



UNIVERSITAT
POLITÈCNICA de
VALÈNCIA



INSTITUT DE DISSENY I FABRICACIÓ (IDF)

**SYNTHESIS AND CHARACTERIZATION OF SOME
NANO-SELENIDES AND THEIR APPLICATION IN
SOLAR CELLS**

BY

SUZAN KAMAL ABDEL HAMIED SABER

Doctoral Thesis

Supervised by: Prof. Dr. Bernabé Marí Soucase

May 2018

Table of Contents

List of abbreviations and symbols	8
List of figures	11
List of tables	15
Dedication	16
Acknowledgements	17
Abstract	18
Motivation and Objective.....	21
Chapter 1. Introduction	
Part I: Basic Photovoltaic Physics	
1. 1.1. Energy.....	19
1.1.2. Power	19
1.1.3. Efficiency.....	20
1.1.4. Electricity.....	21
1.1.4.1. Electric Fields.....	21
1.1.4.2. Current.....	21
1.1.4.3. Voltage.....	22
1.1.4.4. Resistance.....	22
1.1.5. Circuits.....	22
1.1.5.1. Series Circuits.....	22
1.1.5.2. Parallel Circuits.....	23
1.1.5.3. Short Circuits.....	23
1.1.5.4. Open Circuits.....	23
1.1.6. Diffusion.....	24
1.1.7. Atomic Theory.....	24
1.1.7.1. Bohr Model of the Atom.....	25
1.1.7.2. Band Theory of Solids.....	25
1.1.8. Semiconductors: p-n Junctions.....	27
1.1.9. Light.....	28
1.1.9.1. Waves.....	28
1.1.9.2. Electromagnetic Spectrum.....	29

1.1.10. The Solar Spectrum.....	29
1.1.11. Photon Absorption.....	31
1.1.11.1. Photocurrent.....	31
1.1.11.2. Photovoltage.....	31
1.1.11.3. Fill Factor and Maximum Power.....	32
1.1.12. Single-Junction Solar Cell Design.....	33
1.1.13. Multijunction Solar Cell Design.....	33
1.1.14. Bandgap Selection.....	33
1.1.15. Lattice Matching.....	34
1.1.16. Cell Optimization.....	35
1.1.16.1. Current Matching.....	35
1.1.16.2. Power Production.....	35
1.1.16.3. Concentration Systems.....	35
Part II: State of the Art of Thin Film Solar Cells	
1.2. CIGS Thin Film Solar Cells.....	35
1.3 Multiple Junction GaAs Based Thin Film Solar Cells.....	37
1.4. GaAs Solar Cells.....	38
1.5. InP Solar Cells.....	39
1.6. InGaAsP and GaN.....	40
1.7. Plastic Solar Cells.....	41
1.8. Photovoltaic Conversion.....	44
1.8.1. Heterojunction.....	44
1.8.1.1. Open-Circuit Voltage.....	46
1.8.1.2. Short-circuit Current.....	46
1.8.1.3. Fill Factor (FF).....	46
1.8.1.4. Efficiency.....	47
1.8.2. Homojunction.....	47
1.8.3. Schottky Barrier.....	47
1.9. Criteria for the Choice of Heterojunction Pair in the Thin Film Solar Cells.....	47
1.9.1. Band Gap of Absorber.....	47
1.9.2. Band Gap of Window Material.....	47

1.9.3. Electron Affinities.....	48
1.9.4. Lattice and Thermal Mismatch.....	48
1.9.5. Electrical Contacts.....	48
1.9.6. Cell Stability and Life Time.....	48
1.9.7. Deposition Methods.....	48
1.9.8. Materials.....	48
1.9.9. Window Materials.....	49
1.9.10. Absorber Materials.....	49
1.10. Copper Based I–III–VI ₂ Semiconductors.....	49
1.11. Nanocrystalline materials.....	50
References.....	51

Chapter 2. The semiconductor materials. Literature Review

2.1. THE SUN.....	44
2.2. Photovoltaic Power Systems.....	44
2.3. Photovoltaics advantages	46
2.4. Photovoltaic technologies	47
2.5. Photovoltaic effect and principle of solar cell operation.....	49
2.6. A brief history of the I-III-VI ₂ family	51
2.7. A brief history of CZTS based solar cells	57
2.7.1. Introduction into CZTS based solar cells.....	57
2.7.2. Crystal structure, defects, and composition.....	60
2.7.3. Sulphurisation/selenisation and recrystallization.....	63
2.7.4. Electrodeposition of CZTS based solar cells.....	65
2.7.5. Spin/spray/blade coating of CZTS based solar cells.....	67

Chapter 3. Experimental Techniques Methodology and Characterization

3.1. Experimental Techniques Methodology.....	83
3.1.1. Electrochemical deposition (Electrodeposition).....	83
3.1.2. Annealing Process.....	84
3.1.3. Hydrothermal technique.....	85
3.1.4. Reaction Containers.....	87
3.1.5. Spin Coating Process.....	89

3.2. Characterization.....	90
3.2.1. UV- Visible Spectroscopy.....	90
3.2.2. X-ray Diffraction analysis.....	90
3.2.3. Field emission Scanning Electron Microscopy (FESEM).....	92
3.2.4. Energy-dispersive Spectroscopy (EDS).....	93
3.2.5. Transmission electron microscopy (TEM) analysis.....	93
3.3. Electrical Properties of I–III–VI ₂ Compounds.....	95
3.3.1. Mott-Schottky Measurement.....	95
3.3.2. Flat band Potential.....	95
3.3.3. Electrochemical Impedance Spectroscopy(EIS).....	96
3.3.4. Photo electrochemical analysis.....	99

Chapter 4. CIGS thin films

4.1. Objectives.....	100
4.2. Introduction.....	100
4.3. Theory of CIS electrodeposition.....	101
4.4. CIS Structure.....	102
4.5. Experimental Procedure.....	103
4.5.1. Thin film preparation.....	103
4.5.2. Characterization.....	103
4.6. Results and discussion.....	104
4.6.1. XRD analysis.....	104
4.6.2. FE-SEM analysis.....	106
4.7. Optical measurements.....	108
4.8. Mott-Schottky measurements.....	110
4.9. Conclusion.....	115
References.....	115

Chapter 5. CIGS:Cr thin films

5.1. Objectives.....	118
5.2. Introduction.....	118
5.3. Experimental.....	119
5.3.1. Synthesis of nano-precursor powders.....	119

5.3.2. Synthesis of the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ thin films.....	120
5.4. Charaterization and Measurement	120
5.4.1. Structure study for both $\text{CuIn}_x\text{Cr}_y\text{Ga}_{1-x-y}\text{Se}_2$ nano-crystalline powder and thin films...120	
5.4.2. Electrochemical impedance spectroscopy (EIS) measurement.....	121
5.5. Results and discussion.....	122
5.5.1. Structure Study	122
5.5.1.1. XRD of the $\text{CuIn}_x\text{Cr}_y\text{Ga}_{1-x-y}\text{Se}_2$ precursor powder	122
5.5.1.2. XRD of $\text{CuIn}_x\text{Cr}_y\text{Ga}_{1-x-y}\text{Se}_2$ thin films	125
5.5.2. FESEM Analysis	128
5.5.2.1. FESEM Analysis of $\text{CuIn}_x\text{Cr}_y\text{Ga}_{1-x-y}\text{Se}_2$ nano-crystalline powders	128
5.5.2.2. FESEM Analysis of $\text{CuIn}_x\text{Cr}_y\text{Ga}_{1-x-y}\text{Se}_2$ thin films	131
5.5.3. HRTEM analysis	131
5.5.4. EDX analysis	133
5.5.5. Optical Properties and electric measurements	134
5.5.5.1. Optical Properties	134
5.5.5.2. Dielectric spectra analysis.....	137
5.6. Conclusions.....	143
References	144
 Chapter 6. CTZS thin films	
6.1. Objectives	147
6.2. Introduction	147
6.3. Experimental.....	148
6.3.1. Methods.....	148
6.3.2. Materials characterization.....	149
6.3.2.1. Photoelectrochemical and electrochemical analyses.....	149
6.4. Results and discussion.....	150
6.4.1. Structural properties.....	150
6.4.2. Optical Properties.....	152
6.4.3. Scanning Electron Microscopy.....	153
6.4.4. EDS Analysis.....	154
6.4.5. Photoelectrochemical measurements of CZTS.....	155

6.4.6. Conclusion.....	156
References.....	157
Chapter 7. Conclusion	
7.1. Conclusions and Future work.....	159
7.2 Future Research.....	162