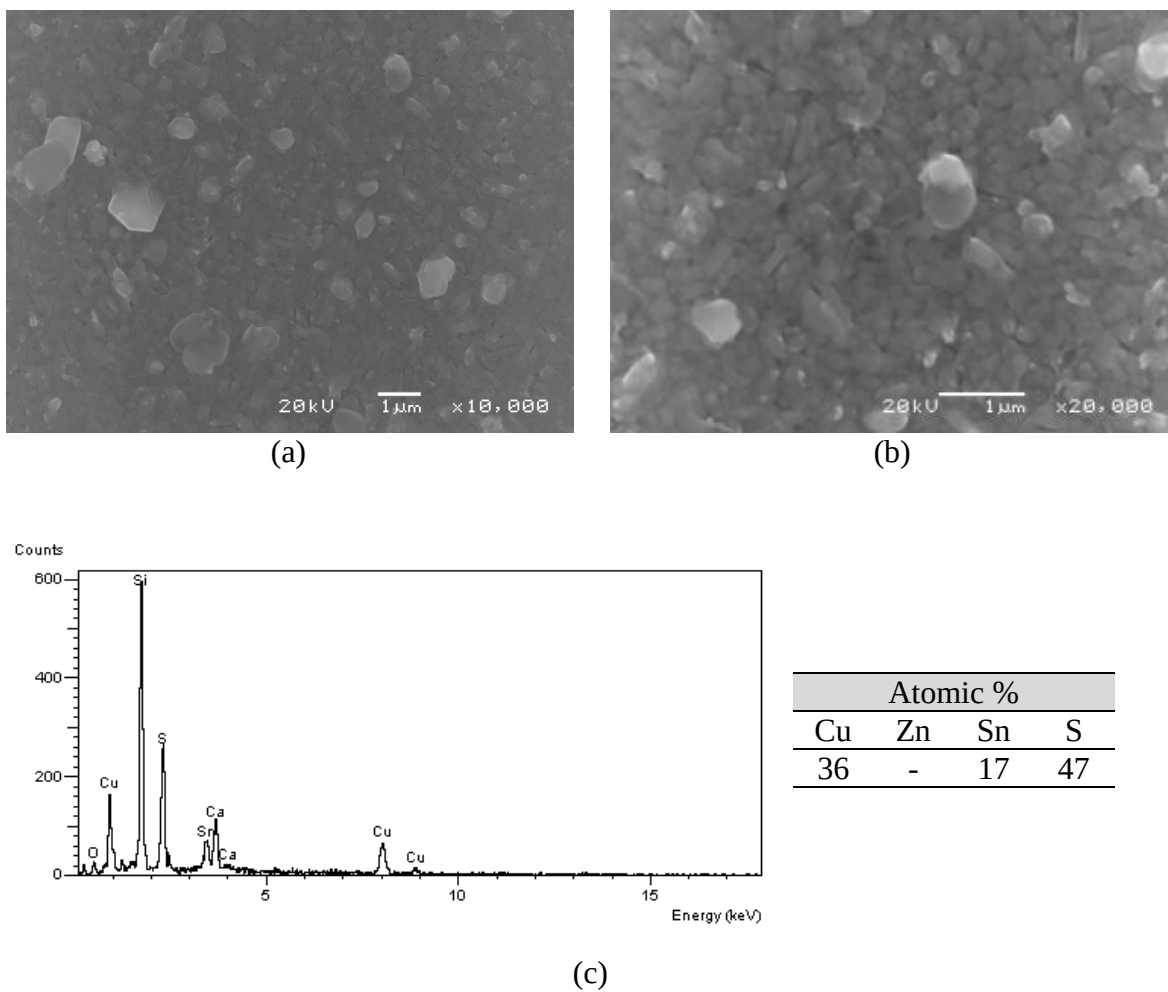


Figure 4.4. SEM images (a,b) and EDS results (c) of the SILAR grown sample obtained in one-stage by using 0.01 M CuCl_2 , 0.005 M ZnCl_2 , 0.01 M SnCl_2 , 0.05 M Na_2S in 50 cycles (each duration in the beakers was 15 s).

4.1.1.2. Modified one-stage SILAR grown films

In order to obtain CZTS film through SILAR method in one cationic solution, we modified deposition parameters. Unlike the section 4.1.1.1, we have dissolved 10 times more zinc source than the stoichiometric value and added 0.5 cc hydrochloric acid into the first and third beakers. After this modification, although smoother and more homogeneous films were obtained, it wasn't detected any zinc content again. Figure 4.5 shows images of the films. Figure 4.6 shows the SEM images of one-stage grown films. While there is not an obvious trend appears with respect to the Cu/Sn molar ratio, surface morphologies of the films change with decreasing the ratio. As can be seen in Figure 4.6a that the film has apparent grain boundaries. The grain sizes are about 250 nm. When Cu/Sn ratio decreases to 1.2, the grain sizes decrease dramatically which is the most significant effect in this sample series.



Figure 4.5. Images of the sulfurized samples obtained in (a) 15 and (b) 30 cycles

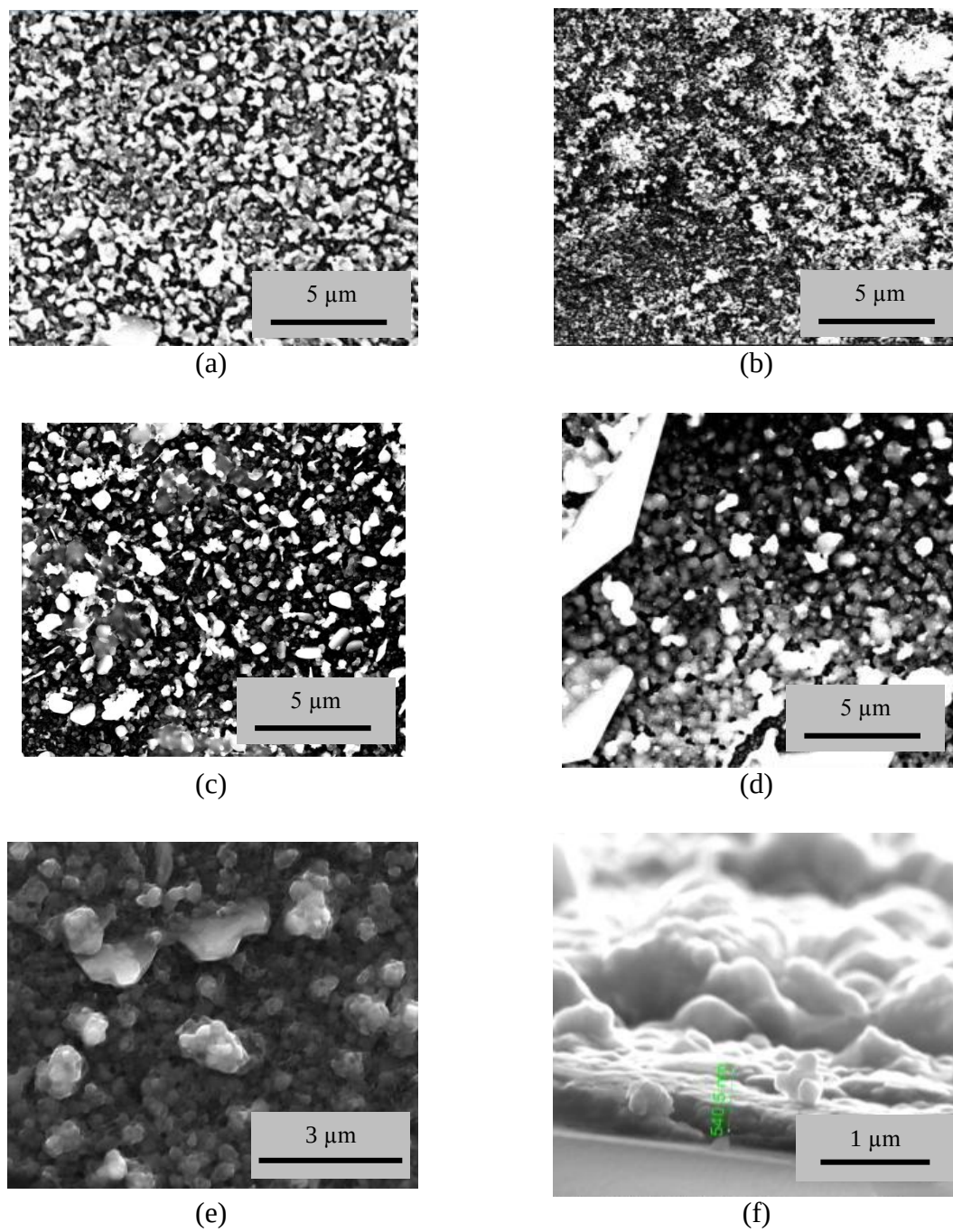
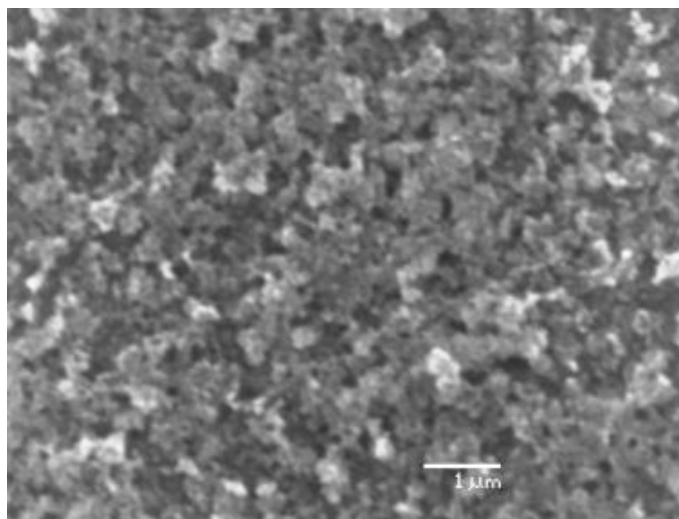


Figure 4.6. SEM images of the modified one-stage SILAR grown samples. M_{Cu}/M_{Sn} : (a) 1.4 (b) 1.2 (c) 1.0 (d) 0.8 (e, f) 0.6.

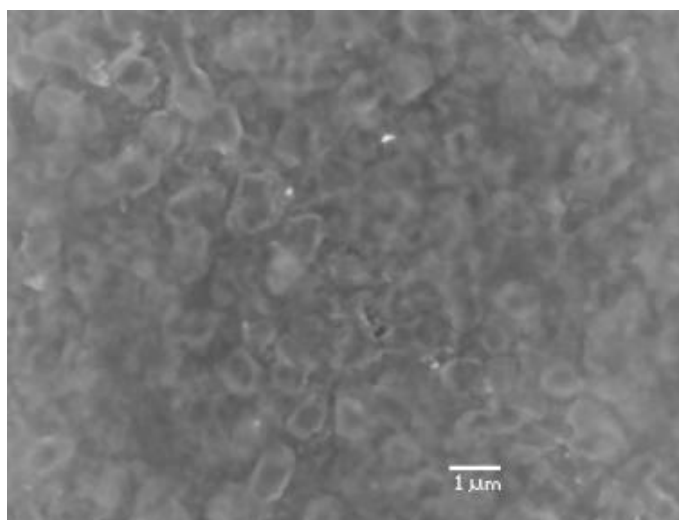
4.1.1.3. Two-stage SILAR grown films for different molar ratios

The films were obtained by sulfurizing $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacked sulfide layers. For the deposition of the Cu_2SnS_3 layer the cation solution was composed of 0.005 M CuCl_2 , 0.01 M SnCl_2 . Triethanolamin was used to adjust the pH value of the solution. For the deposition of the ZnS layer on the Cu_2SnS_3 layer, the cation solution contained 0.1 M ZnCl_2 . To adjust pH value of the ZnCl_2 solution, diluted sulfuric acid was used. Both anion solutions were prepared with 0.05 M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ serving as a source of sulfur. Four different solutions were prepared to investigate the effects of the ratio of copper molarity to tin molarity in precursor solutions. The initial $M_{\text{Cu}}/M_{\text{Sn}}$ ratio was changed as 1/2, 1/4, 1/8, 1/12 and 1/16, respectively. For comparison, Cu_2SnS_3 and ZnS single layers were separately grown on bare glass substrates. Before the annealing, the tube furnace was evacuated to 5×10^{-4} mbar. The samples were annealed at 500 °C for 2 hours. 10 g of elemental sulfur was put into the tube underneath the samples to compensate for possible sulfur loss during the annealing. The heating rate was 5 °C/min. After the annealing process, the samples were allowed to cool naturally to room temperature. Obtained SEM images and atomic composition results are given in Figure 4.7 and 4.8. As can be seen that the surface morphology of the films significantly changes with decreasing $M_{\text{Cu}}/M_{\text{Sn}}$ ratio. From the compositional studies of the samples obtained from the sulfurization of $\text{Cu}_2\text{SnS}_x/\text{ZnS}$ layers, the sample with $M_{\text{Cu}}/M_{\text{Sn}}=1/4$ was found to be nearly stoichiometric. Based on the EDS results, the possible chemical formula of that sample was predicted as $\text{Cu}_{2.00}\text{Zn}_{1.28}\text{Sn}_{1.04}\text{S}_{3.68}$.



Atomic %			
Cu	Zn	Sn	S
25	16	13	46

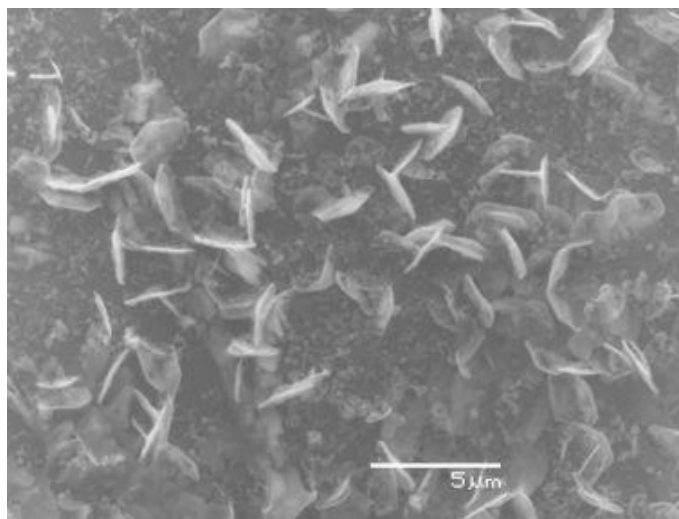
(a)



Atomic %			
Cu	Zn	Sn	S
23	16	24	47

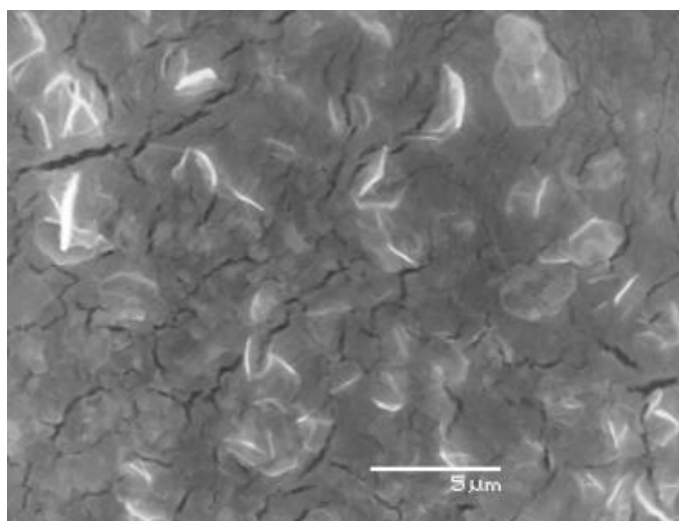
(b)

Figure 4.7. SEM image and EDS result of the two-stage SILAR grown CZTS film via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers. $M_{\text{Cu}}/M_{\text{Sn}}$ is (a) 1/4 (b) 1/8.



Atomic %			
Cu	Zn	Sn	S
08	21	29	42

(a)



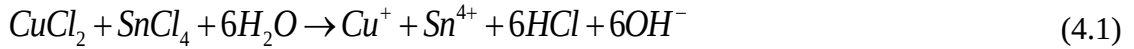
Atomic %			
Cu	Zn	Sn	S
01	18	34	47

(b)

Figure 4.8. SEM image and EDS result of the two-stage SILAR grown CZTS film via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers. $M_{\text{Cu}}/M_{\text{Sn}}$ is (a) 1/12 (b) 1/16.

4.1.1.4. Two-stage SILAR grown films for different deposition cycles

For a thin-film deposition process, the type of growth kinetics is ion-by-ion in which the deposition occurs via nucleation sites on the immersed surfaces (Hodes, 2005). Nucleation takes place as a result of the surface coagulation of these ions and results in a compact adherent film (Lundin and Kitaev, 1965). When the substrate is dipped into the first beaker, Cu^+ and Sn^{4+} cations are adsorbed on the substrate.



Then the substrate is washed with purified water in the second beaker to remove the unwanted reactants. The third beaker contains a Na_2S solution, which gives sulfide ions (S^{2-}) as per the deposition cycle.



Finally, the following reaction takes place between the pre-adsorbed Cu^+ , Sn^{4+} cations and the S^{2-} anion to form a solid Cu_2SnS_3 thin film.



In the second stage, ZnS layer is grown on the previously deposited solid Cu_2SnS_3 thin film through using the same procedure as described above and possible chemical reactions are given below:



Plain view SEM images and EDS results of the sulfurized films are shown in Figure 4.9 and 4.10. It is clear that the films are continuous and composed of homogenously distributed grains. It is well known, in general, that the efficiency of polycrystalline thin film solar cells increases with increasing grain size in the absorber layer. Therefore, larger grains are required for the production of high-performance photovoltaic devices (Yamaguchi et al., 2009; Tanaka et al., 2007; Shinde et al., 2012a).

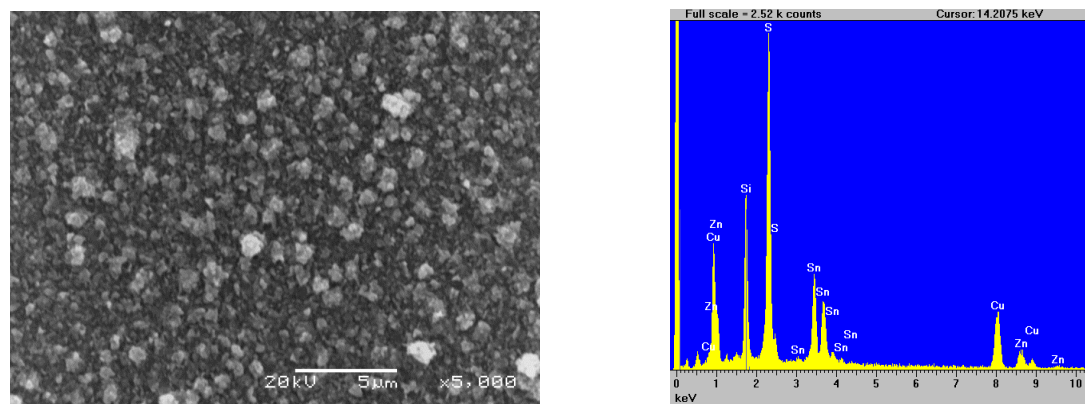
Besides the Cu-Zn-Sn-S, characteristic peaks of Si and O excited from the soda lime glass substrate are also present in the EDS patterns as the primary electron beam penetrates the sulfide film. The number of deposition cycles influences the thickness of the films and the lowest thickness of the sample (prepared via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers of which deposition cycle ratio is 30/40) is also clearly indicated by the highest intensity of the characteristic peaks of Si and O in its EDS pattern. The influence of the number of deposition cycles on the composition of the films is most obviously indicated in the EDS patterns of the samples by variations in the intensity of the characteristic Zn Cu_K peaks at 8.6 and 9.5 eV. The results of the standardless quantitative EDS analyses are presented to just illustrate the relative elemental composition of the samples in Table 4.1. They indicate that we have the $\text{Cu}_2\text{ZnSnS}_4$ -type phase in all samples. It is a desired composition for efficient CZTS based solar cells that the samples 30/40 and 30/20 have slightly Cu-poor and Zn-rich composition while the samples 60/40 and 60/20 do not. Several groups reported that Cu-Zn-Sn-S compounds should be grown under slightly Cu-poor and Zn-rich conditions to improve the optoelectronic properties of the film and to prevent the formation of Cu_{2-x}S or other binary/ternary phases. Katagiri et al., 2008; Katagiri, 2005; Katagiri et al., 1997 and Kobayashi et al., 2005 achieved efficiencies of 1.08%, 3.93%, and 6.77% using Cu-poor absorber layers. Chen et al., 2010a found that Cu-poor conditions improved the efficiency of CZTS solar cells. The Cu deficit enhances the formation of Cu vacancies, which giving rise to shallow acceptors. Another reason to use a

copper-poor composition is the loss of tin, mainly in the form of SnS, which occurs during the sulfurization process (Fernandes et al., 2010b).

Table 4.1. The relative elemental composition of the samples obtained through semi-quantitative, energy-dispersive x-ray spectroscopy (EDS) analysis.

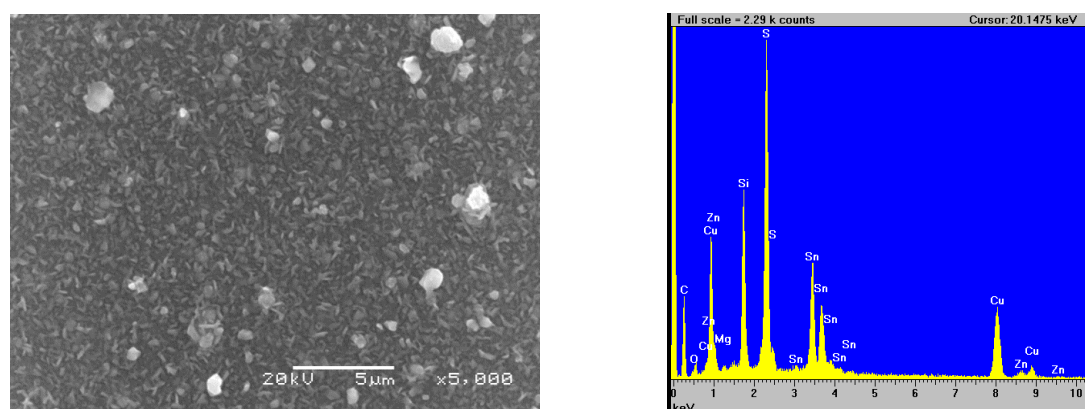
	Number of deposition cycle ratio of Cu ₂ SnS ₃ /ZnS layers							
	60/40		60/20		30/40		30/20	
Element	a.f. (%)	N=8*	a.f. (%)	N=8*	a.f. (%)	N=8*	a.f. (%)	N=8*
Cu	28.19	2.26	33.26	2.66	24.89	1.99	24.64	1.97
Zn	11.14	0.89	3.16	0.25	15.61	1.25	12.85	1.03
Sn	14.48	1.16	17.44	1.40	12.54	1.00	16.18	1.29
S	46.17	3.70	46.14	3.69	46.96	3.76	46.32	3.71
Possible formulation	Cu _{2.26} Zn _{0.89} Sn _{1.16} S _{3.70}		Cu _{2.66} Zn _{0.25} Sn _{1.40} S _{3.69}		Cu _{1.99} Zn _{1.25} Sn _{1.00} S _{3.76}		Cu _{1.97} Zn _{1.03} Sn _{1.29} S _{3.71}	
Cu/(Zn+Sn)	1.10		1.62		0.88		0.85	
Zn/Sn	0.77		0.18		1.24		0.79	

*Composition normalized on 8 atoms per formula unit of CZTS



Atomic %			
Cu	Zn	Sn	S
28	11	15	46

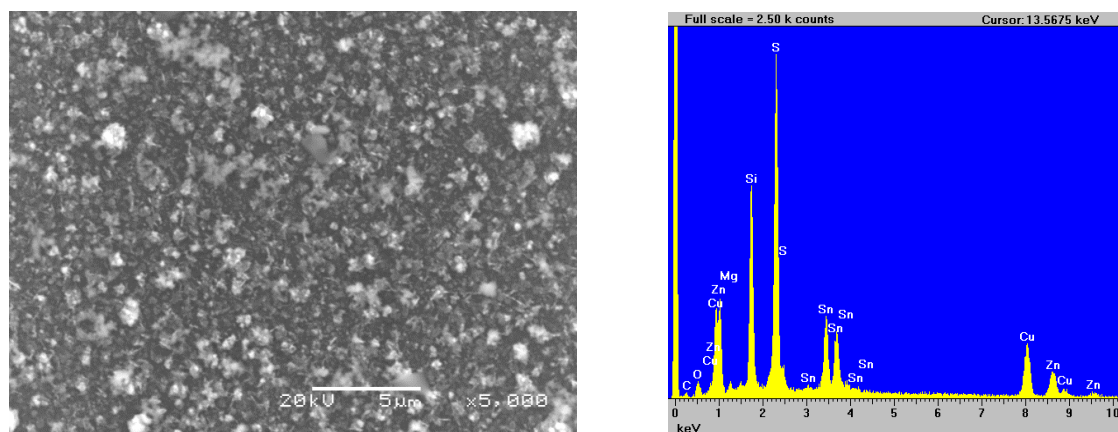
(a)



Atomic %			
Cu	Zn	Sn	S
33	04	17	46

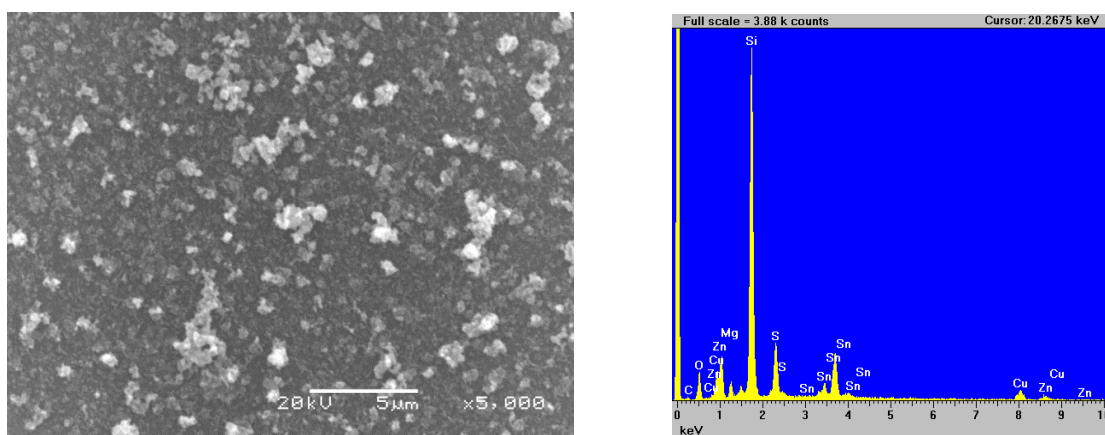
(b)

Figure 4.9. The SEM image and EDS result of the two-stage SILAR grown CZTS films. The number of cycles for the $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers (a) 60/40 (b) 60/20.



Atomic %			
Cu	Zn	Sn	S
25	15	13	47

(a)



Atomic %			
Cu	Zn	Sn	S
25	13	16	46

(b)

Figure 4.10. The SEM images of the two-stage SILAR grown CZTS films. The number of cycles for the $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers (a) 30/40 (b) 30/20.

4.1.2. Sol-gel grown CZTS films

4.1.2.1. Effects of stabilizer content

In order to utilize the sol-gel technique for obtaining crack-free, uniform, transparent and strongly adherent films, sol stabilization is one of the essential steps in the film formation (Kaminski et al., 2005). To stabilize the sol and to reduce the rates of hydrolysis and poly-condensation reactions by forming complex intermediates (Djaoued et al., 2002; Zhang et al., 2009), various stabilization or chelating or complexing agents have been used. Diethanolamine (DEA), diethylenetriamine, monoethanolamine, acetylacetone, acetic acid and polyethylene glycol have widely been used for this purpose. Diethanolamine (DEA) is frequently used as a stabilizer in various sol-gel systems. To investigate the role of DEA in sol-gel spin coated CZTS film deposition process, we have added different amount of DEA into the precursor solutions.

The CZTS precursor solutions were prepared by dissolving copper (II) acetate monohydrate (0.3 M), zinc (II) acetate dihydrate (0.3 M), tin (II) chloride (0.3 M) and thiourea (1.2 M) into 2-methoxyethanol (20 ml). The final solutions were stirred at 45 °C, 850 rpm for 1 h to dissolve the metal compounds completely. During stirring, a certain amount of diethanolamine was dropped slowly into each solution as a stabilizer. The molarity of DEA was changed from 0.3 to 2.5. After 24 hours of aging, it was observed that the prepared solutions were stable. The Mo-coated SLG substrates were used as substrates. To produce the CZTS films, the prepared solutions were spin-coated onto the substrates at 3000 rpm for 30 s followed by solvent-drying at 175 °C for 10 min on a hot plate. The spin-coating and solvent-drying processes were repeated 10 times to obtain the desired thickness of the films. Before the annealing, the tube furnace was evacuated to 5×10^{-4} mbar. The samples were annealed for 2 h at 550 °C in a quartz tube containing certain amount of elemental sulfur. The heating rate was 5 °C/min. After the annealing process, the samples were allowed to cool down naturally to room temperature. SEM images and EDS results of the CZTS films prepared by using different DEA in sol solution are shown in Figure 4.11-26.

Figure 4.11-4.15 show the surface morphology and compositional results of the samples prepared by using 2.5, 2.0, 1.5 and 1.0 M DEA, respectively. They reveal that all samples show a smooth, compact and densely packed morphology. Some cracks and voids were observed in the film prepared with the solution containing 2.5 M DEA (Figure 4.11). When the DEA concentration was decreased the density of the cracks and voids decreased rapidly (Figure 4.12 and 4.13). Finally the cracks and voids disappeared when the DEA concentration was 1 M in the sol solution (Figure 4.14). Hence, it can be deduced that DEA concentration in the sol is very crucial to obtain void/crack-free CZTS thin films. EDS studies of the samples prepared by using different DEA amounts are given the following figures.

According to the EDS results the possible chemical formulations were predicted to be $\text{Cu}_{2.24}\text{Zn}_{0.88}\text{Sn}_{1.20}\text{S}_{3.68}$, $\text{Cu}_{2.64}\text{Zn}_{0.32}\text{Sn}_{1.36}\text{S}_{3.68}$, $\text{Cu}_{2.00}\text{Zn}_{1.20}\text{Sn}_{1.04}\text{S}_{3.76}$, $\text{Cu}_{1.60}\text{Zn}_{1.28}\text{Sn}_{1.20}\text{S}_{3.92}$ for the samples prepared by using the solutions containing 2.5, 2.0, 1.5 and 1.0 M diethanolamine (DEA) as stabilizer, respectively.

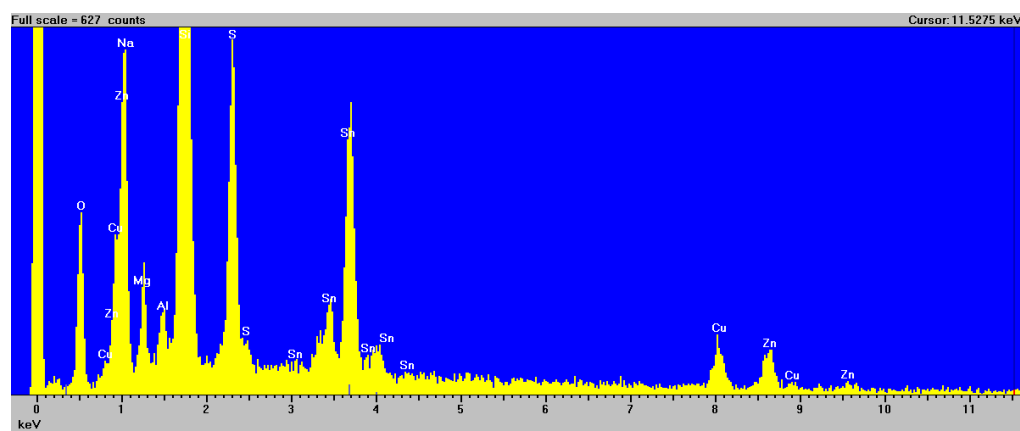
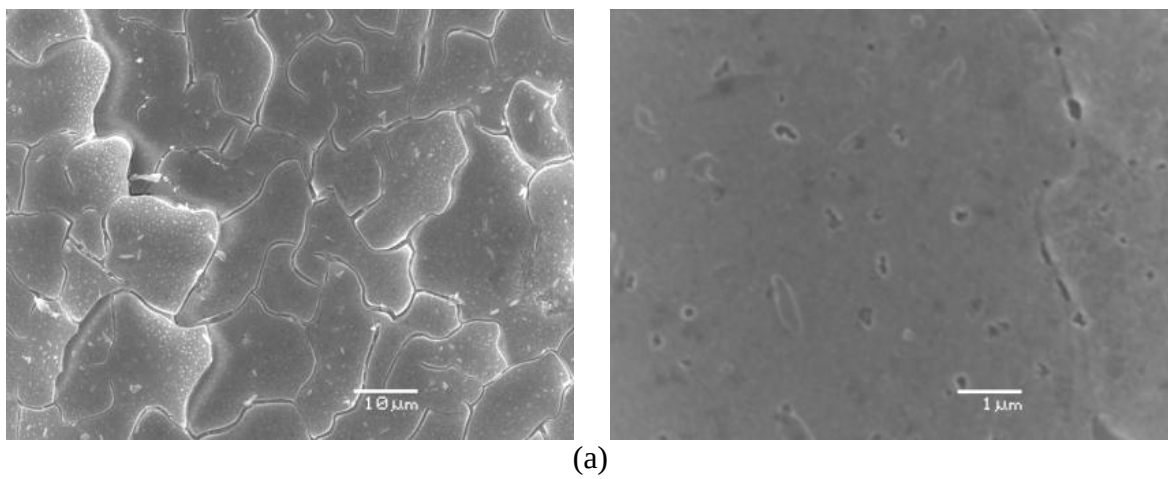
Figure 4.15 shows plain view and cross-section SEM images of the sample prepared by using a solution containing 1.0 M DEA. It is clearly seen in the Figure that the film has a good textured surface morphology with ~400 nm grain size. It can be also seen that there are some big particles on top of textured surface. Through the EDS study, it was found that those residual particles are Cu_{2-x}S .

Figure 4.16 shows plain view and cross-section SEM images of the sample prepared by using a solution containing 0.8 M DEA. It is clear that the film has continuous and dense morphology with micron size grains which is crucial to produce for high efficient solar cells. EDS result of that sample indicates its near-stoichiometry.

Because of high volatility and high vapor pressure of sulfur, an inevitable MoS_2 layer formed in almost all samples after sulfurization (e.g. wide black region in cross-section image, Figure 4.16). Un-damaged Mo layers are seen as thin white line in the image. When DEA concentration is 0.3 in precursor solution, the grain sizes become bigger (about 2 microns) (Figure 4.18).

Figure 4.19-4.24 show the SEM images and EDS results of the samples prepared by using 0.9, 1.1, 1.3, 1.5 and 1.9 M DEA. It can be clearly seen that there are two

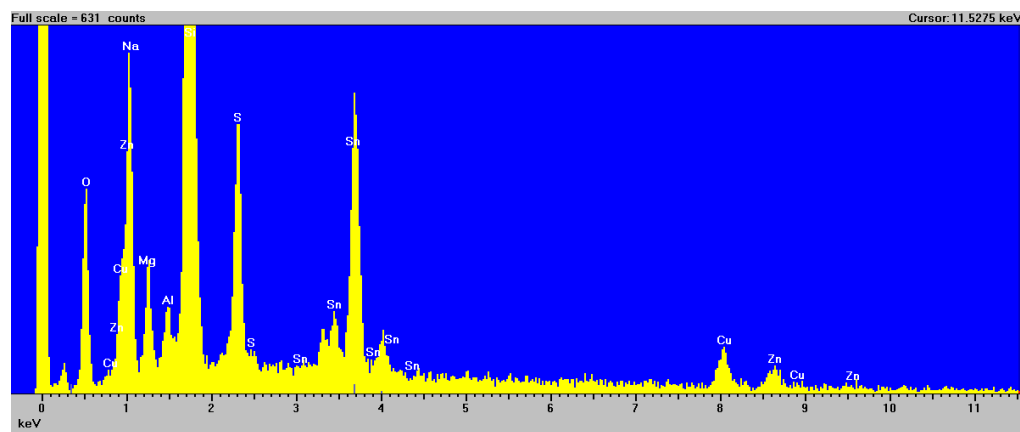
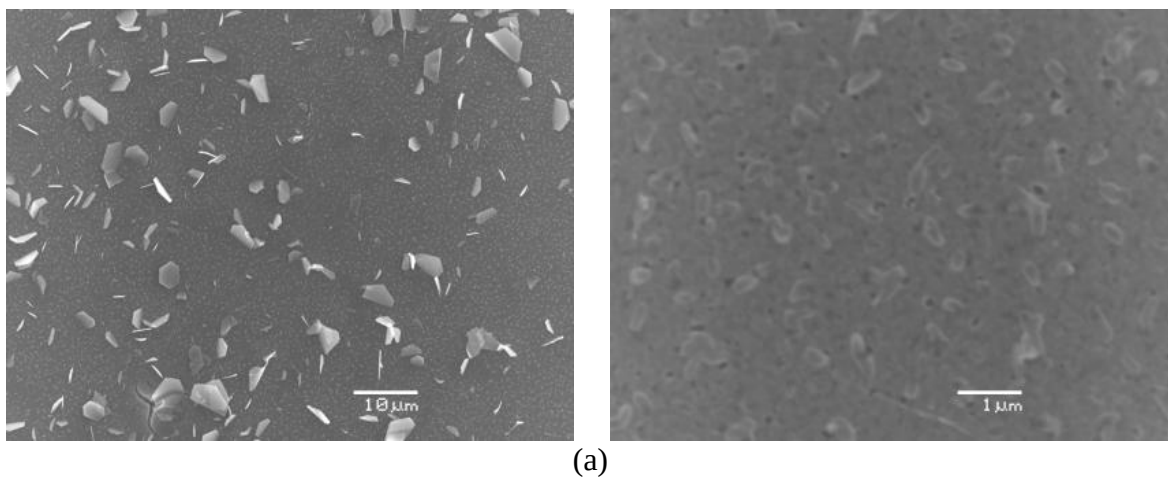
different layers: one is a relatively smooth bottom textured surface and the other one is randomly distributed large particles on top surface. Through EDS studies, it can be deduced that both layers composes of Cu, Zn, Sn and S of which atomic percentages are consistent with stoichiometric ones of CZTS compound. In Figure 4.25, some big hexagonal shaped particles on top of the film surface can be seen. These particles are different from the others and composed of Cu and S of which atomic percentages indicate the presence of Cu_{2-x}S phase. As it will be shown in XRD discussion of this sample, the obtained XRD pattern of this sample proves that big particles are copper sulfide with hexagonal crystal system.



Atomic %			
Cu	Zn	Sn	S
23	12	14	51

(b)

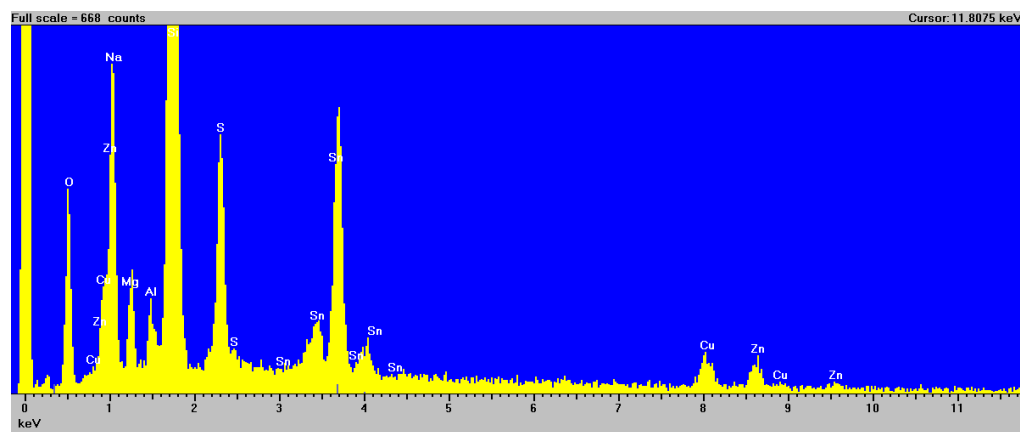
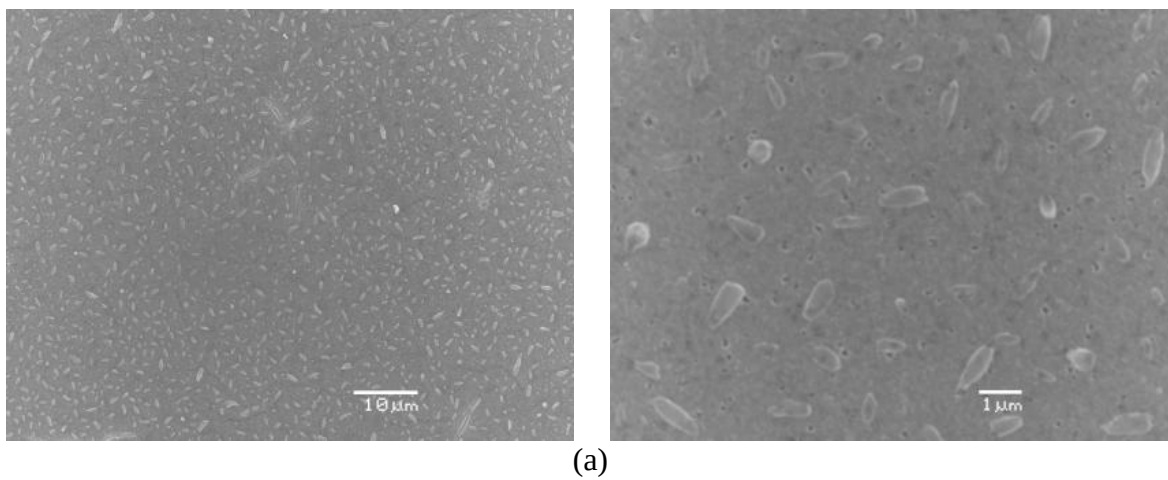
Figure 4.11. (a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 2.5 M DEA (Sulfur pressure: 20 atm)



Atomic %			
Cu	Zn	Sn	S
22	12	14	52

(b)

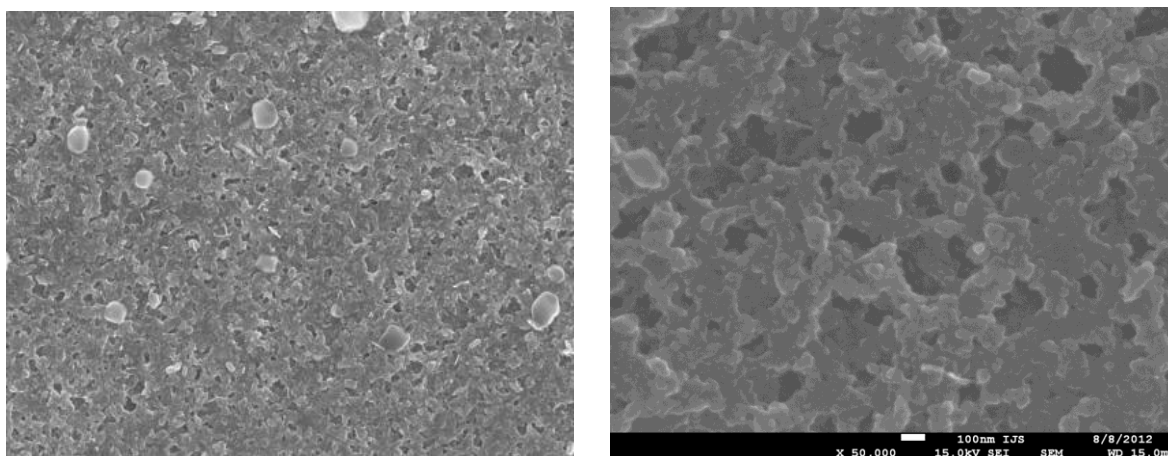
Figure 4.12. (a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 2.0 M DEA (Sulfur pressure: 20 atm)



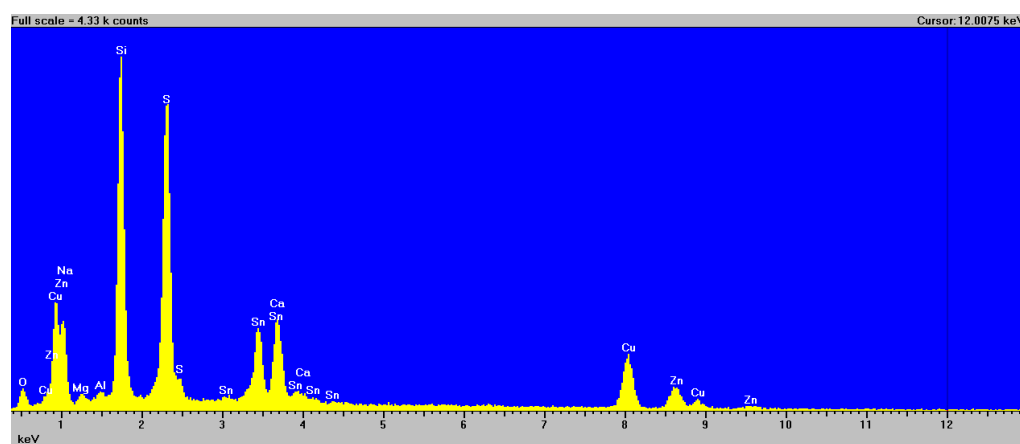
Atomic %			
Cu	Zn	Sn	S
24	12	14	50

(b)

Figure 4.13. SEM images and EDS result of the sol-gel grown sample prepared from solution containing 1.5 M DEA (Sulfur pressure: 20 atm)



(a)



Atomic %			
Cu	Zn	Sn	S
23	13	13	51

(b)

Figure 4.14. SEM images and EDS result of the sol-gel grown sample prepared from solution containing 1.0 M DEA (Sulfur pressure: 20 atm)

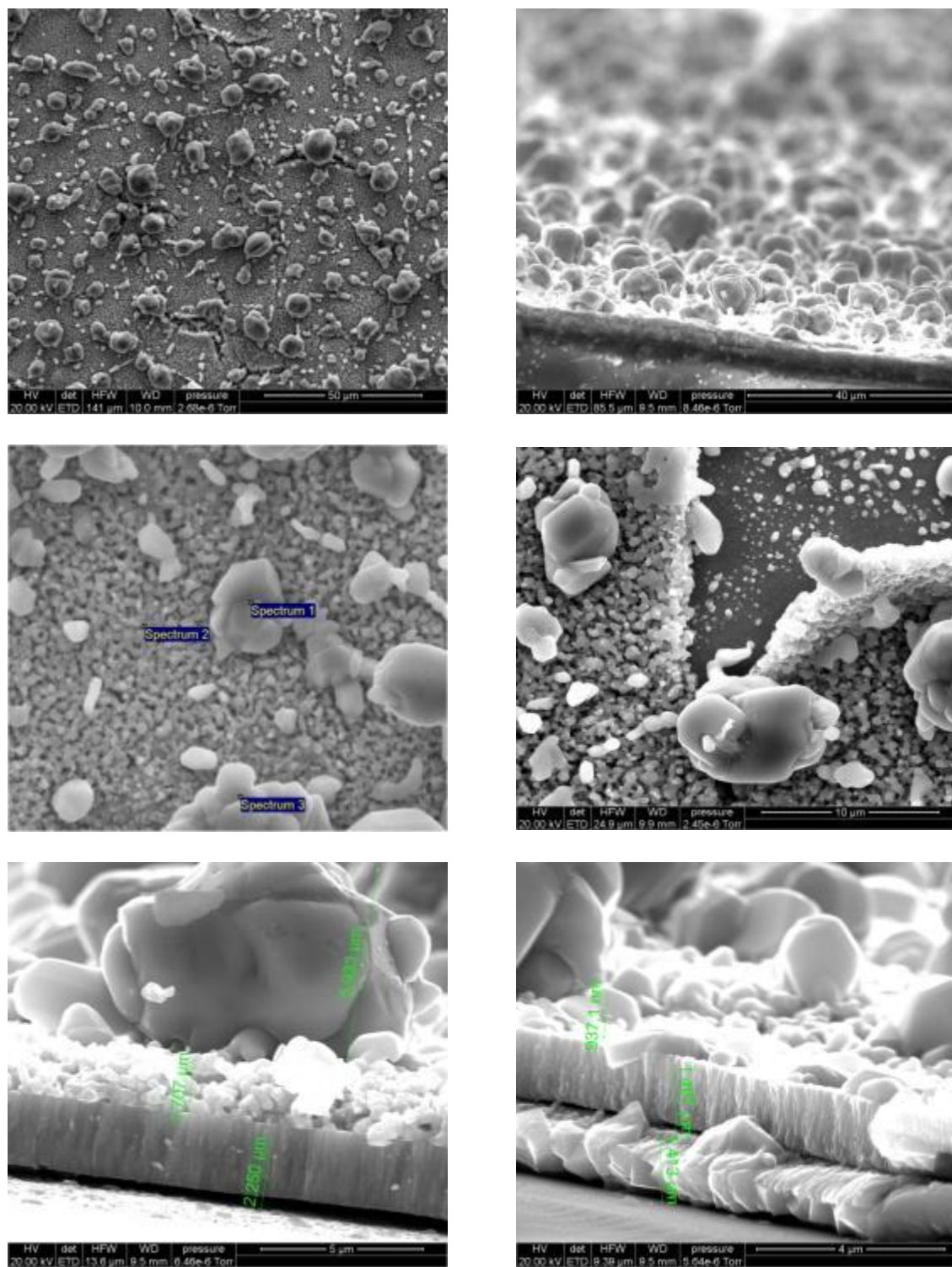
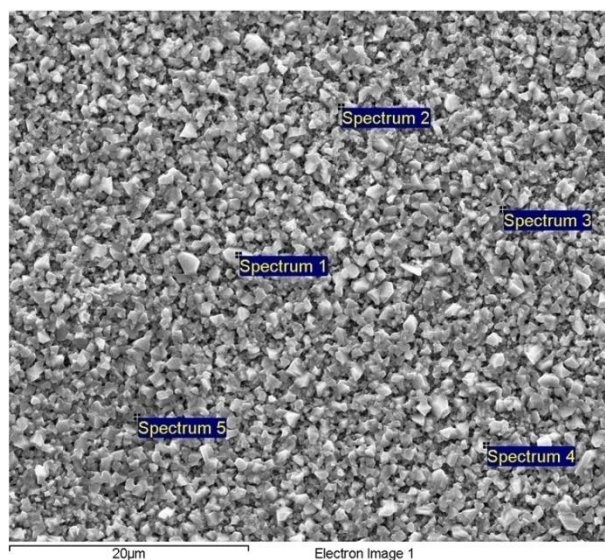
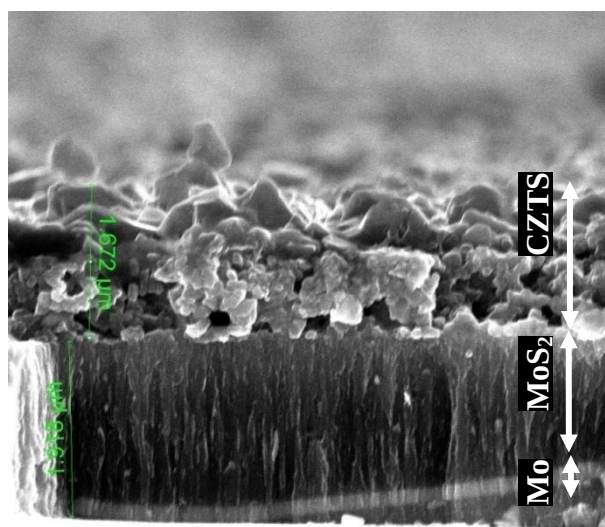


Figure 4.15. Plain view and cross-section SEM images of the sol-gel grown sample prepared from solution containing 1.0 M DEA (Sulfur pressure: 20 atm)



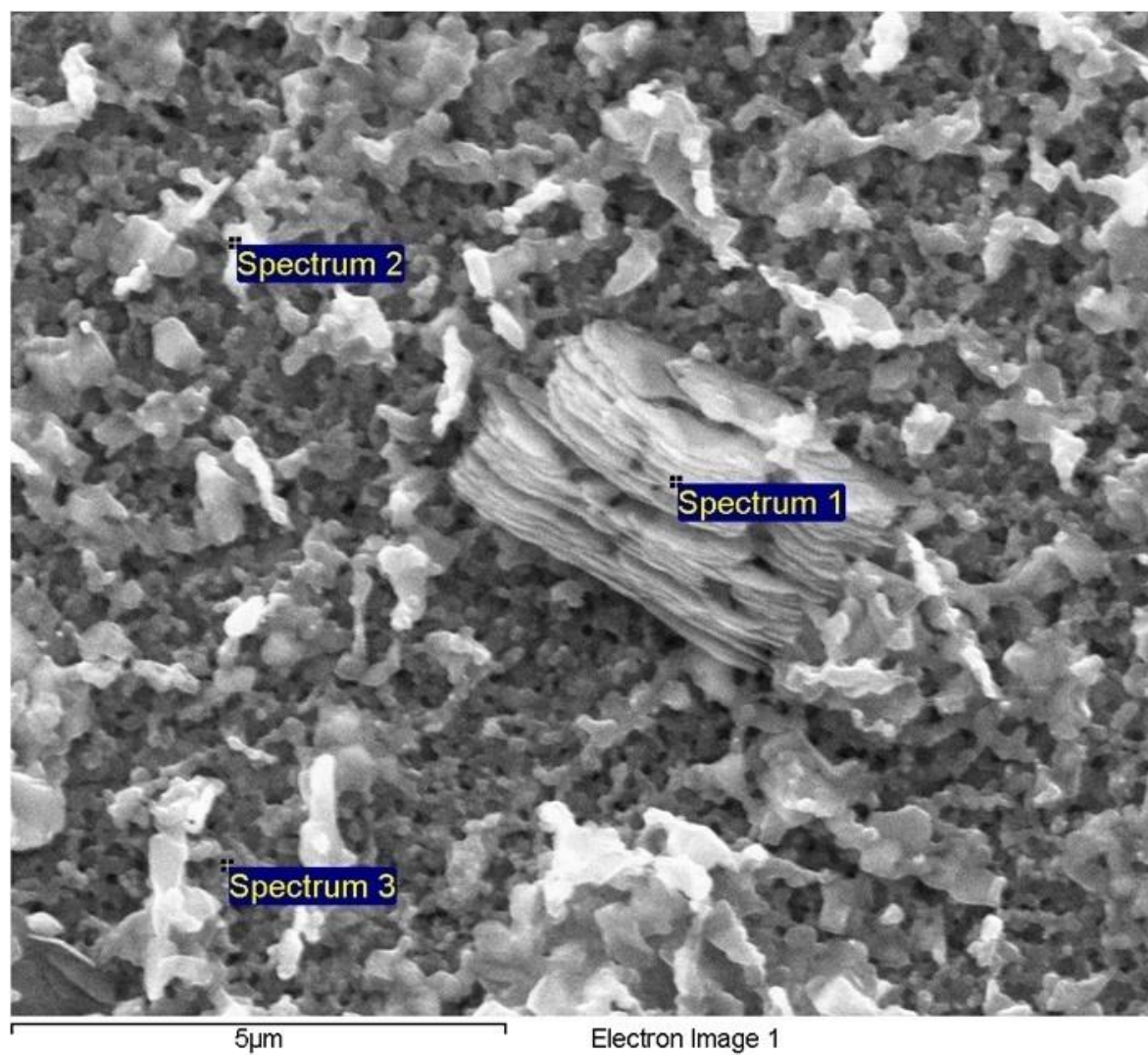
Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	21	11	11	53	4
2	18	10	9	51	12
3	17	9	9	53	12
4	19	11	11	52	7
5	17	10	10	53	10
Mean	18	10	10	52	9

(a)



(b)

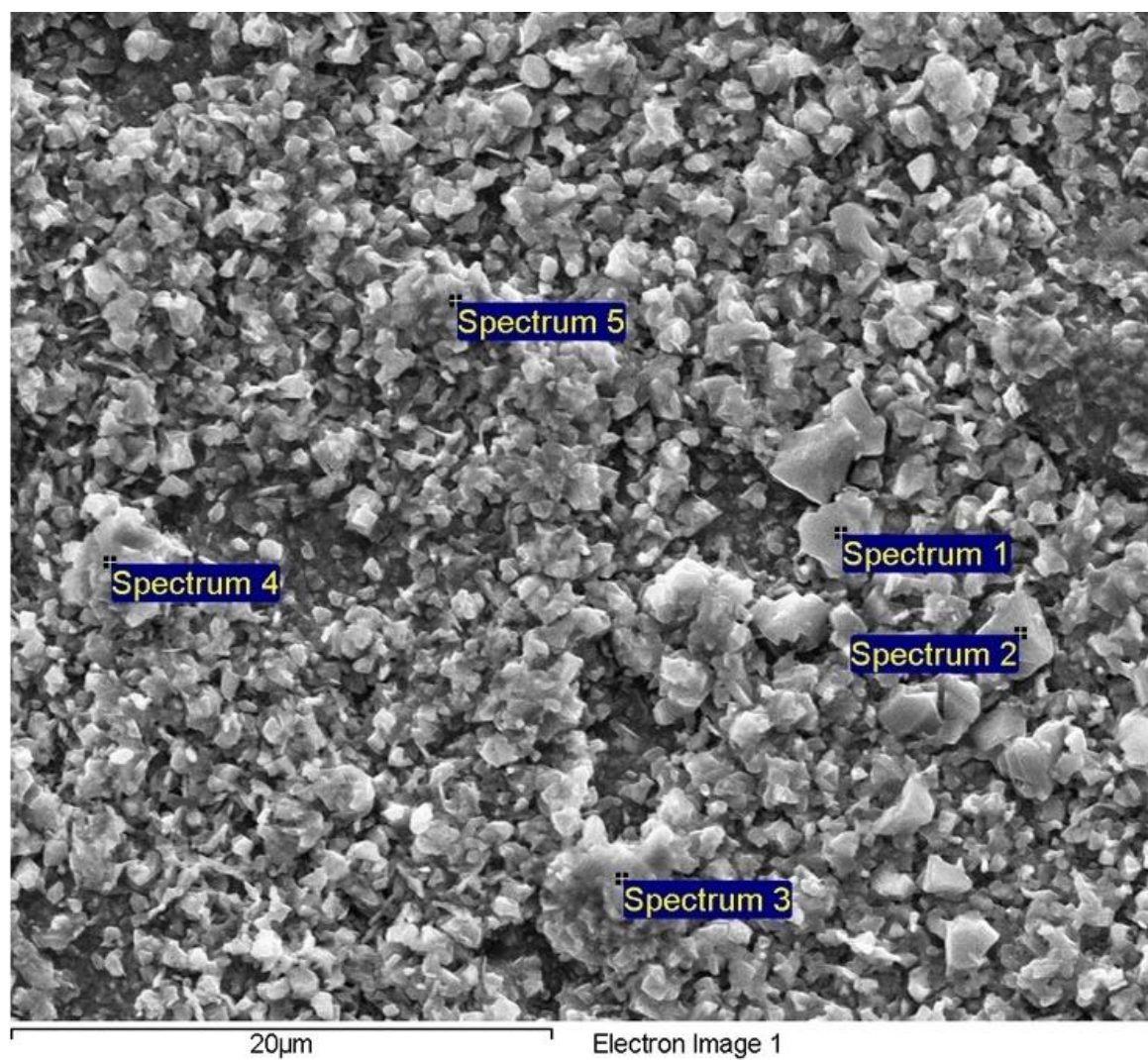
Figure 4.16. (a) EDS results and cross-section SEM image of the sol-gel grown sample prepared from solution containing 0.8 M DEA (Sulfur pressure: 20 atm)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	10	6	20	59	5
2	15	10	9	53	13
3	14	9	9	54	14
Mean [†]	14	10	9	54	14

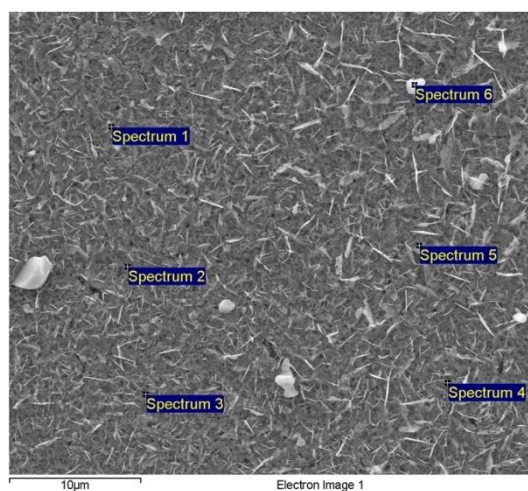
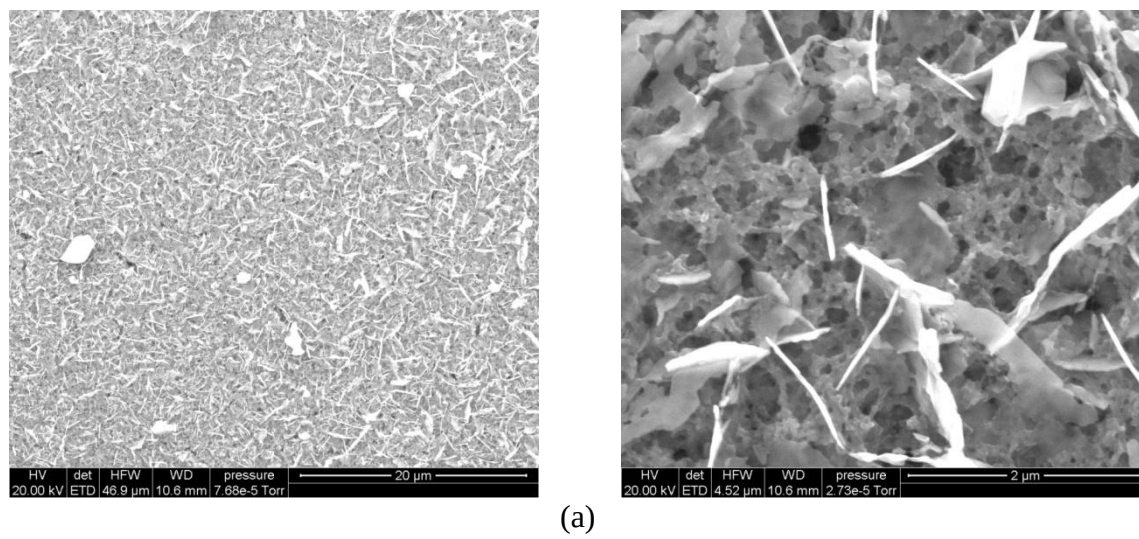
Figure 4.17. SEM image and EDS result of the sol-gel grown sample prepared from solution containing 0.4 M DEA (Sulfur pressure: 20 atm)

[†] Spectrum 1 was not taken into account for the calculation of mean values



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	23	12	12	52	1
2	23	12	13	52	-
3	21	13	13	53	-
4	21	13	13	53	-
5	21	11	13	55	-
Mean	22	12	13	53	-

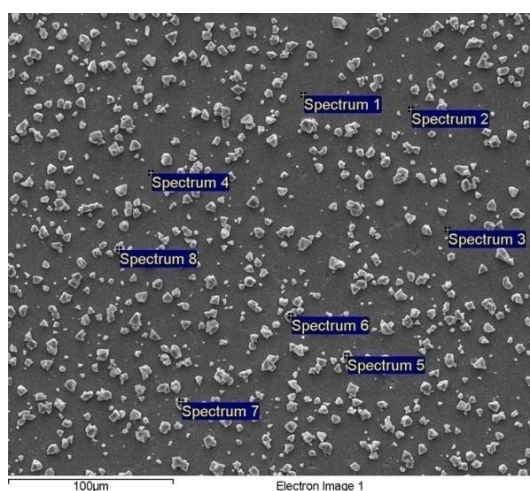
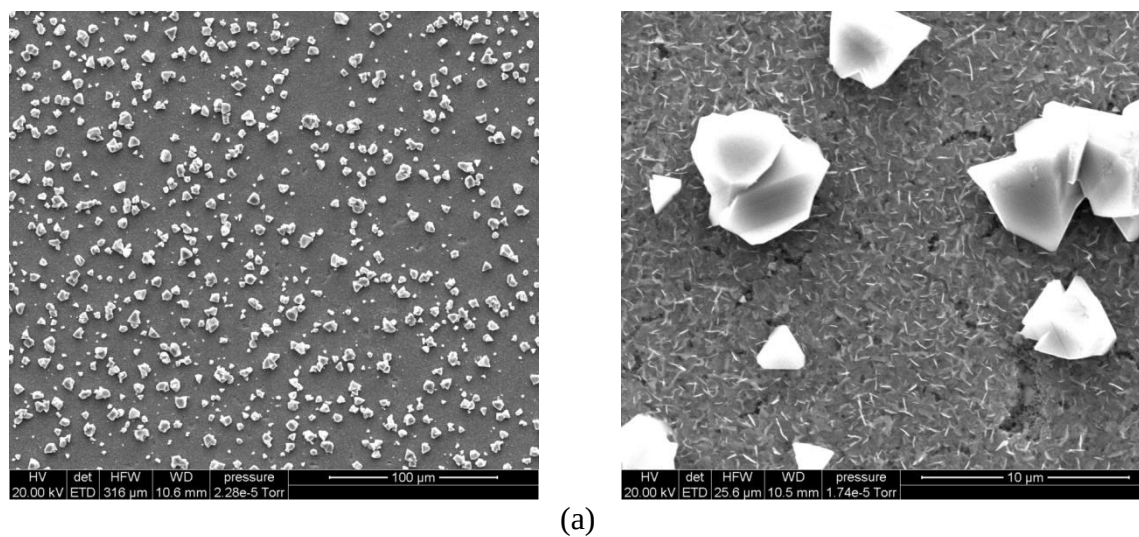
Figure 4.18. SEM image and EDS result of the sol-gel grown sample prepared from solution containing 0.3 M DEA (Sulfur pressure: 20 atm)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	24	10	12	50	4
2	23	10	11	50	6
3	24	10	11	50	5
4	23	9	11	51	6
5	23	10	11	51	5
6	23	10	11	52	4
Mean	23	10	11	51	5

(b)

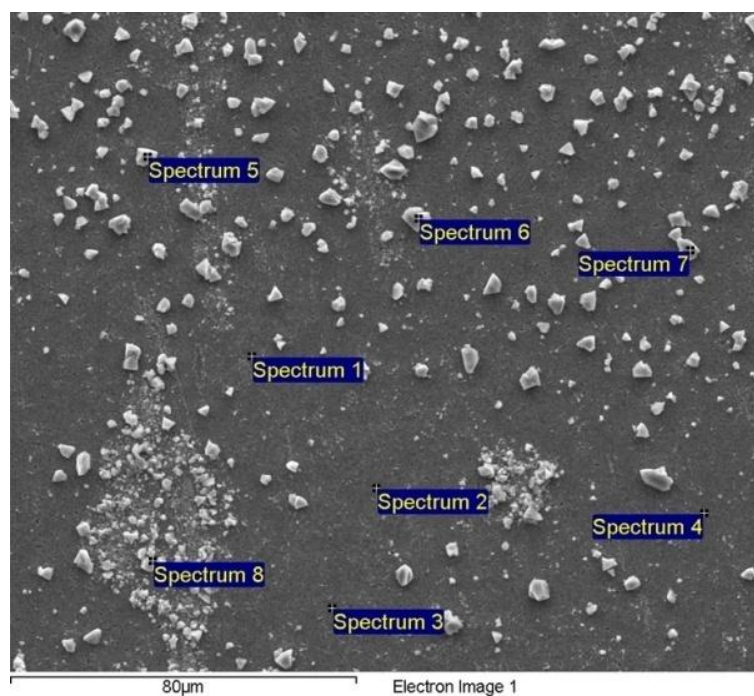
Figure 4.19. (a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 0.9 M DEA (Sulfur pressure: 2.5 atm)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	21	10	12	53	4
2	21	10	12	54	3
3	21	9	12	55	3
4	22	11	12	53	2
5	25	13	13	48	1
6	25	12	13	50	-
7	25	13	13	49	-
8	24	12	13	50	1
Mean	23	11	12	52	1

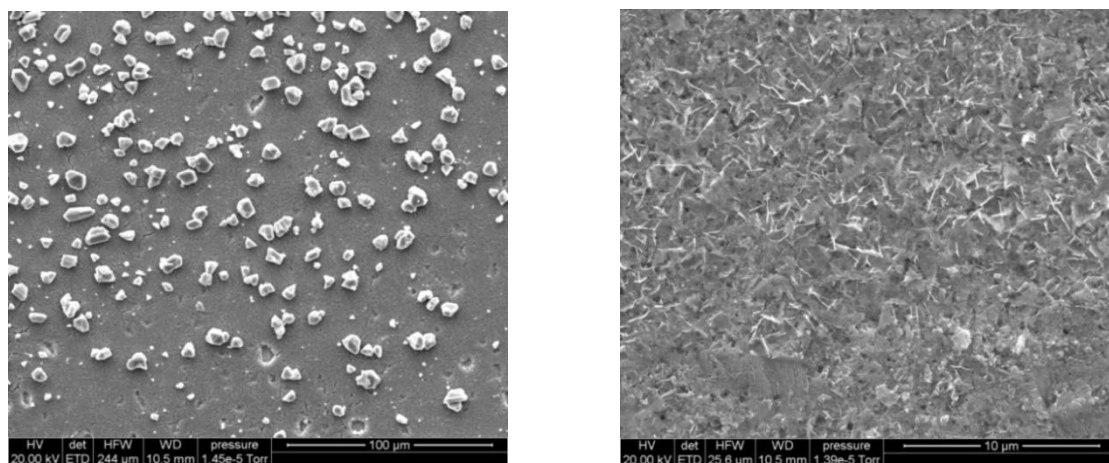
(b)

Figure 4.20. (a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 1.1 M DEA (Sulfur pressure: 2.5 atm)

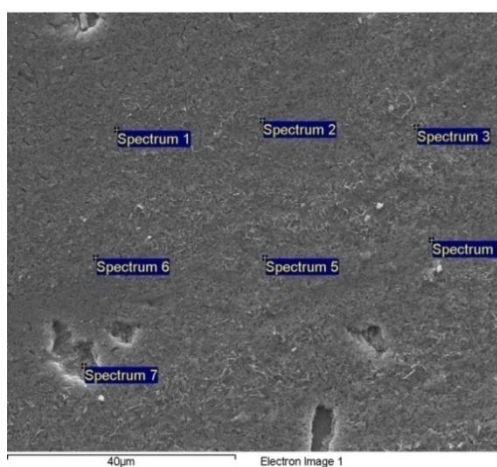


Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	22	11	13	53	1
2	22	11	13	53	1
3	23	11	13	52	1
4	23	10	13	52	2
5	24	13	12	50	1
6	24	13	13	49	1
7	24	12	12	51	1
8	23	11	13	50	3
Mean	23	12	13	51	1

Figure 4.21. EDS result of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 2.5 atm)



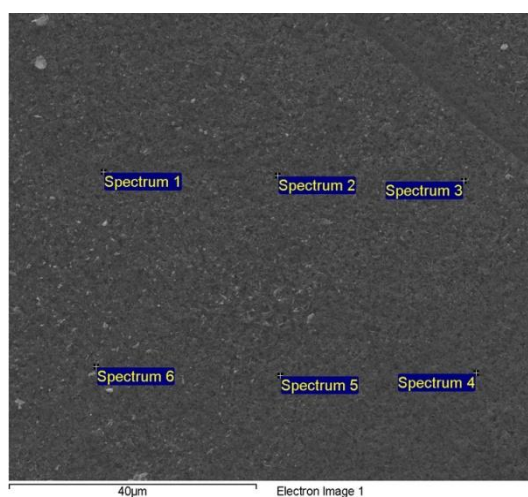
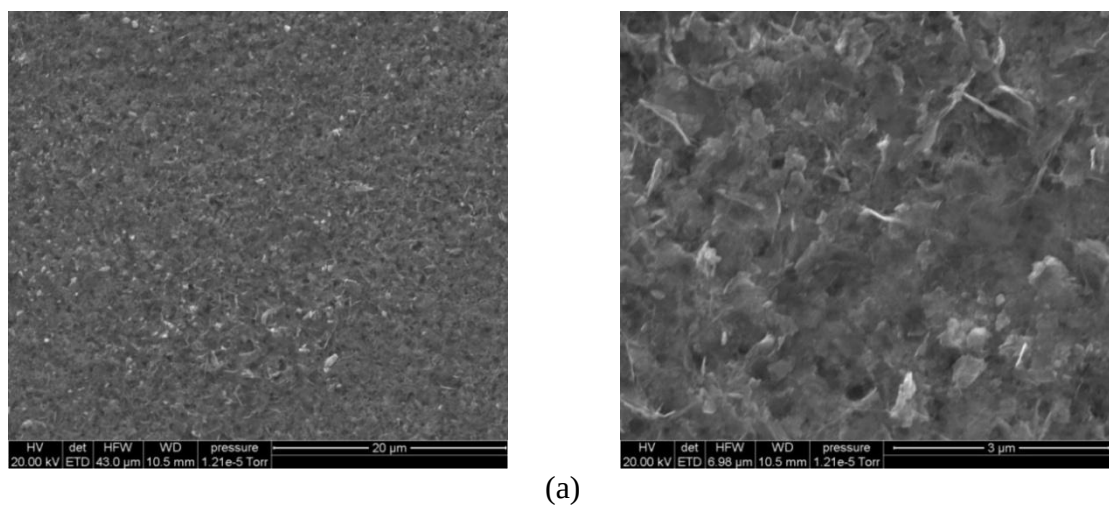
(a)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	21	10	11	52	6
2	22	9	11	51	7
3	21	10	12	51	6
4	20	9	11	52	8
5	21	10	12	51	6
6	22	9	12	51	6
7	2	-	1	60	37
Mean	21	10	12	51	6

(b)

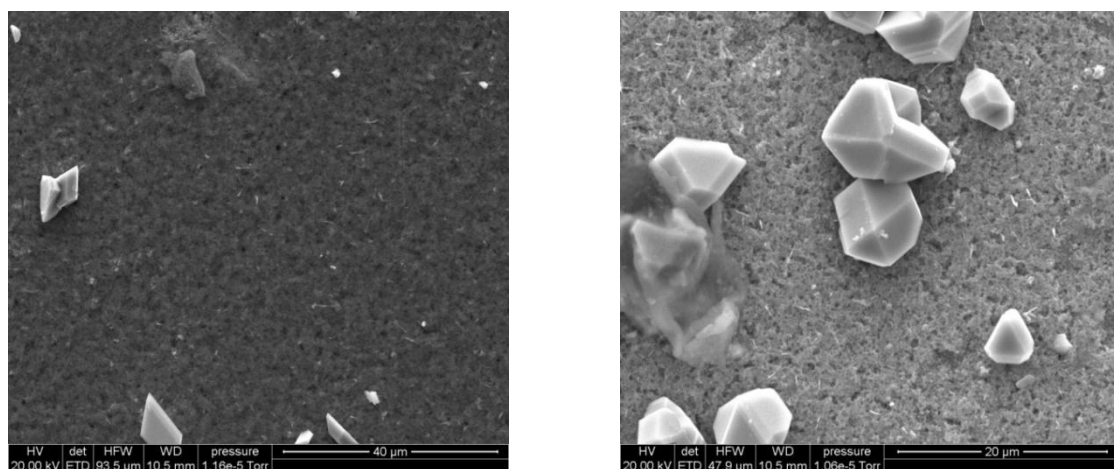
Figure 4.22. (a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 1.5 M DEA (Sulfur pressure: 2.5 atm)



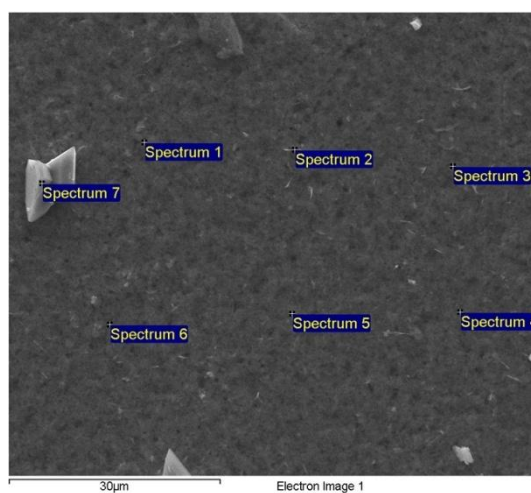
Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	24	10	13	50	3
2	23	11	13	52	1
3	23	10	13	53	1
4	23	11	12	51	3
5	23	10	13	51	3
6	23	11	13	52	1
Mean	23	10	13	52	2

(b)

Figure 4.23. (a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 1.7 M DEA (Sulfur pressure: 2.5 atm)



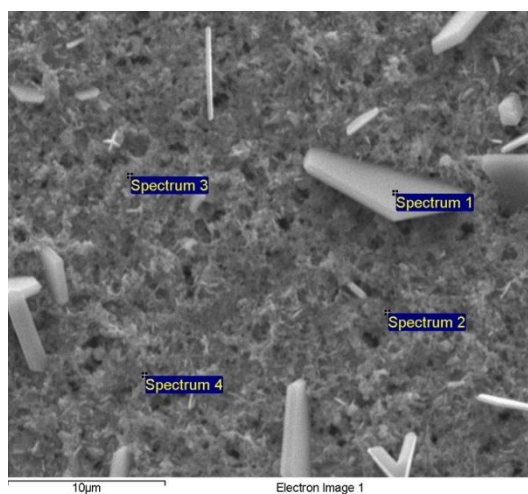
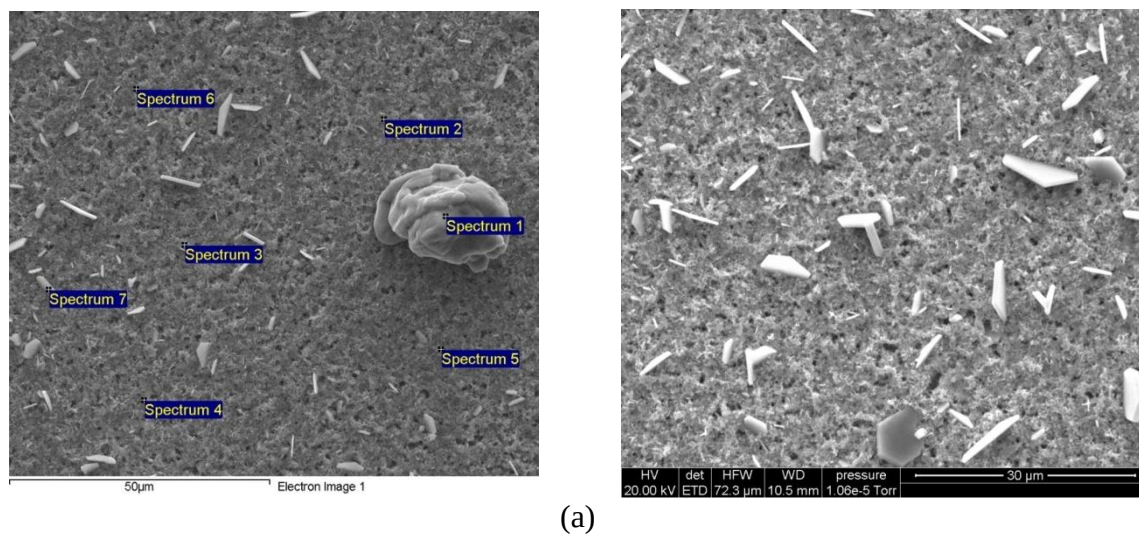
(a)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	26	10	10	51	3
2	25	10	10	52	3
3	26	10	9	52	3
4	25	10	10	52	3
5	25	10	10	52	3
6	24	10	10	50	6
7	25	12	12	50	1
Mean	25	10	10	51	3

(b)

Figure 4.24. (a) SEM images (b) EDS result of the sol-gel grown sample prepared from solution containing 1.9 M DEA (Sulfur pressure: 2.5 atm)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	43	1	1	54	1
2	24	10	8	51	7
3	25	11	8	51	5
4	24	12	9	51	4
Mean	24	11	8	51	5

(b)

Figure 4.25. (a) SEM images and (b) EDS result of the sol-gel grown sample prepared from solution containing 2.1 M DEA (Sulfur pressure: 2.5 atm)

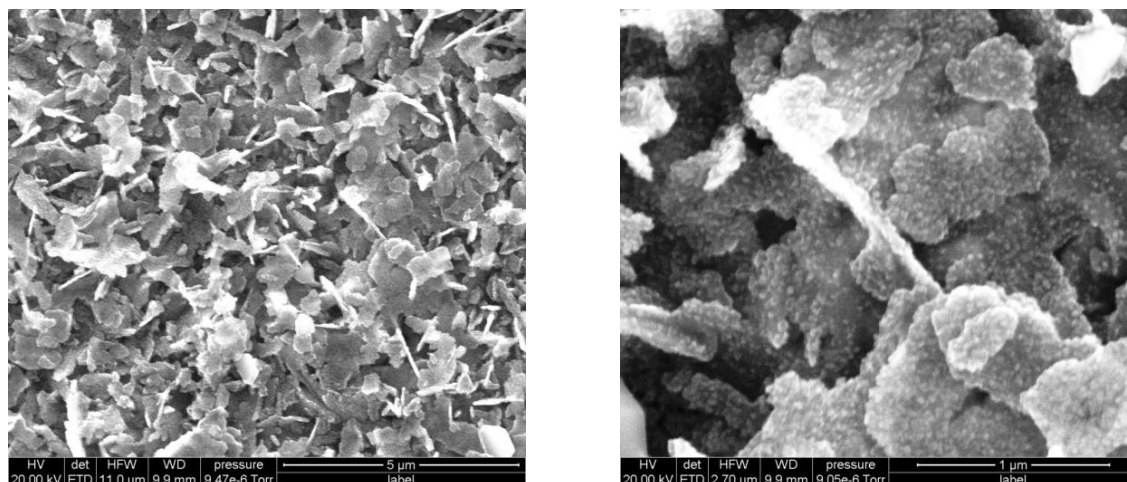


Figure 4.26. SEM images of the sol-gel grown sample prepared from solution containing 1.5 M DEA (Sulfur pressure: 1.0 atm)

4.1.2.2. Effects of sulfur pressure

In the previous section stabilizer amount in the precursor solution was tried to be optimized. The sample obtained by using 1.3 M of diethanolamine was found to have bigger particles without cracks or holes. Therefore, we investigated the effects of sulfur pressure on the samples prepared by using 1.3 M of diethanolamine. To investigate the role of sulfur pressure during sulfurization in sol-gel spin coated CZTS film deposition process, we have sulfurized the samples at the pressures of 0.5, 0.9 and 1.4 atm. The CZTS precursor solution was prepared by dissolving copper (II) acetate monohydrate (0.3 M), zinc (II) acetate dihydrate (0.3 M), tin (II) chloride (0.3 M) and thiourea (1.2 M) into 2-methoxyethanol (20 ml). The final solution was stirred at 45 °C, 850 rpm for 1 h to dissolve the metal compounds completely. During stirring, 1.3 M of diethanolamine (according to the optimization study in the previous section) was dropped slowly into the solution as a stabilizer. After 24 hours of aging, it was observed that the prepared solution was stable. To produce the CZTS film, the prepared solution was spin coated at 3000 rpm for 30 s followed by solvent-drying at 175 °C for 10 min on a hot plate. The spin-coating and solvent-drying processes were repeated 10 times to obtain the desired thickness of the films. The precursor film was cut into four pieces to investigate sulfur pressure effect. Finally, the samples were annealed for 2 h at 550 °C in a vacuumed quartz tube containing

a certain amount of elemental sulfur. The sulfur pressures were adjusted to be 0.5, 0.9 and 1.4 atm. The heating rate was 5 °C/min. After the annealing process, the samples were allowed to cool down naturally to room temperature. SEM images and EDS results of the CZTS films sulfurized under different pressures are shown in Figure 4.27-4.34. Generally, they reveal that sulfur pressure strongly affects surface morphology and grain size. As can be seen that the grains become larger in accordance with the increasing sulfur pressure up to 1.4 atm. The grain sizes of the sample sulfurized at 1.4 atm are about 2 micron which has a key role to produce high efficient CZTS thin film solar cells. In all cross-section images, it can be still seen that there are MoS₂ layer resulted from high vapor pressure/high volatility of sulfur penetrating into the Mo layer coated on glass substrates.

Figure 4.27 and 4.28 show the plain view/tilted SEM images of four different samples prepared with 1.3 M DEA sulfurized at 0.5, 0.9 and 1.4 atm, respectively. It is clear that surface morphologies strongly changes with the increasing sulfur pressure. It can also be concluded that sulfur pressure also affects the crystallization behavior, grain sizes and uniformity of the samples.

From the EDX results, it can be shown that sulfur content in the samples doesn't change with increasing sulfur pressure. Maeda et al., 2011 investigated the influence of H₂S concentration on the properties of CZTS films prepared by sol-gel sulfurization. They sulfurized the samples at 500 °C for 1 h in an H₂S/N₂ mixed gas atmosphere with H₂S concentrations of 3%, 5%, 10%, and 20%. They found that the percentage of S showed almost no dependence on the H₂S concentration. They attributed this independency to a saturation which occurred at even the lowest gas concentration in their study. In our case, mean atomic percentages of sulfur were determined as 52, 52 and 51 in the samples sulfurized at 0.5, 0.9 and 1.4 atm., respectively (Figures 4.30, 4.32 and 4.34). Similarly to the work of Maeda et al., 2011, these constant sulfur values can be attributed to a saturation which happens even at 0.5 atm of sulfur pressure.

According to the tilted SEM images (Figure 4.28, 4.33, 4.34), it is clear that the sample sulfurized under sulfur pressure of 1.4 atm exhibits well defined/interconnected and homogeneously distributed crystalline grains. It should be noted that the sample has slightly

Cu-poor composition. The white big particle on top (Figure 4.30) was evaluated as containing Cu, Sn and S through EDS study.

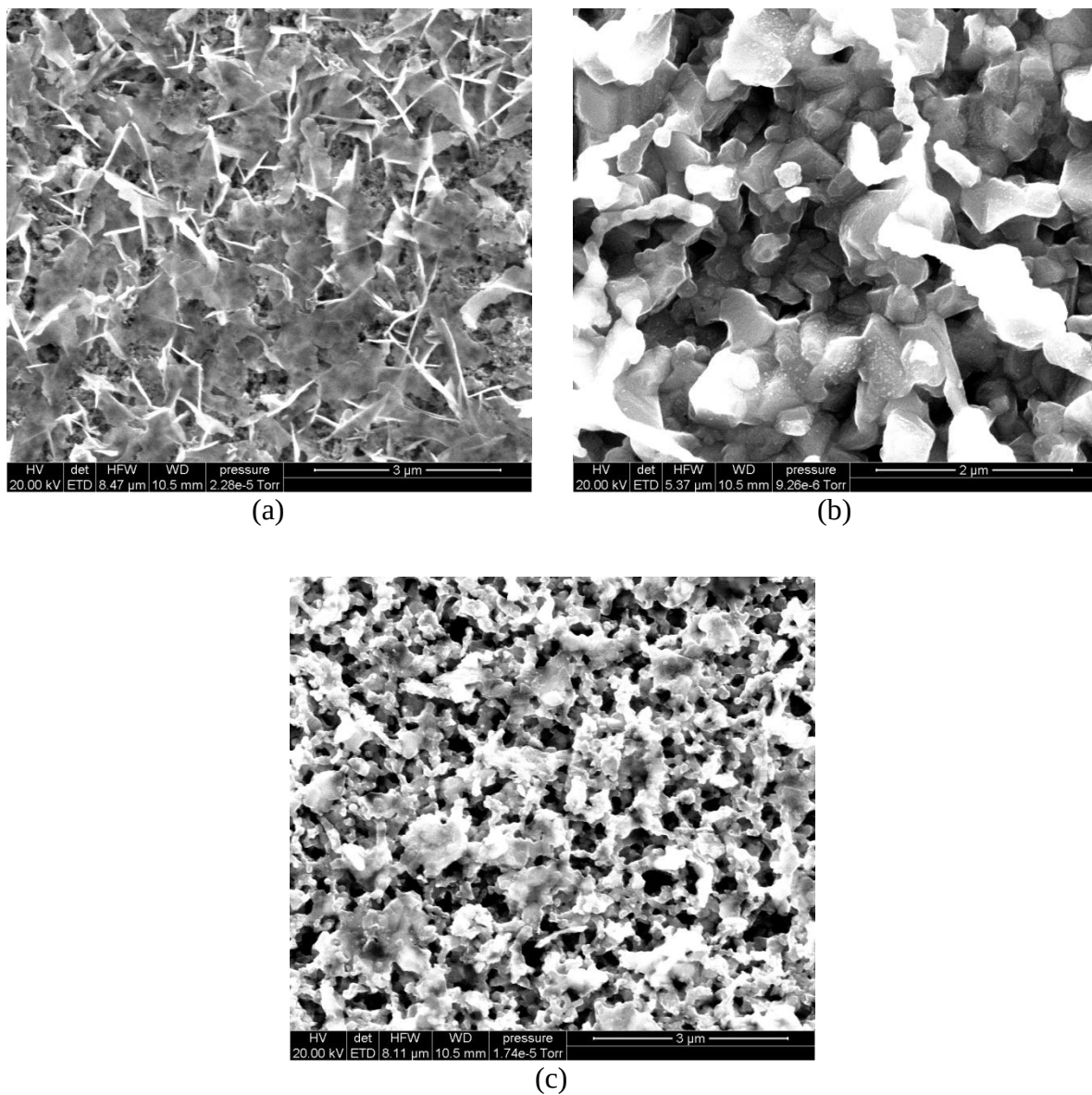


Figure 4.27. SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA under sulfur pressure of (a) 0.5 atm (b) 0.9 atm and (c) 1.4 atm

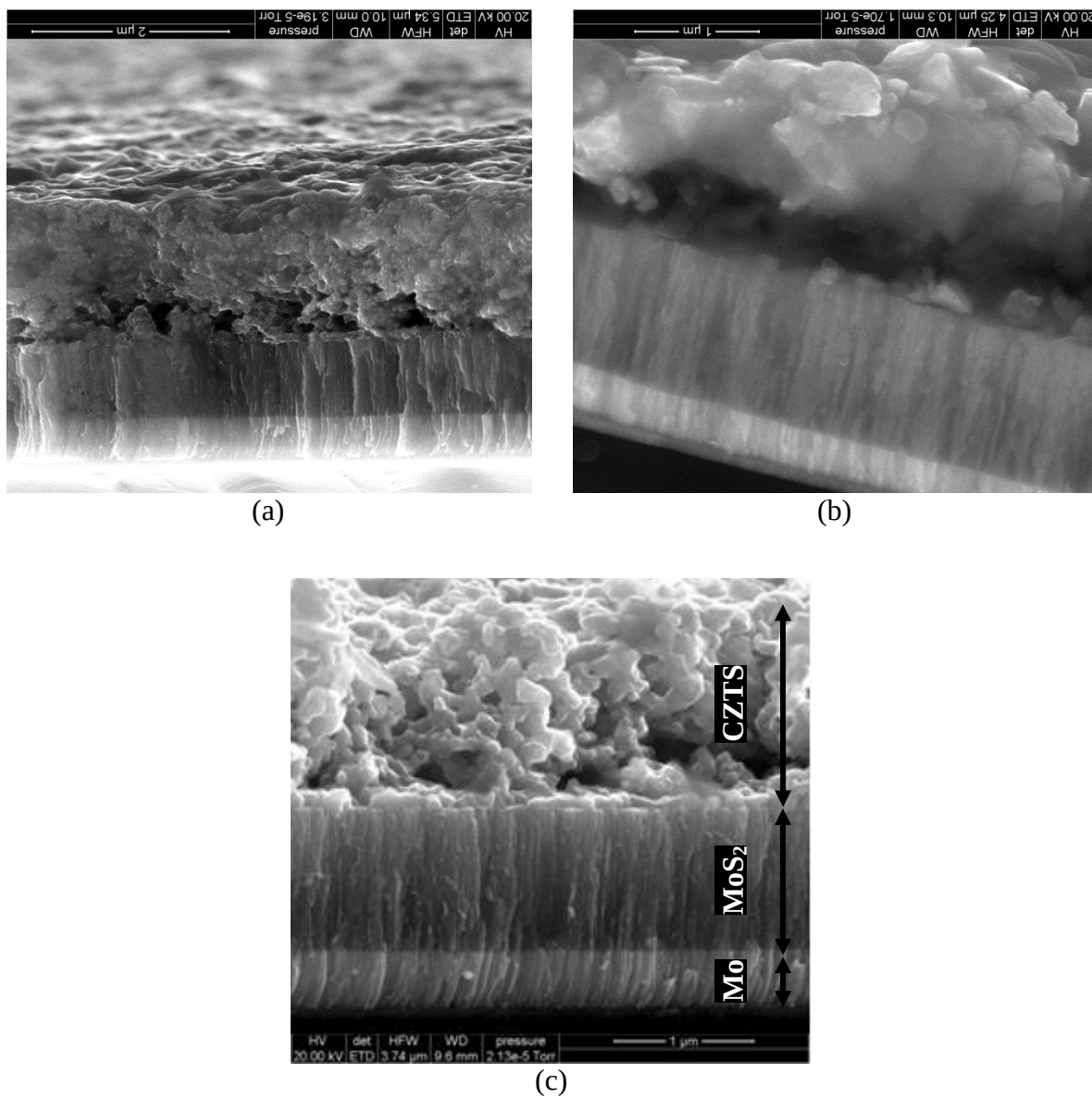


Figure 4.28. Cross section SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA under sulfur pressure of (a) 0.5 atm (b) 0.9 atm and (c) 1.4 atm

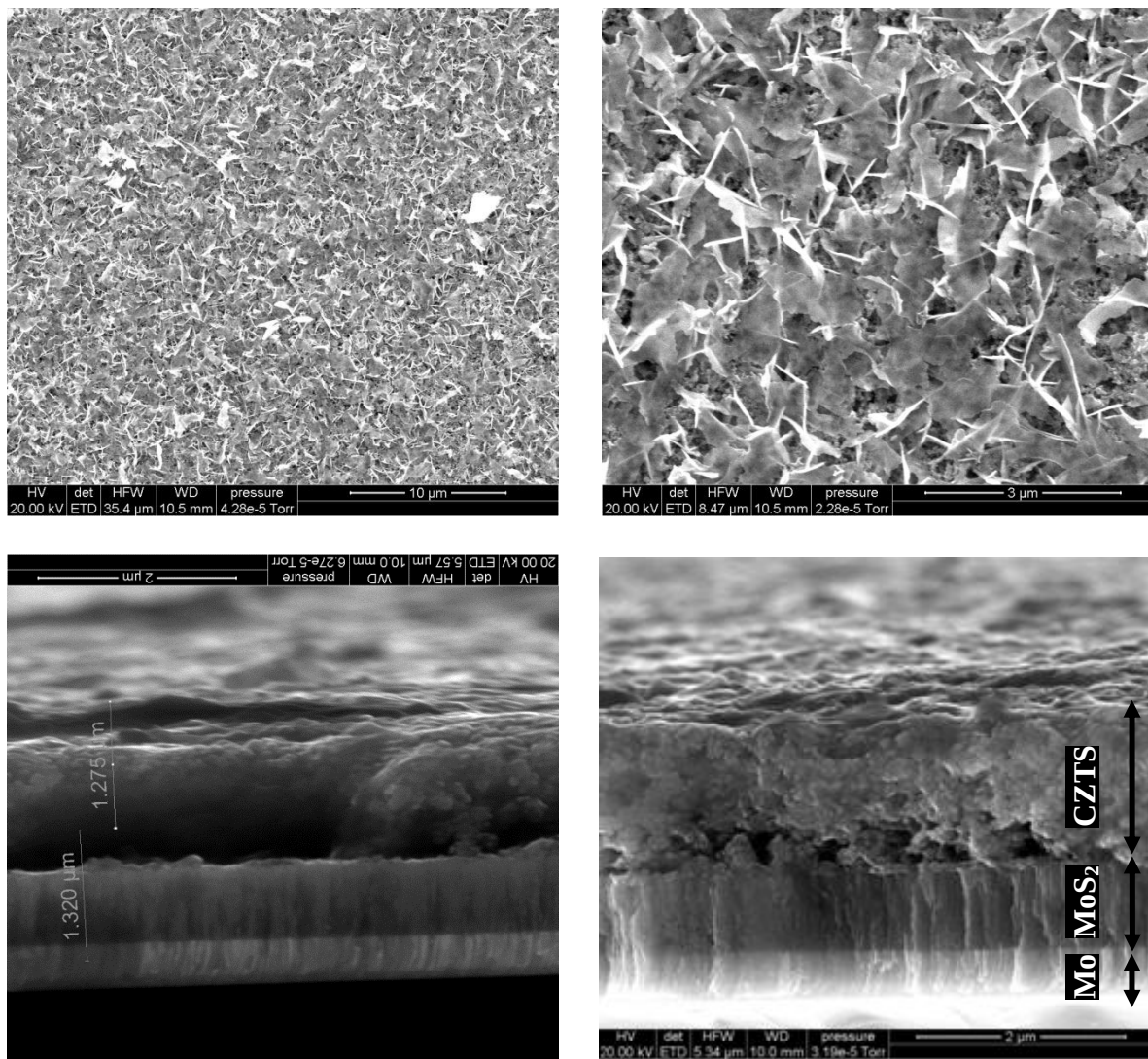
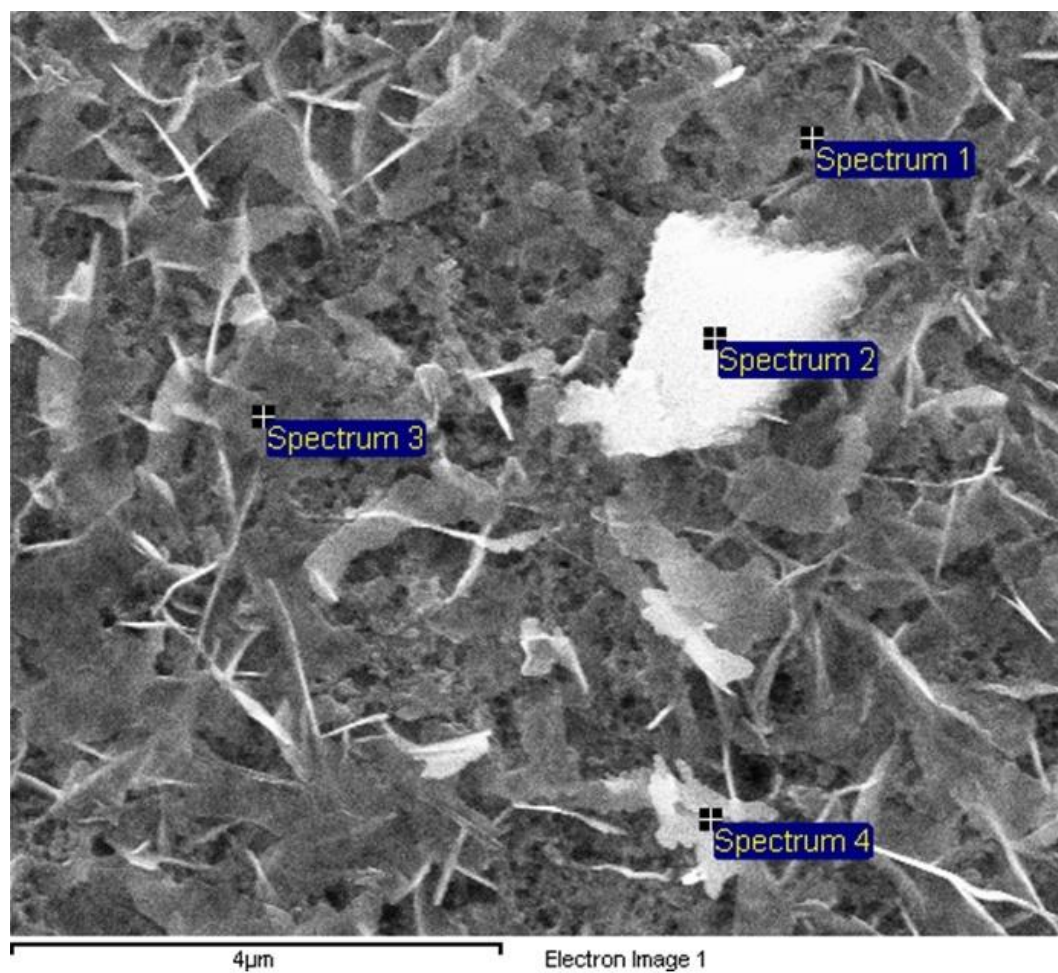


Figure 4.29. SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 0.5 atm)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	16	10	10	52	12
2	6	4	6	61	23
3	16	11	10	52	11
4	16	11	11	52	10
Mean	16	11	10	52	11

Figure 4.30. EDS result of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 0.5 atm)

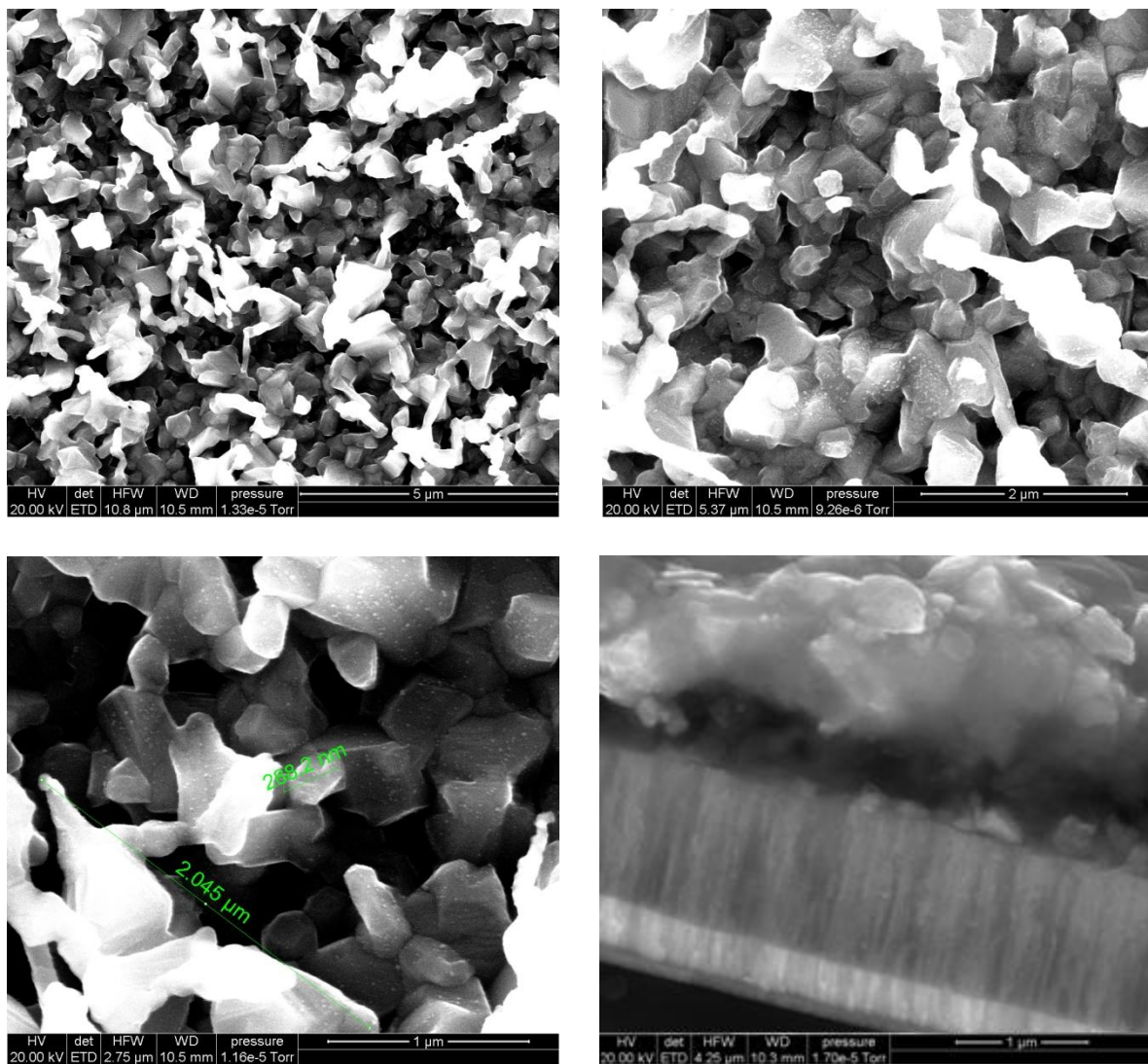
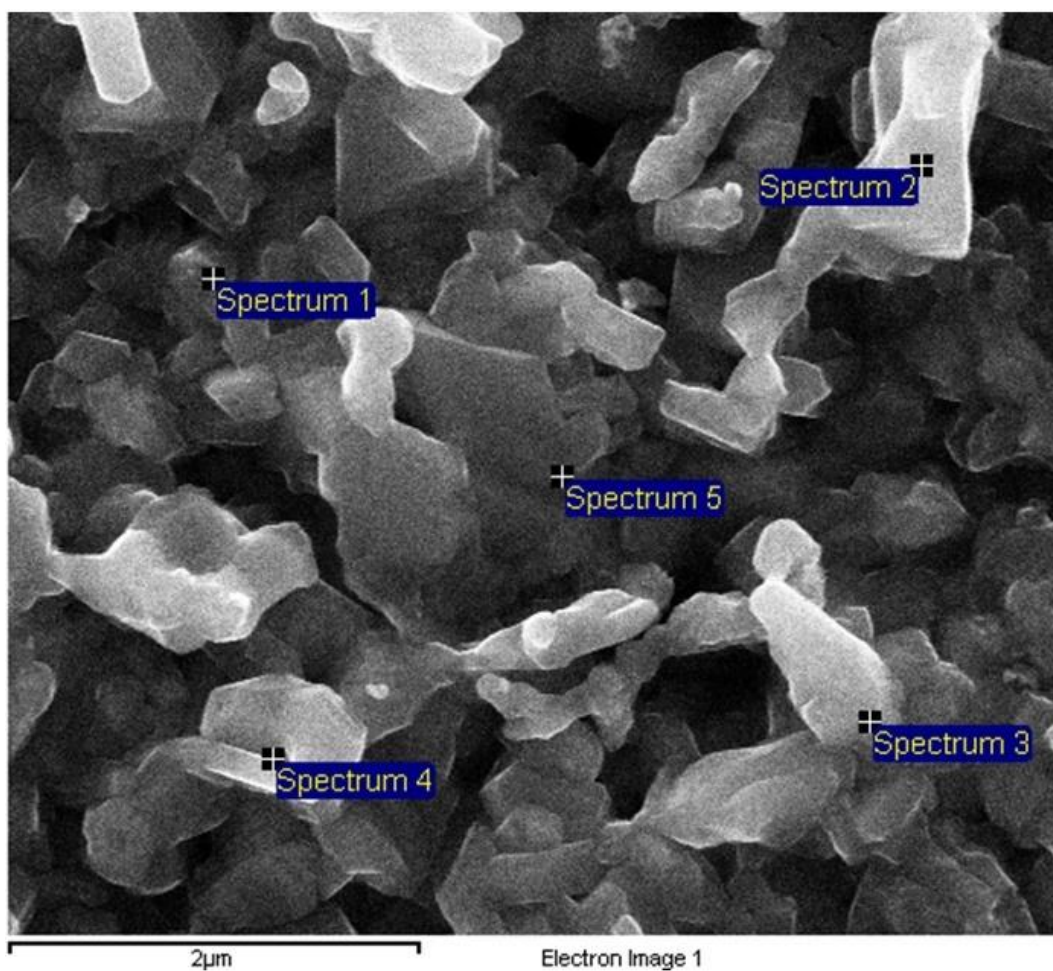


Figure 4.31. SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 0.9 atm)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	17	11	10	51	11
2	20	12	11	51	6
3	20	12	11	52	5
4	19	11	11	51	8
5	18	10	10	54	8
Mean	19	11	11	52	8

Figure 4.32. EDS result of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 0.9 atm)

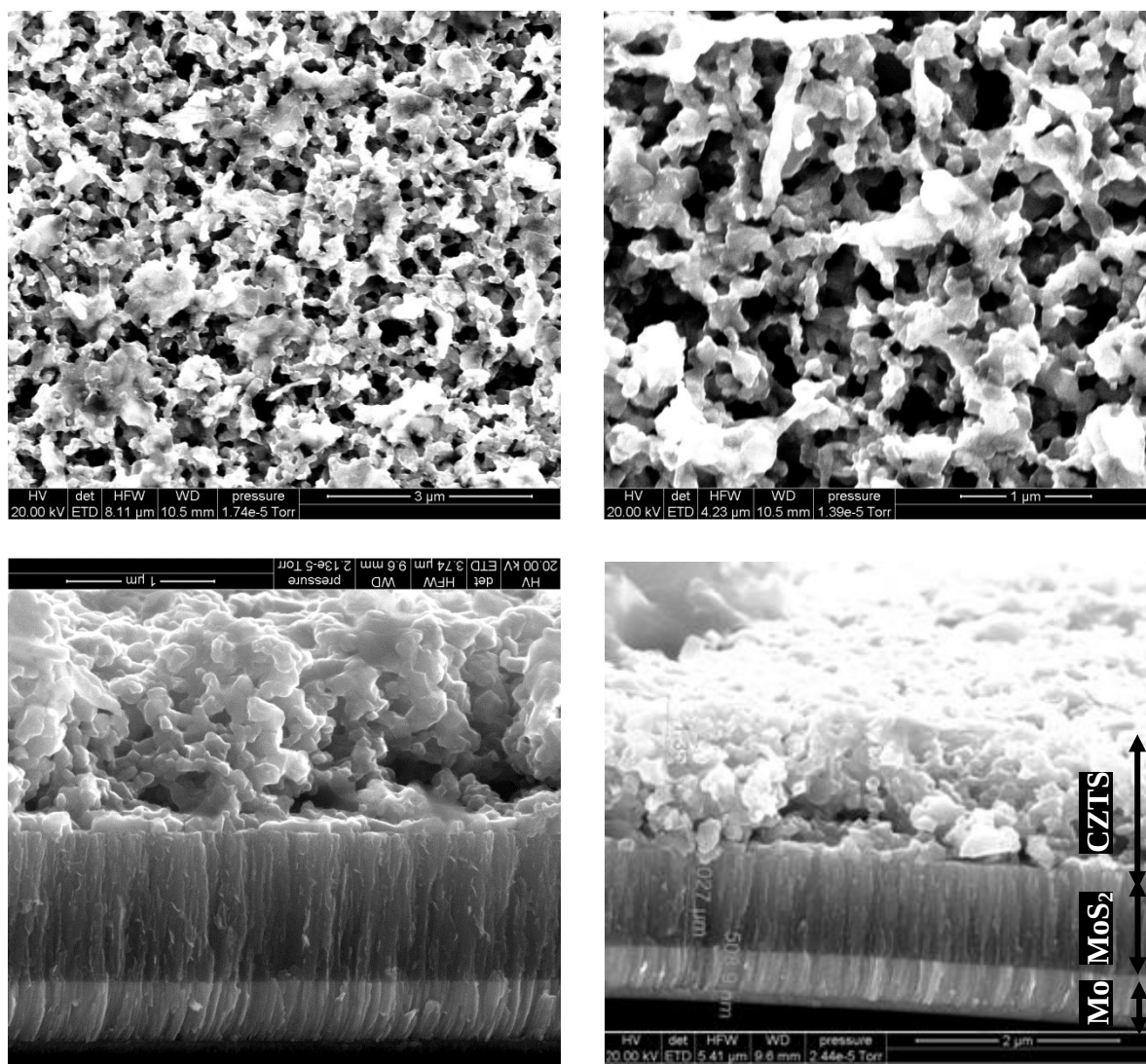
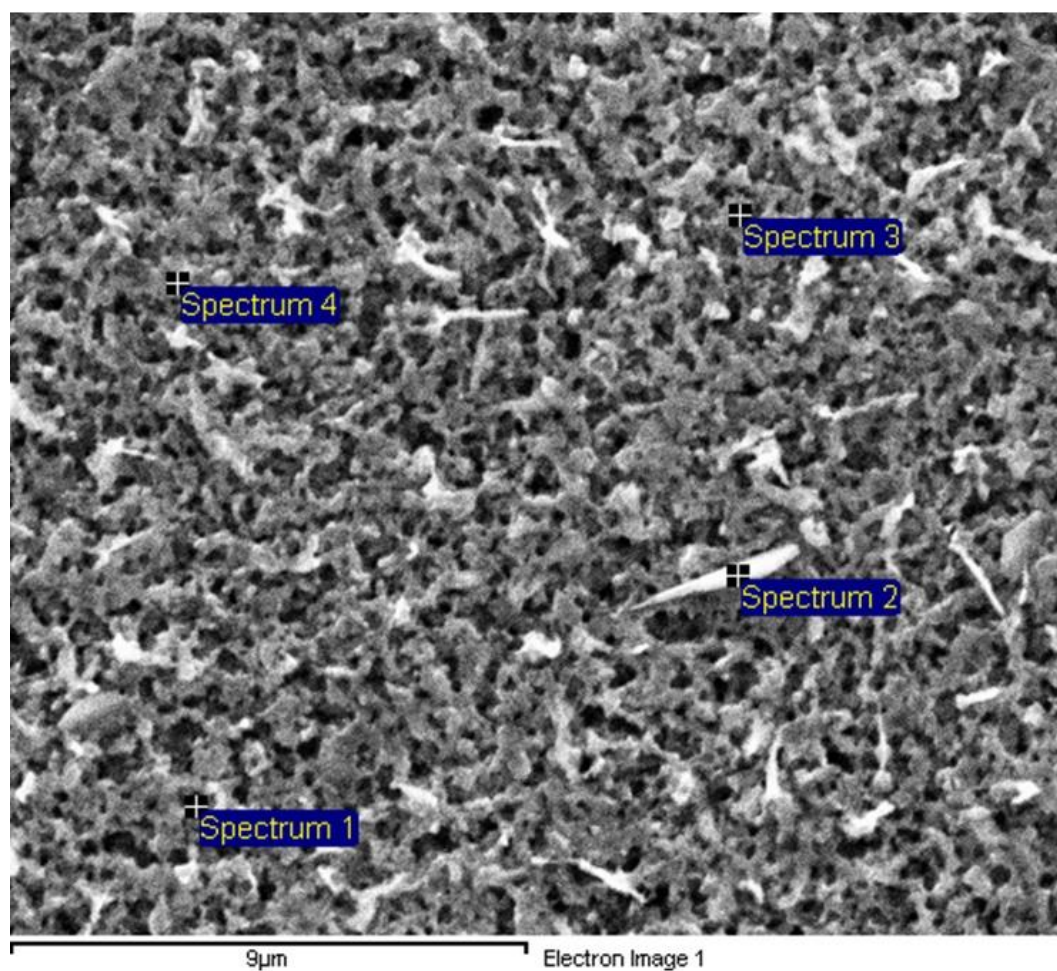


Figure 4.33. SEM images of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 1.4 atm)



Spectrum	Mean atomic %				
	Cu	Zn	Sn	S	Mo
1	18	11	10	50	11
2	14	9	16	55	6
3	18	11	10	51	10
4	19	12	12	51	6
Mean [‡]	18	11	10	51	9

Figure 4.34. EDS result of the sol-gel grown sample prepared from solution containing 1.3 M DEA (Sulfur pressure: 1.4 atm)

[‡] Spectrum 2 was not taken into account for the calculation of mean values

4.1.2.3. Effects of sulfurization temperature

Top-view SEM images of sol-gel grown CZTS films are shown in Figure 4.35-4.37. They reveal that the CZTS films sulfurized at temperatures between 200 and 500 °C are uniform and composed of homogeneously distributed grains with a size of about 100 nm. As will be discussed in structural section of related samples, the sample sulfurized at 700 °C is composed of Cu-Zn-S phases due to tin loss. It is clearly seen in the Figure 4.37 that the decomposition occurring at relatively high temperature deteriorates the surface morphology of the sample. The results of the semi-quantitative, energy-dispersive x-ray spectroscopy (EDS) analysis, which just illustrate the elemental composition of the CZTS films, are showed in Table 4.2. They clearly indicate that the CZTS films sulfurized at temperatures between 200 and 500 °C have a deficit of Cu. Several groups reported that Cu-Zn-Sn-S compounds should be grown under slightly Cu-poor and Zn-rich conditions to improve the optoelectronic properties of the film and to prevent the formation of Cu_{2-x}S or other binary/ternary phases. Katagiri et al (Katagiri et al., 2008; Katagiri, 2005; Katagiri et al., 1997; Kobayashi et al., 2005) achieved efficiencies of 1.08%, 3.93%, and 6.77% using Cu-poor absorber layers. Chen et al, 2010a found that Cu-poor conditions improved the efficiency of CZTS solar cells. The Cu deficit enhances the formation of Cu vacancies, which give rise to shallow acceptors. Another reason to use a copper-poor composition is the loss of tin, mainly in the form of SnS, which occurs during the sulfurization process (Fernandes et al., 2010b).

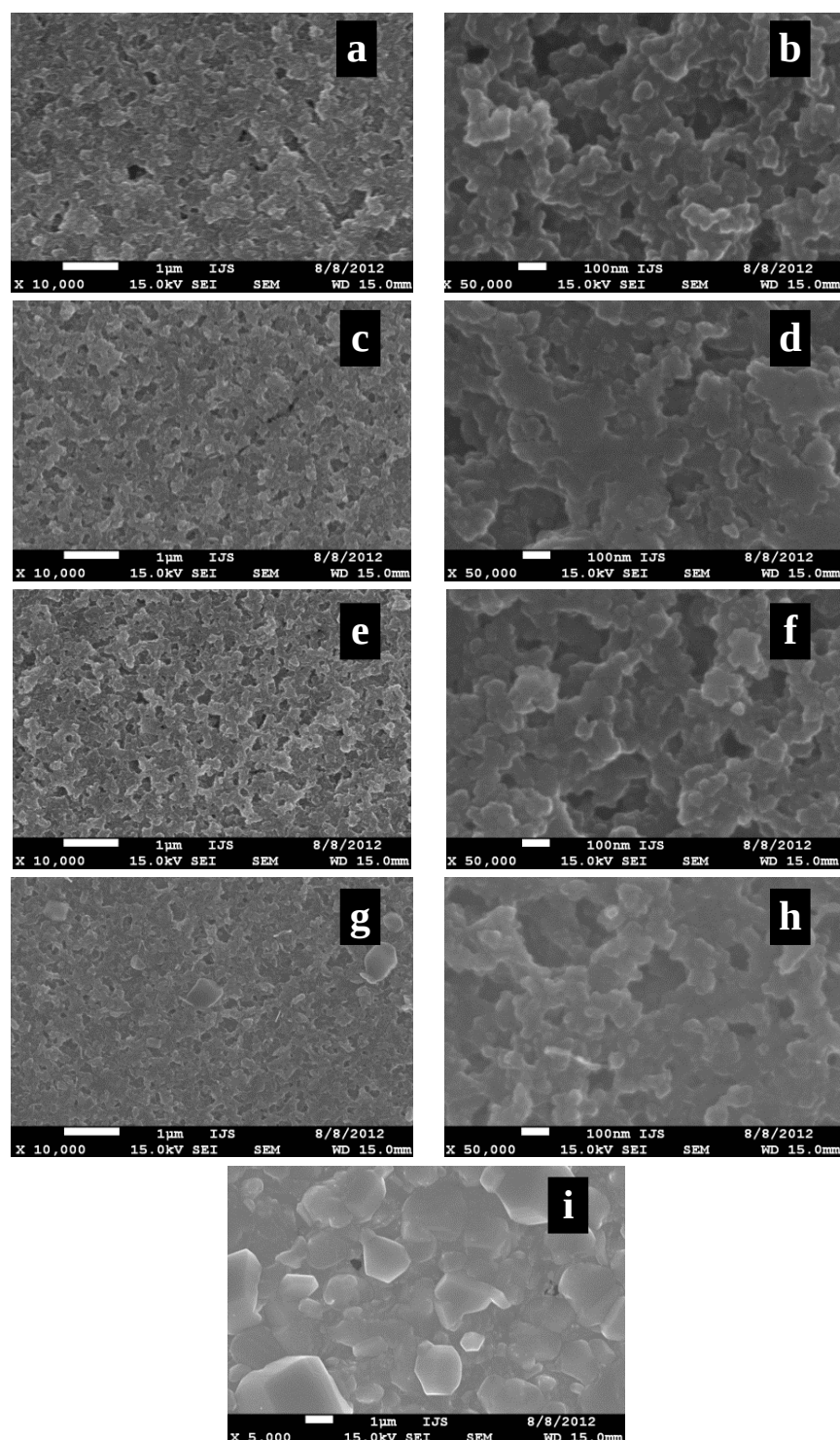
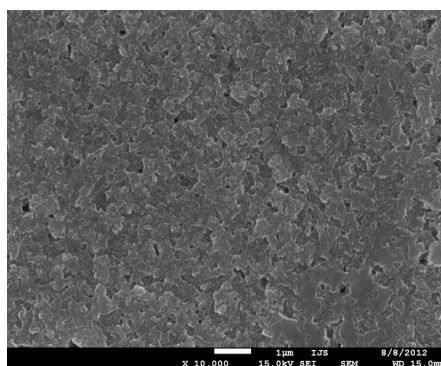


Figure 4.35. SEM images of the sol-gel grown CZTS films sulfurized at (a,b) 200 °C (c,d) 300 °C (e,f) 400 °C (g,h) 500 °C and (i) 700 °C.

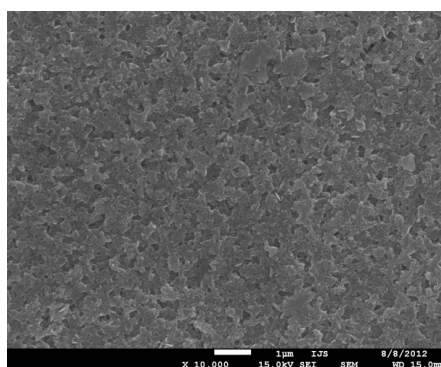
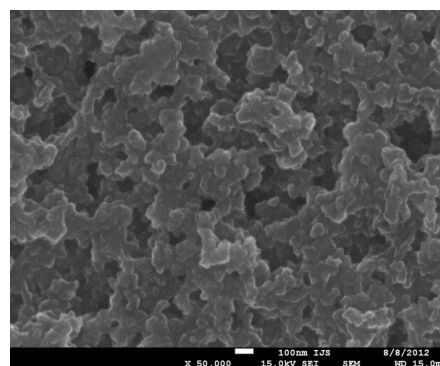
Table 4.2. Semi-quantitative energy-dispersive x-ray spectroscopy analysis of sol-gel grown CZTS films sulfurized at different temperatures.

Element	200 °C		300 °C		400 °C		500 °C		700 °C
	a.f. (%)	N=8*	a.f. (%)	N=8*	a.f. (%)	N=8*	a.f. (%)	N=8*	a.f. (%)
Cu	19.1	1.5	19.4	1.6	19.1	1.5	20.1	1.6	30.2
Zn	16.2	1.3	14.5	1.2	15.0	1.2	16.2	1.3	26.0
Sn	16.5	1.3	16.4	1.3	15.8	1.3	14.6	1.2	0.0
S	48.3	3.9	49.7	4.0	50.2	4.0	49.2	3.9	43.8
Cu/(Zn+Sn)	0.6		0.6		0.6		0.7		
Zn/Sn	1.0		0.9		0.9		1.1		

*Composition normalized on 8 atoms per formula unit of $\text{Cu}_2\text{ZnSnS}_4$



(a)



(b)

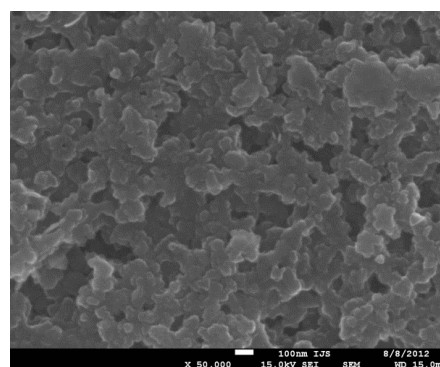
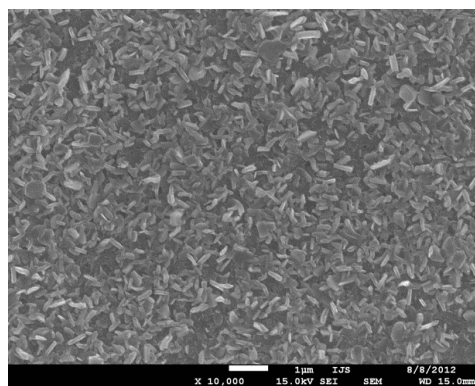
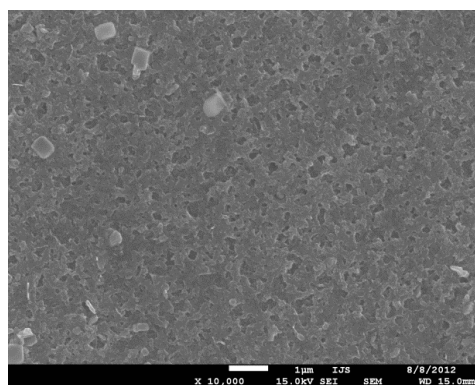
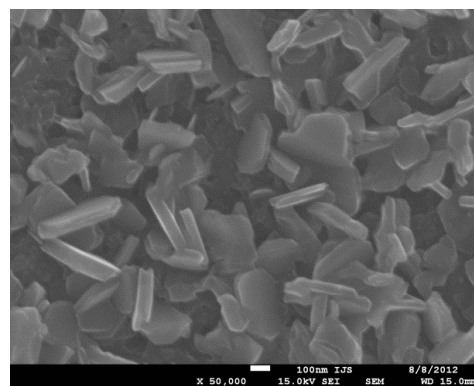


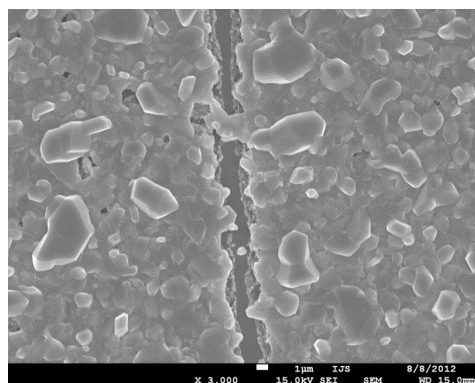
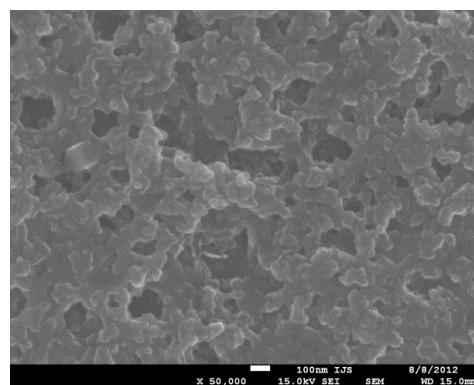
Figure 4.36. SEM images of sol-gel grown CZTS sample sulfurized at (a) 200 °C and (b) 300 °C for 2 h under 20 atm. sulfur pressure ($M_{\text{DEA}}=1$)



(a)



(b)



(c)

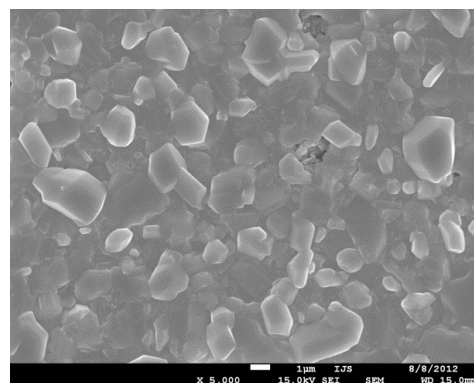


Figure 4.37. SEM images of sol-gel grown CZTS sample sulfurized at (a) 400 (b) 500 and (c) 700 °C for 2 h under 20 atm. sulfur pressure ($M_{\text{DEA}}=1$)

4.2. Structural characterization

4.2.1. SILAR grown films

4.2.1.1. One-stage SILAR grown films

Structural characterization was performed via XRD. The diffraction patterns were obtained at 40 keV operating voltage and 35 mA current. The step size and scan step time were 0.0330° and 1 s, respectively. Figure 4.38 shows the obtained XRD patterns of the samples. In the Figure 4.38, six peaks can be clearly seen at $2\theta=18.09^\circ$, 28.75° , 33.24° , 47.76° , 56.67° and 59.31° . The patterns of the samples match with the Cu_2SnS_3 (JCPDS 01–089–4714: Tetragonal, $a=b=0.5413$ nm, $c=1.0824$ nm, I-42m). Other reference PDFs are also given for comparison. Peaks corresponding to (101), (112), (200), (220), (312) and (224) planes indicate the polycrystalline nature of the films. The highest peak at 28.75° corresponding to (112) plane proves the preferred crystallization. While no peak refers to other binary or ternary phases in the pattern of sample 1, only one weak peak referring covallite $\text{Cu}_2\text{-xS}$ phase at 31.73° of 2θ was detected in the pattern of sample 2. As discussed before, the XRD results support the idea that Cu-poor growth conditions may prevent the formation of secondary phases.

The average crystallite size of the samples was calculated with the peak width at the half maximum of the peak (β), through the Debye–Scherrer equation (Knuyt et al., 1996):

$$D = 0.94\lambda / \beta \cos \theta \quad (4.7)$$

where λ is the wavelength of x-ray radiation, λ is the Bragg angle of the peak, and β is the angular width of the peak at full-width at half maximum (*FWHM*). Each peak obtained in a diffractometer is broadened due to instrumental and physical factors (crystallite size and lattice strains) (Klug and Alexander, 1974). The microstrain (ε) and dislocation density (ρ) for preferential orientation were calculated by using the formulas given below (Suresh et al., 2009):

$$\varepsilon = \beta \cos \theta / 4 \quad (4.8)$$

and

$$\rho = 15\varepsilon / aD \quad (4.9)$$

where a is the lattice constant. The estimations were done by taking into account all diffraction peaks and the obtained values are given in Table 4.3.

Table 4.3. Structural parameters of the one-stage SILAR grown samples (obtained by using 0.01M SnCl_2 and 0.05M Na_2S in 50 cycles)

Samples				Crystallite size	Microstrain	Dislocation density
	M_{CuCl_2}	M_{ZnCl_2}	Duration in beaker	(D) (nm)	(ε) $\times 10^{-4}$	(ρ) $\times 10^{14}$ (cm^{-2})
(1)	0.005	0.01	15	59	7.3	4.82
(2)	0.01	0.005	15	67	5.7	2.45
(3)	0.01	0.01	15	79	5.1	2.13
(4)	0.01	0.01	5	72	5.3	2.28

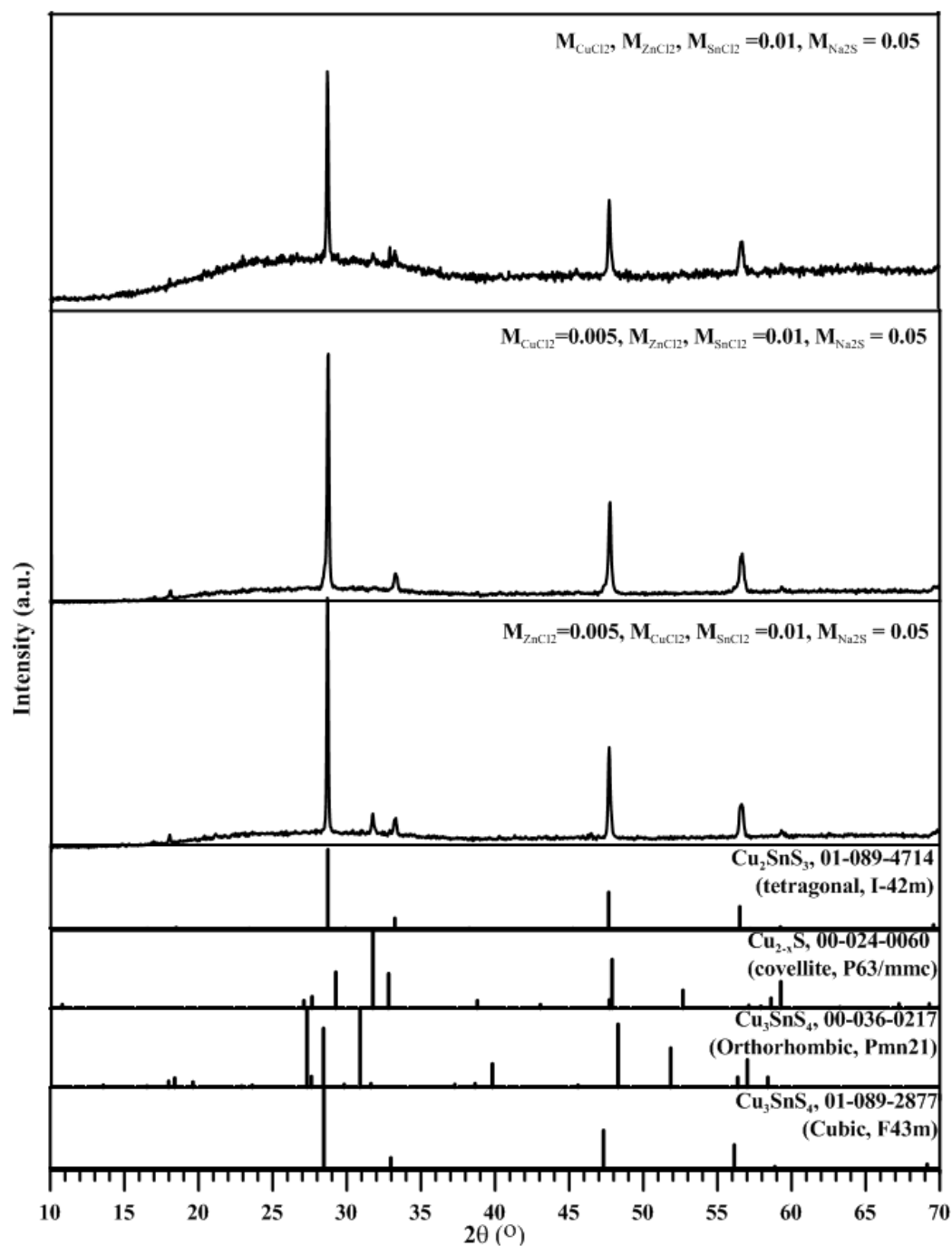


Figure 4.38. The XRD patterns of the one-stage SILAR grown thin film samples prepared by using solutions containing different concentration of metal sources.

4.2.1.2. Modified one-stage SILAR grown films

Four beakers are generally used in SILAR method. First beaker contains anionic solution while third beaker contains cationic precursor solution. Second and fourth beakers contain only de-ionized water. In the case of CZTS growth process in SILAR method, it is very difficult to deposit CTZS compound by using the process described above. Because of competitive adsorption between copper and other ions, zinc deposition is blocked by the copper ions. We tried to overcome this problem via modifying the initial precursor molarities and the volume of hydrochloric acid to adjust the pH value. Cu/Sn molarity ratio in the precursor solutions was also investigated. For this purpose the ratio was changed from 2 (stoichiometric ratio) to 0.6.

Figure 4.39-4.42 show the obtained XRD patterns of the modified one-stage SILAR grown films. It can be seen that there are nine peaks which can be assigned to different phases. The peaks numbered as (1), (7), (8) and (9) can be assigned to the (112), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(6) can be assigned to Cu_{2-x}S ; 00-024-0060. It can be inferred that the patterns cannot indicate/prove the presence of CZTS phase. As a conclusion, it can be said that the modification in the initial parameters is not successful.

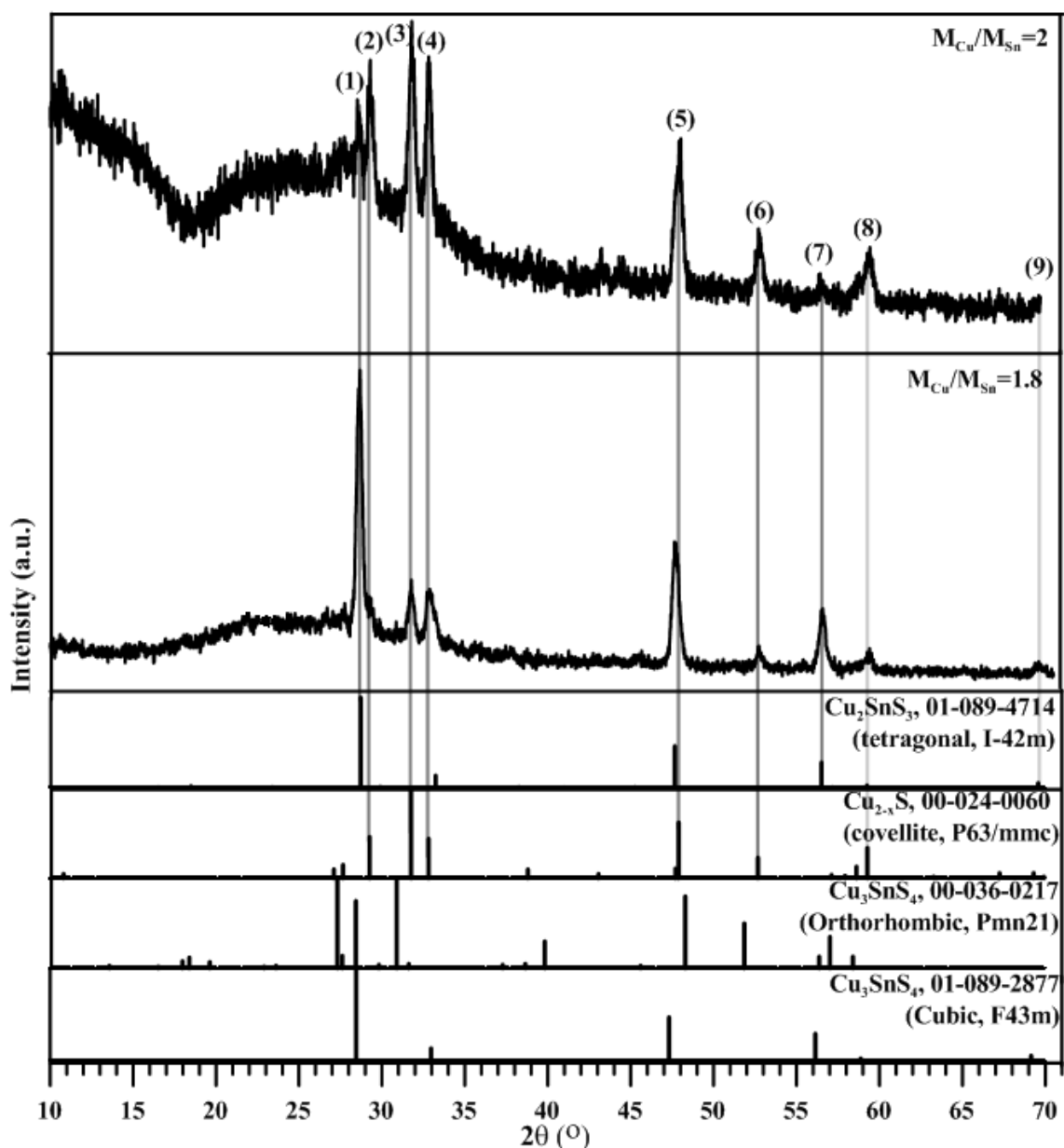


Figure 4.39. The XRD patterns of the modified one-stage SILAR grown films. The peaks (1), (7), (8) and (9) can be assigned to the (112), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(6) can be assigned to $Cu_{2-x}S$; 00-024-0060.

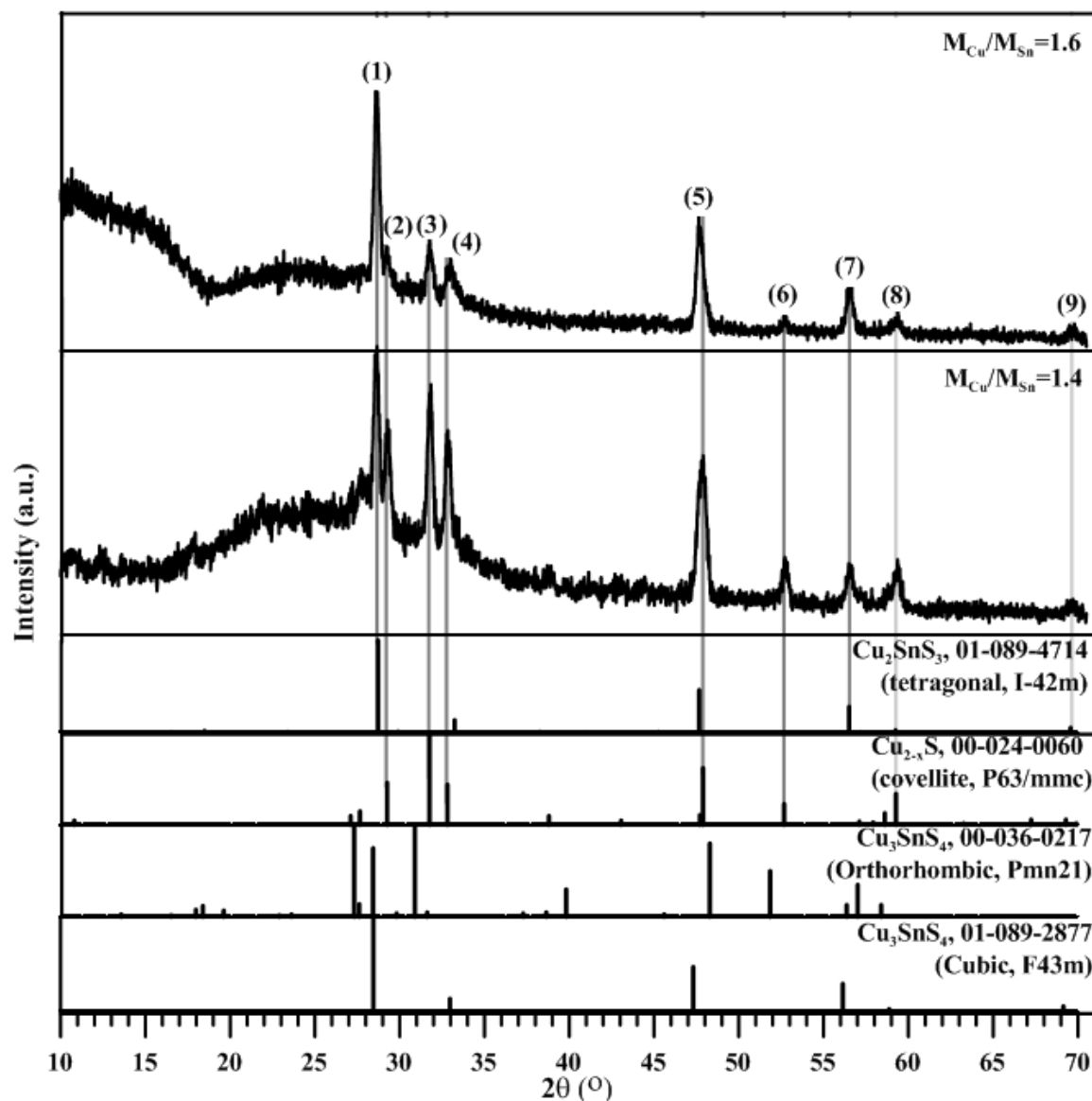


Figure 4.40. The XRD patterns of the modified one-stage SILAR grown films. The peaks (1), (7), (8) and (9) can be assigned to the (112), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(6) can be assigned to $Cu_{2-x}S$; 00-024-0060.

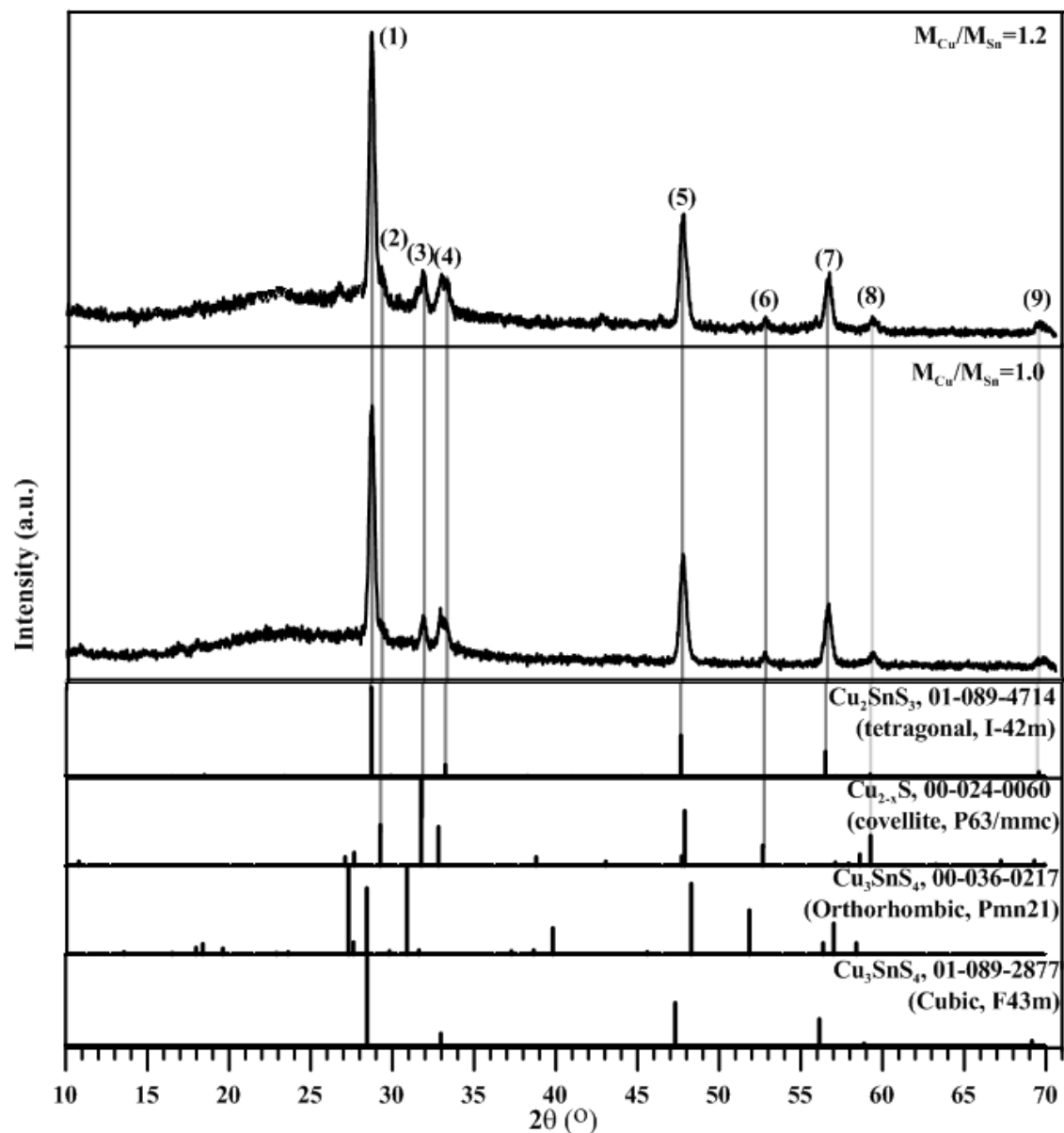


Figure 4.41. The XRD patterns of the modified one-stage SILAR grown films. The peaks (1), (5) and (7)-(9) can be assigned to the (112), (220), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(4) and (6) can be assigned to $Cu_{2-x}S$; 00-024-0060.

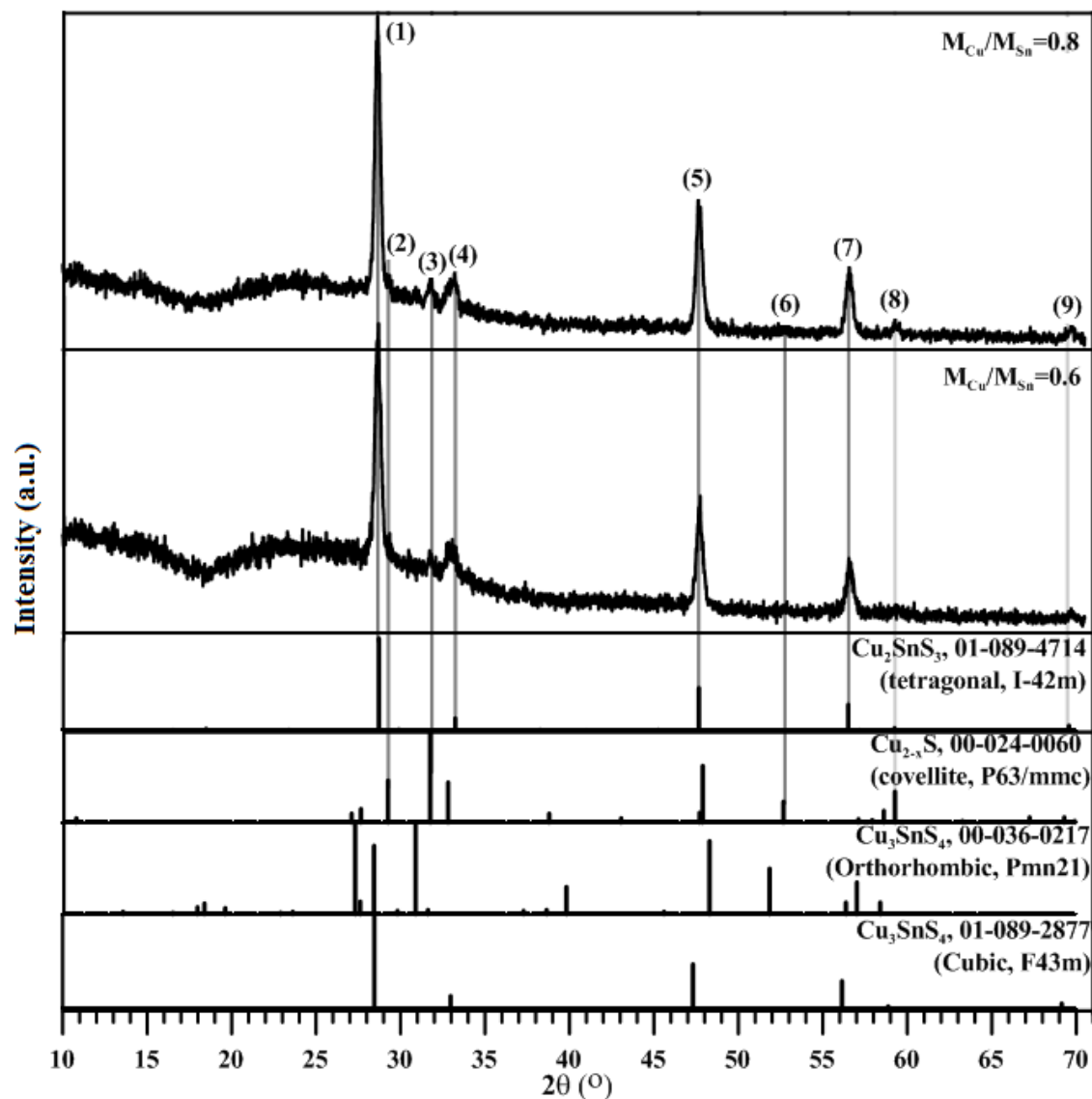


Figure 4.42. The XRD patterns of the modified one-stage SILAR grown films. The peaks (1), (5) and (7)-(9) can be assigned to the (112), (220), (312), (224) and (400) planes of Cu_2SnS_3 ; 01-089-4714, respectively. The peaks (2)-(4) and (6) can be assigned to $Cu_{2-x}S$; 00-024-0060.

4.2.1.3. Two-stage SILAR grown films for different molar ratios

Figure 4.43 shows the XRD patterns of two-stage SILAR grown CZTS film via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers deposited with different $M_{\text{Cu}}/M_{\text{Sn}}$ ratios. In the CZTS growth process, the molarity of copper is very crucial to obtain quality and well crystallized films. The copper molarity higher than the stoichiometric ratio usually causes the formation of Cu_{2-x}S secondary phase while the lower copper molarity causes a significant decrease in the crystallinity of the films. Therefore the effects of copper molarity under stoichiometry were investigated. The pattern of stoichiometric sample was also given in Figure 4.43 for comparison. Five clear peaks were observed at $2\theta=18.30^\circ$, 28.47° , 33.07° , 47.38° and 56.18° in the pattern of stoichiometric sample. The patterns of the samples match very well with the $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 00-026-0575: Tetragonal, $a=b=5.427$ nm, $c=10.848$ nm, I-42m). The peaks corresponding to the (101), (112), (200), (220) and (312) planes indicate the polycrystalline nature of the films. As can be seen in the XRD results, the crystallinity of the film decreases with respect to decreasing copper amount and finally the films become amorphous when the copper/tin molarity is below 1/8. According to these results, it can be concluded that the copper molarity affects the crystal structure remarkably and is very crucial to obtain high quality and well crystallized films.

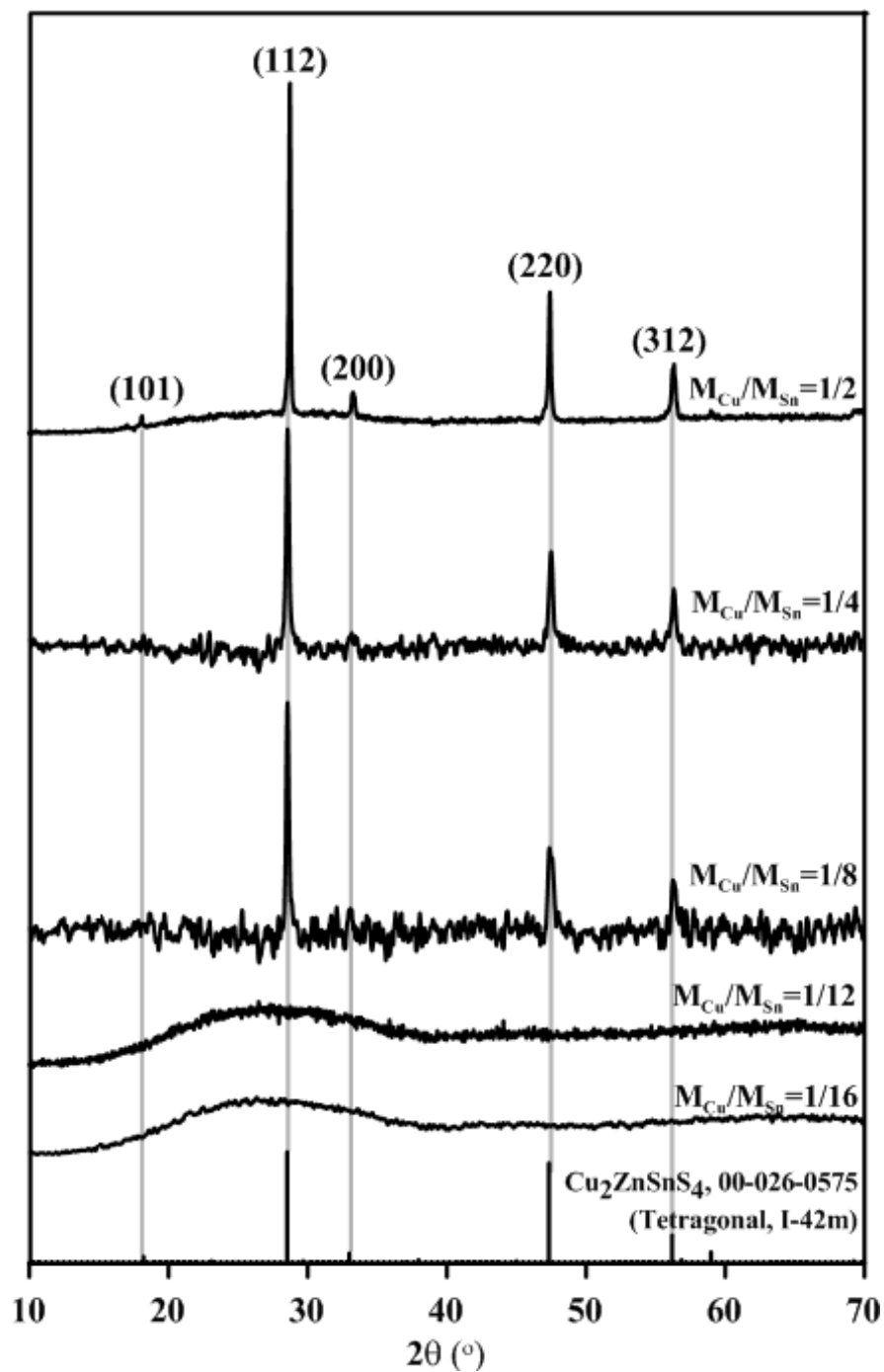


Figure 4.43. The XRD patterns of two-stage SILAR grown CZTS film via sulfurization of Cu_2SnS_3/ZnS stacking layers deposited with different M_{Cu}/M_{Sn} ratios.

4.2.1.4. Two-stage SILAR grown films for different deposition cycles

Figure 4.44 shows the obtained XRD patterns of the samples. Five clear peaks were observed at $2\theta=18.30^\circ$, 28.47° , 33.07° , 47.38° and 56.18° . The patterns of the samples match very well with the $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 00-026-0575: Tetragonal, $a=b=5.427$ nm, $c=10.848$ nm, I-42m). The peaks corresponding to the (101), (112), (200), (220) and (312) planes indicate the polycrystalline nature of the films. The highest peak at 28.47° corresponding to the (112) plane proves the preferred crystallization. While there are no other peaks indicating the presence of binary or ternary secondary phases in the XRD pattern of Sample 60/40, 60/20 and 30/40, a weak peak at 2θ equals to 31.88° , referring to the covallite Cu_{2-x}S phase, was detected in the pattern of Sample 30/20. The XRD patterns of the Cu_2SnS_3 and ZnS precursor layers are given in Figure 4.45. In Figure 4.45, it can be seen that the patterns are in good agreement with those of references. To prove the phase purity or to detect the presence of other possible secondary phases, Raman spectroscopy analyses of the samples over the range 200 to 500 cm^{-1} were also made and the results are given in Figure 4.46. Peaks corresponding to the CZTS compound were observed at 338 and 374 cm^{-1} , in good agreement with the reported Raman data for CZTS (Wang et al., 2010; Shin et al., 2011; Altosaar et al., 2008). The spectrum indicates the absence of any phase separation or the formation of binary/ternary phases such as SnS, SnS_2 and Cu_{2-x}S .

According to the XRD pattern of Sample 30/20, there was a weak peak corresponding to the Cu_{2-x}S binary phase. In contrast, according to the Raman result of Sample 30/20, no Cu_{2-x}S phase could be detected due to the limited penetration depth of the Raman radiation. For a semiconductor, the penetration depth of light, d is roughly given by, $d=1/\alpha$ where α is the absorption coefficient. In the case of the Raman scattering analysis using the back scattering configuration, we must consider that the light has to return and therefore the equation is then $d=1/2\alpha$. Using this equation and knowing α , it is possible to estimate the effective penetration depth. In this study a 532 nm wavelength laser was used. Considering that the absorption coefficients of the CZTS films were of the order of 10^4 cm^{-1} , the effective depths were estimated to be around 545 nm.

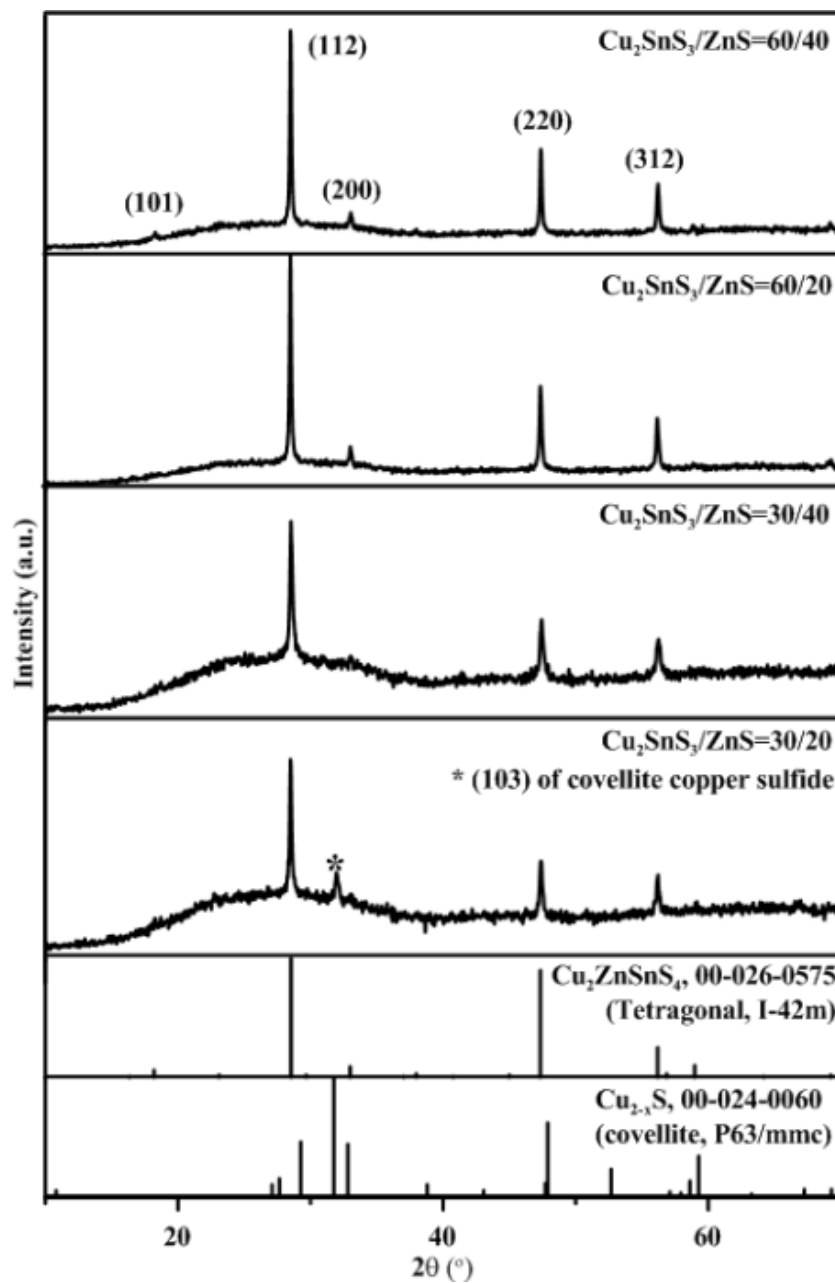


Figure 4.44. The XRD patterns of the two-stage SILAR grown CZTS films via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ layers

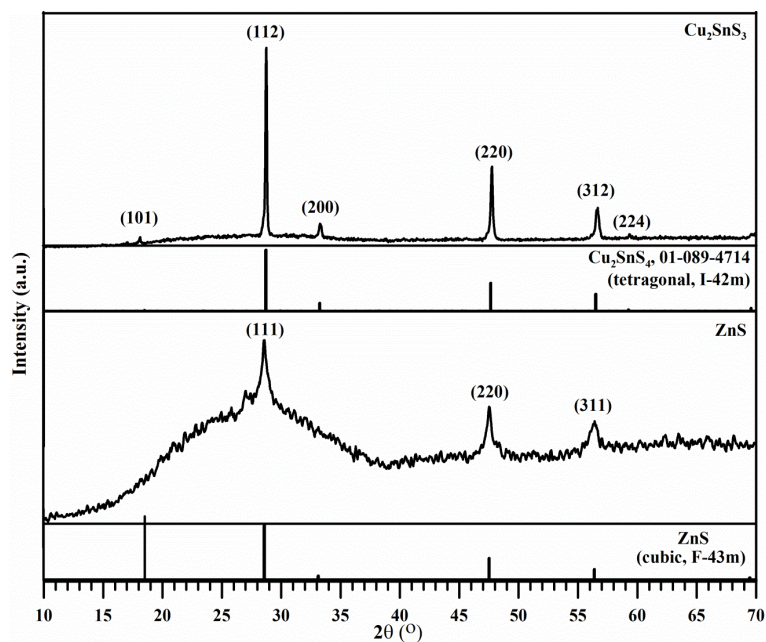


Figure 4.45. The XRD patterns of the Cu_2SnS_3 and ZnS precursor layers.

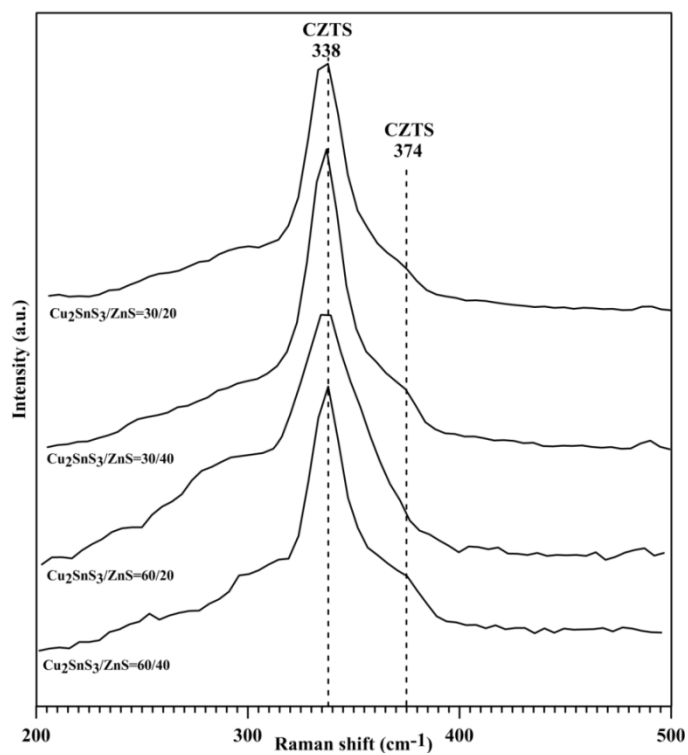


Figure 4.46. The Raman spectroscopy analyses of the samples over the range of 200 to 500cm^{-1} .

4.2.1.5. Two-stage SILAR grown films for different sulfurization temperatures

Under our experimental conditions, it was determined previously that the sample obtained from $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ structure is preferable by means of both composition and crystal structure. To investigate the sulfurization temperature effect, we sulfurized the sample (number of deposition cycle ratio for $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ layers: 30/40) at 200, 300, 400 and 500 °C. The structural characterization was performed using x-ray diffraction (XRD) and Raman techniques. The diffraction patterns were obtained at a 40-keV of operating voltage and a 35-mA current. The step size and the scan step time were 0.0330° and 1 sec., respectively. Figure 4.47 shows the obtained XRD patterns of the sample. Four clear peaks were observed at $2\theta=28.64^\circ$, 47.61° and 56.29° . The patterns of the sample match very well with the $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 00-026-0575: Tetragonal, $a=b=5.427$ nm, $c=10.848$ nm, I-42m). The peaks corresponding to the (112), (220) and (312) planes indicate the polycrystalline nature of the films. There are no other peaks indicating the presence of binary or ternary secondary phases. It can be also seen from the patterns that the crystal structure of the sample improves with increasing temperature.

To investigate the sulfurization temperature effect, we sulfurized the sample ($M_{\text{Cu}}/M_{\text{Zn}}:30/40$) at 200, 300, 400 and 500 °C. Raman spectroscopy analyses of the samples over the range 200 to 500 cm^{-1} were also made to prove the phase purity or to detect the presence of other possible secondary phases. The results are given in Figure 4.48. The peak corresponding to the CZTS compound was observed at 339 cm^{-1} , in good agreement with the reported Raman data for CZTS (Wang et al., 2010; Shin et al., 2011; Altosaar et al., 2008). The spectrum of the samples sulfurized at 200, 300 and 400 °C indicate the absence of any phase separation or the formation of binary/ternary phases such as SnS, SnS_2 and Cu_{2-x}S . However, in the spectrum of sample sulfurized at 500 °C, a strong peak appears corresponding to Cu_{2-x}S phase. This may be attributed to a decomposition occurring at relatively high temperature.

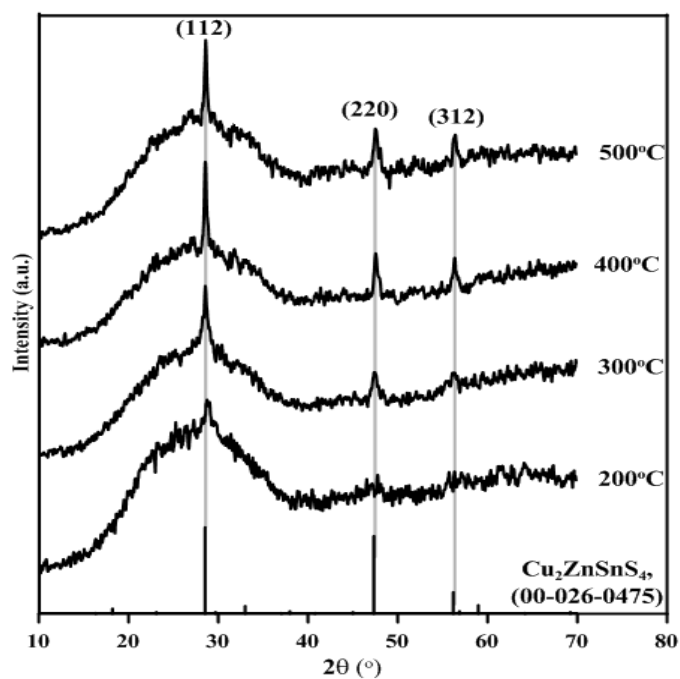


Figure 4.47. The XRD patterns of the two-stage SILAR grown CZTS films via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ layers

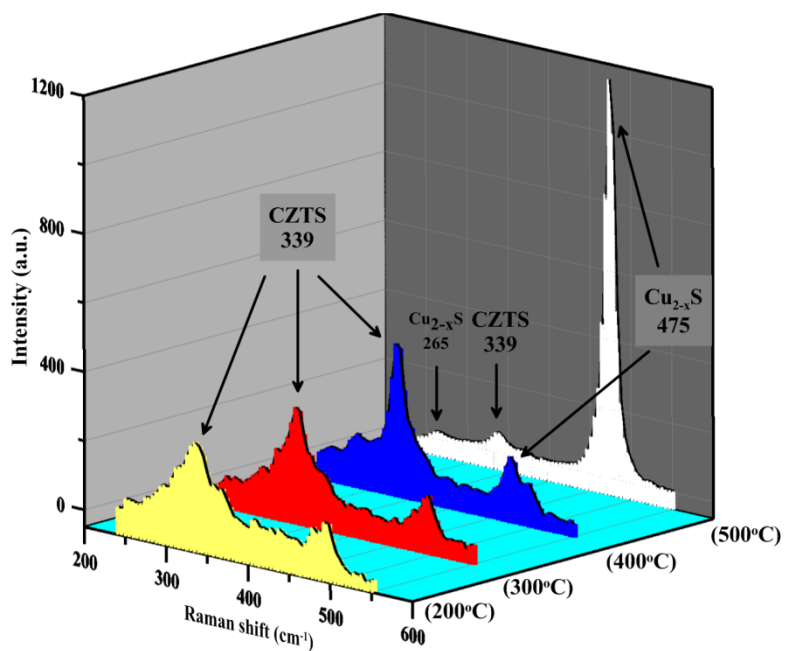


Figure 4.48. The Raman spectroscopy analyses of the sample sulfurized at different temperatures. The sample prepared via sulfurization of $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers. Number of deposition cycle ratio of the layers: 30/40.

4.2.2. Sol-gel grown CZTS films

4.2.2.1. Effects of stabilizer content

In order to utilize the sol–gel technique for obtaining crack-free, uniform, transparent and strongly adherent films, sol stabilization is one of the essential steps in the film formation (Kaminski et al., 2005). Various stabilization or chelating or complexing agents have been used to stabilize the sol and to reduce the rates of hydrolysis and polycondensation reactions by forming complex intermediates (Djaoued et al., 2002; Zhang et al., 2009a). Diethanolamine (DEA), diethylenetriamine, monoethanolamine, acetylacetone, acetic acid and polyethylene glycol have widely been used for this purpose (Murugan et al., 2011; Chen et al., 2007; Djaoude et al., 2008; Yu et al., 2006; Jung et al., 2003; Sanchez et al., 1988, Takahashi et al., 2000). Diethanolamine (DEA) is frequently used as a stabilizer in various sol–gel systems (Takahashi and Matsuoka, 1988; Takahashi and Yamaguchi, 1990; Ohya et al., 1994).

The obtained XRD patterns of the films and the reference patterns for possible secondary phases are given in Figure 4.49 and 4.50. The patterns of the samples match very well with the $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 00-026-0575: Tetragonal, $a=b=5.427$ nm, $c=10.848$ nm, I-42m) and are almost similar with small differences. The peaks corresponding to the (101), (112), (200), (220) and (312) planes indicate the polycrystalline nature of the films. In patterns belong to the samples prepared by using 2.1 M-0.9 M DEA, a peak was detected at about $2\theta=15.03$ corresponding to SnS phase. According to the XRD patterns, it can be concluded that DEA stabilizer amount affects SnS formation above the molarity value 0.9.

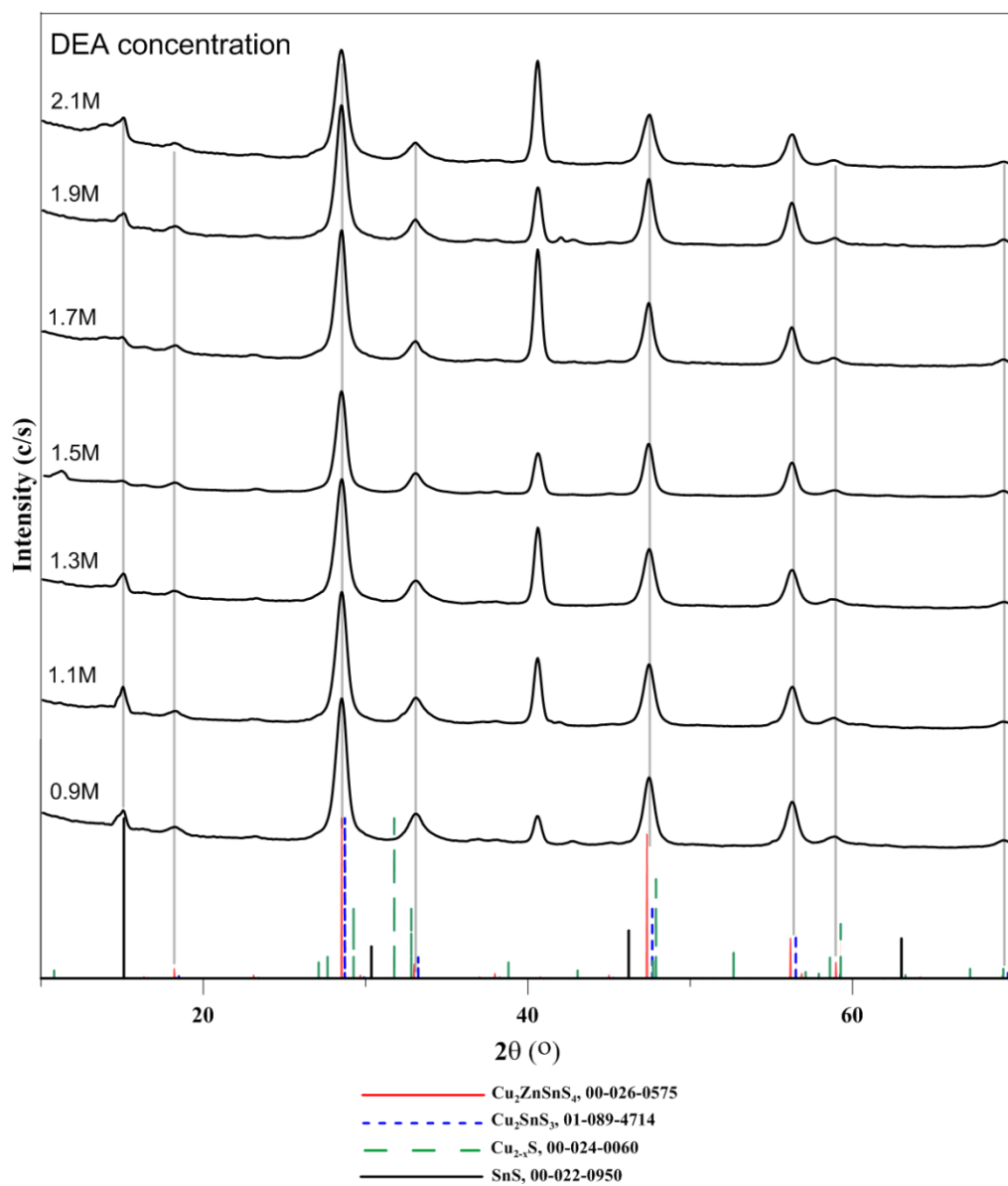


Figure 4.49. XRD patterns of the CZTS films prepared by using different stabilizer amounts

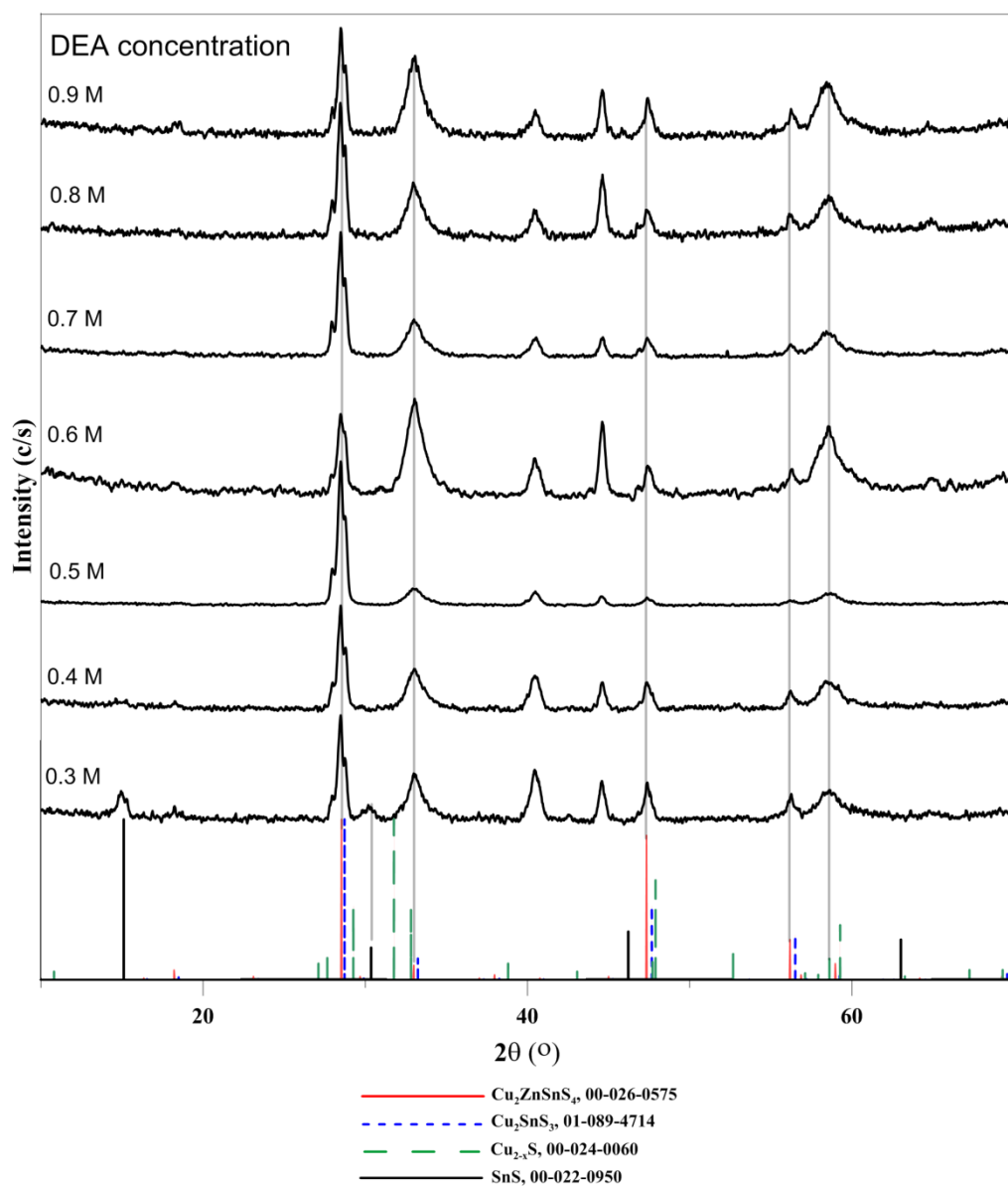


Figure 4.50. XRD patterns of the CZTS films prepared by using different stabilizer amounts

4.2.2.2. Effects of sulfur pressure

The obtained XRD patterns of the films and a reference CZTS pattern for comparison are given in Figure 4.51. The patterns of the samples match very well with the $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 00-026-0575: Tetragonal, $a=b=5.427$ nm, $c=10.848$ nm, I-42m) and are almost similar with small differences. The peaks corresponding to the (101), (112), (200), (220) and (312) planes indicate the polycrystalline nature of the films. It can be seen in the XRD patterns that peaks are broadened with the decreasing sulfur pressure. This means that the crystallite sizes of the films decreases with the decreasing sulfur pressure. As a conclusion, it can be said that sulfur pressure affects the crystallite size of CZTS films.

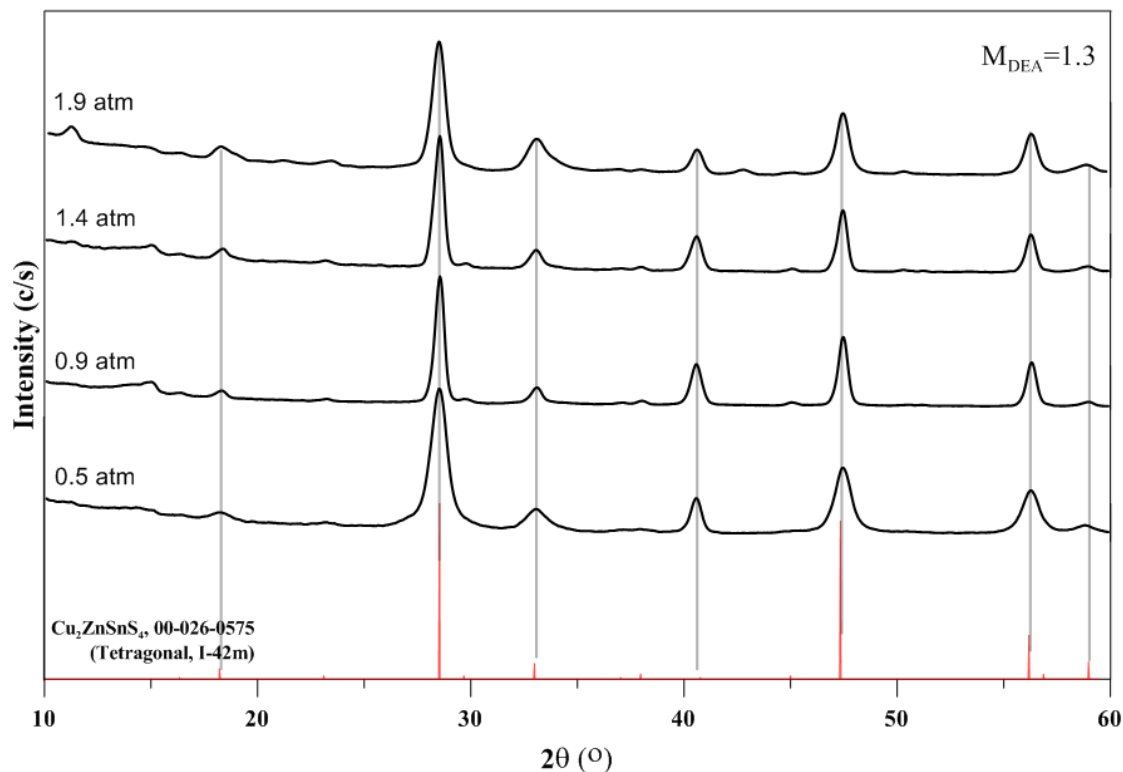


Figure 4.51. XRD patterns of the CZTS films sulfurized at different sulfur pressures

4.2.2.3. Effects of sulfurization temperature

We sulfurized the samples at 200, 300, 400, 500 and 700 °C to investigate the sulfurization temperature effect. The structural characterization was performed using x-ray diffraction (XRD) and Raman techniques. The diffraction patterns were obtained at a 40-keV of operating voltage and a 35-mA current. The step size and the scan step time were 0.0330° and 1 sec., respectively. Figure 4.52 and 4.53 show the obtained XRD patterns of the samples. In the patterns of the samples sulfurized at 200-500 °C, four clear peaks were observed at $2\theta=28.49^\circ$, 32.17° , 47.37° and 56.15° . The patterns of the samples match very well with $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 00-026-0575: Tetragonal, $a=b=5.427$ nm, $c=10.848$ nm, I-42m). Peaks corresponding to the (112), (200), (220) and (312) planes indicate the polycrystalline nature of the films. No other prominent peaks were observed, which suggests that no secondary phases occurred. We can see that the degree of crystallinity of the CZTS films increased with the sulfurization temperatures. A part of the resulting CZTS was sulfurized at 700 °C to see how temperatures above 500 °C affect the structure of the CZTS film. Figure 4.53 shows the XRD pattern of the sample sulfurized at 700 °C. It is clear that this pattern is completely different from the XRD patterns of other samples sulfurized at lower temperatures. All the peaks observed in Figure 4.53 can be attributed to CuS (JCPDS 03-065-0603, covallite) and ZnS (JCPDS 03-065-1691, zinc sulfide). According to the previous studies on CZTS (Weber et al., 2010; Scragg et al., 2011; Yang et al., 2012), tin losses with significant rates occur at temperatures of 550 °C and above. Therefore, the changes at 700 °C can be attributed to tin loss from the CZTS lattice. The results of the EDS analysis also support this attribution. The mean crystallite sizes of the CZTS films were estimated by using Debye Scherrer's formula (Knuyt et al, 1996). The estimated results are 3.6, 6.0, 9.3 and 11.9 nm for the samples sulfurized at 200, 300, 400 and 500 °C, respectively. The increasing crystallite size with sulfurization temperature can be attributed to an enhancement occurring in the lattice structure of the films.

Binary or ternary sulfides such as ZnS, Cu_{2-x}S and Cu_2SnS_3 have similar diffraction patterns to CZTS owing to their similar zinc blend-type structures. Raman spectroscopy analyses of the samples over the range 200 to 500 cm^{-1} were also made to prove the phase purity or to detect the presence of other possible secondary phases, and the results are given

in Figure 4.54. In the Raman spectrum, an obvious major peak at 331 cm^{-1} and a minor peak at 368 cm^{-1} can be clearly seen. This spectral data is in good agreement with the reported Raman spectra of CZTS (He et al., 2013; Gao et al., 2013; Zaberca et al, 2012) and confirms the formation of the CZTS phase. Moreover, the strong major peak is an indication of the good crystalline quality of the compound. It is noticeable that the peaks at 351 and 274 cm^{-1} corresponding to ZnS, the peak at 475 cm^{-1} corresponding to Cu_{2-x}S and the peak at 345 cm^{-1} corresponding to ZnS:Cu (Fernandes et al., 2009; 2011; Owens et al., 2011) do not appear, suggesting the absence of these compounds. The peaks in the Raman spectra of the sample sulfurized at 700°C (as an inset in Figure 4.54) indicate the formation and presence of Cu-Zn-S phases. This spectrum also proves the decomposition of the CZTS resulting from tin loss. The tin loss was also supported by EDS analysis of the sample in section 4.1.2.3

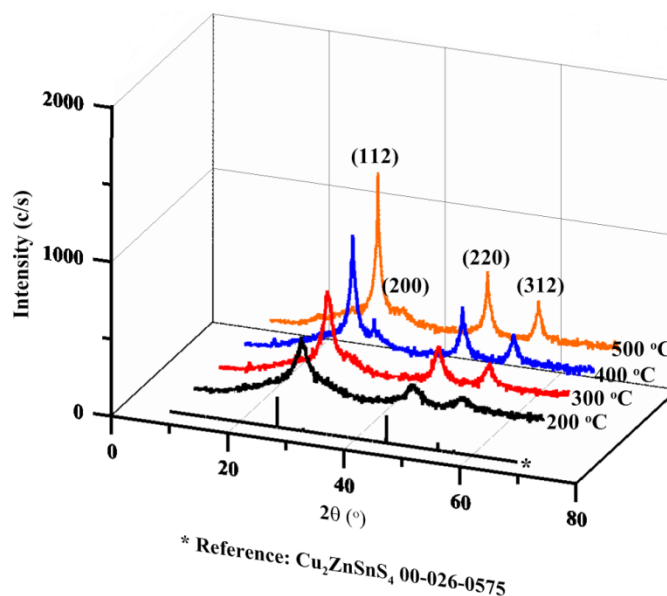


Figure 4.52. The XRD patterns of sol-gel grown CZTS films sulfurized at 200, 300, 400 and 500°C .

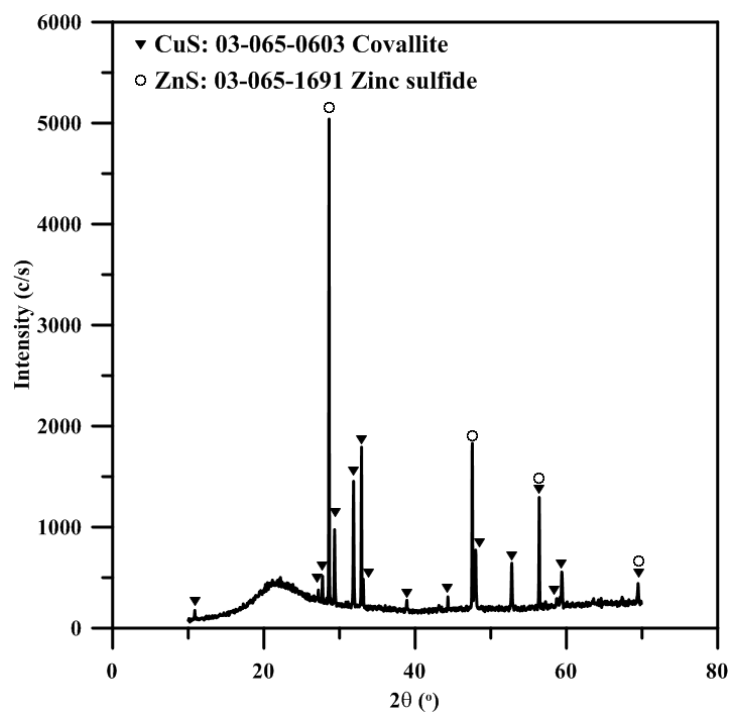


Figure 4.53. The XRD patterns of sol-gel grown CZTS films sulfurized at 700 °C.

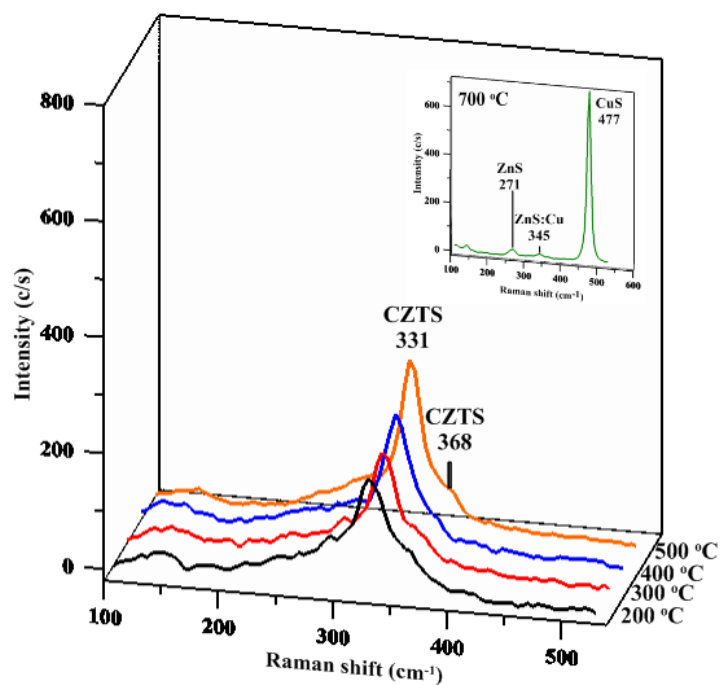


Figure 4.54. The Raman spectra of the sol-gel grown CZTS films sulfurized at different temperatures.

4.3. Photo-conversion efficiency studies of the CZTS films

4.3.1. Sol-gel grown CZTS films

The IPCE value corresponds to the number of electrons generated by monochromatic light in the external circuit, divided by the number of incident photons. Measuring the photovoltaic response of a photo-active material to monochromatic light provides the information about how efficiently the material converts photons of a given wavelength into electrons. This measurement is often also referred to as EQE or external quantum efficiency.

In our experiments the signal of the monochromatic light is split by a chopper (27 Hz) that allows referring the measurement signal to the incoming monochromatic light. The QE curve allows drawing conclusions about the absorption and recombination losses in the material.

The photo-conversion efficiency of the films was examined through using them as photocathode in a photo-electro chemical cell. The measurements were carried out in a 3-arm cell with a Ag/AgCl reference electrode and a platinum basket auxiliary electrode, using a CH Instruments potentiostat. The electrolyte was a 0.1 M KCl/0.1 M $\text{Eu}(\text{NO}_3)_3$ aqueous solution. IPCE data was collected at the wavelength range of 500-900 nm under illumination from filtered (450 nm cutoff filter) and collimated light passing through a grating monochromator, with an applied bias of -350 mV vs Ag/AgCl. Obtained IPCE results of the samples prepared under different conditions are given in Figure 4.55-4.63. Derived IPCE and band gap values are summarized in Table 4.4. The variation of IPCE and band gap values of the sol-gel grown CZTS films with respect to sulfur pressure are given in Figure 4.64.

Table 4.4. IPCE and band gap values of the samples used as a photo-cathode in a photo-electro chemical cell.

M_{DEA}	Sulfur pressure (atm)	EQE/IPCE (%)	Band gap (eV)
0.9	0.5	0.8	1.44
0.9	0.9	1.7	1.47
0.9	1.4	1.1	1.48
1.1	0.5	0.1	1.45
1.1	0.9	0.9	1.47
1.1	1.4	2.1	1.49
1.3	0.5	0.5	1.42
1.3	0.9	1.4	1.47
1.3	1.4	12	1.48

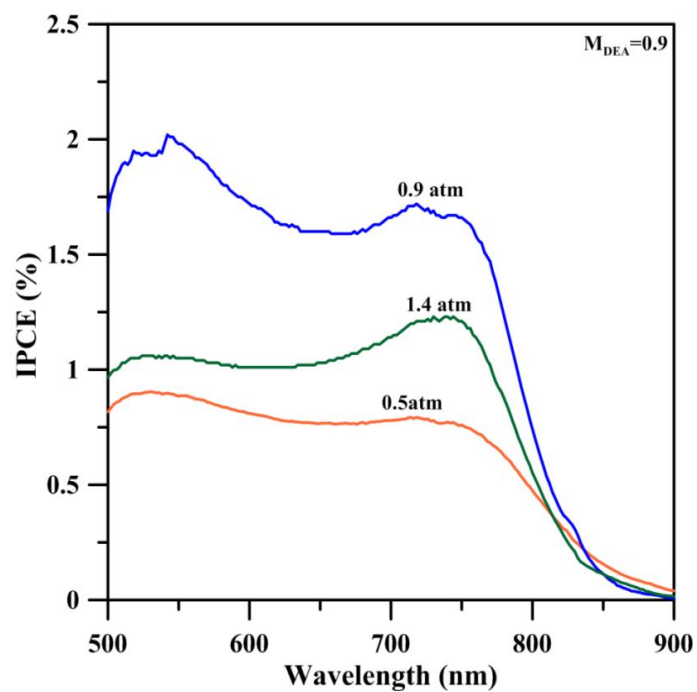


Figure 4.55. IPCE results of the samples prepared under different sulfurization conditions

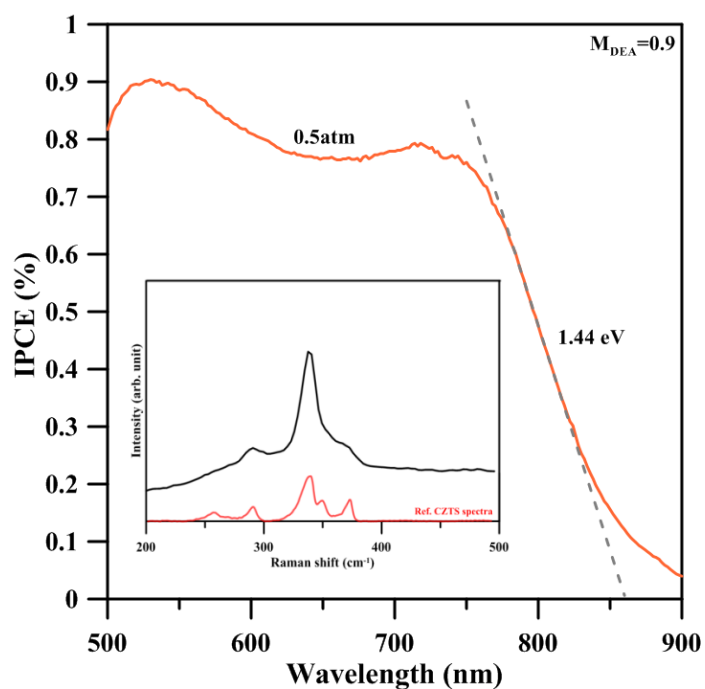


Figure 4.56. IPCE results of the samples prepared by using 0.9 M DEA and sulfurized under sulfur pressure of 0.5 atm (Inset: Raman spectra).

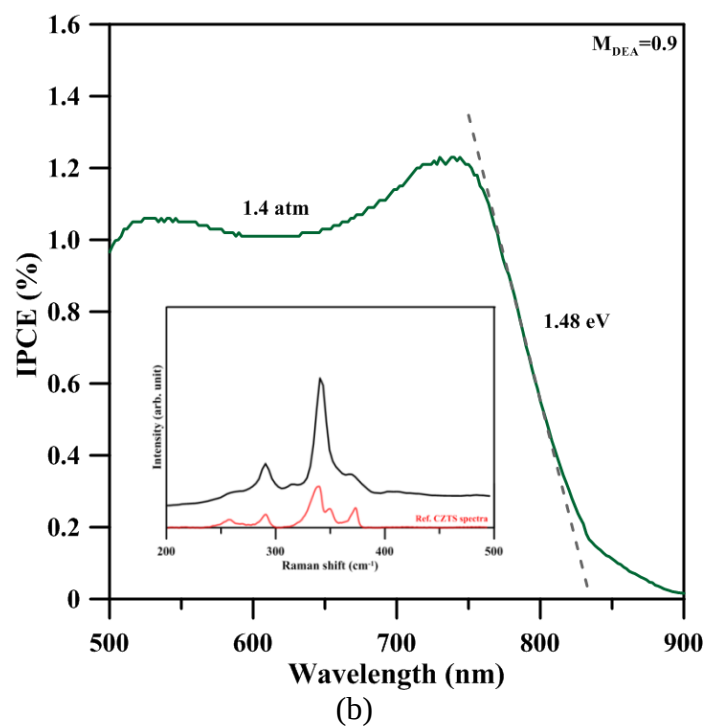
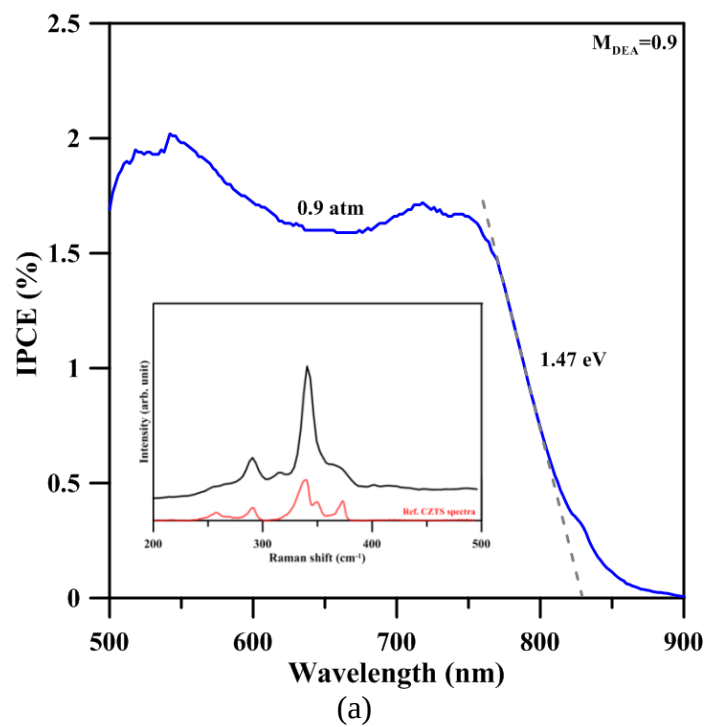


Figure 4.57. IPCE result of the sample prepared by using 0.9 M DEA and sulfurized under sulfur pressure of (a) 0.9 and (b) 1.4 atm (Insets: Raman spectra).

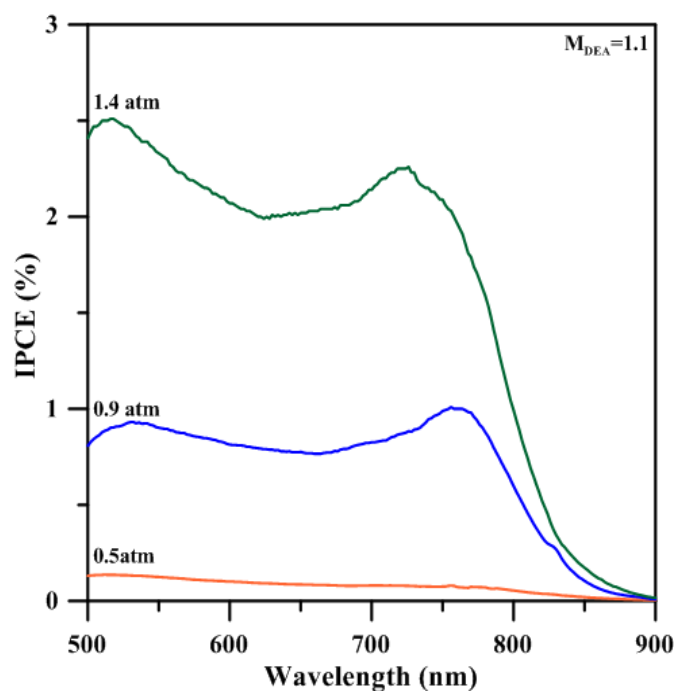


Figure 4.58. IPCE results of the samples prepared by using 1.1 M DEA and sulfurized under sulfur pressure of 0.5, 0.9 and 1.4 atm.

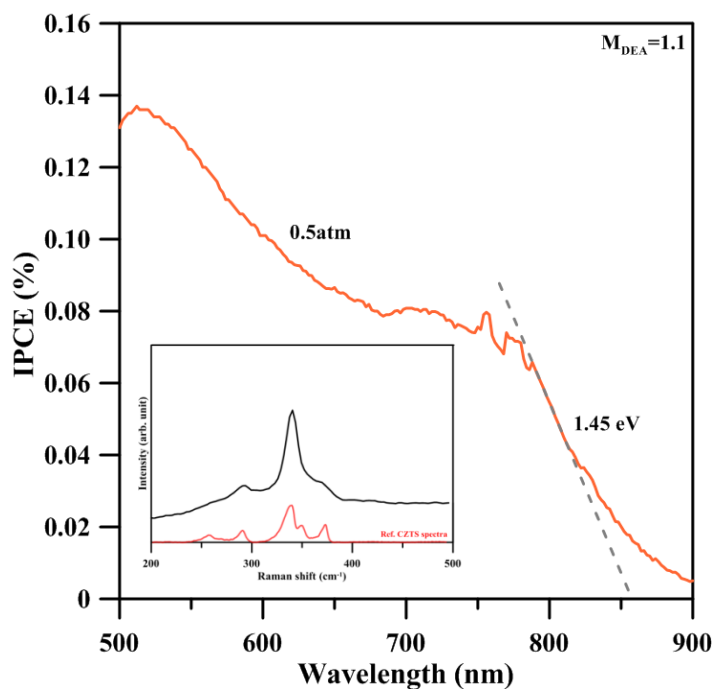


Figure 4.59. IPCE results of the samples prepared by using 1.1 M DEA and sulfurized under sulfur pressure of 0.5 atm (Inset: Raman spectra).

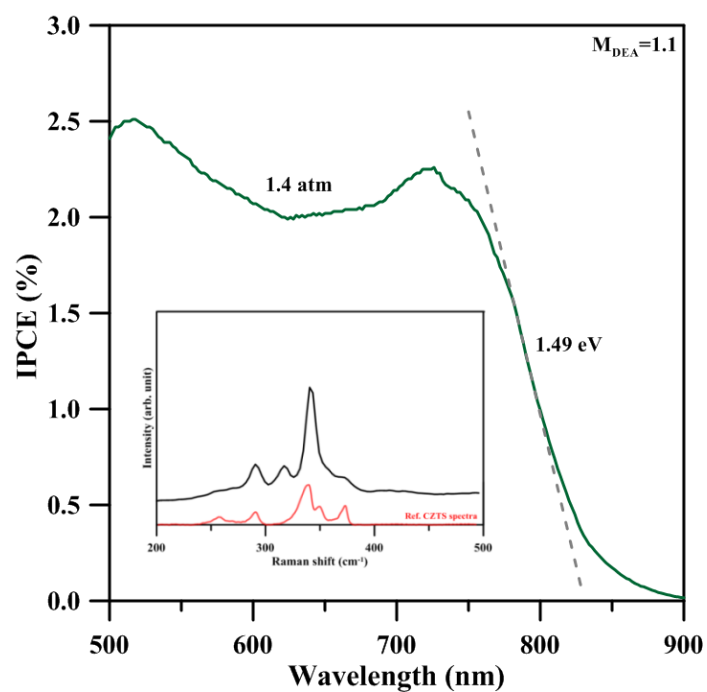
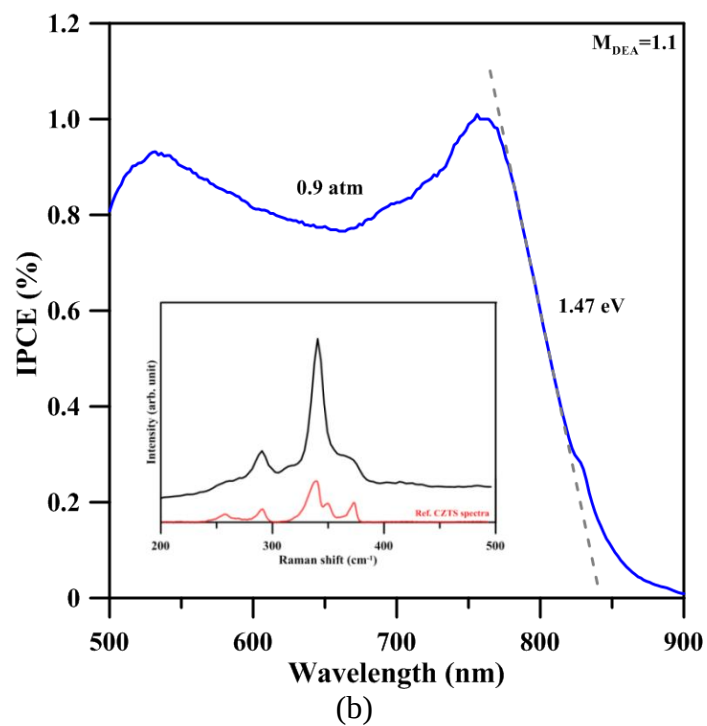


Figure 4.60. IPCE result of the sample prepared by using 1.1 M DEA and sulfurized under sulfur pressure of (a) 0.9 and (b) 1.4 atm (Insets: Raman spectra).

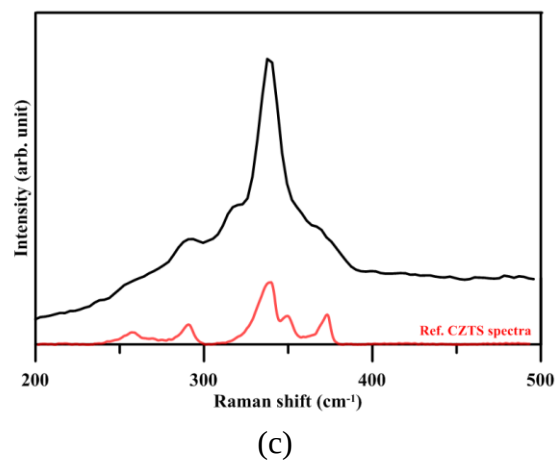
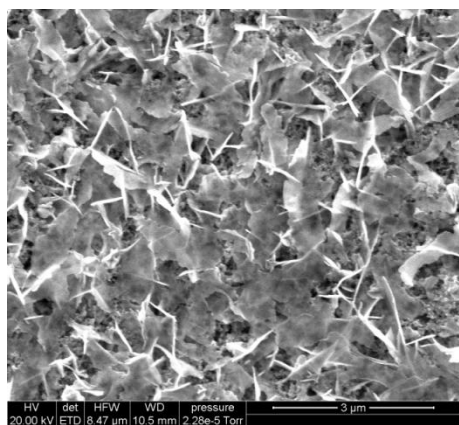
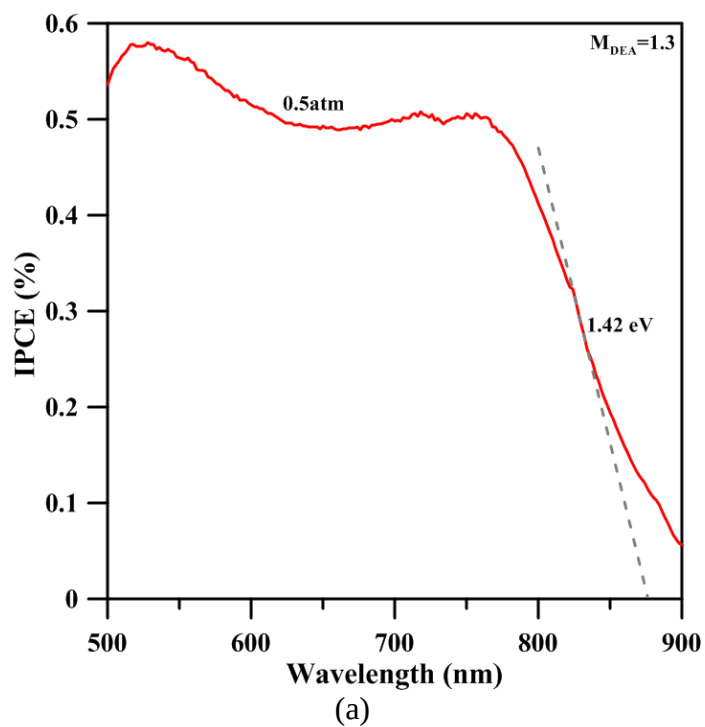


Figure 4.61. (a) IPCE result, (b) SEM image and (c) Raman spectra of the sample prepared by using 1.3 M DEA and sulfurized under sulfur pressure of 0.5 atm.

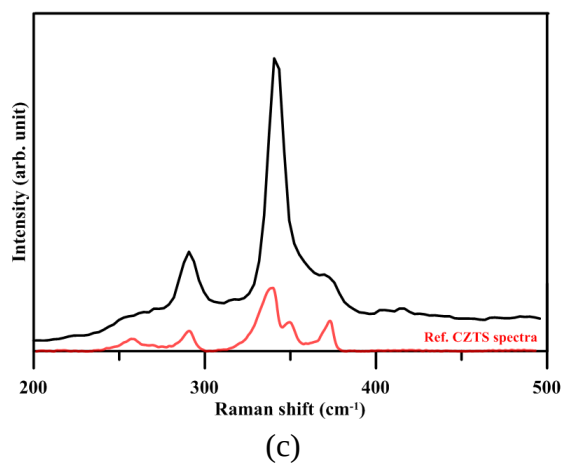
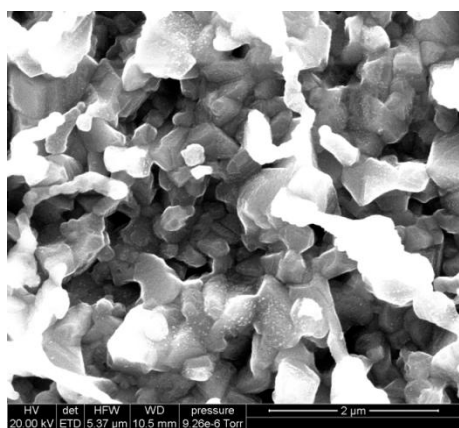
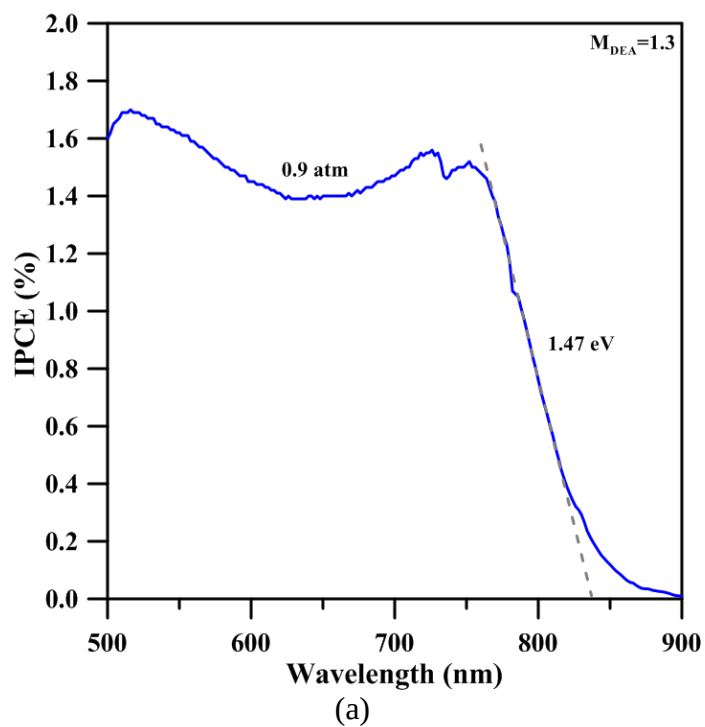


Figure 4.62. (a) IPCE result, (b) SEM image and (c) Raman spectra of the sample prepared by using 1.3 M DEA and sulfurized under sulfur pressure of 0.9 atm.

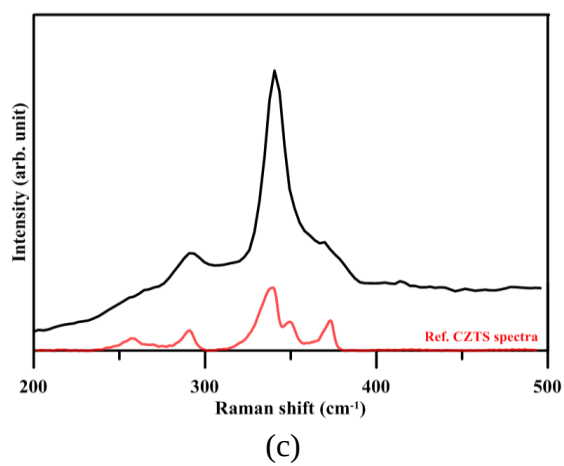
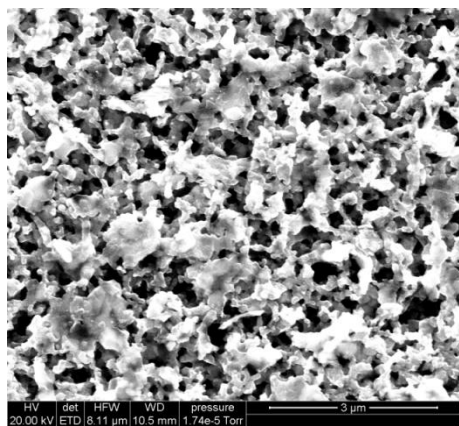
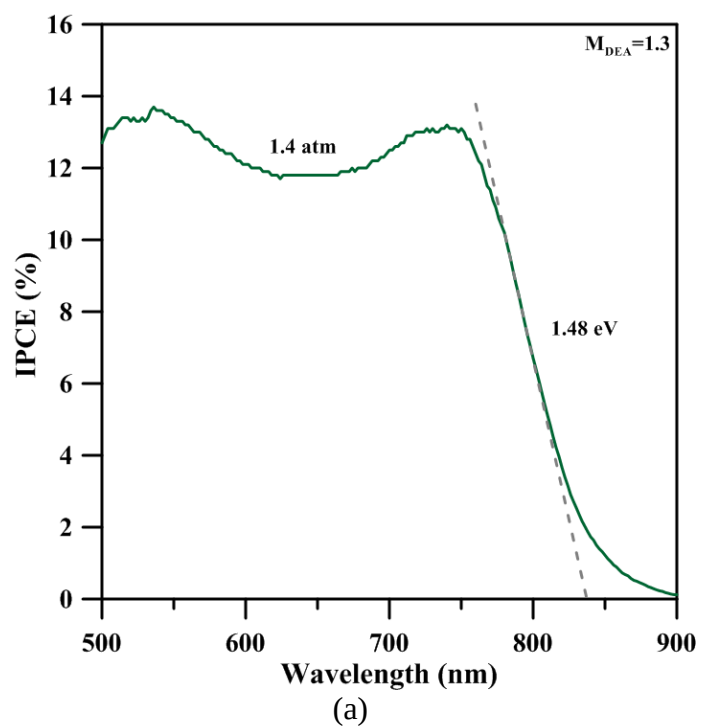


Figure 4.63. (a) IPCE result, (b) SEM image and (c) Raman spectra of the sample prepared by using 1.3 M DEA and sulfurized under sulfur pressure of 1.4 atm.

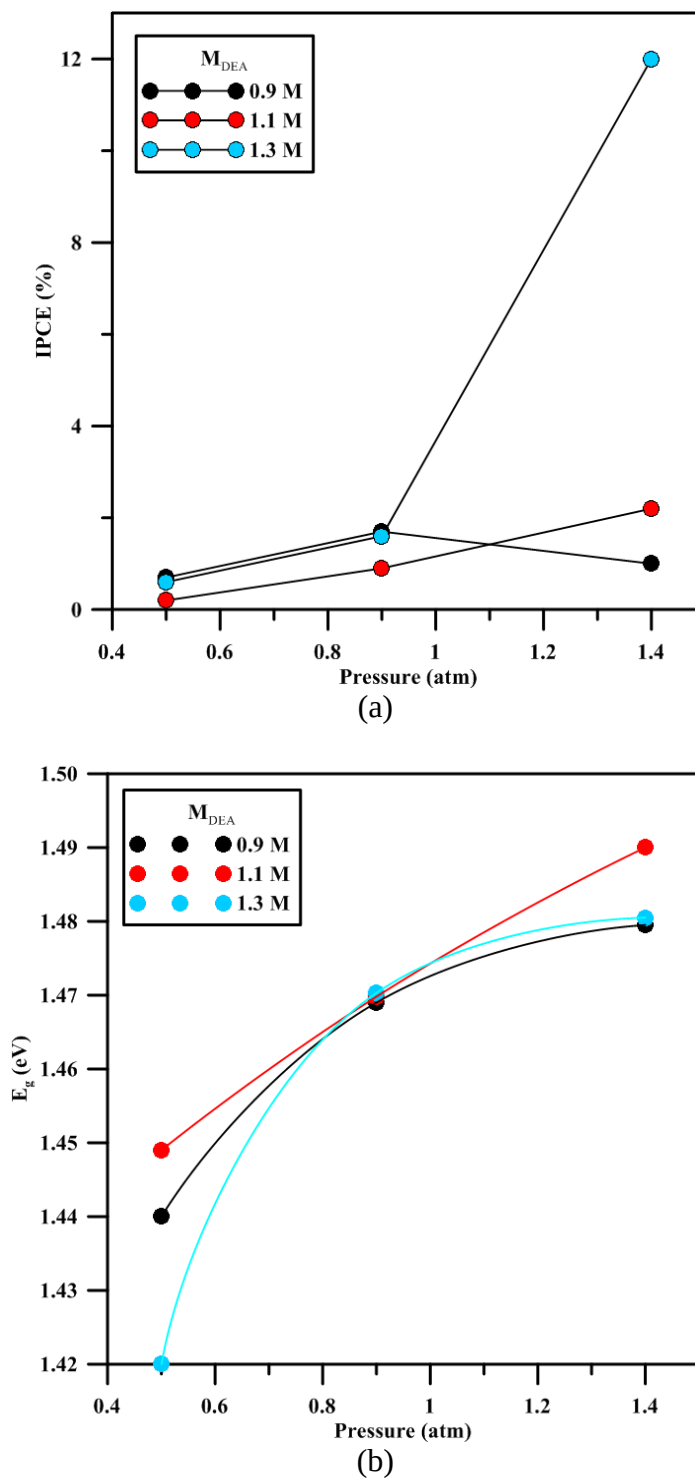


Figure 4.64. Variation of (a) the IPCE and (b) band gap values sol-gel grown CZTS films with respect to sulfur pressure.

4.4. Optical studies of the CZTS films

4.4.1. SILAR grown films

4.4.1.1. One-stage SILAR grown films

The absorption coefficient (α) of the films was calculated from the measured values of the reflectance and transmittance data (Figure 4.65) using the relation (Vipul et al., 2013)

$$\alpha(\lambda) = (1/t) \ln \left[\frac{1-R(\lambda)}{T(\lambda)} \right] \quad (4.10)$$

where α is the absorption coefficient and t is the thickness of the sample. The calculated absorption coefficient values are of the order of 10^4 cm^{-1} . Near the absorption edge or in the strong absorption zone of the transmittance spectra, the absorption coefficient is related to the optical energy gap, E_g following the power-law behavior of Tauc relation (Tauc, 1970)

$$\alpha h\nu = B(h\nu - E_g)^m \quad (4.11)$$

where B is an energy-independent constant, E_g is the optical band gap energy and m is an index that characterizes the optical absorption process and is theoretically equal to 2 and 1/2 for the indirect and direct allowed transitions, respectively. It was found that α was about 10^4 cm^{-1} . It can be seen in the Figure 4.65 that both films are almost opaque in the wavelengths from 200 to 600 nm with a small reflectivity about 10 %. However, compared to the sample (b), the sample (a) covers a slightly wider wavelength zone by means of blocking visible photons. This indicates that non-stoichiometric/copper-poor growth conditions may improve the absorption behavior of Cu_2SnS_3 thin films.

Figure 4.66 shows the band gap photon energy estimation performed via extrapolating the linear region of the plot $(\alpha h\nu)^2$ versus $h\nu$ to the horizontal axis and considering the intersecting point. As can be seen in Figure 4.66, the samples exhibit linear dependence which directly indicates transition nature of the films. Thus, we can choose m

as $1/2$. By plotting the graph of $(\alpha h\nu)^2$ against photon energy $h\nu$, the band gap values were estimated to be 1.45 and 1.35 eV for the samples (a) and (b), respectively.

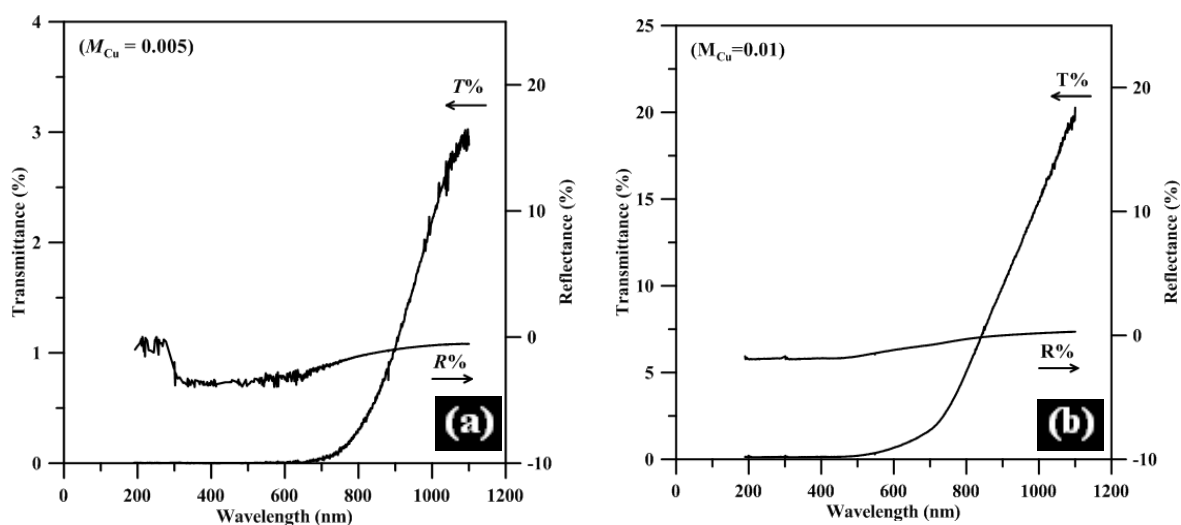


Figure 4.65. Transmittance and reflectance spectra of the samples (a) $M_{Cu} = 0.005$ (b) $M_{Cu} = 0.01$.

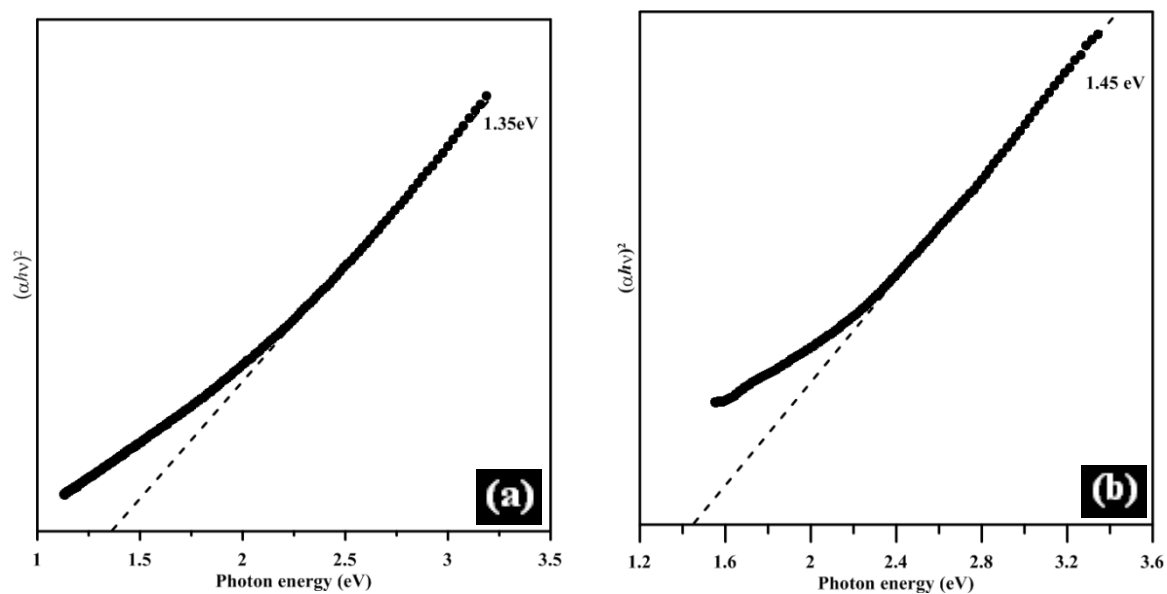


Figure 4.66. Band gap energy estimations of the samples (a) $M_{Cu} = 0.005$ (b) $M_{Cu} = 0.01$.

As a p-type direct band gap semiconductor, the E_g value of Cu_2SnS_3 has been reported in between 0.93 and 1.51 eV (Bouaziz et al., 2009; Onoda et al., 2000; Berg et al., 2012). The difference between the reported values is due to the crystal structure of polymorphic compound Cu_2SnS_3 , where 0.98 eV was measured for a cubic phase and 1.35 eV for a tetragonal phase (Fernandes et al., 2010b). The polymorphic state of grown Cu_2SnS_3 depends on the growing temperature, where the cubic phase is known to form at high temperatures ($>775^\circ\text{C}$) and the monoclinic and triclinic as well as the tetragonal phases are low temperature phases ($<775^\circ\text{C}$) (Berg et al., 2012; Rastogi and Salkalachen, 1982). It can be said that the estimated results are in good agreement with literature values. Such band gap values found in the present study are quite close to the optimum band gap for a solar cell, which make the films promising absorber materials. For the sample (a), the reason for having a slightly higher band gap value may be related to the relatively rich Cu content. As discussed in XRD results, a secondary Cu_xS phase was detected in the pattern of sample (a). The direct optical band gap of Cu_xS reported earlier in the literature varies from 1.7 to 2.16 eV according to the value of x (Rastogi and Salkalachen, 1982). Consequently, the slightly higher band gap value of CTS1 can be attributed to a small amount of Cu_xS phase in the structure.

4.4.1.2. Two-stage SILAR grown films for different deposition cycles

Figure 4.67 shows the band-gap photon-energy estimations performed by extrapolating the linear region of the plot $(\alpha h\nu)^2$ versus to $h\nu$ the horizontal axis and considering the intersecting point. As can be seen in the figure, the samples exhibit a linear dependence, which directly indicates the allowed nature of the films. Thus we can choose m as 1/2. By plotting a graph of $(\alpha h\nu)^2$ against the photon energy $h\nu$, the band-gap values were estimated to be 1.41, 1.50, 1.48 and 1.36 eV for the samples 60/40, 60/20, 30/40 and 30/20, respectively.

The E_g value of CZTS, as a p-type direct-band-gap semiconductor, has been reported to be in between 1.4 and 1.5 eV (Sarswat et al., 2012b; Katagiri et al., 2008;

Schubert et al., 2011; Seol et al., 2003). It can be said that the estimated results are in good agreement with the values in literature and quite close to the optimum band gap for a solar cell. Band gap energy estimations of the ZnS and Cu_2SnS_3 precursor layers are also given in Figure 4.67. ZnS has band-gap values of 3.5–3.7 and 3.7–3.9 eV for cubic zinc-blende and hexagonal wurtzite structures, respectively (Han et al., 2010). The optical band-gap value of 3.62 eV suggests that the precursor ZnS layer has a cubic structure.

As a p-type direct band gap semiconductor, E_g value of Cu_2SnS_3 has been reported in between 0.93 and 1.51 eV for cubic and tetragonal phase, respectively (Kuku et al., 1987; Bouaziz et al., 2009; Bouaziz et al., 2011; Avellaneda et al., 2010; Fiechter et al., 2003). The difference between the reported values is due to the crystal structure of polymorphic compound Cu_2SnS_3 , where 0.98 eV was measured for a cubic phase and 1.35 eV for a tetragonal phase (Fernandes et al., 2010b). It can be said that the estimated results are in good agreement with the values in literature.

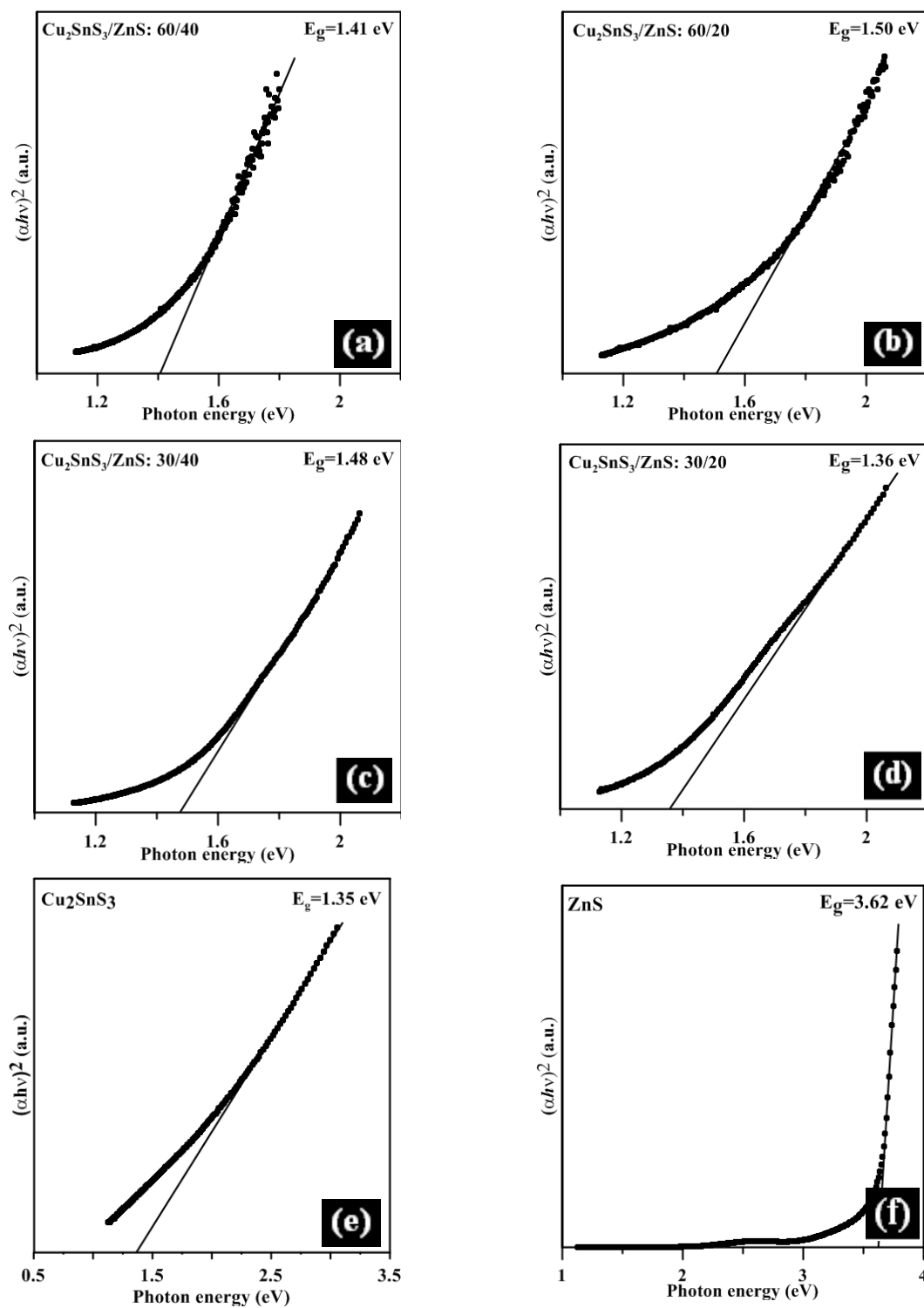


Figure 4.67. Band gap energy estimations of the samples.

4.4.2. Sol-gel grown CZTS films

4.4.2.1. Effects of stabilizer content

Figure 4.68 shows the band-gap photon-energy estimations of the CZTS films prepared by using 1.0, 1.5, 2.0 and 2.5 M diethanolamine (DEA), respectively. The band-gap estimations were performed by extrapolating the linear region of the plot of $(\alpha h\nu)^2$ versus $h\nu$ to the horizontal axis and considering the intersecting point. As can be seen in the figure, the samples exhibit a linear dependence which indicates the directly allowed nature of the films. Thus we can choose m as $1/2$.

By plotting the graph of $(\alpha h\nu)^2$ against the photon energy $h\nu$, the band gap values were estimated to be 1.49, 1.59, 1.52, and 1.48 eV for the samples deposited in the solutions containing 1.0, 1.5, 2.0 and 2.5 M DEA, respectively.

The E_g value of the CZTS compound, as a p-type direct-band-gap semiconductor, has been reported to be between 1.4 and 1.6 eV (Sarswat et al., 2012b; Katagiri et al., 2008; Daranfied et al., 2012; Schubert et al., 2011; Seol et al., 2003). It can be said that the estimated results are quite close to the optimum band gap for a solar cell.

As it is generally known that the additives used in aqueous methods control the surface morphology, crystalline structure, grain size, internal stress, corrosion behavior and even chemical composition (Mouanga et al., 2006; 2007).

In sol-gel method, the sol stabilization which has usually been made by using DEA is one of the essential steps in the film formation (Kaminski et al., 2005). In precursor preparing step, DEA content deeply affects the solution properties such as density, color, amount of dissolved substances and homogeneity. As it is discussed in SEM and XRD studies, DEA amount changed the morphology and structure of the films. Thus, the variation in the optical band gap values of the samples may be attributed to grain size, morphology and chemical composition.

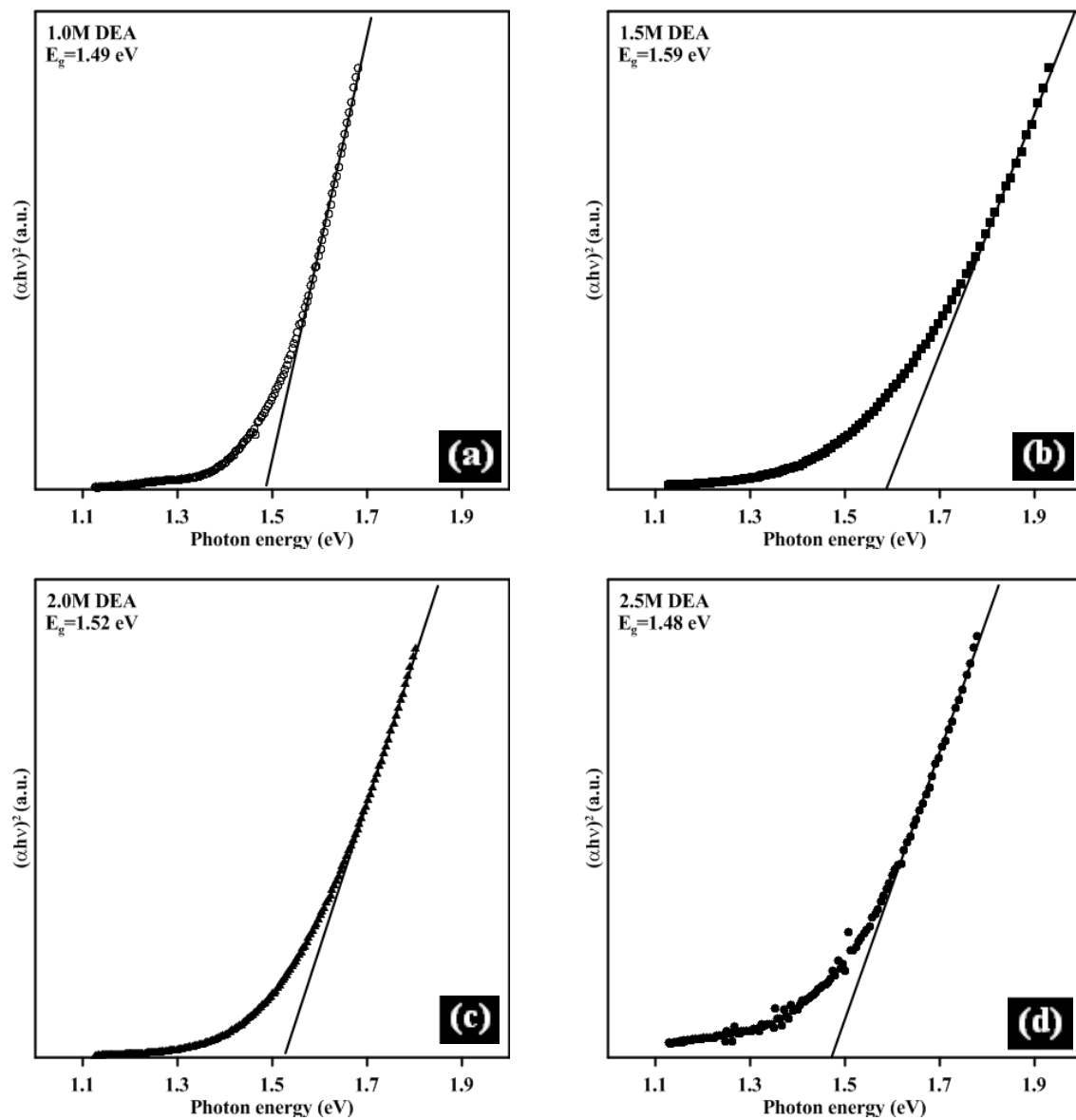


Figure 4.68. Band gap energy estimations of the samples of the sol-gel grown samples obtained by using (a) 1.0 M (b) 1.5 M (c) 2.0 M (d) 2.5 M DEA .

4.4.2.2. Effects of sulfurization temperature

Figure 4.69 shows the band-gap photon-energy estimations of the CZTS films sulfurized at 200, 300, 400, 500 and 700 °C, respectively. The band-gap estimations were performed by extrapolating the linear region of the plot of $(\alpha h\nu)^2$ versus $h\nu$ to the horizontal axis and considering the intersecting point. As can be seen in Figure 4.69 the samples exhibit a linear dependence which indicates the directly allowed nature of the films. Thus we can choose m as 1/2. By plotting the graph of $(\alpha h\nu)^2$ against the photon energy $h\nu$, the band gap values were estimated to be 2.27, 1.47, 1.39, 1.32 and 1.29 eV for the samples sulfurized at 200, 300, 400, 500 and 700 °C, respectively. The E_g value of the CZTS compound, as a p-type direct-band-gap semiconductor, has been reported to be between 1.4 and 1.5 eV (Sarswat et al., 2012b; Katagiri et al., 2008; Schubert et al., 2011; Seol et al., 2003). The higher band gap may be attributed to the residual organic precursor compounds at the sample at relatively low sulfurization temperatures. It can be said that the estimated results are quite close to the optimum band gap for a solar cell. The crystallite size of the films can also be estimated through UV-Vis spectroscopy. By using an effective mass model (Pesika et al., 2003) the crystallite sizes of the samples were estimated to be 2.2, 4.1, 4.7 and 5.7 nm for the samples sulfurized at 200, 300, 400 and 500 °C, respectively. A similar trend in crystallite size was obtained from the XRD analysis.

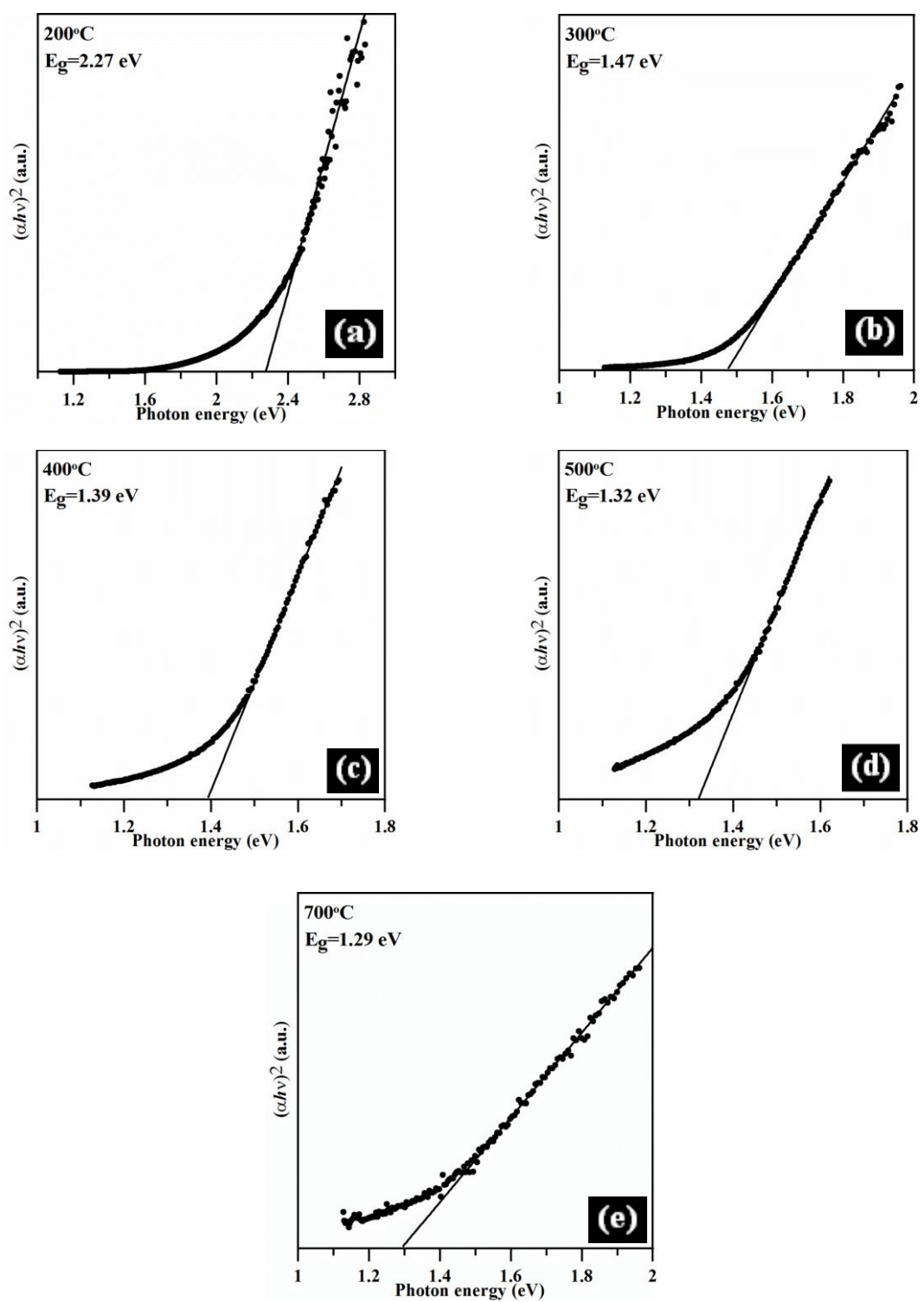


Figure 4.69. Band gap energy estimations of the sol-gel grown samples prepared by using 1.0 M DEA sulfurized at (a) 200 (b) 300 (c) 400 (d) 500 (e) 700 °C.

5. CONCLUSIONS

In this study we have obtained $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin film solar absorbers via successive ionic layer adsorption-reaction (SILAR) and sol-gel spin coating methods. In the SILAR method, we have tried to optimize the deposition conditions and investigated the effects of Cu/Sn initial ratios, number of deposition cycles of each Cu_2SnS_3 and ZnS layers. The role of sulfurization temperature was also discussed. The effects of stabilizer content, sulfur pressure and sulfurization temperature were investigated for the spin coated samples. The experimental conditions were tried to be optimized for the sol-gel spin coated CZTS films. All prepared samples were examined by means of scanning electron microscopy, energy dispersive x-ray photo-electron spectroscopy, Raman spectroscopy, UV-Visible spectroscopy and incident photon to current efficiency (IPCE) method.

Through electron imaging, one-stage SILAR grown films were generally found to be continuous and composed of homogeneously distributed large grains which were affected by copper molarity. Zinc deposition was found to be problematic in the case of single cationic solution. According to the compositional studies of one-stage SILAR grown films, it was concluded that those films have the form of Cu_2SnS_3 rather than $\text{Cu}_2\text{ZnSnS}_4$. This result/problem was attributed to a competitive adsorption between different metal ions. Therefore we prepared $\text{Cu}_2\text{SnS}_x/\text{ZnS}$ stacking layers and sulfurized them to produce CZTS films. The characterizations indicated that we had a $\text{Cu}_2\text{ZnSnS}_4$ -type phase in all samples. It is a desired composition for efficient CZTS based solar cells that some samples had slightly Cu-poor and Zn-rich composition. The study found that copper molarity is very crucial to obtain quality and well crystallized films. The copper molarity below the stoichiometric value decreased the crystallinity while higher molarity caused formation of Cu_{2-x}S secondary phase. Due to the overlap of the XRD patterns of $\text{Cu}_2\text{ZnSnS}_4$, Cu_2SnS_3 , Cu_{2-x}S and ZnS, Raman analysis were made to examine the phase purity of the films.

The study revealed that diethanolamine concentration in the growth solution is very crucial to obtain void/crack-free CZTS thin films. Optimum DEA concentration was tried to be determined in a wide range. Through SEM images the films were found to have continuous and dense morphology with micron size grains which is crucial to produce for high efficient solar cells. EDS results of the samples proved to have near-stoichiometry. It

is a generally encountered problem that Cu_{2-x}S residual particles were detected on the surface of the films in some cases. Majority of these particles were removed via potassium cyanide etching process. Because of high volatility and high vapor pressure of sulfur, an inevitable MoS_2 layer formed in almost all samples after sulfurization. When DEA concentration was 0.3 in the precursor solution, the grain sizes became larger (about 2 micron) than those of the samples prepared by using higher DEA concentrations. XRD diffraction and Raman analysis proved the phase purity of sol-gel grown films.

SEM images and EDS results of the CZTS films sulfurized under different pressures revealed that sulfur pressure strongly affects surface morphology and grain size. It was seen that the grains became larger in accordance with the increasing sulfur pressure up to 1.4 atm. The grain sizes of the sample sulfurized at 1.4 atm were about 2 micron which plays a key role in producing high efficient CZTS thin film solar cells. In cross-section images, it was seen that there were MoS_2 layers as a result of high vapor pressure/high volatility of sulfur penetrating into the Mo layer.

The photo-conversion efficiency of the films was examined through incident photon to current efficiency (IPCE) method. The films which were grown on Mo-coated glass substrates were used/tested as a photocathode in a photo-electro chemical cell. The IPCE values were changed from 0.1 to 12%.

As a conclusion, it was found that low cost SILAR and sol-gel methods can be utilized to obtain high efficient CZTS absorber which is a promising, green and earth-abundant material in the near future.

As this study has shown, there are still many points which should be clarified to achieve marketable CZTS based thin film solar cells. Thus, some proposals for a further research can be suggested:

In the scope of this study, we tried to obtain CZTS films via SILAR method with a single cationic solution. However, our efforts remained inadequate to get a CZTS phase. Therefore, we preferred to grow $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking layers and succeeded to grow CZTS films after sulfurizing them. We believe that single cationic SILAR method is more controllable, repeatable and cost effective. CZTS films can be obtained in with a single cationic solution by changing deposition conditions/parameters in a future study,

Number of deposition cycles of each stacking layer can be investigated in a wider range in the $\text{Cu}_2\text{SnS}_3/\text{ZnS}$ stacking structures to improve the film quality.

Effects of different stabilizer materials and additives can be studied in sol-gel and SILAR systems to get more controllable growth and different morphologies.

Sulfurization temperature of CZTS films can be investigated in a narrow temperature region (e.g. between 500-600 °C with 5 °C step) for the purpose of obtaining exact phase formation temperature region.

Controlling the sulfur pressure during sulfurization is another crucial parameter which directly affects the film characteristics. Effects of sulfurization pressure should be clarified by investigating the optimum sulfur pressure in detail.

Another important problem in CZTS growth process is inevitable MoS_2 layer resulting from penetrating sulfur into the Mo contact during the sulfurization process. A method should be suggested/developed for preventing sulfur penetration into Mo layer.

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ACKNOWLEDGEMENTS

This dissertation would not have been possible without the guidance, help and encouragement of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study.

First and foremost, I offer my sincerest gratitude to Prof. Dr. Hüsnü Salih Güder, for being an amazing advisor and allowing me to follow my research passions. His inspiration, invaluable support and encouragement have guided me all throughout my study. I am very thankful to him for giving me the valuable opportunity to work with him.

I also would like to express my special thanks to the members of my doctoral dissertation committee, Assoc. Prof. Dr. İsmail Hakkı Karahan and Assoc. Prof. Yasin Yücel for their reviewing, valuable advices and constructive criticisms.

I am also extremely grateful to Samed Çetinkaya for his constant help throughout my experiments and characterizations. I thank him for all of his graciously efforts and supports.

My sincere thanks to Assist. Prof. Dr. Slavko Bernik, Mateja Podlogar and all of the members of the K-7 Laboratory in Joseph Stefan Institute, Prof. Dr. Bruce A. Parkinson, Brandon Durant and all members of the Parkinson Group in University of Wyoming who have helped me in some ways at some points of my study.

Last but most definitely not the least, I would like to thank all of my family and friends. Without their support I would not be here today, both literally and figuratively.

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