

National Library of Canada Bibliothèque nationale du Canada

Acquisitions and Bibliographic Services Branch

395 Wellington Street Ottawa, Ontano K1A 0N4 Direction des acquisitions et des services bibliographiques

395, rue Wellington Ottawa (Ontario) K1A 0N4

Your hie - Votre reference

#### NOTICE

AVIS

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments. La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

## Canadä

## Development of Photovoltaic Cells on Electrodeposited CuInSe<sub>2</sub> Films

by Chunong Qiu

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

> Department of Electrical Engineering, McGill University, Montreal, Quebec.

> > Octorber 1995.



National Library of Canada

Acquisitions and Bibliographic Services Branch

Direction des acquisitions et des services bibliographiques

du Canada

Bibliothèque nationale

395 Wellington Street Ottawa, Ontario K1A 0N4 395, rue Wellington Ottawa (Ontario) K1A 0N4

Your Me Votre reférence

Our Me. Notre reterence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission. L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-612-12462-2



#### ABSTRACT

Using polycrystalline thin films of CuInSe<sub>2</sub> (thickness 1.5  $\mu$ m) prepared by an electrodeposition method, photovoltaic cells of the form ZnO/CdS/CuInSe<sub>2</sub> have been fabricated and studied. Before the cell fabrication, properties of the electrodeposited CuInSe<sub>2</sub> were first studied. Conditions for the preparation of high resistivity CdS thin films (thickness 360 Å) by a chemical bath deposition method were then established. This was achieved by varying the deposition temperature and amount of NH<sub>4</sub>OH in the solution. It was observed that the quality of CdS films deposited at a temperature of 60°C and an NH<sub>4</sub>OH concentration of 0.48 M was the best. Thermal stability of low resistivity, In- or Ar-doped, rf-sputtered ZnO thin films (thickness 1 $\mu$ m) was also studied. This was done by heat treating the ZnO films in air, O<sub>2</sub> and N<sub>2</sub> at temperature in a range from 200 to 350°C. It was observed that the amount of increase of resistivity at a given temperature decreased as the doping concentration was increased from 0.5 to 5.3 wt.%. For the films containing 2 wt.% In or Al, the resistivity increased as the treating temperature was increased from 200 to 350°C. For the samples treated at 200°C, the increase in resistivity was about 1 order of magnitude.

The high resistivity CdS and low resistivity ZnO thin films were then deposited on electrodeposited CuInSe<sub>2</sub> to fabricate cells of the form ZnO/CdS(high  $\rho$ )/CuInSe<sub>2</sub>. For comparison, cells of CdS(low  $\rho$ )/CdS(high  $\rho$ )/CuInSe<sub>2</sub> were also fabricated by evaporation of low resistivity CdS. The CuInSe<sub>2</sub> films used were treated either in vacuum or Ar. For those treated in vacuum, very poor properties were observed. The properties improved after a post fabrication heat treatment in air, however, the efficiency of these cells was below 2%. The low

conversion efficiency was due to the low open circuit voltage. From capacitance-voltage measurements, this was found to be due to a high acceptor concentration on the surface of the vacuum treated CuInSe<sub>2</sub> films (10<sup>17</sup> cm<sup>-3</sup>). For the cells fabricated on the CuInSe<sub>2</sub> films treated in Ar, photovoltaic effects were present before the air heat treatment. An efficiency of 6.8% was obtained for one of the best cells, sample J8-4 (with low resistivity CdS window). For cells with ZnO window, a conversion efficiency of 6.3% was obtained (cell O51). For these cells, the acceptor concentration in CuInSe<sub>2</sub> was 10<sup>16</sup> cm<sup>-3</sup>, which was one order of magnitude lower than that of CuInSe<sub>2</sub> films treated in vacuum.

The diffusion length of minority carriers (electrons) in the electrodeposited, p-type  $CuInSe_2$  was first measured using the photocurrent and capacitance methods. For the vacuum treated  $CuInSe_2$  films, the electron diffusion length was small (less than 0.1 µm). For those treated in Ar, values of the electron diffusion length were about 0.5 µm. These values are close to those reported for evaporated  $CuInSe_2$  thin films.

Some of the fabricated cells were also studied using an electron beam induced current (EBIC) method. From the EBIC experiments, the effective diffusion lengths of electrons with values greater than 1  $\mu$ m were obtained. Considering the surface recombination effect, the electron diffusion length of the electrodeposited CuInSe<sub>2</sub> was finally found to be 2.4  $\mu$ m. This large electron diffusion length was consistent with the high short circuit current density observed in I-V measurements of the electrodeposited CuInSe<sub>2</sub> cells.

#### RÉSUMÉ

Des couches minces polycristallines de CuInSe, (épaisseur de 1.5 µm) ont été préparées par électrodéposition. À partir de ces couches minces, des cellules photovoltaïques de la forme ZnO/CdS/CuInSe, ont été fabriquées et étudiées. Avant la fabrication des cellules, les propriétés des couches électrodéposées de CuInSe, ont été étudiées. Les conditions gérant la préparation de couches minces de CdS (épaisseur de 360 Å) à haute résistivité par déposition chimique en bain ont ensuite été établies. Ceci a été obtenu en variant la température de déposition et la quantité de NH,OH dans la solution. Il a été observé que la qualité des films de CdS déposés en utilisant une température de 60 °C et une concentration de NH,OH de 0.48 M était la meilleure. La stabilité thermique des couches minces de ZnO à basse résistivité, déposées par pulvérisation cathodique (rf) et dopées à l'indium ou à l'argon, a également été étudiée. Ceci a été fait par traitement thermique des films de ZnO dans l'air, l'oxygène et l'azote à des températures variant entre 200 et 350 °C. Il a été observé que la valeur de l'augmentation de la résistivité à une température donnée décroît lorsque la concentration des dopants augmente de 0.5 à 5.3 % molaire. Pour les films contenant 2 % molaire d'indium ou d'aluminium, la résistivité augmente lorsque la température du traitement thermique passe de 200 à 350 °C. Dans le cas des échantillons traités à 200 °C, l'augmentation de la résistivité était d'environ un ordre de grandeur.

Les couches minces de CdS à haute résistivité et de ZnO à basse résistivité ont ensuite été déposées sur une couche électrodéposée de CuínSe<sub>2</sub> afin de fabriquer des cellules de la forme ZnO/CdS(haute  $\rho$ )/CuInSe<sub>2</sub>. À titre comparatif, des cellules de CdS(basse  $\rho$ )/CdS(haute

p)/CuInSe<sub>2</sub> ont également été fabriquées par évaporation de CdS à basse résistivité. Certains films de CuInSe<sub>2</sub> utilisés ont été traités sous vide, les autres à l'argon. Dans le cas des films traités sous vide, les propriétés se sont avérées largement inférieures. Les propriétés ont été améliorées par un traitement thermique dans l'air. Toutefois, l'efficacité de ces cellules était de moins de 2 %. La faible efficacité de conversion etait causée par une basse tension en circuit ouvert. Des mesures de capacité-tension ont permis de découvrir que cette basse tension était causée par une concentration élevée d'accepteurs (10<sup>17</sup> cm<sup>-3</sup>) à la surface des films de CuInSe<sub>2</sub> traités à l'argon, les effets photovoltaïques étaient présents avant le traitement thermique dans l'air. Uue efficacité de CdS à basse résistivité). Dans le cas des cellules avec fenêtre de ZnO, une efficacité de conversion de 6.3 % a été obtenue pour l'échantillon O51. Pour ces cellules, la concentration des accepteurs dans le film de CuInSe<sub>2</sub> était de 10<sup>16</sup> cm<sup>-3</sup>, soit un ordre de grandeur plus bas que la concentration dans les films de CuInSe<sub>2</sub> traités sous vide.

La longueur de diffusion des transporteurs minoritaires (électrons) dans le film électrodéposé de  $CuInSe_2$  de type P a premièrement été mesurée en utilisant les méthodes de photocourant et de capacité. Dans le cas des films de  $CuInSe_2$  traités sous vide, la longueur de diffusion des électrons était courte (moins de 0.1 µm). Dans le cas des films traités à l'argon, la longueur de diffusion était d'environ 0.5 µm. Ces valeurs sont près de celles publiées pour les couches minces de CuInSe<sub>2</sub> déposées par évaporation.

Quelques unes des cellules fabriquées ont aussi été étudiées en utilisant la méthode du courant induit par faisceau d'électron (*electron beam induced current* ou *EBIC*). Par cette méthode, des longueurs de diffusion des électrons de plus de 1  $\mu$ m ont été obtenues. Considérant l'effet de recombinaison en surface, la longueur de diffusion des électrons des films de CuInSe<sub>2</sub> électrodéposés était finalement de 2.4  $\mu$ m. Cette valeur élevée de longueur de diffusion des électrons corrobore les hautes densités de courants de courts-circuits observées lors des mesures des caractéristiques de courant-tension des cellules électrodéposées de CuInSe<sub>2</sub>.

#### ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to his supervisor, Dr. Shih, for his guidance and invaluable assistance throughout this study. The author would like to aknowledge Ms. Christine Alain for translating the abstract into French. Special thanks are due Dr. Champness for his generosity in providing some of the equipment needed to complete this work. Special thanks are due to his colleagues in the laboratory, especially to Dr. C.X. Qiu, for their numerous suggestions and assistance. The author would also like to thank the technicians in the workshop for their technical assistance throughout this work.

Acknowledgements are also due to The Natural Sciences and Engineering Reserch Concil of Canada for the financial support.

The author would like to express his gratitude to his parents, wife, brothers and sisters for their love, encouragement and support throughout this study.

## TABLE OF CONTENT

÷

| ABSTRACT  |
|---|
| RÉSUMÉ iii  |
| ACKNOWLEDGEMENTS vi   |
| TABLE OF CONTENT vii  |
| CHAPTER 1 INTRODUCTION 1  |
| CHAPTER 2 LITERATURE SURVEY   |
| CHAPTER 3 THEORY OF SOLAR CELLS 14   3.1. INTRODUCTION 14   3.2. ENERGY BAN DIAGRAM AND STATIC CHARACTERISTICS 14   3.2.1 Homojunction 15   3.2.2 Heterojunction 17   3.3. CURRENT TRANSPORT MECHANISM OF A JUNCTION 18   3.3.1 Ideal Junction 18   3.3.2 Deviation From the Ideal Junction 19   3.4. EFFECTS OF ILLUMINATION ON JUNCTIONS 20   3.5. ADVANTAGES OF HETEROJUNCTION CELLS 22   3.6. CURRENT TRANSPORT MECHANISMS OF A PRACTICAL 23   HETEROJUNCTION SOLAR CELL 23   3.7. CONCLUSIONS 29 |
| CHAPTER 4CHARACTERIZATION OF THE MATERIALS AND DEVICES394.1. INTRODUCTION394.2. SCANNING ELECTRON MICROSCOPY394.3. MEASUREMENT OF THICKNESS FILMS404.4. X-RAY DIFFRACTION434.5. ELECTRICAL RESISTIVITY444.6. OPTICAL TRANSMISSION444.7. CURRENT-VOLTAGE CHARACTERISTICS454.8. CAPACITANCE-VOLTAGE CHARACTERISTICS454.9. SPECTRAL RESPONSE474.10. CONCLUSIONS48  |
| CHAPTER 5 PREPARATION OF CdS FILMS BY CHEMICAL BATH DEPOSITION   AND CdS/Si DEVICES 59   5.1. INTRODUCTION 59   5.2. CHEMICAL BATH DEPOSITION OF CdS 60   |

,

| 5.2.1. Principles of the Chemical Bath Reaction                      | 60   |
|--|------|
| 5.2.2. Preparation of a Deposition Solution                          | 61   |
| 5.2.3. Experimental Technique  | 61   |
| 5.3. FABRICATIONS OF CdS/Si HETEROJUNCTIONS                          | 62   |
| 5.3.1. Si Substrate Preparation                                      | 62   |
| 5.3.2. Contact Formation   | 62   |
| 5.4. RESULTS OF THE CdS FILM DEPOSITION                              | 62   |
| 5.5. RESULTS FOR THEE CdS/Si JUNCTIONS                               | 64   |
| 5.5.1. I-V Characteristics of the CdS/Si Cells                       | 64   |
| 5.5.2. Electrical Contacts to High Resistivity CdS                   | 66   |
| 5.5.3. Effects of Heat Treatment on the CdS/Si Junctions             | 67   |
| 5.5.4. Optical Transmission of CdS Films and Spectral Response of Cd | S/Si |
| Junctions  | 68   |
| 5.6. CONCLUSIONS   | 69   |
|  |      |
| CHAPTER 6 LOW RESISTIVITY AND TRANSPARENT ZnO THIN FILMS             | 80   |
| 6.1. INTRODUCTION  | 80   |
| 6.2. ZnO FILM DEPOSITION   | 81   |
| 6.2.1. Principles of Sputtering                                      | 81   |
| 6.2.2. Sputtering System   | 82   |
| 6.2.3. Target and Substrate Preparation                              | 83   |
| 6.2.4. Deposition Procedure  | 83   |
| 6.3. PROPERTIES OF AS-DEPOSITED ZnO FILMS                            | 84   |
| 6.3.1. Morphological and Thickness of ZnO Films                      | 84   |
| 6.3.2. Crystalline Structure of ZnO Films                            | 84   |
| 6.3.3. Optical Transmission  | 85   |
| 6.3.4. Electrical Resistivity  | 85   |
| 6.4. EFFECTS OF HEAT TREATMENT ON ZnO FILMS                          | 86   |
| 6.4.1. Air Heat Treatment  | 87   |
| 6.4.2. Treatment in Different Gases                                  | 88   |
| 6.5. CONCLUSIONS   | 89   |
|  |      |
| CHAPTER 7 FABRICATION OF THE SOLAR CELLS                             | 101  |
| 7.1. INTRODUCTION  | 101  |
| 7.2. DEPOSITION OF $CuInSe_2$  | 101  |
| 7.2.1. Substrate Preparation   | 101  |
| 7.2.2. Deposition Procedure  | 102  |
| 7.3. Heat treatment of the CuInSe <sub>2</sub>                       | 102  |
| 7.3.1. Treatment in Vacuum   | 103  |
| 7.3.2. Treatment in Inert Gas  | 103  |
| 7.4. CHEMICAL BATH DEPOSITION OF CdS                                 | 104  |
| 7.5. EVAPORATION OF In-DOPED CdS                                     | 104  |
| 7.6. SPUTTERING OF Al-DOPED ZnO FILMS                                | 106  |
| 7.7. AI CONTACT EVAPORATION  | 106  |
|  |      |



.

| 7.8. PATTERNING THE DEVICES  | 107 |
|--|-----|
| 7.8.1. Patterning of the ZnO window  | 107 |
| 7.8.2. Patterning of the Al Contact Area Using a Lift-off Method                         | 108 |
| CHAPTER 8 RESULT OF PHOTOVOLTAIC CELLS ON CuinSe, THIN FILMS                             | 116 |
| 8.1. INTRODUCTION  | 116 |
| 8.2. SOME PROPERTIES OF ELECTRODEPOSITED CuInSe_ FILMS                                   | 117 |
| 8.2.1. Morphological Characteristics of the CuInSe <sub>2</sub>                          | 117 |
| 8.2.2. Crystalline Orientation and Conducting type                                       | 118 |
| 8.2.3. Refractive Index of CuInSe <sub>2</sub> Films                                     | 118 |
| 8.2.4. Absorption Coefficient of CuInSe <sub>2</sub>                                     | 120 |
| 8.2.4.1. Preparation for Absorption Measurements (121)                                   |     |
| 8.2.4.2. Experimental Results (121)  |     |
| 8.3. EFFECT OF HEAT TREATMENT OF CulnSe, ON THE CELLS                                    | 123 |
| 8.3.1. Al/CdS/CuInSe <sub>2</sub> Schottky Junction                                      | 123 |
| 8.3.2. CdS/CuInSe <sub>2</sub> Cells Fabricated on CuInSe <sub>2</sub> Treated in Vacuum | 124 |
| 8.3.3. CdS/CuInSe, Cells Fabricated on CuInSe, Treated in Ar                             | 126 |
| 8.4. Al/CdS/CuInSe, HETEROJUNCTION   | 127 |
| 8.5. Al/ZnO/CdS/CuInSe, HETEROJUNCTION   | 129 |
| 8.6. CONCLUSIONS   | 130 |
| CHAPTER 9 DIFFUSION LENGTH OF ELECTRONS IN CuInSe_                                       | 159 |
| 9.1. INTRODUCTION  | 159 |
| 9.2. MEASUREMENT METHODS   | 160 |
| 9.2.1. Photocurrent-Capacitance (PC) Method  | 160 |
| 9.2.2. Differential Photocurrent (DPC) Method  | 162 |
| 9.3. EXPERIMENTAL SETUP FOR THE MEASUREMENTS   | 164 |
| 9.3.1. Setup for Photocurrent Measurements   | 164 |
| 9.3.2. Setup for Capacitance Measurements  | 165 |
| 9.4. DETERMINATION OF DIFFUSION LENGTH OF CuInSe_  | 165 |
| 9.4.1. Photocurrent-Capacitance Method [PC]  | 166 |
| 9.4.2. Differential Photocurrent Method [DPC]  | 166 |
| 9.5. RESULTS AND DISCUSSION  | 168 |
| 9.6. CONCLUSIONS   | 170 |
| CHAPTER 10 STUDY OF CuinSe2-BASED SOLAR CELLS BY ELECTRON BEAM                           |     |
| INDUCED CURRENT MEASUREMENTS   | 181 |
| 10.1. INTRODUCTION   | 181 |
| 10.2. PRINCIPLE OF THE EBIC METHOD   | 182 |
| 10.2.1. Backscattering of Incident Electrons   | 183 |
| 10.2.2. Energy Dissipation   | 184 |
| 10.3.3. Generation of Electron-Hole Pairs  | 185 |
| 10.2.4. Determination of Diffusion Length From EBIC Measurements                         | 186 |
| 10.3. DETAILS OF THE MEASUREMENTS  | 188 |

•

٠

-

| 10.4. RESULTS AND DISCUSSION                               | 189 |
|--|-----|
| 10.5. CONCLUSIONS  | 192 |
| CHAPTER 11 CONCLUSIONS                                     | 202 |
| 11.1. CdS THIN FILMS PREPARED BY THE CBD METHOD            | 202 |
| 11.2. LOW RESISTIVITY ZNO THIN FILMS BY RF SPUTTERING      | 203 |
| 11.3. ZnO/CdS/CuInSe, PHOTOVOLTAIC CELLS                   | 204 |
| 11.4. MINORITY CARRIER DIFFUSION LENGTH IN CulnSe.         | 205 |
| Appendix 1 Photolithographic Process for Patterning of ZnO | 208 |
| REFERENCES   | 209 |

.

•

2

2

•

.

#### CHAPTER 1 INTRODUCTION

The total amount of conventional non-renewable energy sources on earth, such as coal and petroleum is limited. Since most of these conventional sources are non-renewable, the steady supply of energy to meet long term world need is one of the most important and challenging issues in our society. That stocks of readily available non-renewable energy resources are being exhausted has become apparent with the energy crisis of the 1970's. The energy crisis ended global complacency towards earth's unlimited energy supplies and was the impetus for research on novel sources. In order to avoid the impact of depleting non-renewable energy sources on cur future living conditions, developing alternative renewable energy sources is imperative.

Renewable energy sources include falling water, wind, sunlight, ocean current and wave. Of these, sunlight or solar energy is the most attractive because although not evenly distributed around the earth at any given time, solar energy reaches everywhere of the earth's surface. The amount of solar energy falling on the surface of the earth is approximately  $7.45 \times 10^{17}$  kWh annually. This amount is four orders of magnitude higher than the world energy consumption.

Solar energy may be utilized in photothermal, photochemical, photoelectrochemical, photobiochemical and photovoltaic forms. The cleanest, most direct and efficient mode is the conversion of sunlight into the electrical power through photovoltaic processes. In such processes, Photovoltaic devices or solar cells are used to convert sunlight directly into electricity. Compared with other energy technologies, the photovoltaic technology has several distinct advantages. A photovoltaic system does not require moving parts, does not require extensive maintenance and can be physically located near the load.

At the present, the main applications of solar cells are limited to space vehicles, remote area residential and small electronic components. Most of the cells used in these applications are fabricated on single crystalline Si and GaAs substrates.

The cells fabricated on monocrystalline Si and GaAs are too expensive for large scale terrestrial photovoltaic applications due to the amounts of energy and materials required for the fabrication. One of the logical ways to reduce the cost is to develop thin film solar cells. Compared with monocrystalline cells, thin film cells have the following advantages. Thin films can be fabricated on large substrates, hence, the packaging density can be maximized. In addition, low cost processes such as spray pyrolysis, chemical deposition and electrodeposition can be used.

Theoretically, it is possible to fabricate thin film solar cells with a high energy conversion efficiency with various combinations of materials. However, considering the basic material properties such as optical absorption coefficient and energy band gap, the choice of materials is limited. At the present, the most important semiconductors useful for photovoltaic solar cells are amorphous Si, CdTe and CuInSe<sub>2</sub>.

Among these three materials, the semiconductor  $CuInSe_2$  has received the most attention in recent years.  $CuInSe_2$  is a direct gap material with a band gap of 1.04 [1.1]. The band gap of 1.04 eV is near the optimum value for high efficiency solar cell applications. More importantly, the optical absorption coefficient of  $CuInSe_2$  is the highest ever reported among any known semiconductors ( $6 \times 10^5$  cm<sup>-1</sup>). With the high absorption coefficient, most of the light in the solar spectrum can be absorbed by a film with a thickness less than 1  $\mu$ m. Thus, the amount of material required to fabricate CuInSe<sub>2</sub>-based cells is small. In addition to the above properties, the lattice

mismatch between  $CuInSe_2$  and large band gap window materials CdS or CdZnS is small. Therefore, the density of interfacial states in a cell based on  $CuInSe_2$  can be minimized [1.2]. Finally, no interfacial spike is expected in the conduction band since the electron affinities of CuInSe<sub>2</sub>, CdS and CdZnS are similar [1.3][1.4].

Table 1.1 lists some of the properties of the three semiconductors ZnO, CdS, and CuInSe<sub>2</sub>. A unit cell of CuInSe<sub>2</sub> is shown in Figure 1.1 and unit cells of CdS and ZnO are shown in Figure 1.2. For the formation of thin film solar cells, the preferred lattice plane is (112) for CuInSe<sub>2</sub>, and (002) for CdS and ZnO (see Figure 1.3). The lattice mismatch between (112) CuInSe<sub>2</sub> and (002) CdS is about 0.6%.

Because of the above-described advantages, the semiconductor CuInSe<sub>2</sub> has been the main absorber material of photovoltaic research projects in our laboratory. In addition to the research work on monocrystalline CuInSe<sub>2</sub>, an one-step electrodeposition method has been developed in our laboratory for the deposition of CuInSe<sub>2</sub> films [1.5-1.8]. This method is not only simple but the material utilization rate is high. Furthermore, the energy consumption is low and the deposition system can be easily scaled up. Hence, with further improvement, the process developed is ideal for future large scale production of CuInSe<sub>2</sub> thin film solar cells.

Research work to be described in this thesis thus will concentrate on  $CuInSe_2$  films with the following objectives: (1) to study properties of the electrodeposited  $CuInSe_2$  films before and after a heat treatment, (2) to determine if the electrodeposited  $CuInSe_2$  thin films are suitable for fabrication of photovoltaic cells with ZnO as the window, and (3) to determine the diffusion length of minority carriers in  $CuInSe_2$ .

The arrangement of the thesis is as follows. A brief survey of the development of CuInSe<sub>2</sub> thin film solar cells is first given in Chapter 2. Chapter 3 describes the principles of operation of a solar cell. Chapter 4 describes some of the characterization techniques used to study the semiconductor materials and solar cells. In Chapter 5, a chemical bath deposition process for CdS thin films and some of the characteristics of n-CdS/p-Si junctions are described. Chapter 6 presents the properties of the doped ZnO films deposited on glass substrates. In Chapter 7, the detailed processes of fabricating ZnO/CdS/CuInSe<sub>2</sub> solar cells are presented. In Chapter 8, results on cell characterization are presented. In Chapter 9 experiments on the minority carrier diffusion lengths by the capacitance methods are described. Chapter 10 presents the results on the study of CuInSe<sub>2</sub>-based solar cells by an electron beam induced current method. Finally, in Chapter 11 conclusions for the present CuInSe<sub>2</sub> work are given.

| Material            | E <sub>g</sub> (eV) | χ (eV) | Туре | Structure    | Lattice<br>constant(Å) | ê <sub>r</sub> | Melting<br>point<br>(°C) | μ <sub>e</sub> μ <sub>h</sub><br>cm²/V-s |
|---------------------|---------------------|--------|------|--------------|------------------------|----------------|--------------------------|--|
| ZnO                 | 3.3                 | 4.2    | n    | Wurtzite     | a=3.25<br>c=5.21       | 9              | 1975                     | 20,                                      |
| CdS                 | 2.4                 | 4.5    | n    | Wurtzite     | a=3.82<br>c=6.26       | 8              | 1750                     | 400, 15                                  |
| CuInSe <sub>2</sub> | 1.04                | 4.15   | n, p | Chalcopyrite | a=5.78<br>c=11.62      | 10             | 990                      | 320, 10                                  |

Table 1.1 Properties of three semiconductor materials for photovoltaic cells.



Figure 1.1 A unit cell of  $CuInSe_2$  with a chalcopyrite structure.



Figure 1.2 A unit cell for hexagonal CdS or ZnO.



Figure 1.3 (a) Atomic structure on the (112)-plane of chalcopyrite CuInSe<sub>2</sub>, (b) the (002)-plane of hexagonal CdS, (c) the (002)-plane of hexagonal ZnO. The lattice mismatch between the (112)-plane CuInSe<sub>2</sub> and (002)-plane CdS is the smallest (0.6%). The lattice mismatch between the (112)-plane CuInSe<sub>2</sub> and the (002)-plane ZnO is large (11.4%).

#### CHAPTER 2 LITERATURE SURVEY

In this chapter, a brief survey of research work done in the area related to this thesis is given. It consists of a survey on the past work on CuInSe<sub>2</sub>-based solar cells first with CdS and then with ZnO as the window. A brief survey of work on the development of low cost methods for CuInSe<sub>2</sub> films is also given.

Demonstration photovoltaic solar cells of  $CuInSe_2$  were first reported on monocrystalline substrates [2.1][2.2][2.3]. These cells were fabricated by depositing an n-CdS window on p- $CuInSe_2$  single crystals. A cell with  $V_{oc}$  of 0.5 V,  $I_{sc}$  of 38 mA/cm<sup>2</sup>, F.F. of 0.6 and an efficiency of 12% has been obtained by Shay et. al in 1975 [2.2]. The early work on single crystalline cells gave a strong motivation for further development of CuInSe<sub>2</sub> thin film solar cells.

Almost at the same time when high efficiency monocrystalline solar cell was reported, experiments on polycrystalline thin films of CuInSe<sub>2</sub> were started. The initial work on CuInSe<sub>2</sub> thin films had been reported by Elliott [2.4] and Kazmerski [2.5]. The first generation thin film cells of the form n-CdS/p-CuInSe<sub>2</sub> were fabricated by evaporating CdS onto polycrystalline CuInSe<sub>2</sub> films prepared by vacuum evaporation [2.6]. The highest solar to electrical energy conversion efficiency of these cells was 5.7%. Although the efficiency of the first generation thin film cells was low compared with those fabricated on monocrystalline CuInSe<sub>2</sub>, it did demonstrate that the thin film cell concept was feasible for the second generation cell development (with efficiency more than 10%).

Within 15 years after the report of successful deposition of CuInSe<sub>2</sub> thin films, CuInSe<sub>2</sub> cells with high conversion efficiencies were reported by several workers. These cells used

vacuum evaporated CdS or CdZnS thin films as the window layers. In these studies, different deposition methods have been used to deposit polycrystalline CuInSe<sub>2</sub> thin films. The methods include thermal evaporation, selenization of metal layers (Cu/In), sputtering and electrodeposition [2.7-2.12]. The devices were formed with either single- or double-layer of CuInSe<sub>2</sub> thin films. The purpose of the double-layer CuInSe<sub>2</sub> is to control the concentrational depth profile in order to increase the open circuit voltage. The energy conversion efficiency for the best second generation thin film cells on CuInSe<sub>2</sub> with CdS or CdZnS as the window was 12.4% [2.7].

The efficiency of the second generation CdS/CuInSe<sub>2</sub> cells is limited by the relatively small energy gap value of the CdS window. The window semiconductor CdS, with an energy gap of 2.4 eV, absorbs those photons in the solar spectrum with energies higher than this value. Hence, the high energy photons will not reach the absorber layer (CuInSe<sub>2</sub>) and contribute to carrier generation. The replacement of CdS with higher energy band gap CdZnS has been limited by the lack of effective dopants for CdZnS. In fact, it is very difficult to deposit low resistivity and transparent CdZnS film with Zn content higher than 20%. Since the energy gap of Cd<sub>0.8</sub>Zn<sub>0.2</sub>S is about 2.48 eV, only a small increase in transmission over that of CdS is expected for this material.

The semiconductor ZnO ( $E_g$ =3.3 eV), is a very attractive window material for solar cell applications because of its excellent optical and electrical properties [2.13][2.14]. In earlier work, low resistivity ZnO thin films were obtained by controlling ratio of Zn/O. However, thermal stability of low resistivity ZnO films obtained by controlling the Zn/O ratio was very poor. If the thermal stability can be improved, ZnO would be an ideal window material for many optoelectronic devices. Figure 2.1 shows the solar spectrum under AM1.5 condition. The absorption edges of the semiconductors CdS,  $Cd_{0.5}Zn_{0.2}S$ , ZnO and CuInSe<sub>2</sub> are labelled on the diagram.

It is seen that by replacing the traditional small band gap window CdS by the large band gap ZnO, the total solar light which can reach the cell will increase by 10%. This will cause an increase not only in the short circuit current density but also the efficiency. In a more recent work, ZnO was used to replace the traditional CdS and CdZnS windows in thin film cell fabrication [2.15]. Unfortunately, the interface properties of the ZnO/CuInSe<sub>2</sub> cells were very poor due to the large lattice mismatch between ZnO and CuInSe<sub>2</sub> (the lattice mismatch is 11.4%). When the lattice mismatch is large, the density of interface states in the junction will be large. In a cell with a large interface density, recombination dominates the current transport mechanism and the conversion efficiency is low.

In order to reduce the interfacial state density of the ZnO/CuInSe<sub>2</sub> cells, a thin layer of CdS or CdZnS can be deposited on CuInSe<sub>2</sub> prior to the deposition of ZnO to form the third generation cells. The third generation solar cells of the form ZnO/CdS(CdZnS)/CuInSe<sub>2</sub> have been fabricated by vacuum deposition with a relatively good performance [2.16]. However, the thickness of the CdS or CdZnS layer has to be small in order to minimize the absorption.

Extensive research work on cells with the ZnO/CdS/CuInSe<sub>2</sub> structure has been carried out in recent years by the vacuum methods. Solar cells with an efficiency as high as 15.4% were reported [2.16-2.19]. The efficiency of 15.4% is the highest value reported so far for CuInSe<sub>2</sub> thin film cells prepared by the vacuum methods. For the best cell, the short circuit current density was 41.2 mA/cm<sup>2</sup>, open circuit voltage was 0.515 V and fill factor was 0.726 [2.19].

To increase further the energy conversion efficiency of the CuInSe<sub>2</sub> thin film cells, it is

required to improve the properties of the absorber layer. One of the methods is to increase the energy gap. This can be achieved by adding a small amount of Ga to the ternary compound, CuInSe<sub>2</sub>, to form a quaternary compound, CuInGaSe<sub>2</sub>. The quaternary compound, CuInGaSe<sub>2</sub>, has an energy gap which is greater than that of CuInSe<sub>2</sub>. Cells fabricated with this quaternary compound have been shown to have a higher open circuit voltage [2.20-2.22]. Although the short circuit current density was reduced some what, a ZnO/CdS/CuInGaSe<sub>2</sub> cell with a conversion efficiency of 16.9% has been successfully fabricated [2.18]. For this cell, V<sub>oc</sub> was 0.641 V, I<sub>sc</sub> was 35.8 mA/cm<sup>2</sup> and FF was 0.735.

From the above brief literature survey, it is clear that high efficiency thin film solar cells can be fabricated on vacuum deposited  $CuInSe_2$  or  $CuInGaSe_2$ . Since the fabrication cost of cells by the vacuum methods is too high for large scale terrestrial photovoltaic applications, it is required to develop alternate low cost methods for the thin film deposition and cell fabrication.

Useful alternate methods for thin film solar cell fabrication should satisfy all of the following conditions. These conditions include: (1) low energy consumption, (2) high material utilization rate, (3) short processing time and (4) good reproducibility. Several non-vacuum methods, such as spray pyrolysis and electrodeposition, have been studied in the past decade for the fabrication of CuInSe<sub>2</sub>-based photovoltaic solar cells.

Spray pyrolysis is a low cost process which has been used for the deposition of several semiconductor thin films including ITO. This method has also been used for the deposition of CuInSe<sub>2</sub> thin films [2.23]. However, the electronic properties of CuInSe<sub>2</sub> prepared by spray pyrolysis were poor and the conversion efficiency of cells fabricated was less than 2%.

Electrodeposition is another low cost method which has been used extensively in industry

for the deposition of metal films. Using a sequential electrodeposition method, Kapur and coworkers [2.24] have deposited metallic In and Cu layers onto Mo substrates. Thin films of CuInSe<sub>2</sub> were formed by a post-deposition selenization for cell fabrication. The post-deposition selenization process used by Kapur and coworkers involved the toxic H<sub>2</sub>Se gas. Furthermore, the selenization was carried out at a relatively high temperature.

In our laboratory, a novel one-step electrodeposition method has been successfully developed for the deposition of CuInSe<sub>2</sub> thin films [1.4][1.5]. In this method, polycrystalline thin films of CuInSe<sub>2</sub> are deposited on conduction substrates such as Mo or Mo-coated glass substrates, without the need of the selenization step. The deposition rate is high and does not require expensive equipment. Hence, this method can meet all of the requirements for future terrestrial photovoltaic solar cell fabrication. In the present work, special efforts will be made to study devices fabricated on CuInSe<sub>2</sub> films and to identify the possible limitations associated with this electrodeposition method.



Figure 2.1 Solar spectrum under AM1.5 conditions. The absorption edges of CdS, Cd<sub>0.8</sub>Zn<sub>0.2</sub>S, ZnO, CuInSe<sub>2</sub> are indicated in this figure.

#### CHAPTER 3 THEORY OF SOLAR CELLS

#### 3.1 INTRODUCTION

A solar cell is a device that converts sunlight directly to electricity without moving parts. A solar cell consists of three functional elements, namely an absorber, a junction and a collector. The purpose of the junction is to separate minority carriers generated in the absorber and sweep them to the collector. Once the minority carriers generated in the absorber cross the junction, they become majority carriers. The collector distributes the majority carriers to external loads in the form of current.

• Different types of junctions can be used for solar cells, such as (1) a p-n homojunction, (2) a p-n heterojunction, (3) a Schottky junction, and (4) a metal-insulator-semiconductor junction. Among them, the homojunction is the simplest and the theory developed for it can be used to understand operation of other devices such as heterojunctions and Schottky junctions. Hence, the characteristics of a homojunction solar cell are presented first in this chapter. Because the solar cells to be studied in this work have a heterojunction structure, the characteristics of a heterojunction cell are also presented. The theory of p-n junction solar cells is very well developed. Detailed treatments can be found in various references [3.1-3.3].

#### 3.2 ENERGY BAND DIAGRAM AND STATIC CHARACTERISTICS

In this section, the energy band diagram of a homojunction is first presented. Characteristics of the homojunction in open circuit condition are then discussed. The properties of a heterojunction are finally described.

#### 3.2.1 Homojunction

A homojunction is formed in a semiconductor piece with two regions having different conductivity types, namely, n- and p-types. For simplicity, it is assumed that the acceptor impurity concentration in one region,  $N_A$ , is constant. At the interface, the concentration changes abruptly to another value,  $N_D$ , for donors. This type of junction is called an abrupt anisotropic homojunction.

Figure 3.1a shows a schematic diagram of an abrupt p-n junction. The device is divided into three regions, the neutral p region, the neutral n region and the depletion region. The space charge distribution of the p-n junction in thermal equilibrium is shown in Figure 3.1b. The electric field in the junction is plotted against distance, x, in Figure 3.1c. The maximum electric field occurs at the metallurgical junction, x=0. The potential variation with distance in the junction is shown in Figure 3.1d. Here, the potential  $V_d$  is called the built-in potential of the junction and is related to the device parameters by the following expression:

$$qV_{d} = E_{g} - (qV_{n} + qV_{p}) = kT \ln(\frac{n_{no}p_{po}}{n_{i}^{2}}) - kT \ln(\frac{N_{A}N_{D}}{n_{i}^{2}})$$
(3.1)

Where  $N_A$  and  $N_D$  are acceptor and donor concentration in p and n region of the junction, respectively. The band diagram of the p-n junction is shown in Figure 3.1e.

The maximum electric field  $(E_m)$  and built-in potential  $(V_d)$  can be expressed as:

$$E_m = (qN_d x_n) / \epsilon_s \tag{3.2}$$

$$V_d = \frac{1}{2}E_m(x_n + x_p)$$
(3.3)

Here  $\varepsilon_i$  is the dielectric constant of the semiconductor. The depletion width, w, can be expressed

$$w = \sqrt{\frac{2\epsilon_s V_d (N_A + N_D)}{q N_A N_D}}$$
(3.4)

For a one-sided abrupt junction, the above expression is simplified to:

$$w = \sqrt{\frac{2\epsilon_s V_d}{q N_B}} \tag{3.5}$$

where  $N_B = N_A$  when  $N_D \gg N_A$  and  $N_B = N_D$ , when  $N_D \ll N_A$ .

When a junction is biased to a voltage, V, the total electrostatic potential difference across the junction is  $V_d$ -V. The band diagram of a homojunction under forward and reverse bias is shown in Figure 3.2. For the one-sided junction with the bias voltage applied, the depletion width is:

$$w = \sqrt{\frac{2\epsilon_s (V_d - V)}{qN_B}}$$
(3.6)

The depletion-layer capacitance, C, of the junction varies with the depletion width, w (or bias voltage, V). Therefore, the capacitance per unit area, C, can be expressed as a function of bias voltage:

$$C = \frac{dQ_C}{dV} = \frac{\epsilon_s}{w} = \sqrt{\frac{q\epsilon_s N_B}{2(V_d - V)}}$$
(3.7)

and

$$\frac{dC^{-2}}{dV} = \frac{2}{q\epsilon_s N_B} \tag{3.8}$$

## From Equation (3.8), it is expected that a plot of $C^{-2}$ versus V would yield a straight line.

The slope of the line would give the doping concentration, N<sub>B</sub>.

#### 3.2.2 Heterojunction

A junction formed between two different semiconductors (1 and 2) is called a heterojunction. Figure 3.3 shows the energy band diagram for a heterojunction. The built-in potential,  $V_d$ , is:

$$V_d = \phi_p - \phi_n = V_{dp} + V_{dn} \tag{3.9}$$

Here,  $\phi_p$  and  $\phi_n$  are the work functions of the semiconductors p and n, and  $V_{dp}$  and  $V_{dn}$  are the built-in potentials in the two semiconductors.  $\chi_n$  and  $\chi_p$  are the electron affinity in the two semiconductors. The difference in the energy of the conduction edges in the two semiconductor is denoted by  $\Delta E_c$  and that of the valence band edges by  $\Delta E_v$ . When one side of a heterojunction is much more heavily doped than the other side, the junction is an one-sided heterojunction. For solar cell applications, a structure consisting of a window layer and an absorber layer is often employed. Normally, the window layer is a highly transparent and heavily doped semiconductor with a large band gap, and the absorber is a lightly doped layer with a small band gap. The ideal I-V characteristics that describes an one-sided homojunction can be used to describe an one-sided heterojunction.

To form a good quality heterojunction, the following conditions must be satisfied. (1) The difference of lattice constants of the window and the absorber materials should be small in order to minimize the density of interface states, (2) the difference of electron affinities of the two materials should be small to minimize energy band discontinuities, and (3) the thermal expansion coefficients of the two materials should be close. The last requirement is needed in order to

minimize defects which can form during fabrication and post fabrication heat treatment. The model of an ideal heterojunction also assumes an abrupt junction that is free of dipoles and localized interface states.

In practical junctions, because of a finite lattice mismatch and an elemental inter diffusion effect, localized band-gap states can form at the interface (called interface states). Such states can store electrical charges and produce an interfacial unipole. Interface states are very important in solar cells because they act as recombination centers or trapping sites for generated electrons and holes. There are two types of localized states, acceptor state and donor state. The acceptor state is neutral when it is vacant and is negative when occupied by an electron (ionized). The donor state is neutral when occupied by an electron and positive when it is vacant.

#### 3.3 CURRENT TRANSPORT MECHANISMS OF A JUNCTION

In this section, the current transport mechanisms of ideal homojunctions and heterojunctions are presented first. Deviations of practical junctions from an ideal one are then discussed.

#### 3.3.1 Ideal Junction

Several assumptions are made to derive the current-voltage characteristics of an ideal p-n junction: (1) the junction is abrupt, (2) Boltzman relations are valid, (3) low-injection conditions are valid, and (4) no generation and recombination of carriers in the depletion region.

When a junction is biased, the band bending and carrier distribution are changed. For the ideal junction, the current is determined by diffusion of minority carriers. The total current

density for a biased p-n junction is:

$$J = J_o \left[ e^{\frac{qV}{kT}} - 1 \right]$$
(3.10)

where q, k, and T are the electron charge, Boltzmann constant and absolute temperature respectively.  $J_0 = qD_pp_{n0}/L_p + qD_nn_{p0}/L_n$  is the reverse saturation current density,  $D_p$  and  $D_n$  are the diffusion coefficients for electrons and holes,  $p_{n0}$  and  $n_{p0}$  are the equilibrium minority carrier concentrations, and  $L_p$  and  $L_n$  are the minority carrier diffusion lengths.

Figure 3.4 shows an I-V curve of an ideal p-n junction under dark condition. When a forward voltage, V, (V\*kT/q) is applied to the junction, the current density varies exponentially with the applied voltage. The reverse current density will reach J<sub>s</sub> when a reverse voltage, V « -kT/q is applied to the junction.

#### 3.3.2 Deviations From the Ideal Diode

For a practical junction under reverse bias, the magnitude of the current will be greater than I, because of the generation of carriers in the depletion region. When the magnitude of the reverse bias voltage continues to increase, junction breakdown eventually occurs.

The deviations of the practical junction from the ideal one under forward bias are due to the following factors: (a) recombination in the depletion region, (b) high level injection and (c) resistance associated with the bulk region and metal semiconductor contact. Figure 3.5 shows deviations of a practical junction from an ideal one under bias.

When a practical junction is forward biased, the current-voltage relation can be simplified

$$J_F = J_o \exp\left(\frac{qV}{nkT}\right) \tag{3.11}$$

where n is the ideality factor and is a measure of the deviations from an ideal junction. The ideality factor n is equal to 1 when diffusion current dominates and equal to 2 when recombination current dominates. When both the mechanisms are comparable, n lies between 1 and 2.

#### 3.4 EFFECTS OF ILLUMINATION ON JUNCTIONS

When an incident light reaches the absorber semiconductor, electron and hole pairs are generated. The generated minority carriers in the neutral regions (electrons in p-semiconductor or holes in the n-semiconductor) will diffuse towards the depletion layer. The carriers generated inside the depletion region and the carriers diffused into the depletion region will be separated by the strong electric field. The holes will be swept into the p-side and the electrons will be swept into the n-side. Figure 3.6 shows the generation, diffusion and separation processes in a homojunction under illumination. Here, the electrons and holes generated by the incident photons inside the depletion region (1 and 2) are separated. The electrons are swept towards the right-hand side and the holes are swept towards the left-hand side. It is noted that the minority carriers generated in the neutral regions (3 and 4) within diffusion lengths, can diffuse into the depletion region and be separated by the electric field in the depletion region. It is thus clear that the performance of a solar cell is determined by the diffusion of charge carriers generated in the absorber. In the present work, special efforts will be made to determine the value of electron

diffusion length in CuInSe<sub>2</sub> and see how this parameter is related to the cell performance.

The effect of illumination can be seen from the current voltage (I-V) characteristics of the junction. Figure 3.7a shows an equivalent circuit for a solar cell under illumination and Figure 3.7b shows the I-V characteristics of this cell.

The I-V relationship for the cell under illumination can be written as:

$$I - \frac{V - IR_s}{R_{sh}} = I_s \{\exp[q(V - IR_s) / nkT] - 1\} - I_L$$
(3.12)

There are several important solar cell parameters which need to be explained.

(1) The short circuit current of the cell  $(I_{sc})$  is defined as the current that flows through the junction under illumination at zero bias. In the ideal case,  $R_s = 0$  and  $R_{sh} = \infty$ , and  $I_{sc} = I_L$ .

(2) The open circuit voltage  $(V_{oc})$  is the voltage across the junction under illumination with no current flowing through the device. Under the open circuit condition, the cell would have to bias itself to the open circuit voltage,  $V_{oc}$ . The relation between  $V_{oc}$  and  $I_{sc}$  is given below, in Equation (3.13).

$$V_{OC} = \frac{nkT}{q} \ln\left(\frac{I_{SC}}{I_s} + 1\right)$$
(3.13)

The power output of the cell at a given voltage, V, is given by:

$$P = IV = I_{S}V[\exp\left(\frac{qV}{nkT}\right) - 1] - I_{SC}V \qquad (3.14)$$

The maximum power point  $(I_m, V_m)$  on the curve of Figure 3.7(b) can be obtained by setting  $\delta P/\delta V = 0$ .

(3) The fill factor (FF) of a cell is the ratio of the maximum output power to the product of the short circuit current and the open circuit voltage.

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}}$$
(3.15)

(4) The energy conversion efficiency  $(\eta)$  of a cell is defined as the ratio of the maximum output power to the incident photon power.

$$\eta = \frac{I_m V_m}{P} \tag{3.16}$$

(5) The spectral response  $(SR(\lambda))$  of a cell is defined as the photocurrent collected at each wavelength divided by the number of incident photons per unit time. The internal spectral response is the ratio of the number of electron-hole pairs collected by the cell under short circuit condition to the number of photons that have entered the cell surface.

$$SR(\lambda) = \frac{J_{SC}}{qF(\lambda) [1-R(\lambda)]}$$
(3.17)

here,  $F(\lambda)$  is the number of photons incident on the device at wavelength  $\lambda$  per square centimeter per second per unit bandwidth,  $R(\lambda)$  is the reflectance of photons at wavelength  $\lambda$ .

The external spectral response is the ratio of the number of electron-hole pairs collected to the number of photons reaching the surface of the device.

$$SR(\lambda)_{Err} = SR(\lambda) [1-R(\lambda)]$$
(3.18)

#### 3.5 ADVANTAGES OF HETEROJUNCTION CELLS

Since CuInSe<sub>2</sub>-based, heterojunction solar cells are studied in this work, it is specially interesting to compare performance of a heterojunction cell with that of a homojunction cell. The performance of a heterojunction cell may be affected by several factors such as compatibility of

the thermal expansion coefficient and the lattice constant of the two materials, interdiffusion at the metallurgical junction and discontinuity of the energy band diagram. However, the heterojunction cells have several advantages over homojunction cells. Firstly, a heterojunction allows the use of semiconductors that can only be doped either n- or p-type, (such as ZnO or CdS for windows). Secondly, low cost processes can be developed for the heterojunctions.

# 3.6 CURRENT TRANSPORT MECHANISMS OF A PRACTICAL HETEROJUNCTION SOLAR CELL

In addition to interfacial states, deep energy states also exist in the bulk region of the semiconductors. The density of the deep energy states can be large in a polycrystalline semiconductor such as CuInSe<sub>2</sub>. Therefore, some carriers generated in the neutral region will recombine before reaching the depletion region.

Figure 3.8 shows a one-sided heterojunction with a window-layer. The absorber is lightly doped compared with the window. Therefore, the build-in potential is mainly due to the band bending of the p-type absorber. The net current density, J, at x = W is:

$$J = -[J_{p}(W) + J_{p}(W)]$$
(3.19)

The minus sign indicates that the current is in the fourth quadrant when the junction is under illumination (in an J-V plot). The current component,  $J_n(W)$ , is the minority carrier current flow in the quasi-neutral region,  $W \le x \le W + L$ . It can be expressed as [3.1]:
$$J_{n}(W) = J_{LB} - J_{dg} \{ \exp \left[ E_{Fn}(W) / kT \right] - 1 \}$$
(3.20)

where  $E_{Fn}$  is the electron quasi-Fermi level at x = W and  $J_{LB}$  is the photocurrent generated in the neutral region (W $\leq x \leq W+L$ ).  $J_{LB}$  can be expressed as:

$$J_{LB} = e \phi_o \left\{ \left[ \frac{\beta_1^2 e^{-\beta_1}}{\beta_1^2 - \beta_2^2} \right] \left[ \frac{\beta_3 \beta_2 / \beta_1 - 1}{\beta_3 \sinh \beta_2 + \cosh \beta_2} \right] + \left[ \frac{\beta_1^2}{\beta_1^2 - \beta_2^2} \right] \left[ \left[ 1 - \left( \frac{\beta_2}{\beta_1} \right) \left( \frac{\beta_3 \cosh \beta_2 + \sinh \beta_2}{\beta_3 \sinh \beta_2 + \cosh \beta_2} \right) \right] \right\}$$
(3.21)

and

$$J_{dif} = \frac{eD_n n_{p0}}{L_n} \left[ \frac{\beta_3 \cosh\beta_2 + \sinh\beta_2}{\beta_3 \sinh\beta_2 + \cosh\beta_2} \right]$$
(3.22)

The second term of Equation (3.20) is the bucking recombination and diffusion current developed in this quasi-neutral region. It is thus clear that, in order to collect all of the carriers generated in the absorber, the diffusion length  $L_n$  must be large.

The dimensionless  $\beta$  numbers appearing in Equations (3.21) and (3.22) are given by  $\beta_1 = L\alpha$ ,  $\beta_2 = L/L_n$  and  $\beta_3 = L_n S_n/D_n$ . Here,  $\alpha$  is the absorption coefficient,  $L_n$  is the diffusion length of electrons,  $D_n$  is the diffusivity of the electrons in the absorber, and  $S_n$  is the recombination velocity of the electrons at the back surface.

 $J_p(W)$  in Equation (3.20) is not a minority carrier current. Consequently, it cannot be treated as easily as  $J_n(W)$ . Using the continuity equation for the depletion region,  $J_p(W)$  can be expressed as:

$$J_{p}(W) = e \int_{0}^{W} G dx - \int_{0}^{W} R dx - J_{r}$$
(3.23)

The first and second terms are photogeneration and recombination in the depletion region, respectively and J<sub>r</sub> is the interface recombination current density. In Equation (3.23), it is assumed that the recombination takes place in the absorber. It is also assumed that the current arising from holes injected over the valance band barrier at x=0 is negligible due to the large discontinuity,  $\Delta V$ .

The generation current can be expressed as:

$$\int_{0}^{W} Gdx = e\phi_{o}(1 - e^{-\alpha W})$$
(3.24)

Here,  $\phi_o$ , is the photonflux and  $\alpha$  is the absorption coefficient of the absorber. The recombination current is expressed as:

$$\int_{0}^{W} Rdx = J_{SCR}[\exp(\frac{V}{nkT}) - 1]$$
(3.25)

The quantity,  $J_{SCR}$ , is a prefactor characterizing the depletion region recombination current. Assuming that the interface recombination current,  $J_r$ , is controlled by the electron and hole concentrations at  $x=0^+$ , then it can be expressed as:

$$J_{r} = J_{IR} \left\{ \exp\left[\frac{E_{FR}(0+)}{kT}\right] - 1 \right\}$$
(3.26)

Here,  $J_{IR}$  is a prefactor. For Equation (3.26), the hole quasi-Fermi level is assumed to be flat across the depletion region. This same assumption is not made for electrons. The quantity,  $E_{Fn}(0^+)$ , is larger then the bias voltage, V.

It is further assumed that the capture cross section area,  $\sigma$ , of the recombination is the same for electrons and holes. The prefactor in Equation (2.26) can be express as [3.1]:

$$J_{IR} = \frac{e\sigma V_{th} N_I N_C \exp[-\frac{E_g}{2kT}]}{\exp[\frac{E_g}{2kT} - \frac{V_p}{kT} - \frac{V_{Bi}}{kT} + \frac{V}{kT}] + 2 + \exp[\frac{E_g}{2kT} - \frac{V_p}{kT} - \frac{V_{Bi}}{kT} + \frac{V}{kT}] \exp[\frac{E_{Fn}(0^+)}{kT}]}$$
(3.27)

Here,  $V_{uh}$  is the thermal velocity of the electrons,  $N_I$  is the number of localized states per unit area,  $N_c$  is the effective density of the states in conduction band of the absorber,  $V_p$  is the Fermi level with respect to the valence band edge at thermodynamic equilibrium in the absorber. The quantity  $J_{IR}$  depends on bias voltage and  $E_g$  through  $E_g/2-V_p-V_{Bi}$ . The energy,  $E_g/2-V_p-V_{Bi}$ , locates the Fermi level in thermodynamic equilibrium, at, x=0.

Substituting Equations (3.24)-(3.26) into (3.23) and substituting Equations (3.20) and (3.23) into (3.19), Equation (3.28) is obtained.

$$J = J_{IR} \exp\left[\frac{E_{Fn}(0+)}{kT}\right] - 1 + J_{SCR}\left[\exp\left(\frac{V}{nkT}\right) - 1\right] + J_{dy}\left(\exp\left[\frac{E_{Fn}(W)}{kT}\right] - 1\right) - J_{LB} - J_{LSC}$$
(3.28)

The last term of Equation (3.28), J<sub>LSC</sub>, is the generation current in the depletion region from

Equation (3.24). Equation (3.28) demonstrates that the photocurrent,  $J_{LB}+J_{LSC}$ , generated in an one-sided heterojunction is opposed by three bucking current mechanisms. They are recombination at the interface, recombination in the depletion region, and recombination-diffusion in the absorber.

As can be seen from Equation (3.28), the recombination current at the interface is driven by the electron quasi-Fermi level at x=0. The recombination-diffusion current in the absorber is driven by the electron quasi-Fermi level at x=W. If the electron quasi-Fermi level is flat or in other words, if across the depletion region,  $E_{Fn}(0)=E_{Fn}(W)=V$ , the electrons face no difficulty in crossing from x=W to X=0. However, if the electrons do face difficulties crossing the depletion region, the electron quasi-Fermi level will rise as shown in Figure 3.8. A transport factor,  $F_s$ , can be defined to characterize the electron transport across W≥x>0. It quantificatifies the tendency of an electron to back-diffuse away from the junction because of the difficulty the electrons face in crossing W≥x>0. The transport factor can be expressed as:

$$F_a = \frac{J_{sweep}}{J_{dif} + J_{sweep}}$$
(3.29)

The sweep current density can be expressed as:

$$J_{sweep} = en_{p0} \mu_n kT \int_0^w \exp(-\psi/kT) dx \qquad (3.30)$$

Here,  $\psi$  is the conduction band edge as a function of position.

Similarly, a transport factor, F<sub>1</sub>, can be defined to characterize the electron emission from

the absorber to the window material at x=0.

$$F_{I} = \frac{J_{TH} \exp(-V/kT)}{J_{IR} + F_{c} J_{dif} + J_{TH} \exp(-V/kT)}$$
(3.31)

The thermionic emission current density is given by:

$$J_{TH} = A^{*}T^{2} \exp[(-E_{g} - V_{p} - V_{Bi})/kT]$$
(3.32)

Here,  $A^*$  is the effective Richardson's constant. If  $F_i=0$ , the electrons will not face difficulties crossing the metallurgical junction. The photogenerated carriers from the absorber will be injected into the window material by thermionic emission.

The values of the electron quasi-Fermi level at x=0 and x=W depend on the transport factors  $F_1$  and  $F_4$ . If  $F_1=1$ , then  $E_{Fn}(0^+)=V$ . If  $F_1=F_4=1$ , then  $E_{Fn}(0^+)=E_{Fn}(W)=V$ .

After the introduction of the transport factors, the current density of the heterojunction solar cell in Equation (3.28) can be expressed as:

$$J = F_{I}J_{IR}[\exp(\frac{V}{kI}) - 1] + J_{SCR}[(\frac{V}{nkI}) - 1] + F_{I}F_{a}J_{dif}[\exp(\frac{V}{kI}) - 1] - F_{I}F_{a}J_{LB} - F_{I}J_{LSC}$$
(3.33)

Equation (3.33) is a mathematic model for electron transport in a one-sided heterojunction solar cell.

To see the effect of interface states in the window side on the recombination current component, it is assumed that  $F_a=F_1=1$ . Using the continuity equation for an electron near the interface:

$$\frac{\partial n}{\partial t} = G_n - R_n + \frac{1}{e} \frac{\partial j_n}{\partial x}$$
(3.34)

 $G_n$  and  $R_n$  are the generation and the recombination rates, respectively. If Equation (3.34) is applied in the vicinity of the interface under the steady state condition  $\partial n/\partial t=0$  then,

$$J_{n}(0^{+}) - J_{n}(0^{-}) = e \int_{0^{-}}^{0^{+}} R_{n} dx = e n_{I} S_{I}$$
(3.35)

and

$$J_{n}(0^{+}) = J_{LO} = J_{n}(0^{-}) + en_{I}S_{I} = J_{L} + en_{I}S_{I}$$
(3.36)

Here,  $J_{LO}$  is the generated current density that reaches the junction from the absorber,  $J_L$  is the current density that leaves the junction on the window side, and  $S_I$  is the interface recombination velocity. The quantity  $en_IS_I$  is the recombination current density,  $n_I$  is the density of electrons on the window side and  $S_I$  is the effective recombination velocity. The current density component,  $J_L$ , can be expressed as:

$$J_r = e n_r \mu \xi \tag{3.37}$$

Where,  $\mu$  is the electron mobility and  $\xi$  is the electric field at the interface on the window side. Substituting Equation (3.37) into (3.36):

$$J_{LO} = e n_I \mu \xi + e n_I S_I \tag{3.38}$$

and

$$J_{L} = en_{I}\mu\xi = J_{LO}\frac{\mu\xi}{\mu\xi+S_{I}} = F^{*}J_{LO}$$
(3.39)

 $F^*$  is a transport factor and  $F^* \leq 1$ . The quantity  $\mu \xi/(\mu \xi + S_1)$  is the ratio of the drift velocity at x=0<sup>•</sup> to the sum of the drift velocity and the recombination velocity. In Equation (3.39), it is seen that the collection of photogenerated current is sensitive to the electric field value at interface.

# **3.7 CONCLUSIONS**

From the above discussion, it is apparent that the most important layer of a heterojunction solar cell is the absorber in which light-induced transitions produce mobile charge carriers. The window material is a large energy gap semiconductor which does not absorb significant amounts of sunlight. Generally, a semiconductor with large optical absorption coefficients and long minority diffusion lengths is desirable for absorber applications. An absorber layer with a low surface carrier concentration can result in a wide depletion region. Therefore, the carrier generation takes place mainly inside the depletion region and in the bulk region near the junction. The window layer is a large band gap semiconductor with high conductivity. Hence, the resistivity loss can be minimized. The lattice constants of the absorber layer and window layer should be similar to ensure a low density of interface states. Finally, the metal contacts should cover only a small portion of the cell surface to maximize the photocurrent.



•



Figure 3.1 Schematic diagrams of an abrupt junction showing: (a) cross-section view, (b) space charge distribution, (c) electric field distribution, (d) potential distribution and (e) band diagram.



Figure 3.2 Energy band diagrams of a p-n junction under (a) forward- and (b) reverse-bias conditions.

.







Figure 3.4 I-V characteristics of an ideal p-n junction, plotted in (a) linear scale, (b) semi-logarithmic scale.



Figure 3.5 I-V characteristics of a practical p-n junction showing the deviations.



Figure 3.6 A band diagram showing the carrier generation, collection and separation in a p-n junction under illumination.



Fig 3.7 (a) An equivalent circuit of a solar cell and (b) typical I-V characteristics of a p-n junction under illumination.



Figure 3.8 Energy band diagram of a practical n<sup>+</sup>-p heterojunction under illumination.

# 4.1 INTRODUCTION

Before fabrication of a solar cell, it is essential to have a basic understanding of properties of the semiconductor materials involved. These include crystalline structure, morphology, composition, electronic and optical properties. A detailed study of these properties is particularly important for high efficiency cell fabrication. The electronic properties to be studied include conduction type, resistivity, and concentration of the carriers. The optical properties include optical transmission and refractive index.

After fabrication, the complete solar cells will be characterized by carrying out currentvoltage (I-V), capacitance-voltage (C-V) and spectral response measurements. These measurements will be done in order to obtain essential parameters such as reverse saturation current  $I_o$ , ideality factor n, diffusion voltage  $V_D$ , depletion width x, series resistance  $R_s$  and other relevant parameters.

In this chapter, the measurement techniques for both the semiconductor thin films and the fabricated devices will be discussed. The principles and the equipments used for the measurements will also be described.

# 4.2 SCANNING ELECTRON MICROSCOPY

The Scanning Electron Microscopy (SEM), is extensively used for characterization of various semiconductor materials[4.1][4.2]. In a secondary electron mode, the SEM can be used to reveal microscopic morphological structure. In back scattering electron mode, the

crystallographic structure, in addition to the morphological structure, can be studied. The resolution of the SEM operating in secondary electron mode is better than 100 Å. An energy dispersive X-ray attachment (EDX) can be added to characterize X-rays generated in the sample by the incident electrons. This will allow us to obtain quantitative compositional characteristics of the material being examined.

Figure 4.1 shows a schematic diagram of a scanning electron microscope. The electron gun consists of a tungsten filament which emits electrons. The electrons are accelerated by the strong electrical field applied between the electron gun and the specimen to form a beam. The scanning coils incorporated in the vicinity of the final lens cause the beam to scan the sample. The collector collects the output signal from the sample as back scattered electrons, secondary electrons or X-rays. The output signal is amplified and displayed in the cathode ray tube (CRT). In the present work, a JOEL model JSM-6100 scanning electron microscope is used for studying the semiconductor materials and devices prepared. In the same SEM system, an attachment can be added for electron beam induced current measurements (EBIC). It will be shown in a later chapter that this attachment can be used to obtain the diffusion length of minority carriers in a semiconductor.

# 4.3 MEASUREMENT OF THICKNESS OF FILMS

The thickness of each layer of materials of a solar cell must be known because it plays a critical role in the optimization of the cell. Knowledge of the thickness of a film deposited using one particular deposition method, enables one to design a standard procedure for the film deposition. One of the techniques for the determination of film thickness is by examining the semiconductor sample in SEM. Another technique commonly used is an optical measurement method. The optical method is particularly useful for large band gap semiconductors, such as CdS and ZnO. In this section, the optical method used for the thickness determination will be described. This method is based on light interference within the film. When a monochromatic light in the visible region is incident on the surface of a film, the interaction of the rays causes the intensity of the light to increase or decrease in a specific direction [4.3].

As shown in Figure 4.2, when the incident light (AO) reaches the top surface of a thin film, it will be partially reflected (OR) and partially refracted (OC). As the refracted light (OC) reaches the bottom surface of the film, it will be partially reflected (CO1) and refracted (CT) again. For a transparent film, the intensity of reflected light is much lower than that of refracted light. Therefore, it is sufficient to consider only the interference between the first two reflected rays. The intensity of subsequently reflected rays does not interfere appreciably with the first two reflected rays.

The difference in the optical path of the first two reflected rays is:

$$\Delta l = (OC + O_1 C) n - OF = \frac{2nt}{\cos\beta} - 2t \tan\beta \sin\alpha \qquad (4.1)$$

where n is the refractive index of the material and t is the film thickness. Since  $n = \sin\alpha/\sin\beta$ , one can show that:

$$\Delta l = 2tn\cos\beta = 2t\sqrt{n^2 - \sin^2\alpha} \qquad (4.2)$$

When a light is reflected from a material with a high refractive index into a material with a low refractive index, the light defracted. When a light is reflected from a material with a high refractive index back to a material with a low index, a phase change of 180° occurs (for instance, the refractive index of CdS or ZnO is greater than that of the glass substrate). The effective difference in the optical path is then given by the following equation:

$$\Delta I_{eff_{\star}} = \Delta I - \lambda/2 \tag{4.3}$$

When  $\Delta l_{eff.} = k\lambda$  or  $\Delta l = (2k+1)\lambda/2$ , the maximum interference occurs. By knowing k,  $\lambda$ ,  $\alpha$  and n, the thickness t of a deposited film can be obtained from the following equation.

$$t = \frac{(2k+1)\lambda}{4\sqrt{n^2 - \sin^2 \alpha}}$$
(4.4)

here k is the maximum number of interference fringes.

The thicknesses of the ZnO and CdS films deposited in the present work for photovoltaic solar cells have been determined from the optical measurements. During the measurements, the sample was placed under an optical microscope and the number of interference fringes in the edge region of the sample was counted. Filtered light with a wavelength of 6300 Å was used because the fringes can clearly be seen under the microscope. At 6300 Å wavelength, the refractive index of ZnO is about 3 and is 2.29 for CdS. Thus from equation (4.4), each interference fringe in ZnO corresponds to an incremental thickness of 0.21  $\mu$ m and is 0.28  $\mu$ m for CdS.

The method described above is simple and nondestructive. Hence, it can be used to determine the film thickness after each step of the fabrication. For a film with a very small thickness, such as chemical bath deposited CdS, the present method is not accurate enough. Other methods will have to be used to determine the thickness.

#### 4.4 X-RAY DIFFRACTION

X-ray diffraction (XRD) is an effective method for the determination of the crystalline structure of a material. It is a nondestructive method which gives information on the crystalline phases and grain sizes in the sample [4.4][4.5]. A schematic diagram of an X-ray diffractometer is shown in Figure 4.3. The X-ray diffractometer consists of three main parts, an X-ray tube to generate radiation, a detector to detect the diffracted radiation and a goniometer to rotate the sample and the detector simultaneously (at different angular speeds).

The radiation spectrum detected by the detector is first translated into a pulse spectrum. The pulse spectrum is then amplified and converted into a graphic record of intensity versus diffraction angle. The relation between the angle for maximum diffraction of X-ray by a material and the wavelength of the X-ray is given by the Bragg's law,

$$2d\sin\theta = n\lambda \tag{4.5}$$

where n is an integer,  $\lambda$  is the wavelength of the incident X-ray, d is the spacing between the crystal planes and  $\theta$  is the incident angle of the X-ray. Because scattered waves interfere with each other, maximum intensity is obtained only when the above Bragg condition is satisfied. From the recorded data, the incident angles  $\theta$  at the peak positions and the height of the peaks can be obtained. The d spacing value can then be calculated from Bragg's equation. The crystalline structure of a film can be determined from ASTM data. By comparing the height and the width of the peaks, the crystalline quality can be determined. In general, the higher and narrower the peaks, the better is the crystalline quality of the sample.

In the present work, an Siemens X-ray diffractometer is used. This diffractometer has a Cuk $\alpha_1$  source with a Ni filter (wavelength = 1.54 Å).

# 4.5 ELECTRICAL RESISTIVITY

The electrical resistivity of a film can be measured using a conventional four-point probe technique [4.3]. A schematic diagram of the four-point probe is shown in Figure 4.4. The four probes are equally spaced and adjusted to the same height. A small dc current is supplied by a battery through the two outer probes and the voltage developed between the two inner probes is measured. The resistivity of the film,  $\rho$ , is then calculated using the follow equation:

$$\rho = \frac{V}{I}tCF \qquad (4.6)$$

here t is the thickness of the film and CF is the correction factor. When the probe spacing is much larger than the thickness of the film (which is typically, 1  $\mu$ m), the value of CF is 4.54. This method has been used in this work to determine the resistivity of the ZnO and CdS films deposited on glass substrates.

#### 4.6 OPTICAL TRANSMISSION

Optical transmission of the window material in heterojunction solar cells determined the amount of light reaching the absorber for electron generation. Therefore, it is important to know how the transmission characteristic will vary with processing conditions of semiconductors. In the present work, the optical transmission values of the two semiconductor window materials ZnO and CdS (deposited on glass substrates) have been measured by the set-up shown in Figure 5.5.

The setup includes a Bechman Model 2400 monochromator with a wavelength range from 0.4 to 2.0  $\mu$ m. The wavelength of the output is selected by adjusting the orientation of a prism. During the measurements, the slit width of the monochromator is kept at 0.5 mm. A Si detector

(United Detector, Model No. 6-PIN) is used for the intensity measurements in the 0.4 to 1.1  $\mu$ m wavelength range. In the 1.0 to 2.0  $\mu$ m wavelength range, an InSb photovoltaic detector (Jadson Infrared Inc.) is used. The short circuit current of the detectors under illumination is measured using an HP semiconductor parameter analyzer (Model No. 4145A).

#### 4.7 CURRENT-VOLTAGE CHARACTERISTICS

The experimental setup for the determination of current-voltage characteristics of a junction is shown in Figure 4.6. The DC voltage is supplied by the HP semiconductor parameter analyzer which is controlled by an IBM personal computer. Current output at each bias voltage is measured more than 10 times and the average value is obtained.

For routine photovoltaic measurements, a Bausch & Lomb tungsten light source is used to illuminate the samples. The light source is adjusted to near AM1 intensity. From the dark and illuminated I-V characteristics, the ideality factor n, reverse saturation current  $I_0$ , open circuit voltage  $V_{oc}$ , short circuit current  $I_{sc}$ , fill factor FF, and the energy conversion efficiency of the cells are obtained.

# 4.8 CAPACITANCE-VOLTAGE CHARACTERISTICS

Information on capacitance-voltage characteristics of a junction is important for the determination of basic parameters [4.6]. The basic parameters include carrier concentration of the base material (CuInSe<sub>2</sub>), depletion width and diffusion potential.

In a semiconductor junction, the depletion width varies with the bias voltage applied. When the magnitude of the reverse voltage across the junction in Figure 4.7 (a) is increased by  $\Delta V$ , the depletion width increases. The increase of the depletion width causes an increase in the total charge in the depletion region by  $\Delta Q$ . As shown in Chapter 3, the depletion (differential) capacitance per unit area is defined as:

$$C = dQ/dV \tag{4.7}$$

here, dQ is the incremental charge per unit area due to a change of the applied voltage, dV. For an one-side abrupt junction (Figure 4.7(b)), the capacitance per unit area is given by:

$$C = \frac{dQ}{dV} = \frac{d(qN_BW)}{[(qN_B/2\epsilon_s)W^2]} = \frac{\epsilon_s}{W} = \left[\frac{2(V_{bl}+V-2kT/q)}{q\epsilon_sN_B}\right]^{-\nu_k}$$
(4.8)

here  $N_B$  is the impurity concentration of the substrate,  $V_{bi}$  is the built-in potential of the junction, T is temperature, W is the depletion width and  $\varepsilon_s$  is the permittivity of the substrate semiconductor. From Equation (4.8), expression of  $1/C^2$  and  $d(1/C^2)/dV$  can be obtained:

$$\frac{1}{C^2} = \frac{2(V_{bl} - V - 2kT/q)}{q\epsilon_s N_B}$$
(4.9)

$$\frac{d(1/C^2)}{dV} = -\frac{2}{q\epsilon_s N_B}$$
(4.10)

It is clear from Equations (4.9) and (4.10) that, by plotting  $1/C^2$  versus V, a straight line should result for the one-sided abrupt junction. The slope of the straight line gives the impurity concentration of the substrate (N<sub>B</sub>), and the intercept (at  $1/C^2=0$ ) gives V<sub>bi</sub>-2kT/q. Since, V<sub>bi</sub>»2kT/q, the intercept is approximately equal to the build-in potential. Figure 4.8 shows a typical  $1/C^2$  versus V plot. The depletion width of a junction can be obtained from equation (4.8):

$$W(V) = \frac{\epsilon_s}{C(V)} \tag{4.11}$$

In the present work, the differential capacitance of a cell was measured using an HP multifrequency LCR meter (Model 4274A). A block diagram of the experimental setup for this measurement is shown in Figure 4.9. The reverse bias voltage to the cell was supplied by the LCR meter. The actual dc bias of the cell was measured by an HP 3478A multimeter. During the capacitance measurements, a small ac signal was superimposed on the reverse bias voltage. The amplitude and the frequency of this ac signal were set to 0.02 V and 100 kHz. The depletion capacitance of the cell under illumination with the reverse biased voltage applied was recorded.

### 4.9 SPECTRAL RESPONSE

Spectral response (SR( $\lambda$ )) is another important parameter for a solar cell. The spectral response is directly related to the device configuration and properties of the materials involved. The materials and devices may be improved by the information obtained from the spectral response measurements.

The experimental setup for photoresponse measurements is shown in Figure 4.10. A tungsten filament lamp (Oriel, Model No. 6325) is used as a light source. The incident light passes through a monochromator (Beckman, Model No. 2400) to generate monochromatic light. During the measurements, the output setting of the power supply (Oriel, Model No. 6329) for the tungsten lamp is kept constant. The slit width of the monochromator is set at 0.5 mm and the wavelength of the monochromatic light is varied from 0.45 to 1.3  $\mu$ m. The current output of the cell is measured directly using an HP semiconductor parameter analyzer. The photon flux or

power density of the incident light that reached the cell at each wavelength was determined using calibrated photodetectors.

The spectral response of the cell is finally calculated:

$$SR(\lambda) = \frac{J_{cell} R hv}{J_{det} e}$$
(4.12)

where  $J_{cell}$  and  $J_{det}$  are the current densities in the cell and the detectors, respectively. R is the responsivity (in V/W) of the detector at a specific wavelength and hu is the photon energy (in eV) at this wavelength.

# 4.10 CONCLUSIONS

In this chapter, facilities and set-up used in the present work for routine characterization of semiconductor thin films and devices have been briefly described. These facilities allowed one to determine both optical and electrical properties required for the improvement of fabrication processes for thin film CuInSe<sub>2</sub>, CdS and ZnO.



Figure 4.1 A simplified schematic diagram of a scanning electron microscope.

.



Figure 4.2 Light interference in the semiconductor film/glass structure.

50

.

•







Figure 4.4 A schematic diagram of the four-point probe unit used for resistivity measurements.

<u>~</u>



Figure 4.5 A schematic diagram of the experimental setup for optical transmission measurements.



Figure 4.6 A schematic diagram of the experimental setup for current-voltage measurements.

•

*.* .



Figure 4.7 Schematic diagrams of p-n junctions showing changes of depletion width with biasing, (a) a p-n junction, and (b) a p-n<sup>+</sup> junction.



Figure 4.8 A plot of  $C^2$  versus bias voltage of a junction for determination of,  $V_d$ ,  $N_g$ , and w.



.

÷.,

Figure 4.9 A schematic diagram of the experimental sctup for differential capacitance measurements.



Figure 4.10 A schematic diagram of the experimental setup for the cell spectral response measurements.

ບ ເ

# CHAPTER 5 PREPARATION OF CdS FILMS BY CHEMICAL BATH DEPOSITION AND CdS/Si DEVICES

### 5.1 INTRODUCTION

One of the low cost methods for the preparation of large area thin films of CdS is the chemical bath deposition method (CBD) [5.1][5.2]. In this method, thin films of CdS are deposited on substrates in a solution containing thiourea (source of sulphur) and a Cd salt. Growth of CdS films on the substrates takes place by nucleation. When the product of the sulphur ion concentration and that of the cadmium complexes in the solution is larger than the product of solubilities, nucleation begins. The nucleation rate is controlled by adjusting the pH value, the temperature and the relative concentrations of the ions and complexes in the solution. Since the reaction takes place at a low temperature (below 60°C), the deposition can be carried out on various substrate materials. This method has also been successfully used to deposit CdZnS films [5.3][5.4].

Although results of the CBD deposition cf CdS films have been described in literature, detailed conditions for high quality films were not reported. To produce good quality, high resistivity CdS thin films for CdS(low  $\rho$ )/CdS(high  $\rho$ )/CuInSe<sub>2</sub> and ZnO(low  $\rho$ )/CdS(high  $\rho$ )/CuInSe<sub>2</sub> solar cells, the deposition conditions must be established in our laboratory. However, the preparation of CuInSe<sub>2</sub> thin films involving several steps such as deposition and heat treatment. In addition, the quality of the CuInSe<sub>2</sub> films may vary from run to run, making the comparison of CdS to be difficult in the development stage of the CBD method. Hence, it is not appropriate to use CuInSe<sub>2</sub> as the substrate in development stage of CBD CdS. In stead of
$CuInSe_2$ , monocrystalline Si substrates are used in the work to be described in this chapter. CdS/Si devices are fabricated under different conditions and the results obtained have been used to determine the optimum conditions for CdS.

# 5.2 CHEMICAL BATH DEPOSITION OF CdS

Several authors have reported that cadmium acetate is preferred over cadmium chloride as a Cd source in CdS deposition solutions. This is because heterogeneous growth of CdS occurs more readily with cadmium acetate, without the need of an ammonia salt buffer [5.5][5.6]. If the ammonia salt buffer is used, then there is no significant difference between cadmium acetate and cadmium chloride, since the surface morphology of the resulting CdS thin films will be similar. Hence, the advantage of using the ammonia salt buffer in the bath is that either cadmium acetate or cadmium chloride may be used for the deposition.

# 5.2.1 Principles of the Chemical Bath Reaction

The constituents of the deposition solution are  $CdCl_2$ , thiourea,  $NH_4Cl$  and  $NH_4OH$ . The  $CdCl_2$  supplies the cadmium ions, the thiourea provides the sulphur ions and the  $NH_4Cl$  serves as the deposition buffer. The  $NH_4OH$  provides  $OH^2$  for decomposition of the thiourea. The deposition reaction is as follows:

$$CdCl_2 + 4NH_3 = Cd(NE_3)_4Cl_2$$
(5.1)

 $Cd(NH_3)_4Cl_2$ , OH<sup>-</sup> and thiourea diffuse towards the surface of the substrates. Thiourea dissociates in the ammonia on the surface of the substrates:

$$(NH_2)_2CS + OH^- = CH_2N_2 + H_2O + HS^-$$
 (5.2)

Bivalent sulphide ions are then formed:

 $HS^{-} + OH^{-} = S^{2-} + H_2O$  (5.3)

Film of CdS finally form on the substrate:

$$Cd(NH_{3})_{4}^{2*} + S^{2*} = CdS + 4NH_{3}$$
 (5.4)

The formation of CdS films on the substrate can take place either heterogeneously or homogeneously. In the latter case, CdS precipitates in the solution. The homogeneous process is highly undesirable, since CdS precipitates could be absorbed by the substrate producing powdery and non-adherent CdS films.

#### 5.2.2 Preparation of a Deposition Solution

Materials of  $CdCl_2$ ,  $(NH_2)_2CS$  and  $NH_4Cl$  are carefully weighed using an electron balance (Mettler, Model No. AE100). A solution containing  $CdCl_2$ ,  $(NH_2)_2CS$  and  $NH_4Cl$  (solution A) is then prepared. To prepare the deposition bath, 25 ml of the above solution and 55 ml of deionized water are mixed in a beaker and 0.483 M of  $NH_4OH$  is added to the beaker.

### 5.2.3 Experimental Technique

The experimental setup for the deposition is shown in Figure 5.1. Water bath temperature is regulated by maintaining a constant flow of hot water. A thermal meter is placed in the water bath to monitor the temperature. When the temperature is at 60°C, the solution is placed in the water bath. After 10 minutes, substrates are immersed to the solution. After the CdS deposition is completed, the samples are thoroughly rinsed with deionized water and spun-dry.

#### 5.3.1 Si Substrate Preparation

The substrates used in this experiment were p-type, (100) oriented, monocrystalline Si wafers with a resistivity from 1.5 to 5  $\Omega$ -cm. Before the CBD deposition, the substrates were cleaned using the following process. The wafers were first immersed in trichloroethylene (TCE) and introduced in an ultrasonic bath for 10 minutes. After this, they were immersed in acetone (ACE). The wafers were finally etched in buffered HF for 1 minute, then rinsed and finally dried.

# 5.3.2. Contact Formation

After the deposition, the CdS on the back surface of the Si wafers was removed by applying diluted HCl (5%). The back surface was then etched using buffered HF to remove a thin layer of SiO<sub>2</sub> formed during the CBD process. Al or In was thermally evaporated onto the back of the Si substrates to form ohmic contacts. Either In or Al was then evaporated onto the CdS surface through a metal mask (containing several circular regions with an area 0.078 cm<sup>2</sup>) to form ohmic contacts. A schematic cross-sectional diagram of the completed device is shown in Figure 5.2.

#### 5.4 RESULTS OF THE CdS FILM DEPOSITION

Before actual deposition of CdS films on Si substrates, several experimental runs were made to observe the effect of solution temperature on the reaction rate. It was found that the reaction rate was very slow and the films were not uniform when deposited at a temperature below 55°C. At temperature above 70°C, the reaction rate was very fast, making the control of deposition to be difficult. Furthermore, the films were rough and did not adhere well to the substrates. Films with the best quality were obtained at a solution temperature of 60°C. Hence, in subsequent experiments to determine the effect of  $NH_4OH$  concentration, the temperature of solutions was kept at 60°C.

To observe the effect of NH<sub>4</sub>OH concentration on the CdS quality, several runs have been made. About 5 minutes after the solution was placed in the water bath, the solution reached a temperature of 60°C. In the first 10 minutes after being placed into the water bath, the solutions that contained less than 0.77 M of NH<sub>4</sub>OH changed to a very light, yellow colour. The colour indicated the initiation of CdS formation in the solutions. The solutions that contained 0.77, 0.97, and 1.16 M of NH<sub>4</sub>OH changed to a very light, white colour. This colour suggested that of Cd(OH)<sub>2</sub> had precipitated in the solutions. The solution containing 0.72 M of NH<sub>4</sub>OH started to turn yellow 10 minutes after the samples were placed in the solution bath. The solutions containing 0.97 and 1.12 M of NH<sub>4</sub>OH began to turn yellow only 30 minutes after the substrates were placed in the solutions. In order to obtain CdS films of a reasonable thickness, the deposited on both the glass and Si substrates from solutions with different amounts of NH<sub>4</sub>OH. The deposited films were found to be adherent and reflecting. The films on the glass substrates showed a light yellow colour. Most of the films on the Si substrates showed a green colour.

The thickness of CdS deposited on the Si substrates was measured using a DEKTAK surface profile measuring system (Model No. 3030) to determine the deposition rate. The deposition rate is plotted against the concentration of NH<sub>4</sub>OH in the solution as shown in Figure

5.3. One can see that the deposition rates of the films from solutions containing less than 0.48 M and more than 0.77 M of  $NH_4OH$  are very low. The deposition rates of CdS films from the solutions containing 0.48 to 0.68 M of  $NH_4OH$  are high. Here it is noted that the deposition time for films from solutions containing 0.19, 0.39, 0.97 and 1.16 M of  $NH_4OH$  was 60 minutes. For the other films, the deposition time was 30 minutes. The thickness of the CdS, which was dependent on the deposition time, varied from 460 to 800 Å.

# 5.5 RESULTS FOR THE CdS/Si JUNCTIONS

Contacts were deposited on the samples fabricated in section 5.4 to obtain devices for electrical measurements. The current-voltage (I-V) measurements were carried out using an HP semiconductor parameter analyzer. A tungsten lamp was used as a light source. Because the front contact of each junction was opaque, carriers was only generated in the areas outside of the contact. The carriers then diffused to the junction and were then collected. Although the diffusion length of minority carriers in monocrystalline Si was large, the effective area that contributed to the photocurrent was small. Therefore, the photocurrent generated from these junction was very small comparing with solar cells with fine grid front metal contacts. Never-the-less, the open circuit voltage ( $V_{oc}$ ), short circuit current ( $I_{sc}$ ), fill factor (F.F.) and ideality factor (n) obtained from the I-V measurements were used to determine the quality of these junctions.

# 5.5.1 I-V Characteristics of the CdS/Si Cells

Both dark and illuminated I-V characteristics of one of the samples, CdS22-1 are shown in Figure 5.4(a). The CdS film for this sample was deposited from a solution containing 0.48 M of NH<sub>4</sub>OH. The as-deposited CdS film had a high resistivity and was photoconductive. From four-point probe measurements, the resistivity for this film was found to be  $5\times10^{\circ}$   $\Omega$  cm. Under simulated AM1 illumination, the resistivity of the CdS film decreased by a factor of more than 100. Results similar to the present work have been reported in [5.7]. In Figure 5.4(a), it is noted that there is a cross-over between the dark and illuminated I-V curves, indicating a decrease in series resistance under illumination. The dark current-voltage characteristics of the sample are shown in a semilogarithmic-linear scale in Figure 5.4(b). There are two linear regions in the forward direction. In the voltage range of 0.05 to 0.35 volt, the ideality factor is 1.93. For bias voltages greater than 0.35 volt, the current is limited by the series resistance. In reverse direction, there is no clear sign of saturation as the bias voltage increases. In addition to ideality factor and reverse current, open circuit voltage and short circuit current were measured to determine the quality of the junctions.

Table 5.1 summarizes parameters obtained from the 8 samples deposited from solutions containing different concentrations of NH<sub>4</sub>OH. As mentioned before, the CdS deposition rates of the four samples deposited for 1 hour were lower than those deposited for 30 minutes. It is seen in Table 1 that the open circuit voltages of the samples deposited in solutions containing 0.19 and 0.39 M of NH<sub>4</sub>OH are small. The deposition rate of CdS using a solution containing 0.39 M or less of NH<sub>4</sub>OH is low and the  $V_{oc}$  value of the resulted junction is small. Hence, the solution with 0.39 M or less of NH<sub>4</sub>OH is not recommended for the CdS deposition. The samples deposited in solutions containing 0.97 and 1.16 M of NH<sub>4</sub>OH had large open circuit voltages and short circuit currents. However, the deposition rate is low and the time required to deposit the CdS for solar cell fabrication would be too long.

For the samples deposited from solutions containing 0.48 to 0.77 M of NH<sub>4</sub>OH, the open circuit voltage varies from 0.17 to 0.25 volt and the short circuit current varies from 105 to 163  $\mu$ A. The one with the best performance is sample 22-1, which was deposited from a solution containing 0.48 M of NH<sub>4</sub>OH. In addition to the performance, the deposition rate is high. Hence, this solution is considered to be more appropriate for photovoltaic cell fabrication. In solar cell fabrication to be described in subsequent chapters, the high resistivity thin CdS films were always deposited from the solution containing 0.48 M of NH<sub>4</sub>OH.

# 5.5.2. Electrical Contacts to High Resistivity CdS

Since Al was used to make ohmic contact on the thermally evaporated low resistivity CdS, Al was selected as the material for ohmic contact with the CBD CdS. In ref. [5.8], In was used as an ohmic contact for the CdS. In this work, one sample (CdS21) was cut into two pieces, one for Al evaporation (CdS21-1) and the other for In evaporation (CdS21-3). The purpose of the experiments is to compare the two metals for the CBD CdS prepared in this work. The dark and illuminated I-V characteristics of the two samples are shown in Fig. 5.5. Table 5.2 lists the parameters obtained from the two devices.

It is clearly seen that the quality of the sample with Al front contact (CdS21-1) is better than that with In front contact (CdS21-3). The dark forward current of the sample with Al front contact is greater than that of the sample with In front contact. Under simulated AM1 illumination, the forward current of the sample with In front contact shows a saturation effect, suggesting that there is a second junction between In and CdS (which is in series with the CdS/Si junction). Hence, for most of the experiments, Al was employed as the ohmic contact for the CBD deposited high resistivity CdS.

### 5.5.3 Effects of Heat Treatment on the CdS/Si Junctions

The ultimate objective of work on CBD CdS is to establish a process for the fabrication of ZnO/CdS/CuInSe<sub>2</sub> solar cells. In the fabrication of these cells, the samples may be heated to a temperature of about 200°C. Hence, it is specially interesting to study the effect of heat-treatment on the CBD CdS films.

After the deposition, samples of CdS/Si were placed in a glass tube with valves at both ends. The tube was then placed in a furnace initially at room temperature. The glass tube was evacuated using a Varian rotary pump (Model No. SD-300). After this, the pump was switched off and Ar was allowed to pass through the treatment tube. This pumping/filling process was repeated three times to ensure that the oxygen in the tube was a minimum. The power to the furnace was then turned on and the temperature of the furnace was allowed to rise to 200°C (in about 10 minutes). The heat treatment was prolonged for twenty minutes after the temperature of the furnace had reached 200°C. Following this, the furnace power was turned off and Ar flow was continued until the furnace cooled to room temperature. The samples were removed from the glass tube, and the contacts were deposited.

Dark and illuminated I-V characteristics of two samples (one with heat-treated CdS and the other with as-deposited CdS) are shown in Figure 5.6. The parameters of the two cells are listed in Table 5.3. It is seen that the performance has been improved with the heat treatment. The heat treatment quadrupled the short circuit current and increased the open circuit voltage. It is believed that the density of interface states has been reduced after the heat treatment, which causes a decrease in recombination and an increase in the short circuit current. In a separate experiment, a heat treated CdS/Si sample and an as-deposited sample were immersed in diluted HCl solution. It was found that the etching rate of CdS for the treated sample is lower than the as-deposited one.

# 5.5.4 Optical Transmission of CdS Films and Spectral Response of CdS/Si Junctions

Optical transmission measurements were made on thin CdS films deposited on glass substrates and the results for one of the samples (A2) are shown in Figure 5.7. The thickness of sample A2 was 0.16  $\mu$ m, which was much larger than that required for ZnO/CdS/CuInSe<sub>2</sub> solar cell fabrication. It is seen that the optical transmission value of the CdS film increases with the increase of the wavelength of the incident light. At 0.5  $\mu$ m (bandgap of CdS is 2.4 eV), the transmission is 80%. In the wavelength range of 0.5 to 1.2  $\mu$ m, the transmission value increases from 80 to 98%.

The spectral responses of the two cells CdS21-1 (with as-deposited CdS) and CdS21-2 (with heat treated CdS) were measured and the results obtained are shown in Figure 5.8. At short wavelengths, the spectral response values of the two devices are large comparing with spectral response values at long wavelengths. This fact confirms that absorption of light near the absorption edge of CdS is very small because of the small thickness of the CdS layers (about 700 Å). The decrease in the response value with the increase of wavelength is due to the decrease of absorption coefficient in Si. It is also clear that the spectral response values of the cell with the as-deposited CdS (CdS21-2) are larger than that of the cell with the as-deposited CdS (CdS21-1).

From the experiments described in this chapter, the deposition rate and quality of CdS films on Si substrates prepared by the CBD method were observed to be affected by the deposition conditions. An optimum temperature of 60°C was obtained in the work to prepare uniform CdS films with good adhesion. From results of electrical measurements on CdS/Si heterojunctions, it was concluded that the solution containing 0.48 M of NH<sub>4</sub>OH was the best one to prepare high quality CdS films. The electrical resistivity of the CBD CdS films with a thickness of 700 Å was about  $5 \times 10^4 \Omega$ -cm. The CBD conditions established in the present work have been used for photovoltaic thin film cell fabrication, which will be described in subsequent chapters.

In addition to the fabrication of thin film solar cells, the CBD conditions described in this chapter has been used in a separate experiment to develop photovoltaic cells based on Bridgmangrown monocrystalline CuInSe<sub>2</sub>. Recently, high quality cells with an efficiency exceeding 10% have been successfully developed in our laboratory [5.9].

| Sample No.        | NH₄OH<br>(M) | Ι <sub>sc</sub> (μΑ) | V <sub>oc</sub> (V) | n    | F.F. | I (μA) at<br>V=-1 V |
|-------------------|--------------|----------------------|---------------------|------|------|---------------------|
| 26-1*             | 0.19         | 107                  | 0.15                | 1.95 | 0.39 | 14.2                |
| 27-1*             | 0.39         | 156                  | 0.16                | 2.14 | 0,36 | 48.8                |
| 22-1*             | 0.48         | 145                  | 0.25                | 1.93 | 0.36 | 50.5                |
| 23-1+             | 0.58         | 144                  | 0.20                | 2.10 | 0.38 | 44.0                |
| 24-1*             | 0.68         | 105                  | 0.19                | 1.81 | 0.39 | 28.0                |
| 16-1+             | 0.77         | 163                  | 0.17                | 2.03 | 0.37 | 33.2                |
| 28-1              | 0.97         | 163                  | 0.21                | 1.90 | 0.38 | 45.6                |
| 29-1 <sup>•</sup> | 1.16         | 175                  | 0.23                | 2.09 | 0.40 | 51.3                |

Table 5.1 Parameters of CdS/Si devices with CdS deposited from solutions with different NH<sub>4</sub>OH concentrations.

\*Deposition time 1 hour.

+Deposition time 30 minutes.

Table 5.2 Parameters of two CdS/Si junctions with Al or In front contact.

| Sample No. | Front | I <sub>sc</sub> (μA) | V <sub>oc</sub> (V) | n    | F.F.  | I(μA)at                |
|------------|-------|----------------------|---------------------|------|-------|------------------------|
| 21-1       | Al    | 73.1                 | 0.23                | 1,69 | 0.434 | v <u></u> =-1 v<br>7.2 |
| 21-3       | In    | 46.6                 | 0.19                | 1.83 | 0.347 | 13.0                   |

~

| Sample No. | CdS       | I <sub>sc</sub> (μΑ) | $V_{oc}(V)$ | n    | F.F.  | I <sub>sc</sub> (μA) at |
|------------|-----------|----------------------|-------------|------|-------|-------------------------|
|            | Treatment |                      | 1           |      |       | V=-1(V)                 |
| CdS21-1    | по        | 73.1                 | 0.23        | 1.69 | 0.437 | 7.2                     |
| CdS21-2    | yes       | 279.6                | 0.25        | 3.91 | 0.377 | 170.9                   |

Table 5.3 Parameters of two CdS/Si junctions, one with heat-treated CdS and the other with asdeposited CdS.



Figure 5.1 A schematic diagram of a chemical bath deposition system.

1.1



Figure 5.2. A schematic cross-sectional diagram of the completed CdS/Si junction.



Figure 5.3. Deposition rate of CdS plotted against content of NH<sub>4</sub>OH in the solution.



Figure 5.4. (a) Current-voltage characteristics of a CdS/Si junction (CdS22-1) under dark and illuminated conditions, (b) dark current -voltage characteristics of the same junction plotted in semi-logarithmic scale.



Figure 5.5. Current-voltage characteristics of two cells under dark and simulated AM1 illumination, (a) junction with Al front contact and (b) junction with In front contact.





Figure 5.6. Current-voltage characteristics of two cells under dark and simulated AM1 illumination, (a) junction with heat-treated CdS and (b) junction with as-deposited CdS.

 $^{+}$ 

.



Figure 5.7 Optical transmission of a CBD CdS film plotted versus wavelength.



Figure 5.8 Spectral response of the two cells, one with heat treated CdS and the other with as-deposited CdS.

# 6.1 INTRODUCTION

The semiconductor ZnO is one of ideal materials for the fabrication of heterojunction solar cells, particularly those involving CuInSe<sub>2</sub> thin films. Comparing with the most popular window material CdS, the semiconductor ZnO has several advantages. The energy gap of ZnO is about 3.3 eV, therefore, photons with an energy greater than the energy gap of CdS (2.4 eV) but smaller than that for ZnO will be allowed to reach the absorber (CuInSe<sub>2</sub>) to generate electron-hole pairs. In addition, ZnO is less expensive and is not toxic.

Thin films of ZnO have been deposited by various methods such as reactive evaporation [6.1], reactive sputtering [6.2], spray pyrolysis [6.3], and rf sputtering [6.4][6.5]. For high quality heterojunction cell fabrication, the resistivity of ZnO must be low and the optical transmission must be high. In addition, the films must be thermally stable. It is well known that conventional low resistivity ZnO films are not stable. For these films, the resistivity is controlled by controlling ratio of Zn/O [6.6]. The resistivity of ZnO increases when heated in an environment containing  $O_2$ . During the fabrication of photovoltaic cells on CuInSe<sub>2</sub>, it is often required to heat treat the sample in air in order to improve the junctions properties. Hence, the conventional low resistivity ZnO obtained by controlling the stoichiometry is not appropriate for such cell fabrication.

The main objective of research work to be described in this chapter is to improve the conditions of the rf deposition method in order to obtain low resistivity, transparent and thermally stable ZnO thin films for photovoltaic cell fabrication. In stead of controlling the stoichiometry,

the resistivity of ZnO will be controlled by doping using elements from Group III of the periodic table (In and Al). The electrical properties, optical properties and thermal stability of the deposited ZnO thin films will be specifically studied.

### 6.2 ZnO FILM DEPOSITION

In the present work, an rf magnetron sputtering method has been used to deposit the ZnO thin films [6.6-6.12]. Impurities such as In, Al were introduced into the ZnO during the deposition to reduce the resistivity. The deposition system and the deposition procedure used are described in this section.

# 6.2.1 Principles of Sputtering

Sputtering is one of the effective methods for the deposition of good quality thin films [6.13]. There are two sputtering methods, namely, the cathode sputtering method and the rf sputtering method. The principle of sputtering is as follows. The material to be sputtered is used as target and a glow discharge is formed in an inert gas (e.g. Ar) at low pressure. Positive ions (Ar<sup>+</sup>) created from the discharge are accelerated by the potential difference between the target and substrate (ground) to bombard the target. The material is removed on target surface by the bombardment and deposits on the substrate to form a film. The cathode sputtering method can not be used effectively to deposit nonconductive materials because of a surface charging effect. For the rf sputtering method, the target is not necessary to be electrically conductive. During the deposition, secondary electrons are created when the inert gas is ionized. The secondary electrons can obtain a sufficiently high energy in the glow space to cause ionization collisions. Therefore,

they will help to maintain the glow discharge. However, the electrons will impinge the substrate with a high energy and cause an increase of substrate temperature.

In order to minimize the rise of substrate temperature due to secondary electron bombardment and to increase the ionization efficiency, an axial magnetic field is often introduced to form an rf magnetron sputtering system. This magnetic field, which is parallel to the target surface, is formed in the space between the target and the substrate. It will force the secondary electrons to follow a helical path, which is longer than the distance between the substrate and the target. Hence, the probability of ionization collisions with Ar atoms/ions before these electrons reach the target will increase. Because the probability of collisions between the electrons and the Ar atoms/ions increases, the impinging speed of the electrons on the substrate is reduced. Furthermore, the direction of the velocity of the electrons near the substrate is not normal to the surface. Therefore, the rise of substrate temperature is decreased by the usage of the magnetic field.

# 6.2.2 Sputtering System

The rf magnetron sputtering system used in this work includes a Varian vacuum unit (Model No. Turbo-V450) and an rf power supply unit. The vacuum unit consists of a 12-inch glass chamber, a Varian turbo pump (Model No. 969-9042) and a rotary pump (Model No. SD-300). A chamber pressure of 10<sup>-7</sup> torr can be achieved in less than 1 hour. A 4-inch diameter rf sputtering gun (US Inc.) is connected to an rf power supply (Advance Energy, Model No. ATX600) and an rf tuner (Advance Energy, Model No. RFX600). A schematic diagram of the rf sputtering chamber is shown in Figure 6.1.

#### 6.2.3 Target and Substrate Preparation

High purity ZnO powder (99.999%) and high purity  $In_2O_3$  and  $Al_2O_3$  powder (99.999%) were weighed using an electronic balance and mixed thoroughly in a clean beaker. The mixed powder was then pressed into an aluminum holder by using a hydraulic compressor. The target was mounted on top of the rf gun for the deposition.

Pre-cleaned microscope glass slides from Fisher Scientific with an area of  $75 \times 25 \text{ mm}^2$  were used as substrates. These were mounted on an Al sample holder inside the chamber. In order to study effects of substrate position on the properties of ZnO films, substrates were placed either perpendicular or parallel to the target surface (as shown in Figure 7.1). The distance between the target and the substrate holder was about 4 cm.

### 6.2.4 Deposition Procedure

Once the substrates and target have been mounted in the vacuum chamber, the vacuum system was turned on and set at a full speed. The pressure of the chamber reached  $10^{-6}$  torr in about 45 minutes and the pumping speed was reduced to 70% of the full value. High purity Ar gas was then introduced into the chamber. The pressure of the chamber was first increased to about 10 mtorr by adjusting the incoming flow rate of the Ar gas. The rf power supply and the rf generator were turned on to initiate the plasma. The pressure was then reduced to 5 mtorr by decreasing the flow rate of the Ar gas. During the sputtering, the incident rf power was maintained at 60 W. After the deposition, the rf power was turned off and the samples were finally removed from the substrate holder.

#### 6.3 PROPERTIES OF AS-DEPOSITED ZnO FILMS

Several measurements were made to determine thickness, crystalline quality, optical and electrical properties of the deposited ZnO thin films. The results obtained are presented in this section.

### 6.3.1 Morphology and Thickness of ZnO Films

The deposited ZnO films on glass substrates were examined under SEM. Figure 6.2 shows a photograph of a ZnO film. The ZnO films were observed to have a columnar microstructure with the long-axis of the grains perpendicular to the surface of the substrates. The films were smooth and uniform. Thickness of the films was about 1  $\mu$ m.

The variation of thickness with distance from projection of target center was also measured to determine the thickness uniformity. The thickness measurements were carried out using the optical method described in Chapter 4. The results obtained for two In-doped samples are shown in Figure 6.3, where it is clearly seen that the films are not uniform along the substrate surface. The thickness decreased steadily from the central region toward the outer region. The two samples were deposited on substrates mounted parallel to the target surface. For the sample deposited on vertical substrates, the variation of thickness with distance was smaller.

### 6.3.2 Crystalline Structure of ZnO Films

In order to determine the crystalline quality of the deposited ZnO films, several samples were examined by X-ray diffraction. The results for two samples doped with 2 wt% In are shown in Figure 6.4. Curve (a) was obtained for a film deposited on a substrate mounted parallel to the target surface and curve (b) on a substrate perpendicular to the target surface. The thickness of regions examined was about 1  $\mu$ m. It is seen that there are two diffraction peaks for each sample. By comparing with ASTM data, it was concluded that the ZnO films were polycrystalline with a wurtzite structure. From the magnitude of peak at 34°, it is evident that these films have a (002) preferred orientation. Furthermore, it is noted that peak magnitude for sample deposited on the perpendicular substrate (b) is twice of that for the parallel substrate (a). Hence, the crystalline quality of the ZnO film deposited on the perpendicular substrate.

### 6.3.3 Optical Transmission

Figure 6.5 shows variation of optical transmission coefficient with wavelength for two ZnO films with different In contents. The transmission coefficient increases as the wavelength is increased from 0.38  $\mu$ m and reaches 90% at 0.45  $\mu$ m for the film with 2wt% In. The transmission value is essentially constant when the wavelength is increased further from 0.45 to 0.8  $\mu$ m. For the ZnO films with 5.3% In, the transmission coefficient at a given wavelength is smaller than that for the one with 2% In. The difference in transmission coefficient between the two samples could be due to a difference in free carrier concentrations. The optical transmission characteristics of Al-doped (2 wt%) ZnO films were also determined and results are similar to those for the Indoped films (2 wt%).

### 6.3.4 Electrical Resistivity

In addition to thickness, the electrical resistivity of the horizontal samples was found to

vary with the position. This effect is shown in Figure 6.6, where the resistivity of three samples doped with 2wt% In is plotted versus distance from the projection of target centre. It is noted that the resistivity values of the three samples are high in the central region (from 0 to 2 cm) and are low in the outer region (from 3 to 6 cm). In the central region, the impinging Zn/O particles have a large momentum component perpendicular to the substrate. In the outer region, the substrate is outside the main projection area of the target. Hence, the perpendicular momentum component in the outer region is smaller than that in the central region. As a result, the microscopic quality of the ZnO films varies with the distance.

The resistivity of ZnO films with 2 wt% Al was also measured and the results are shown in Figure 6.7. It is seen that the variation of resistivity with distance is similar to that shown in Figure 6.6. The resistivities of vertical ZnO films (deposited on substrates mounted perpendicular to the target surface) were also studied, showing a smaller variation with the distance. The resistivity values of the vertical samples were generally lower than those of the horizontal samples. The lowest resistivity value on vertical ZnO films was  $3 \times 10^{-4}$  ohm-cm.

# 6.4 EFFECTS OF HEAT TREATMENT ON ZnO FILMS

Thermal stability of ZnO films is very important for device applications. This is because the material ZnO will be subjected to a heat treatment during the device processing (up to 200°C). For undoped low resistivity ZnO films, it has been reported that the resistivity increased significantly after a high temperature treatment [6.7]. It is thus specially important to know whether the doped ZnO thin films prepared in present work are stable when treated at a high temperature in air. In the following section, results on effect of heat treatment on ZnO thin films with different In contents will be reported.

#### 6.4.1 Air Heat Treatment

In order to study the effect of In doping on the thermal stability of ZnO, several films with different In concentrations were prepared and then heat treated in atmosphere. The heat treatment was carried out in an oven. The oven was first pre-heated to 250°C and the samples contained in a dish were inserted into the oven. After a period of time (e.g. 10 minutes), the samples were removed and cooled down slowly (20 minutes). The resistivity of the ZnO films ar room temperature was then measured. After the measurements, the heat treatments and resistivity measurement were repeated.

The results obtained from the above experiments for six samples are shown in Figure 6.8. The resistivities of all these samples increased with the increase of heat treatment time. For the ZnO film without In, the resistivity increased by four orders of magnitude after the first heat treatment (10 minutes) and the value continued to increase with further heat treatment. For the ZnO film with 0.5 wt% In, the resistivity increased only by about 1 order of magnitude. The amount of increase in resistivity decreased with the increase of In concentration. For the film containing 5.3 wt% In, the electrical resistivity remained roughly constant after the first heat treatment step.

For undoped ZnO films, the donor levels are created by oxygen vacancies. During the air heat treatment, oxygen atoms can easily diffuse into the films and compensate these donor states. For the doped films, most of donor levels are created by impurity atoms. It is believed that these levels can not be easily compensated by oxygen atoms at the treatment temperature (for instance, 250°C). The resistivity of the heavily doped ZnO (5.3 wt% In) in the above experiments remained constant during the main treatment process. From the present results, it is thus evident that the In doped ZnO films are much more stable than the undoped ones when heat treated in air.

To obtain further information on the thermal stability, several ZnO films with 2 wt% In were treated at different temperatures. The experiments were carried out in a temperature range from 200 to 350°C in a step of 50°C. For the high temperature heat treatments, the selected samples were placed in a pyrex tube. The tube with the samples were inserted into the furnace and kept in the furnace for a fixed period of time.

The result obtained for six samples are shown in Figure 6.9. At 200°C, the sheet resistance was roughly constant throughout the treatment process. For the two samples treated at 300°C, the sheet resistance increased by 1 order of magnitude after the 2 hour treatment. An even larger increase (2-3 orders of magnitude) was observed for the two samples treated at 350°C. From the results described above, it is clear that the air heat treatment of devices containing a doped low resistivity ZnO film window must be carried out at temperatures below 250°C in order to avoid the large increase of resistivity.

# 6.4.2 Treatment in Different Gases

In order to clarify the cause for the increase of resistivity of the ZnO films after the air heat treatment at high temperatures, several ZnO thin films containing 2 wt% Al were heat treated in air,  $O_2$  and  $N_2$  respectively. The results are shown in Figure 6.10. The resistivity remained essentially constant for the two samples treated in  $N_2$ . For the two samples treated in air, the resistivity increased by about 2 orders of magnitude. For the two samples treated in oxygen, the resistivity increased drastically even after the first 10 minutes. The resistivity continued to increase for one of the samples to more than three orders of magnitude of the original values during the subsequent heat treatment process.

At the same treatment temperature, more oxygen atoms could diffuse into the ZnO when treated in pure  $O_2$  to result in the large resistivity increase. From the above results, it can be concluded that the resistivity increases in ZnO films at high temperatures is mainly due to the diffusion of oxygen.

#### 6.5 CONCLUSIONS

High quality ZnO films have been deposited on glass substrates by using the rf magnetron sputtering technique from ZnO targets containing In and Al. From the X-ray diffraction, it was confirmed that all of the ZnO films were single phase with a preferred (002) orientation. The optical transmission values of the low resistivity ZnO films were determined. The cut-off wavelength was about 0.38  $\mu$ m and transmission values in the wavelength range from 0.5 to 0.8  $\mu$ m were about 90% for ZnO films doped with 2 wt% In or Al. The values were slightly lower (80%) for these with 5.3 wt% In. In addition to doping concentration, the resistivity of ZnO films was affected by the orietation of the substrates. For the samples deposited on horizontal substrates, the resistivity was further affected by the distance from the projection of target centre. The resistivity values were found to decrease by 2 orders of magnitude at a distance 2 cm away from the projection of the target center.

The doped ZnO films were found to be more stable thermally and the stability improved as the doping concentration was increased. The reason of the drastic increase of resistivity for undoped samples in the initial air treatment was due to the diffusion of oxygen atoms, which compensated the donor levels created by oxygen vacancies. For the heavily doped samples, most of the donor levels were created by the impurity atoms which can not be compensated easily at low temperatures. At 350°C, the resistivity of the horizontal ZnO films with 2 wt% In increased more than three orders of magnitude after a period of 2 hours. Therefore, during the fabrication of semiconductor devices involving the doped low resistivity ZnO, the processing temperatures must be limited to below 250°C.



Figure 6.1 A schematic diagram of the rf sputtering system for ZnO films.



Figure 6.2 A SEM photograph of a ZnO film deposited on a glass substrate.

ζ,

1.7



Figure 6.3 Variation of thickness of In-doped ZnO films versus the distance from the projection of target center, showing a continuous decrease of thickness.

::



Figure 6.4 X-ray diffraction scans of two ZnO films deposited (a) on a horizontal substrate and, (b) on a vertical substrate, showing the higher peak for the vertical sample.



Figure 6.5 Variation of optical transmission coefficient with wavelength for two ZnO films with different In doping concentrations.

.

 $\mathcal{U}$


Figure 6.6 Resistivity of three In-doped ZnO films plotted versus distance from the projection of target center, showing the positional effect.



Figure 6.7 Resistivity of two Al-doped ZnO films plotted versus distance from the projection of target center, showing the positional effect.



Figure 6.8 Resistivity of ZnO films plotted heat treatment time, showing effect of In content on the thermal stability of the films.



Figure 6.9 Sheet resistance of 2 wt% In-doped ZnO films versus heat treatment time at different temperatures, showing effect of treatment temperature on the increase of resistance.



Figure 6.10 Resistivity versus heat treatment time for six 2 wt% Al-doped ZnO samples in oxygen, air and nitrogen.

# CHAPTER 7 FABRICATION OF THE SOLAR CELLS

### 7.1 INTRODUCTION

In this chapter, detailed procedures for the fabrication of  $CuInSe_2$ -based Schottky-like junction and heterojunction solar cells will be presented. The procedure for a Schottky-like junction, in the form of Al/CdS(high  $\rho$ )/CuInSe<sub>2</sub>, is first described. The purpose of the Schottkylike junction is for studying the properties of the electrodeposited CuInSe<sub>2</sub> films. The Schottkylike junction also helps to the optimize heat-treatment conditions for the CuInSe<sub>2</sub> films. Procedures for solar cells of two different configurations are then developed. One is for solar cells employing In-doped CdS as the window material. The other is for cells using Al-doped ZnO as the window.

#### 7.2 DEPOSITION OF CuInSe

 $CuInSe_2$  thin films are electrodeposited onto Mo or Mo-coated glass. This is a one step deposition process developed in our laboratory [7.1-7.4]. In this section, the deposition process is presented.

## 7.2.1 Substrate Preparation

Mo sheets are first cut into strips with an area of  $1.1 \times 25$  cm<sup>2</sup>. The strips of Mo are then thoroughly cleaned in solvents (TCE and ACE) to remove any surface grease and immersed in 50% aqua regia for 30 seconds. The aqua regia removes superfluous material as well as the grease from the surface of the strips. The Mo strips are then removed from the acid and rinsed with deionized water. This procedure often leaves thin layers of oxidized Mo (black residue) on some areas of the Mo sheet. These black regions may be removed from the sheet by etching the sheet in diluted sulphuric acid for one minute. The sheet is rinsed with deionized water again and it is ready for the deposition.

Mo coated glass plates are also used for the deposition of  $CuInSe_2$  thin films. The glass plate are cut into  $1.2\times6$  cm<sup>2</sup> area strips. The Mo-coated glass strips are rinsed with deionized water to prevent sullying of the surface.

#### 7.2.2 Deposition Procedure

The deposition setup is shown in Figure 7.1. There is an electrical heater immersed in a bath of deionized water. A solution bath sits on a few Teflon blocks in the water bath. The temperature of the water bath is monitored by a type-J thermocouple and is maintained via a temperature controller. During the deposition, the solution bath is agitated using a motor driven Teflon rod. A platinum mesh serves as the anode and the Mo or Mo-coated glass substrate is the cathode. Before the deposition, the water bath is preheated to 95°C. The substrate is then inserted into the solution bath. A typical deposition time for a sample is about 10-20 minutes. After the deposition, the solution bath and rinsed with deionized water. The sample is then dried under an infrared light bulb for about 30 seconds.

#### 7.3 Heat Treatment of the CuInSe.

After the CuInSe<sub>2</sub> is electrodeposited onto the substrate, heat treatment of the CuInSe<sub>2</sub> films in vacuum or in an inert gas is carried out to improve the crystalline quality. The

experiments are carried out in two resistive furnaces.

# 7.3.1 Treatment in Vacuum

The experimental setup for the vacuum heat treatment of the CuInSe<sub>2</sub> films is shown in Figure 7.2. The substrates are placed in a glass tube (one end sealed) and the glass tube is connected to a rotary pump via a rubber hose. The furnace used in this experiment is a Lindberg/Hevi-Duty furnace. The temperature of the furnace is set at a predetermined value. The glass tube is pumped for at least five minutes before placing in the center of the furnace. The glass tube is typically kept in the furnace for 20 minutes. After 20 minutes, the tube is withdrawn from the furnace in one step. The glass tube is allowed to cool while the rotary pump continues to pump residual gas from the tube.

## 7.3.2 Treatment in Inert Gas

The heat treatment of  $CuInSe_2$  films in inert gas (Ar) is carried out in another resistive furnace. A schematic diagram of the heat treatment system is shown in Figure 7.3. The films are placed in a small glass tube which is in turn placed in a second tube that is part of the furnace assembly. Around the second tube are coiled elements that generate heat. The temperature of the furnace is monitored by a type-J thermocouple. One valve, Valve 1, controls the supply of inert gas to the furnace. Two other valves, Valve 2 and Valve 3 control the path of the exiting gas flow, respectively. The samples are placed in the furnace while the furnace is at room temperature. The rotary pump starts to pump when Valves 1 and 3 are closed and Valve 2 is open. After a few minutes, Valve 2 is closed and Valve 1 is opened. Ar gas is allowed to flow

đ.

into the tube. Once the pressure of the tube reaches atmospheric pressure, Valve 3 is opened and Ar is allowed to flow through the tube continuously for a few minutes. Valves 1 and 3 are closed again, and Valve 2 is opened. The rotary pump pumps away the gas from the tube. This process is repeated three times to make sure that the residual oxygen inside the tube is a minimum. When the tube is filled with Ar the third time, the Ar gas is again allowed to flow continuously. The furnace is then turned on and the temperature of the furnace is allowed to rise to a value in the range of 200 to 400°C. Once the temperature of the furnace reaches the setting point, heat treatment is prolonged for twenty minutes. After the heat treatment, the furnace is turned off and Ar flow is continued until the furnace cools to room temperature. The samples are removed from the glass tube.

## 7.4 CHEMICAL BATH DEPOSITION OF CdS

A thin layer of CdS film is then deposited on the heat treated CuInSe<sub>2</sub> by the CBD method. Details of the CBD method for CdS have been described in Chapter 5. For device applications, the thickness of the CBD CdS required is about 500 Å. During the deposition, the CuInSe<sub>2</sub> substrates are held vertically in the solution.

# 7.5 EVAPORATION OF In-DOPED CdS

Low resistivity In-doped CdS films are deposited using a thermal evaporation process [7.5]. Once a thin layer of high resistivity CdS is deposited onto the CuInSe<sub>2</sub> substrates, n-type low resistivity CdS is evaporated. This low resistivity CdS serves as the window for the cells.

A vacuum coating system (Edwards Model No. E306A) is used for the evaporation of the

CdS window. Figure 7.4 is a schematic diagram of the evaporation system. High purity (99.999%) CdS powder is thoroughly mixed with high purity (99.999%)  $In_2S_3$  powder (2 w.t.%). This powder mixture is loaded into a three-compartment tantalum boat. A tantalum cover is placed on top of the boat. There is a hole in the center of the boat cover which acts as a path for evaporation. During the deposition, this evaporation path is covered with tungsten wool to prevent spattering of the powder.

The substrates are mounted on the substrate holder which is attached to a circular heater. A cooling water tube is attached to the substrate holder to cool the substrate after the deposition. A metal shutter is placed between the evaporation boat and the substrate holder to control the evaporation process. Aluminum masks with either circular or square openings are positioned on top of the substrate for CdS defined area evaporation. A piece of glass slide is also mounted on the substrate holder for the determination of CdS thickness. A type-J thermocouple is attached to the substrate holder. The temperature of the substrate is maintained via a temperature controller.

After the substrate holder and the evaporation boat are loaded into the chamber of the coating system, the chamber is evacuated. The pressure in the chamber reaches  $2 \times 10^{-5}$  mbar after about 1 hour of pumping. The substrate holder is then heated to  $180^{\circ}$ C in about 20 minutes. Ten minutes after the substrate holder reaches the desired temperature, electrical current is applied to the boat. How much current is applied to the boat depends on the characteristics of the particular boat. With the shutter is closed, a current of about 75% of the full output is applied to the boat. After 3 minutes, the shutter is opened. Current is kept constant for 10 minutes. The current is then increased to 85% of the full power supply output, and the contents in the boat are

evaporated for 5 minutes. The current supplied to the boat is subsequently increased to 95% of the full power supply output, and the contents of the boat are evaporated for a final 5 minutes. The power to the substrate heater and the power to the boat are turned off. Cold water is allowed to circulate through the substrate holder for about 45 minutes to cool it to room temperature.

## 7.6 SPUTTERING OF AI-DOPED ZnO FILMS

An Al-doped ZnO film is deposited on the CBD CdS coated CuInSe<sub>2</sub> using the conditions described in Chapter 6. During the sputtering process, the sputtered particles approach the substrate at a very high velocity. If the substrate is held parallel to the target surface, the probability that these sputtered particles will bombard the substrate at right angles is high. Bombardment of the substrate at right angles is not desirable, since this type of bombardment reduces film crystalline quality. In Chapter 6, it has been shown that the crystalline quality of the ZnO films is affected by the orientation of the substrate. Hence, for heterojunction solar cells, the deposition of ZnO is carried out with the sample holder held at a  $45^{\circ}$  angle from the target surface (Figure 7.5). As such, the probably of high energy particles hitting the substrate at right angles is substantially less. Cooling water is fed to the substrate holder to cool the substrate during the sputtering process. The CuInSe<sub>2</sub>, with dip-coated CdS substrates, is fixed onto the substrate holder. ZnO films with a thickness of about 1 $\mu$ m can be obtained after sputtering for a period of 5 hours at a sputtering power of 80 W.

## 7.7 AI CONTACT EVAPORATION

Aluminum contact areas are evaporated onto the substrate to complete the solar cells. An

Edwards Coater (the same system used for the low resistivity CdS deposition) is used for the Al evaporation. Aluminum wires are hung on a tungsten filament. An aluminum mask containing windows is positioned on the substrate over the area where deposition is desired. There is also a metal shutter placed between the filament and the substrate. After the aluminum wires and the substrate are loaded into the vacuum chamber, the chamber is evacuated to  $2\times10^{-5}$  torr in about 1 hour. When the power supply to the filament is turned on, the Al wires start to melt into a few small balls with some surface particulate matter. After the matter on the surface of the metal balls evaporates, the shutter is opened. When the aluminum is completely evaporated, the power supply to the filament is turned off. Samples are removed from the chamber 10 minutes after the deposition.

## 7.8 PATTERNING OF THE DEVICES

#### 7.8.1 Patterning of the ZnO Window

When the opening of the metal mask used to establish the ZnO film deposition boundaries on the substrate is small, the resistivity of the ZnO films is high. This high resistance leads to a higher ohmic loss than is desired. In this work, no mask is employed during deposition of the ZnO films. The films are deposited over the entire substrates. After this, a photolithographic process is carried out to define the area of the ZnO films and therefore, the area of the cells.

Details of the photolithographic process will be discussed in Appendix 1. A positive photoresist (Shipley AZ1350) is employed in this work. The photomask used is depicted in Figure 7.6. After the photolithographic process, the ZnO film under the opaque regions of the photomask

remain on the substrate. The areas under the transparent region are removed by etching the samples in diluted HCl acid.

7.8.2 Patterning of the Al Contact Areas Using a Lift-off Method

In this instance, the photolithographic process is carried out before the Al deposition. After the developing process, some fine lines of photoresist are removed and Al is deposited on the photoresist film. The remaining photoresist is then removed from the substrate along with the Al on top of the photoresist. Figure 7.7 shows a top view of a completely patterned Al/ZnO/CdS/CuInSe<sub>2</sub> cell. Fine lines of Al are deposited directly on the remaining ZnO. Areas of the cell formerly covered by the Al contact areas are now available for photon penetration and hence, carrier generation.



Figure 7.1 A schematic diagram of system used for the electrodeposition of CuInSe<sub>2</sub> films.



Figure 7.2 A schematic diagram of a vacuum heat-treatment setup.



Figure 7.3 A schematic diagram of an inert gas heat-treatment setup.

111



. U









Figure 7.6 A photomask that used for ZnO patterning.





.

# CHAPTER 8 RESULTS OF PHOTOVOLTAIC CELLS ON CuInSe<sub>2</sub> THIN FILMS

## **8.1 INTRODUCTION**

As described before, the ternary compound semiconductor  $CuInSe_2$  is one of the most important materials for future terrestrial photovoltaic applications (the other two materials are  $\alpha$ -Si and CdTe). The energy gap of CuInSe<sub>2</sub> is direct and the optical absorption coefficients in the main solar spectrum are the highest among any known semiconductors. Hence, only a thin layer of CuInSe<sub>2</sub> (less than 1 µm) is sufficient to absorb most of photons with energies above the band gap (1.04 eV).

For terrestrial photovoltaic applications, it is required to prepare thin films of CuInSe<sub>2</sub> in an efficient way. In our laboratory, a novel electrodeposition method has been developed for the preparation of CuInSe<sub>2</sub> thin films [8.1]. The processing of CuInSe<sub>2</sub> by this novel method can be carried out at a low temperature with a rather short deposition time. Since the energy consumption in such deposition is very small and the required equipment is simple, compared to that for vacuum deposition methods such as evaporation and sputtering, the electrodeposition method developed in this laboratory is specially important and has potential for photovoltaic cell fabrication in the future.

In the previous work, photovoltaic cells of the form CdS/CuInSe<sub>2</sub> have been demonstrated using electrodeposited CuInSe<sub>2</sub> thin films [8.1]. In that work, the CdS films used were deposited by vacuum evaporation (thickness about 3  $\mu$ m). Since the energy gap of CdS is only 2.4 eV, this material can absorb high energy photons in the solar spectrum. For future large scale photovoltaic applications, it is required to use a large band gap window semiconductor (such as ZnO, E<sub>g</sub>=3.3 eV) to replace the CdS.

The research work to be described in this chapter thus will concentrate on the development of a cell with ZnO as the window and the electrodeposited CuInSe<sub>2</sub> as the absorber. To minimize the effect of interface states on the cell performance, a thin layer of CdS (less then 500 Å) will be introduced. This thin CdS layer will be deposited by the CBD method described in Chapter 5.

In this chapter, some of properties of the electrodeposited  $CuInSe_2$  films will first be described. Results on cells fabricated on the electrodeposited  $CuInSe_2$  will then be presented.

## 8.2 SOME PROPERTIES OF ELECTRODEPOSITED CuInSe, FILMS

In this section, some of the properties of the electrodeposited  $CuInSe_2$  films will be given. These properties include morphology, crystallinity, refractive index and absorption coefficient.

8.2.1 Morphological Characteristics of the CuInSe,

The as-deposited CuInSe<sub>2</sub> films on Mo substrates or Mo-coated glass substrates were examined under an optical microscope. It was found that while the films on the Mo substrates had the texture of substrates, the films on the Mo-coated glass substrates were very smooth. The morphology of the CuInSe<sub>2</sub> films was observed to be affected by the metal ratio of the films. Films with Cu/In ratios larger than unity (Cu-rich) were bluish with very fine grains. Films with Cu/In ratios less than unity (In-rich) were light grey with larger grains.

Under SEM, the CuInSe, films were observed to have a columnar microstructure with the long-axis of the grains perpendicular to the surface of the substrates. The films had a very uniform thickness and a smooth surface. Figure 8.1 shows an SEM picture for the cross section of a  $CuInSe_2$  deposited on a Mo-coated glass substrate. The thickness of this films was about 1.5  $\mu$ m.

#### 8.2.2 Crystalline Orientation and Conducting Type

From X-ray diffraction experiments, all of the electrodeposited  $CuInSe_2$  films were found to have a chalcopyrite structure with a (112) preferred orientation [1.7]. Figure 8.2 shows results of X-ray diffraction for one of the  $CuInSe_2$ .

To determine the conducting type, hot probe measurements were carried out on films deposited under different conditions. It was found that all of the samples tested were p-type even for the ones with a very small Cu/In ratio. This result is different from that obtained of vacuum deposited CuInSe<sub>2</sub> films. For the vacuum deposited CuInSe<sub>2</sub> films, n-type conduction was found. Those with Cu/In ratio in a range of 0.67 to 0.75 were n-type [8.2]. The difference is believed to be due to higher oxygen content in the electrodeposited CuInSe<sub>2</sub> films, which were prepared in a water solution.

#### 8.2.3 Refractive Index of CuInSe<sub>2</sub> Films

The refractive index is an important optical parameter for categorising semiconductor materials because it influences the optical reflectance of materials. If the refractive index of a material is known, the reflectance of the material at different wavelengths can be estimated. Refractive index can be determined from optical interference the material [8.3].

The CuInSe, films used for refractive index measurements were deposited on Mo-coated

glass substrates. The thickness of the Mo layers was about 0.8 µm. When a monochromatic light is incident on the surface of the CuInSe<sub>2</sub>, the light will be partially reflected and partially refracted. When the refracted portion reaches the interfaces between the bottoms of the CuInSe<sub>2</sub> films and the Mo surfaces, the majority of the light will be reflected back by the shiny Mo surfaces. The light reflected from the CuInSe<sub>2</sub> surface and from the Mo surface hava an optical path difference of 2nt. Here, n, is the refractive index of CuInSe<sub>2</sub> and t is the thicknesses of the CuInSe<sub>2</sub> films. When reflectance of the CuInSe<sub>2</sub>/Mo structure is plotted against wavelength of incident light, there are maxima and minima due to interference. The minima occurres when the following condition is satisfied:

$$2nt = (l + \frac{1}{2})\lambda, \quad l = 0, 1, 2, 3, \cdots$$
 (8.1)

The maxima occurrs when:

$$2nt = l\lambda, \quad l = 1, 2, 3, \cdots$$
 (8.2)

The CuInSe<sub>2</sub> films used were p-type with carrier concentration greater than  $10^{16}$  cm<sup>-3</sup>. Reflectance from the films was measured using a Perkin-Elmer spectrophotometer (Model 13U) with the monochromatic light chopped at 86 Hz. The experimental setup for the measurements is shown in Figure 8.3.

The incident light intensity was measured by replacing a sample with a gold coated glass substrate. The reflectance of the gold film was assumed to be 99%. The reflectance of the CuInSe<sub>2</sub>/Mo was then obtained from the ratio of the intensities of the light reflected from the CuInSe<sub>2</sub>/Mo and the gold mirror. During the measurements, an InSb photovoltaic detector operated at 77 K was used to determine intensity of both the incident and reflected light in the 2 to 5  $\mu$ m wavelength range. For the 5 to 10  $\mu$ m wavelength range, a HgCdTe photoconductive detector was used.

Positions of the CuInSe<sub>2</sub>/Mo sample and the detector were adjusted so that the angle between the incident beam and the reflection beam was about 15°. Samples used were CuInSe<sub>2</sub> films with thicknesses ranging from 1.5 to 2  $\mu$ m and with an area about 1×1 cm<sup>2</sup>. The reflection measurements were carried out on both as-deposited and heat-treated CuInSe<sub>2</sub> films.

After the deposition, a sample, No. R-3, was cut into four  $1 \times 1$  cm<sup>2</sup> pieces. The four pieces were heat-treated in vacuum for 15 minutes at 200, 250, 300 and 350°C, respectively. After the heat-treatment, reflection measurements were carried out. There were two maxima peaks and two minima in each reflectance curve in the 5 to 10  $\mu$ m wavelength range. From the maxima and minima on each curve, the refractive index was calculated using Equations (8.1) and (8.2).

It is noted that the post-deposition vacuum heat treatment does not have a strong effect on the refractive index values. From the above results, an average refractive index value of 4.7was obtained for the CuInSe<sub>2</sub> in the wavelength range studied.

## 8.2.4 Absorption Coefficient of CuInSe,

Absorption coefficient is a rather important physical parameter of a semiconductor material, especially for solar absorber applications. This is because the absorption coefficient of an absorber in a heterojunction solar cell directly affects the absorption length. Therefore, the absorption coefficient determines the minimum thickness of the thin film needed for the effective absorption of the incident solar radiation. The absorption coefficient of the electrodeposited CuInSe<sub>2</sub> prepared in this work was determined from the reflectance and transmittance measurements.

#### 8.2.2.1 Preparation for Absorption Measurements

In order to perform reflectance and transmittance measurements simultaneously on CuInSe<sub>2</sub> films, semi-transparent substrates are needed. In this experiment, the substrate used for deposition of the CuInSe<sub>2</sub> films consisted of a semi-transparent Mo/Cr multi-layer deposited on a glass substrate. The thin Cr film (thickness<100 Å) was first deposited on a pre-cleaned glass slide by electron beam evaporation. A layer of thin Mo film was then deposited on top of the Cr using the same system. Because sheet resistance of the semi-transparent Cr/Mo films was too high to be used as the electrode in the deposition of CuInSe<sub>2</sub> films, an additional thick metal layer was deposited (Figure 8.4). The thick metal layer was deposited onto most of the glass substrate, except for a thin strip with a width of about 2 mm which was covered with aluminum foil. The purpose of the thick metal layer is to reduce the effective resistance of the substrate.

Using the above described substrate, a thin layer of  $CuInSe_2$  film (0.3 µm) was then deposited. After the deposition, a brief heat treatment of the films was carried out. Because the substrate was opaque except for the thin strip, the CuInSe<sub>2</sub> deposited on the thin strip was used for transmittance and reflectance measurements.

#### 8.2.2.2 Experimental results

The transmittance and reflectance of the films at wavelength in the range from 0.9 to 1.7  $\mu$ m wavelength range were determined. For transmittance measurements, a Mo/Cr/glass substrate

without  $\text{CuInSe}_2$  was used as reference. A gold film was used as reference for the reflectance measurements. The results of one of the samples measured (sample A-2) are shown in Figure 8.5. It was found that both the reflectance and the transmittance of this sample varied with the wavelength of the incident light. From the measured reflectance and transmittance, the absorbance  $A(\lambda)$  of the film can be obtained from the following equation.

$$A(\lambda) = 1 - R(\lambda) - T(\lambda)$$
(8.3)

Here  $R(\lambda)$  and  $T(\lambda)$  are the reflectance and transmittance of the film. The absorbance,  $A(\lambda)$ , can also be expressed as a function of absorption coefficient,  $\alpha(\lambda)$ , and thickness of the film, x:

$$A(\lambda) = \exp[-\alpha(\lambda)x]$$
(8.4)

The variation of the absorption coefficient with the variation of energy of incident photons was determined and the results are shown in Figure 8.6(a). The absorption coefficients of the films above the energy band gap (1 eV) were as high as  $5 \times 10^4$  cm<sup>-1</sup>. The value decreased as the photon energy was decreased. The transition region for the absorption coefficient in the electroplated CuInSe<sub>2</sub> films was not as sharp as that obtained by other researchers on vacuum deposited CuInSe<sub>2</sub>.

For a direct band gap transition, the absorption coefficient ( $\alpha$ ) is related to the photon energy (hu) by the following equation [3.3]:

$$\alpha h \upsilon = A (h \upsilon - E_{e})^{\frac{1}{2}}$$
(8.5)

Here A is a constant and  $E_g$  is the energy gap. Therefore, for a direct band gap semiconductor, a plot of  $(\alpha h \upsilon)^2$  versus photon energy, h $\upsilon$ , should yield a straight line. The intercept with the photon energy axis gives the value of the band gap. The values of  $(\alpha h \upsilon)^2$ , plotted against photon energy hu, are shown in Figure 8.6(b) for Sample A-2. The energy gap obtained from the intercept on the photon energy axis is 1 eV. This value is approximately the same as that reported for vacuum deposited CuInSe. (1.04 eV).

Figure 8.7 shows plots of  $(\alpha h \upsilon)^2$  versus photon energy, for two other samples. The energy gap values obtained from this plot varied from 0.94 to 1 eV.

## 8.3 EFFECT OF HEAT TREATMENT OF CuInSe, ON THE CELLS [1.8][7.3]

A heat treatment of  $CuInSe_2$  in vacuum and Ar can improve the crystalline quality of the films as evident from X-ray diffraction. In addition to the crystalline quality, the composition may be affected by the heat treatment. In the present work, it was found that there was also a loss of Se during the treatment. This was observed from the deposition of Se on the glass tube used for heat treatment experiment. For the films treated in inert gas (Ar), the loss of Se was less than that from the films treated in vacuum. It is thus specially interesting to determine the effect of heat treatment on the performance of photovoltaic cells fabricated using ZnO and CBD CdS. In this section, results on studies of cells fabricated on  $CuInSe_2$  films after different treatments will be presented.

# 8.3.1 Al/CdS/CuInSe<sub>2</sub> Schottky Junction [7.3]

Schottky-like junctions with an Al/CdS/CuInSe<sub>2</sub> structure have been fabricated for studying the properties of junctions formed with the electrodeposited CuInSe<sub>2</sub>. After the heat treatment, a layer of high resistivity CdS was dip-coated by the CBD method. Al contact areas were finally deposited to complete the fabrication.

I-V characteristics of one of the Schottky-like junction (D7) are shown in Figure 8.8. The CuInSe<sub>2</sub> film used in Junction D7 was deposited on Mo sheet and heat treated in Ar. The reverse leakage current of this junction was small. The series resistance of this junction, obtained from Figure 8.10, was about 36  $\Omega$  cm. Figure 8.9 shows the C-V characteristics of the junction D7. From the slop of the curve, an average acceptor concentration of 2.3×10<sup>16</sup> cm<sup>-3</sup> was obtained.

Figure 8.10 shows dark and illuminated I-V characteristics of another Schottky-junction (E19). Although the thickness of Al contact was too large for light to pass, some excess carriers still were generated in areas outside the contact. The carriers generated near the contact were able to diffuse towards the depletion region and got collected by the junction. However, the photocurrent of this type of junction was very small compared with a heterojunction with transparent window layer. A typical short circuit current obtained from this junction was about 0.12 mA. Figure 8.11 shows C-V characteristics of Sample E19 taken under dark and illuminated conditions. It is noted that there are two main sections in the plots, indicating the difference in the acceptor concentrations.

#### 8.3.2 CdS/CuInSe<sub>2</sub> Cells Fabricated on CuInSe<sub>2</sub> Treated in Vacuum

All of the cells fabricated using vacuum treated CuInSe<sub>2</sub> on Mo substrates were either shorted or very leaky, with a small photovoltaic effect. The leakage current can be reduced by an air treatment for 10 minutes at about 180°C. An additional treatment beyond 10 minutes was found to improve further the I-V characteristics of the cells. For the cells fabricated on Mo-coated glass substrates with a vacuum treatment, both rectification and photovoltaic effect were readily obtained although a heat treatment in air generally improves the conversion efficiency. Figure 8.12 shows I-V characteristics of one of the samples, 14-5-3, which was fabricated on a Mo substrate. The total area of the sample (covered by low resistivity CdS) is 0.16 cm<sup>2</sup> and active area is 0.11 cm<sup>2</sup>. The photovoltaic effect in the as-fabricated cell was usually small. After a heat treatment for 10 minutes in air at 180°C, the sample showed an increase in the photovoltaic effect although the conversion effeciency was only about 0.95% and reverse dark current was large. After another air heat treatment for a period of 20 minutes, all of the parameters for the cell improved. The measured  $J_{sc}$ ,  $V_{oc}$ , FF and  $\eta$  were 35.4 mA/cm<sup>2</sup>, 0.177 V, 0.41, and 2.1% respectively. The relatively low conversion efficiency of cell on the vacuumtreated CuInSe<sub>2</sub> is due to the small open circuit voltage (less than 0.2 volt). If the open circuit voltage can be improved by improving the fabrication condition, cells with a high conversion may be obtained.

In addition to I-V measurements, C-V characteristics were measured for 14-5-3 after treatment in air of 30, 50 and 70 minutes. The results are shown in Figure 6.13. From the slope of the C-V curves, the average acceptor concentration in the CuInSe<sub>2</sub> was determined. The concentration was  $1.04 \times 10^{17}$  cm<sup>-3</sup> after the 30 minute treatment and was  $7.7 \times 10^{16}$  cm<sup>-3</sup> after 50 minute treatment. The one obtained after a total the 70 minute treatment had two sections with distingue slopes. This indicated that the acceptor concentration profile is not uniform across the junction. The concentration near the junction ( $5.8 \times 10^{16}$  cm<sup>-3</sup>) was lower than that in the bulk region ( $1.08 \times 10^{17}$  cm<sup>-3</sup>). From intercepts of the C-V curves with the axis, the diffusion potentials of the cells after different heat treatment stages were 0.38, 0.58, and 0.53 V respectively.

During the vacuum treatment, both the Se and  $O_2$  content near the surface of CuInSe<sub>2</sub> were reduced. Hence, the stoichiometry deviated from the as-deposited films. In the air heat

treatment of the completed cell, oxygen atoms diffused into the CuInSe<sub>2</sub>. The diffused oxygen atoms occupied the vacant Se sites and inproved the junction fabricated on vacuum treated CuInSe<sub>2</sub> films.

#### 8.3.3 CdS/CuInSe, Cells Fabricated on CuInSe, Treated in Ar

More than 200 CdS/CuInSe<sub>2</sub> cells were fabricated on CuInSe<sub>2</sub> films treated in Ar and these were studied. The cells showed strong rectification and photovoltaic effect. However, the I-V characteristic of these cells were not improved by a post-fabrication heat treatment. Various heat treatment were carried out.

Figure 8.14(b) shows the dark and illuminated I-V curve for a cell I5-6 (intensity of light was 125 mW/cm<sup>2</sup>). The open circuit voltage of this cell, 0.33 V, was larger than the cells fabricated on vacuum treated CuInSe<sub>2</sub>. The J<sub>sc</sub>, FF and  $\eta$  were 44.2 mA/cm<sup>2</sup>, 0.533, and 6.2% respectively. Fig 8.14(a) shows dark I-V curves plotted in a semi-log scale. From the forward current curve, the n factor was found to be 1.63.

Figure 8.15 shows C-V characteristics measured for the same sample, showing two main sections with different slopes. Near the junction, the acceptor concentration was  $9.3 \times 10^{14}$  cm<sup>-3</sup> and was  $2.7 \times 10^{15}$  cm<sup>-3</sup> in region away from the junction. Comparing with the cell 14-5-3, the capacitance value of I5-6 was much smaller. This difference suggested that the depletion width in the cell I5-6 was larger than in 14-5-3.

Figure 8.16 shows I-V characteristics for another sample, J20-1 which was fabricated on a CuInSe<sub>2</sub> treated in Ar. The J<sub>sc</sub>, V<sub>oc</sub>, FF and  $\eta$  were 33.7 mA/cm<sup>2</sup>, 0.28 V, 0.533, and 6.0% respectively. The ideality factor was found to be 1.64. Figure 8.17 shows C-V characteristics of the sample J20-1. The acceptor concentration of the CuInSe<sub>2</sub> in this cell obtained from the slop of the C-V characteristics was about  $6.68 \times 10^{15}$  cm<sup>-3</sup>.

# 8.4 Al/CdS/CdS/CuInSe, HETEROJUNCTION [1.7]

After the study of CdS(high  $\rho$ )/CuInSe<sub>2</sub> devices fabricated by depositing CBD CdS on the CuInSe<sub>2</sub> films, photovoltaic cells of the form CdS(low  $\rho$ )/CdS(high  $\rho$ )/CuInSe<sub>2</sub> were fabricated. Hence, the low resistivity CdS was deposited by vacuum evaporation. Current-voltage characteristic measurements have been carried out and the results for one of the solar cells (Sample J8-4) are given in Figure 8.18. The thicknesses of the CuInSe<sub>2</sub>, high  $\rho$  CdS, the low  $\rho$  CdS and were 1.5, 0.05 and 3  $\mu$ m, respectively. The area of the cell (the low resistivity CdS covered area) was 0.176 cm<sup>2</sup>. The active area of the cell was 0.11 cm<sup>2</sup>. The power density of the simulated illumination was 125 mW/cm<sup>2</sup>.

Under the illumination, the open circuit voltage, short circuit current density and fill factor for the cell J8-4 were 0.35 V, 43.6 mA/cm<sup>2</sup>, and 0.56, respectively. The corresponding active area energy conversion efficiency was about 6.8%.

It was also found that conversion efficiency of Cell J8-4 improved after being exposed to illumination for a period of time. After the illumination, the fill factor of the cell increased From 0.56 to 0.57, a 2% increase. This improvement in fill factor led to a 2.3% increase in conversion efficiency. This effect has been reported by Willet and Kuriyagawa [8.6] and was attributed to populating long-live trap state defects or to the phsical breaking and rearrangement of bonds.

The capacitance-voltage measurements were carried out under dark conditions. Figure 8.19

shows C<sup>-2</sup> versus bias voltage for the cell. It can be seen that the C<sup>-2</sup> value decreased as the reverse bias voltage was decreased. From the slopes of the C<sup>-2</sup> versus bias voltage characteristics, an average acceptor concentration, of  $1.23 \times 10^{16}$  cm<sup>-3</sup> was obtained for Sample J8-4.

From the C-V characteristics, the carrier concentration in the vicinity of the depletion region was also calculated and plotted versus the depletion width in Figure 6.20. Although the average acceptor concentration was about  $10^{16}$  cm<sup>-3</sup>, the concentration near the surface of the CuInSe<sub>2</sub> (w<0.1 µm) was higher than the average concentration. It would be interesting to determine the carrier concentration in region very close to the interface. However, if the depletion region were reduced by alliving a large forward bias, diffusion capacitance would contribute to the measured capacitance. Therefore, the acceptor concentration of the CuInSe<sub>2</sub> near the interface could not be determined accurately by this method.

The spectral response of Sample J8-4 was also determined for the 0.4 to 1.4  $\mu$ m wavelength range. The results are shown in Figure 8.22. In the short wavelength region, the response was limited by the low transmittance of the low resistivity CdS layer.

For a Schottky-like cell, the spectral response can also be used for estimation of the barrier height of the junction. The spectral response (S.R.) may be given by [3.3]:

$$S.R. = A(hv - hv_o)^2$$
 (8.6(a))

or,

$$(S.R)^{\frac{1}{2}} = B(hv - hv_{o})$$
(8.6(b))

Here, A and B are constants and  $hv_0$  is the barrier height. A plot of the square root of the spectral response as a function of photon energy is a straight line. The intercept on the energy

axis is the barrier height of the junction. Figure 8.22 shows a plot of  $(S.R.)^{4}$  of sample J8-4 versus energy of incident photons. From the intercept of the straight line with the energy axis, the barrier height of the junction was estimated to be about 0.7 eV.

## 8.5 Al/ZnO/CdS/CuInSe, HETEROJUNCTION [8.4][8.5]

After the above-described studies, photovoltaic cells of the form Al/ZnO/CdS/CuInSe\_/Mo were finally fabricated. A layer of high resistivity CdS (thickness about 360 Å) was first deposited by the CBD method on a heat-treated CuInSe\_. After the CdS deposition, the sample was loaded into the rf sputtering system to deposit a layer of low resistivity ZnO.

Figure 8.23 shows a SEM photograph of the cross section of a ZnO/CdS/CuInSe2 cell. The thickness of the CuInSe<sub>2</sub> film was about 1.2  $\mu$ m and that for the ZnO layer was about 1.4  $\mu$ m. It is seen that both the electrodeposited CuInSe<sub>2</sub> and rf sputtered ZnO films have a columnar structure.

Numerous cells of the form ZnO/CdS/CuInSe<sub>2</sub> have been fabricated and the results for the best one are described below. Figure 8.24 shows the I-V characteristics for the sample O51. The thicknesses of CuInSe<sub>2</sub>, high resistivity CdS, ZnO and Al used were 1.5, 0.05, 1 and 1  $\mu$ m, respectively. The area of the cell (ZnO covered area) was 0.104 cm<sup>2</sup>. The active area (ZnO not covered by Al) of the cell was 0.078 cm<sup>2</sup>. The power density of the simulated illumination was 125 mW/cm<sup>2</sup>. For this best cell, the open circuit voltage, short circuit current density and fill factor were 0.328 V, 42.4 mA/cm<sup>2</sup> and 0.566, respectively. The corresponding active area energy conversion efficiency was about 6.3%.

Capacitance-voltage characteristic measurements were also performed and the C<sup>-2</sup> versus

bias voltage results for the Sample O51 are shown in Figure 8.25. From the slope of C<sup>-2</sup> versus V curve, the average acceptor concentration in the CuInSe<sub>2</sub> was found to be about  $1.17 \times 10^{16}$  cm<sup>-3</sup>.

From the C-V characteristics, the carrier concentration in the neutral region near the depletion edge was also calculated and plotted against the depletion width. The results are shown in Figure 8.26. Although the average acceptor concentration was near the optium value of about  $10^{16}$  cm<sup>-3</sup> for a high performance heterojunction cell, the concentration is not uniform across the depletion region. Since the concentration values near the CuInSe<sub>2</sub> surface are not obtainable, it is not known whether the surface concentration is higher than the average bulk value.

The spectral response of Cell O51 was also determined and the results obtained are shown in Figure 8.27(a). It was found that the spectral response of the cell in short wavelength range was enhenced as compared to that for a CdS/CuInSe<sub>2</sub> cell (see Figure 8.21). At a wavelength of 0.5  $\mu$ m, the quantum efficiency was close to 80%. In the long wavelength region, it decreased gradually as wavelength was increased. Compared to the cell with the a thick CdS window layer, the cell with the ZnO window layer had high quantum efficiency in the short wavelength region. The overall smaller quantum efficiency for this ZnO/CdS/CuInSe<sub>2</sub> cell might be due to different treatment conditions for the CuInSe<sub>2</sub> films.

The square root of the spectral response  $(S.R.)^4$  was also plotted against energy of incident photons and the results are shown in Figure 8.27(b). It was found that the cell barrier height which was determined from the energy axis intercept in the plot of Figure 8.27(b), was about 0.83 volt.

# 8.6 CONCLUSIONS

Solar cells of the forms CdS(low  $\rho$ )/CdS(high  $\rho$ )/CuInSe<sub>2</sub> and ZnO/CdS(high  $\rho$ )/CuInSe<sub>2</sub> with an efficiency over 6% have been fabricated. This is the highest efficiency ever obtained on the cell fabricated on the electrodeposited CuInSe<sub>2</sub> films. It was confirmed that the CuInSe<sub>2</sub> treated in Ar yielded the best cell. This is partly due to the decrease of the accptor concentration in the surface region after the Ar treatment.

.


Figure 8.1 A SEM photograph showing a cross section of a CuInSe<sub>2</sub> thin film deposited on a Mo-coated glass substrate.



Figure 8.2 X-ray diffraction pattern of a CuInSe<sub>2</sub> film.

.



Figure 8.3 A schematic diagram of the system for reflectance measurements.



Figure 8.4 A schematic diagram of a cross section of a CuInSe<sub>2</sub> sample used for optical absorption coefficient measurement.



Figure 8.5 Reflectance and transmittance of Sample A-2 versus wavelength of incident light.



Figure 8.6 (a) Absorption coefficient of Sample A-2, calculated from the reflectance and transmittance measurements, versus energy of incident photons, (b)  $(\alpha h\nu)^{\mu}$  calculated from (a) plotted versus the photon energy. The intercept with the energy axis gives an energy gap of 1 eV for CuInSe<sub>2</sub>.



Figure 8.7 ( $\alpha h\nu$ )<sup>%</sup> value versus the energy of incident photons of three samples, A-5, A-1, A-2. The intercepts yield an energy gap close to 1 eV.



Figure 8.8 Current-voltage characteristics of a Schottky-like junction D7.



Figure 8.9 Capacitance-voltage characteristics of the junction D7.



Figure 8.10 Dark and illuminated I-V characteristics of a Schottky-like junction E19.



Figure 8.11 Capacitance-voltage characteristics of the junction E19 under dark and illuminated conditions.

J



Figure 8.12 Current-Voltage characteristics of the cell 14-5-3 fabricated on a CulnSe<sub>2</sub> film treated in vacuum, showing the effect of treatment time.



Figure 8.13 Capacitance-voltage characteristics of the cell 14-5-3 taken after each of three heat treatment stages, showing the change of acceptor concentration.





Figure 8.14 Current-voltage characteristics of cell I5-6 fabricated on the CuInSe<sub>2</sub> film treated in Ar. Note the cell performance is better than that of the cells deposited on a CuInSe<sub>2</sub> film treated in vacuum.



Figure 8.15 Capacitance-voltage characteristics of cell 15-6.

;



Figure 8.16 Current-voltage characteristics of cell J20 fabricated on a CuInSe<sub>2</sub> film treated in Ar.



Figure 8.17 Capacitance-voltage characteristics of cell J20.



Figure 8.18 Dark and illuminated I-V characteristics of Sample J8-4 showing a high short circuit current.



Figure 8.19 C<sup>-2</sup> versus bias voltage of Sample J8-4 under dark conditions. The slope of the curve gives an acceptor concentration of  $1.23 \times 10^{16}$  cm-3.



Figure 8.20 Acceptor concentration versus depletion width of Sample J8-4 obtained from C-V characteristics.



Figure 8.21 Spectral response of sample J8-4 versus wavelength of incident light.



Figure 8.22 Square root of the spectral response of sample J8-4 versus energy of incident photons, the intercept of the linear portion of the curve gives a barrier height of 0.7 V.

.

÷ 1



Figure 8.23 SEM pictures of cross section view of ZnO/CdS/CuInSe\_/glass.







Figure 8.25 C<sup>-2</sup> versus bias voltage of Cell OS1 under dark conditions. The slope of the curve gives an average acceptor concentration of  $1.17 \times 10^{16}$  cm-3.

÷



Figure 8.26 Acceptor concentration versus depletion width of Sample OS1 obtained from C-V characteristics.



Figure 8.27 (a) Spectral response of Sample O51 versus wavelength of incident light. (b) Square root of the spectral response of sample O51 versus energy of incident photons. The intercept of the curve with the vertical axis gives a barrier height was 0.83 V.

Ξ.

# CHAPTER 9 DIFFUSION LENGTH OF ELECTRONS IN CuinSe,

# 9.1 INTRODUCTION

Photons with an energy larger than the bandgap of the absorber (CuInSe<sub>2</sub>) create electronhole pairs in the solar cell. Minority carriers (electrons in p-type CuInSe<sub>2</sub>) diffuse toward the depletion region and are separated from majority carriers (holes) to produce a photocurrent. The minority carriers created at a distance greater than the diffusion length from depletion region edge can not contribute to the photocurrent. Hence, the operation and energy conversion efficiency of a solar cell are determined by the value of minority carrier diffusion length. The operation of other optoelectronic devices, is also affected by the diffusion length. For instance, the injection efficiency of a solid state laser is a function of the minority carrier diffusion length value.

Various methods can be used to determine minority carrier diffusion length in a semiconductor. These methods include the surface voltage method [9.1-9.3], photoluminescence method [9.4-9.6], photoresponse method [9.7-9.9] and the electron beam induced-current method (EBIC) [9.10][9.11]. The first three methods require knowledge of precise optical absorption coefficients of the semiconductor material being examined.

To understand the characteristics of the solar cells fabricated on electrodeposited CuInSe<sub>2</sub> thin films, it is necessary to carry out the minority carrier diffusion length measurements. The measurements must be carried out before one can determine if the electronic properties of the CuInSe<sub>2</sub> thin films prepared by the novel electrodeposition are good enough for future large scale photovoltaic applications.

In the present work, diffusion length measurements have been carried out on CdS/CuInSe<sub>2</sub>

and ZnO/CdS/CuInSe<sub>2</sub> heterojunction solar cells fabricated on electrodeposited CuInSe<sub>2</sub>. Two non-destructive methods have been employed for the diffusion length measurements. One is the photocurrent-capacitance (PC) method [9.14-9.17] and the other is the differential photocurrent (DPC) method [9.18]. The diffusion length of the semiconductor CuInSe<sub>2</sub> was measured without the prior data of absorption coefficient. The results obtained from the above two methods will be presented in this chapter [8.4][8.5]. Another method involving an electron beam (EBIC) has also been used and the results will be given in the next chapter.

#### 9.2 MEASUREMENT METHODS

In this section, the principles of the PC and DPC methods are discussed. Each method requires a heterojunction solar cell fabricated on the absorber with appropriate contacts. In the solar cell for the diffusion length measurements, the window layer should be a large band gap semiconductor so that absorption of incident light in the window layer can be neglected.

# 9.2.1 Photocurrent-Capacitance (PC) Method

When a monochromatic light beam is incident on a heterojunction cell, a photocurrent develops in the cell. The photocurrent may be represented by:

$$I_{ph} = eI_o TA[1 - \exp(-\alpha x) + \alpha L/(1 + \alpha L)\exp(-\alpha x)]$$
(9.1)

where  $I_0$  is the intensity of incident light, T is the transmission of the window layer including reflection losses, A is the area of the device and  $\alpha$ , L and x are the absorption coefficient, the minority carrier diffusion length and the depletion width of the absorber, respectively.

If the wavelength of the incident light is chosen so that  $\alpha x \ll 1$ , the absorption of the

incident light in the depletion layer is negligible, Equation (9.1) cab be simplified to:

$$I_{ph} = eI_0 T \alpha A (L+x) / (1+\alpha L)$$
 (9.2)

The depletion capacitance, C, of the junction is given by:

$$C = \epsilon_0 \epsilon_r A / x \tag{9.3}$$

where  $\varepsilon_0$  is the permittivity of vacuum and  $\varepsilon_r$  is the relative dielectric constant of the absorber (CuInSe<sub>2</sub>). From Equation (9.3), the depletion width of the absorber can be obtained from capacitance measurements:

$$x = \epsilon_0 \epsilon_r A / C \tag{9.4}$$

Substituting Equation (9.4) into Equation (9.2), the following relation is obtained:

$$I_{ph} = k(1/C + L/\epsilon_0 \epsilon_A) \tag{9.5}$$

Here  $k = eI_0 L\alpha A^2 \epsilon_0 \epsilon_r / (1+\alpha L)$ . It is assumed that, at a given wavelength, the absorption coefficient and the diffusion length of the absorber are independent of the bias voltage. Therefore, when the cell is illuminated by light of a fixed wavelength, k is a constant.

Since the capacitance, C, is a function of the reverse bias voltage, the photocurrent under constant monochromatic illumination,  $I_{ph}$ , will change when the reverse bias varied.

In Equation (9.5), it is noted that a plot of  $I_{ph}$  versus 1/C will yield a straight line with the intercept on the 1/C axis at -L( $\epsilon_0 \epsilon_r A$ ). Hence the diffusion length of the minority carriers can be obtained from the follow equation.

$$L = -\epsilon_0 \epsilon_A / C \tag{9.6}$$

Several assumptions have been made in the above derivation for the PC method.

(1) The absorption of the incident light in the window layer can be neglected. Therefore, carriers generated in the window layer can be neglected.

(2) The thickness of the absorber layer is larger than the diffusion length, L. Incident photons passing the absorber without being collected can be neglected.

(3) The electron-hole recombination in the depletion region and at interface can be neglected.

(4) The junction is a  $n^+$ -p junction, so the depletion layer is located only on the absorber side.

#### 9.2.2 Differential Photocurrent (DPC) Method

When an one-sided heterojunction under monochromatic light is reverse biased at a voltage V, the photocurrent is given by Equation (9.5). When the applied reverse voltage is changed by  $\Delta V$ , the changes in depletion width and photocurrent are  $\Delta x$  and  $\Delta I_{ph}$ , respectively. The change in the depletion layer width can be expressed as:

$$\Delta x = -\epsilon_0 \epsilon_0 \Delta V/ex N(x) \tag{9.7}$$

where e is the electron charge, x is the depletion width,  $\varepsilon_0$  is the permittivity of vacuum,  $\varepsilon_r$  is the relative dielectric constant of the absorber and N(x) is the carrier concentration at the depletion layer edge. The depletion width x can be obtained from capacitance-voltage measurements.

At the reverse bias voltage,  $V_1 = V + \Delta V$ , the photocurrent can then be expressed as:

$$I_{ph} = eI_0 TA (1 + \alpha L - \exp[-\alpha (x + \Delta x)]) / (1 + \alpha L)$$
(9.8)

When Equation (9.8) is differentiated, the following equations are obtained:

$$\frac{\Delta I_{ph}}{\Delta x} = \frac{eI_0 TA\alpha}{1+\alpha L} \exp(-\alpha x)$$
(9.9)

and

$$\ln\left(\frac{\Delta I_{ph}}{\Delta x}\right) = -\alpha x + \ln\left[\frac{eI_0 T A \alpha}{1 + \alpha L}\right]$$
(9.10)

From the last equation, a plot of  $\ln(\Delta I_{ph}/\Delta x)$  versus the depletion width, x, of the junction will be a straight line with a slope of - $\alpha$  at the wavelength of the incident light. Therefore, the optical absorption coefficient of the absorber of the junction,  $\alpha$ , can be determined by this method. Using the absorption coefficient value obtained,  $\exp(-\alpha x)$  values at different depletion widths, x of different reverse bias voltages can then be calculated. A plot of photocurrent,  $I_{ph}$ , against  $\exp(-\alpha x)$  can be made. From Equation (9.1), it is clear that this plot is linear. Extrapolation of the photocurrent at  $\exp(-\alpha x) = 1$ , where x = 0, gives:

$$[I_{ph}]_{x=0} = \frac{eI_0 T A \alpha L}{1 + \alpha L}$$
(9.11)

At x = 0, Equation (9.9) becomes:

5

$$\left[\frac{\Delta I_{ph}}{\Delta x}\right]_{x=0} = \frac{eI_0 TA\alpha}{1+\alpha L}$$
(9.12)

Combining Equations (9.11) and (9.12), the diffusion length of the minority carriers can be obtained:

$$L = [I_{ph}]_{x=0} / [\frac{\Delta I_{ph}}{\Delta x}]_{x=0}$$
(9.13)

The assumptions made for the photocurrent-capacitance method also apply for the differential photocurrent method. Since the recombination of carriers at the interface has been ignored in the above treatment, the diffusion lengths obtained by the present methods may be small than their true value.

# 9.3 EXPERIMENTAL SETUP FOR THE MEASUREMENTS

The equipment used for the photocurrent measurements and capacitance measurements to determine the minority carrier diffusion length is briefly described in this section.

#### 9.3.1. Set-up for Photocurrent Measurements

A schematic diagram of the setup for photocurrent measurements is shown in Figure 9.1. A tungsten filament lamp (Oriel, Model No. 6325) was used as a light source. The incident white light passed through a monochromator (Beckman, Model No. 2400) which converted the white light to monochromatic light. During the measurements, setting of the power supply (Oriel, Model No. 6329) to the tungsten lamp was fixed at 7 A. The slit width of the monochromator was set at 0.5 mm and the wavelength of the monochromatic light was adjusted at a value from 1.1 to 1.3  $\mu$ m.

A reverse bias voltage was applied to the junction through an HP semiconductor parameter analyzer (Model No. 4145A) and the current output was measured. The current at each bias voltage was measured 256 times and the average value was then taken. The reverse bias applied to the cell varied from -0.1 to -2 volts in steps of 0.1 V. The dark current  $(I_D)$  of the cell was first measured at different reverse biases. The current  $(I_{ill})$  of the cell under illumination was then measured at the same reverse biases. The photocurrent of the cell is given by:

$$I_{ph} = I_{ill} - I_D \tag{9.14}$$

#### 9.3.2. Set-up for Capacitance Measurements

The depletion capacitance of the cells under monochromatic illumination was measured using an HP LCR meter (Model No. 4274A) controlled by an IBM personal computer. The reverse bias to the cell, which was supplied by the LCR meter, was varied from 0.1 to 2 volts in steps of 0.1 volts. The actual dc bias of the cell was measured by an HP multimeter (Model No. 3478A). During the measurements, a small ac signal was superimposed on the reverse bias voltage. The amplitude and the frequency of this ac signal were set to 0.02 V and 100 kHz. The depletion capacitance of the cell under illumination and the reverse bias voltage were recorded. A schematic block diagram of the experimental setup for the measurements is shown in Figure 9.2. During the measurements, the setting of the monochromator was the same as that described in Section 9.3.1.

## 9.4 DETERMINATION OF DIFFUSION LENGTH OF CuInSe,

Several photovoltaic cells of the form CdS/CuInSe<sub>2</sub> fabricated in the laboratory have been studied. Detailed experimental results for one of the cells, sample J20-1, will be specially described in this section. The CuInSe<sub>2</sub> film used was treated in Ar. The wavelengths of the incident monochromatic light selected were 1.1, 1.15, 1.2 and 1.25  $\mu$ m. The total area of the J20-1 was 0.178 cm<sup>2</sup> with an active area of 0.11 cm<sup>2</sup>. The dielectric constant of CuInSe<sub>2</sub> used was

chosen to be 10.

9.4.1 Photocurrent-Capacitance Method [PC]

Differential capacitance of sample J20-1, under reverse bias voltages ranging from 0 to 2 volts was measured at 100 kHz. During the measurements, monochromatic light was allowed to incident on the sample. Figure 9.3 shows a plct of 1/C versus the reverse bias voltage. The photocurrent of the sample was also measured under the same biases and illumination. Figure 9.4 shows the variation of photocurrent ( $I_{ph}$ ) with reverse bias for Sample J20-1.

From the results of Figure 9.3 and Figure 9.4, a plot of the sample photocurrent versus 1/C was obtained (Figure 9.5). From intercepts of the straight lines with the 1/C axis, the diffusion lengths of the electrons in p-type CuInSe<sub>2</sub> were obtained from Equation (9.6). The diffusion lengths obtained under incident monochromatic light of wavelengths, 1.1, 1.15, 1.2 and 1.25  $\mu$ m were 0.54, 0.52, 0.45 and 0.39  $\mu$ m.

# 9.4.2 Differential Photocurrent Method [DPC]

To determine the minority carrier diffusion length by the DPC method, the depletion layer width must be known. The depletion width of the sample was calculated by Equation (9.15) from the 1/C versus reverse bias plot shown in Figure 9.3.

$$\mathbf{x}(\mathbf{V}) = \epsilon_0 \epsilon_{\mathbf{A}} / C(\mathbf{V}) \tag{9.15}$$

A plot of depletion width versus reverse bias under illumination, for the sample J20-1, is shown in Figure 9.6. From the plot, the increment of the depletion width,  $\Delta x_i$ , at a reverse bias of V<sub>i</sub> can be obtained.

$$\Delta x_i = x_i - x_{i-1} \tag{9.16}$$

The differential current of the sample at a reverse bias of  $V_i$  can be obtained from Figure 9.4.

$$\Delta I_i = I_i - I_{i-1} \tag{9.17}$$

From the values calculated using Equations (9.16) and (9.17), values of  $\ln(\Delta I/\Delta x)$  for the sample J20-1 at different reverse biases could be calculated. The results are plotted against depletion width in Figure 9.7. From the slope of the straight lines, the optical absorption coefficients of the CuInSe<sub>2</sub> could be calculated. The optical coefficients were 1.06, 1.19, 1.09 and 1.01  $\mu$ m<sup>-1</sup> at 1.1, 1.15, 1.2 and 1.25  $\mu$ m respectively. From the intercepts of the straight lines with the ln( $\Delta I/\Delta x$ ) axis, the [ $\Delta I/\Delta x$ ]<sub>x=0</sub> values, at incident wavelengths of 1.1, 1.15, 1.2 and 1.25  $\mu$ m, were then obtained. The [ $\Delta I/\Delta x$ ]<sub>x=0</sub> values were 74.5, 79.5, 69.7 and 49.5 A/m, respectively.

Using the optical absorption coefficients obtained in the above measurements, value of  $e^{-\alpha x}$  at different depletion widths and different reverse bias voltages were computed. The variation of photocurrent  $I_{ph}$  versus  $e^{-\alpha x}$  was plotted. The results are displayed in Figure 9.8. The extrapolated photocurrent at  $e^{-\alpha x} = 1$ , where x = 0, was obtained. The values of  $I_{ph}$ , at x = 0, of sample J20-1, were 18.4, 17.7, 13.9 and 9.1  $\mu$ A at wavelengths of 1.1, 1.15, 1.2 and 1.25  $\mu$ m.

The diffusion length of the absorber  $CuInSe_2$  in the sample J20-1 was finally obtained from the ratio of  $[I_{ph}]_{x=0}$  to  $[\Delta I/\Delta x]_{x=0}$ . The diffusion length values of the sample J20-1 obtained using the differential photocurrent method, were 0.25, 0.23, 0.20 and 0.18 µm at incident wavelengths of 1.1, 1.15, 1.2 and 1.25 µm respectively.
Detailed measurements using the PC and DPC methods described above have been carried out on several other samples and the results obtained are reported below.

### 9.5 RESULTS AND DISCUSSION

Table 9.1 shows the parameters of the six CdS/CuInSe<sub>2</sub> jeterojunction cells used for the diffusion length experiments. The acceptor concentration in the CuInSe<sub>2</sub> of these cells varied from  $6.2 \times 10^{15}$  to  $1.9 \times 10^{16}$  cm<sup>-3</sup>. The open circuit voltages of these cells under simulated AM1 illumination varied from 0.27 to 0.32 Volt. The short circuit current varied from 3.2 to 4.86 mA. All the cells listed in this table are CdS/CuInSe<sub>2</sub> junctions.

Table 9.2 shows results of diffusion length measurements obtained using the photocurrentcapacitance and the differential photocurrent methods on the same six samples. The diffusion lengths measured using the differential photocurrent method were shorter than those measured using the photocurrent-capacitance method. The difference in diffusion lengths between the two method was large especially for the two samples, J17-4 and J19-1. Similar to that from the PC method, the diffusion lengths obtained with DPC method varied with the incident photon energy. The diffusion lengths of the cells measured using the two methods showed no significant concentration dependence when samples had acceptor concentration less than  $2.0 \times 10^{10}$  cm<sup>-3</sup>.

The optical absorption coefficients of the CuInSe<sub>2</sub> obtained from the above experiments are also listed in Table 9.2. The  $\alpha$  values did not vary as expected. With the exception of Sample J16-1, there were no sharp decreases in the  $\alpha$  values near the energy gap (1 eV). In sample J16-1, a sharp decrease in the  $\alpha$  values occurred at a wavelength of 1.3 µm. This wavelength, 1.3 µm, corresponded to a photon energy of 0.954 eV which is close to the energy gap reported for vacuum-deposited thin films of  $CuInSe_2$ . The energy gap of electrodeposited  $CuInSe_2$  films prepared in this experiment could be smaller than that reported for thermally evaporated films.

One of the assumptions for the two methods used for diffusion length measurements is that the current transport mechanism in the cells is dominated by diffusion. However, if the diffusion component of the current is less than  $eI_0T\alpha A$ , the intercept of  $I_0$  with the 1/C axis will be less than the diffusion length,  $\bot$ . Hence, the real diffusion length of the CuInSe<sub>2</sub> should be greater than the lengths obtained from the PC method. The diffusion length values of two samples K16-3 and J8-4 were 0.52 and 0.53 µm, respectively, at a wavelength of 1.2 µm. These values are very close to the reported value of 0.6 µm for vacuum evaporated CuInSe<sub>2</sub> films[9.12].

Diffusion length measurements were also carried out on cells with a ZnO/CdS/CuInSe<sub>2</sub> structure. In these measurements the plot of  $ln(\Delta I_{ph}/\Delta x)$  versus x for these samples did not yield a straight line. Therefore, the diffusion length was determined only from the PC method. Table 9.3 shows the results of these measurements. It is noted that the only difference between these cells and the CdS/CuInSe<sub>2</sub> cells is the window material used. The L values obtained from the PC method for the three cells were very close to the values of CdS/CuInSe<sub>2</sub> cells described in this section.

#### 9.6 CONCLUSIONS

Minority carrier diffusion length of  $CuInSe_2$  was measured using the PC and the DPC methods. These two methods are simple and are non-destructive. Values of the minority carrier diffusion length of the CuInSe<sub>2</sub> films prepared by the novel electrodeposition method were close to the values reported by other researchers for evaporated CuInSe<sub>2</sub> films [9.12]. Diffusion lengths

values determined using the DPC method were smaller than those from the PC method. It was  $\therefore$ so found that, the diffusion lengths in the CdS/CuInSe<sub>2</sub> cells were close to that in ZnO/CdS/CuInSe<sub>2</sub> cells. Hence, the electronic quality of the CuInSe<sub>2</sub> films were not affected strongly by the CBD process for deposition of high resistivity CdS and the rf deposition process for ZnO. Furthermore, it was found that the diffusion length in CuInSe<sub>2</sub> with acceptor concentration less than  $2 \times 10^{16}$  cm<sup>-3</sup> was not dependent on the concentration. However, for the samples with higher acceptor concentrations, the diffusion length decreased with the increase in carrier concentration. Although, the optical absorption coefficient of the CuInSe<sub>2</sub> measured using the DPC method did not show a rapid decrease near the reported band gap. The values obtained were approximately equal to those from the direct measurements presented in Chapter 8.

÷

| Sample No | J <sub>sc</sub> (mA) | V <sub>oc</sub> (V) | N <sub>B</sub> (cm <sup>-3</sup> ) |
|-----------|----------------------|---------------------|------------------------------------|
| J8-4      | 4.86                 | 0.32                | 1.80×10 <sup>16</sup>              |
| J16-1     | 3.73                 | 0.28                | 1.40×10 <sup>16</sup>              |
| J17-4     | 3.20                 | 0.27                | 6.17×10 <sup>15</sup>              |
| J19-1     | 4.48                 | 0.32                | 1.92×10 <sup>16</sup>              |
| J20-1     | 4.64                 | 0.28                | 6.63×10 <sup>15</sup>              |
| K16-3     | 4.80                 | 0.28                | 8.73×10 <sup>15</sup>              |

Table 9.1. Parameters of the samples used for the diffusion length measurement.

\*Average acceptor concentration calculated from C-V characteristics taken at 100 kHz under monochromatic illumination of wavelength, 1.2  $\mu$ m.

14

÷

| Sample<br>No |  | λ=1.1µm               | λ=1.15µm              | λ=1.2 μm              | λ=1.25µm              | λ=1.3µm              |
|--------------|--|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|
| J8-4         | α(μm <sup>-1</sup> )<br>L(μm)(P-C)<br>L(μm)(DPC) | 2.48<br>0.56<br>0.19  | 2.85<br>0.56<br>0.16  | 2.90<br>0.53<br>0.15  | 3.02<br>0.49<br>0.13  | 2.35<br>0.45<br>0.21 |
| J16-1        | α(μm <sup>-1</sup> )<br>L(μm)(P-C)<br>L(μm)(DPC) | 1.51<br>0.37<br>0.12  | 1.78<br>0.31<br>0.095 | 1.60<br>0.28<br>0.078 | 2.0<br>0.18<br>0.028  | 0.08<br>0.15<br>0.14 |
| J17-4        | α(μm <sup>-1</sup> )<br>L(μm)(P-C)<br>L(μm)(DPC) | 1.21<br>0.32<br>0.056 | 1.13<br>0.26<br>0.035 | 0.83<br>0.20<br>0.041 | 0.96<br>0.17<br>0.014 |                      |
| J19-1        | α(μm <sup>-1</sup> )<br>L(μm)(P-C)<br>L(μm)(DPC) | 3.31<br>0.34<br>0.068 | 3.55<br>0.33<br>0.061 | 3.16<br>0.29<br>0.063 | 3.01<br>0.27<br>0.059 |                      |
| J20-1        | α(μm <sup>-1</sup> )<br>L(μm)(P-C)<br>L(μm)(DPC) | 1.06<br>0.54<br>0.25  | 1.19<br>0.52<br>0.22  | 1.09<br>0.45<br>0.20  | 1.01<br>0.39<br>0.18  |                      |
| K16-3        | α(μm <sup>-1</sup> )<br>L(μm)(P-C)<br>L(μm)(DPC) | 1.44<br>0.63<br>0.18  | 1.63<br>0.51<br>0.11  | 1.40<br>0.52<br>0.14  | 1.66<br>0.289<br>0.25 |                      |

Table 9.2. Results of the diffusion length measurements for the six samples listed in Table 9.2.

Table 9.3. Results of diffusion lengths measured using the PC method on three samples with the  $ZnO/CdS/CuInSe_2$  structure.

| Sample No.  | L (μm)<br>λ=1.1 μm | L (μm)<br>λ=1.15 μm | L (μm)<br>λ=1.2 μm | L (μm)<br>λ=1.25 μm | L (μm)<br>λ=1.3 μm |
|-------------|--------------------|---------------------|--------------------|---------------------|--------------------|
| <b>O</b> 51 | 0.65               | 0.61                | 0.54               | 0.37                | 0.37               |
| X31-4       | 0.22               | 0.20                | 0.15               | 0.11                | 0.092              |
| x41-7       | 0.19               | 0.14                | 0.14               | 0.13                | · 0.094            |



Figure 9.1 A schematic block diagram of the photocurrent measurement setup.

 $\sim 11$ 

с., К.,



Figure 9.2 A schematic block diagram of the capacitance measurement setup.

174



Figure 9.3 Reciprocal capacitance versus reverse bias voltage of sample J20-1 under monochromatic illumination at different wavelengths.



Figure 9.4 Photocurrent versus reverse bias voltage of sample J20-1 under monochromatic illumination at different wavelengths.

\_\_\_\_\_

176

2

.



Figure 9.5 Photocurrent versus reciprocal capacitance of sample J20-1 under monochromatic illumination at different wavelengths.



Figure 9.6 Depletion width versus reverse bias voltage of sample J20-1 under monochromatic illumination at different wavelengths.

÷

7

 $\sim$ 



Figure 9.7  $\ln(\Delta I_{ph}/\Delta x)$  versus the depletion width of sample J20-1 under monochromatic illumination at different wavelengths.



Figure 9.8 Photocurrent versus e<sup>-ax</sup> of sample J20-1 under monochromatic illumination at different wavelengths.

# CHAPTER 10 STUDY OF CuInSe<sub>2</sub>-BASED CELLS BY ELECTRON BEAM INDUCED CURRENT MEASUREMENTS

#### **10.1 INTRODUCTION**

In Chapter 9, results of minority carrier diffusion length on electrodeposited CuInSe<sub>2</sub> films by optical methods were presented. In those experiments, the values of electron diffusion lengths were deduced from depletion capacitance and photocurrent measurements. As described in Chapter 9, the diffusion length values thus obtained might be smaller than the actual values due to the recombination process in the junctions. Therefore, in this chapter, research work will be carried out to determine diffusion lengths by an electron beam induced current method (EBIC).

This method has been extensively used to determine diffusion length and lifetime of minority carriers in various semiconductors. The EBIC method is a more direct and independent method for the determination of minority carrier diffusion lengths. It is thus necessary to obtain values by the EBIC method on the electrodeposited  $CuInSe_2$  films and compare them with those obtained by the PC and DPC methods.

Some of work reported in the literature on diffusion length determination by the EBIC method is briefly reviewed below. Hackett used the EBIC method to determine the minority carrier diffusion length of an angle lapped GaP p-n junction [10.1][10.2]. Jastrzebski and coworkers measured the electron beam induced diffusion current across a cleaved GaAs p-n junction [10.3][10.4]. In another paper by Ryan, measurements were carried out by scanning an electron beam along the surface of a planner junction [10.5]. Diffusion length was also determined by measuring the luminescent response of bulk semiconductors and p-n junctions to

181

incident electrons, as a function of excitation energy [10.6][10.7].

From the above brief description, it is clear that EBIC measurements can be carried out either on a cleaved or lapped p-n junction or on a planar junction. For the solar cells fabricated in this work on the electrodeposited CuInSe<sub>2</sub> thin films, it is difficult to obtain a high quality cleaved surface by fracturing. Hence, the EBIC measurements to be described were performed on the planar surface. In this chapter, the principle of the EBIC method used for the determination of minority carriers diffusion length is first described. Details of the experimental procedure are then presented. The results obtained on several solar cells are finally described.

## 10.2 PRINCIPLE OF THE EBIC METHOD

When a beam of electrons is incident on a photovoltaic solar cell, a significant fraction of electrons may be backscattered when they collide with nuclei or electrons of the target material. These electrons will not contribute to the carrier generation process. The rest of the electrons are absorbed by the target. All of the energy of the absorbed electrons dissipates within a given distance from the surface of the target. As a result, excess electron-hole pairs are generated. Only the excess carriers that diffuse into the depletion region and are separated by the electric field of the depletion region (before the recombination) will be able to contribute to the short circuit current. Therefore, it is very important to understand how electrons in the beam interact with the target material.

The interaction of high energy electrons with solid material has been studied extensively [10.8-10.13]. In such study, the primary electrons were assumed to travel straight into the target material to a certain depth [10.10]. At this depth, the electrons diffuse randomly in all directions,

transferring energy to the target material. The incident electrons thus can be considered as a point source. The distance that the primary electrons travel straight into the target is defined as the *depth of complete diffusion*,  $X_D$  [10.10]. The complete path of the electrons that diffuse evenly in all directions is called the Bethe range,  $R_B$ .

#### 10.2.1 Backscattering of Incident Electrons

When the primary electrons enter the target, some of them are scattered back, away from the target. These electrons will not contribute to electron-hole pair generation. The energy associated with these electrons can be expressed as:

$$\frac{\Delta E}{E_0} = \frac{1}{2} \left( 1 + \frac{\mu R_B x_D}{2} \right) \exp\left( -\mu R_B x_D \right)$$
(10.1)

where  $\mu$  is the absorption coefficient of the target material, R<sub>B</sub> is the Bethe range, x<sub>D</sub>, which is a constant, is only dependent on the average atomic number of the target material, Z and x<sub>D</sub>  $\approx$ 4/(Z+4) over the whole range of nonrelativistic energy. The value of the parameter  $\mu$ R<sub>B</sub> shows little dependence on energy and atomic number. In this work, a value of 11 was taken for  $\mu$ R<sub>B</sub> [10.10]. The energy associated with the scattered electrons is then only dependent on the average atomic number of the target material. This energy was calculated using Equation (10.1) and is plotted against atomic number of the target in Figure 10.2. For CuInSe<sub>2</sub>, the average atomic number is 36.5. Hence, from Figure 10.2, about 25% of the energy is associated with scattered electrons.

#### 10.2.2 Energy Dissipation

In order to understand the profile of excess carrier distribution when a target is bombarded with a beam of high energy electrons, it is necessary to determine the differential energy loss, dE/dX, of the electrons. The differential energy loss of the electrons for a given material may be expressed as:

$$\frac{dE}{dX} = \left(\frac{E_0}{R_B}\right) \left(\frac{\mu R_B}{4}\right) \left(1 + \mu R_B |x - x_D|\right) \exp\left(-\mu R_B |x - xD|\right)$$
(10.2)

Here, x is the integrated path length,  $x = X/R_B$  (X is the distance from the target surface). The  $(\mu R_B/4)(1+\mu R_B | x-x_D |)\exp(-\mu R_B | x-x_D |)$  is an universal depth-dose function, which determines the shape of the dissipation energy along the direction of penetration of the incident electrons. This function is independent of incident energy but dependent on the atomic number of the target material.

The Bethe range  $R_B$  is an energy dependent value. The mass-range ( $\rho R_B$ ), for a target material with atomic number greater than 30 at different incident energy values can be found from the Bethe Law. The values of  $\rho R_B$  were 0.8, 1.15, and 1.75 mg/cm<sup>2</sup> for incident energies of 12, 15, and 20 KeV [10.10]. Since the density of CuInSe<sub>2</sub> was 5.65 g/cm<sup>-3</sup>, values of  $R_B$  were 1.42, 2.04, and 3.10 µm for incident energy of 12, 15, and 20 keV respectively.

The differential energy loss of the incident electrons was then calculated and plotted against depth from the target surface for three incident energies. The results are shown in Figure 10.3. The area under each curve represents the total energy loss of electron at that energy. For all three curves, most of the energy of the incident electrons will be absorbed by the target in a distance less than 1  $\mu$ m from the surface. The effective depth for the energy loss increases as the

electron energy is increased. Hence, it is preferred to use an electron beam with a low energy for the study of thin film devices. In this work, beams with electron energies of 12 and 15 KeV will be used.

## 10.3.3 Generation of Electron-Hole Pairs

The energy loss of the incident electrons is transferred to the electrons in the target to generate free electron-hole pairs. Assume  $E_A$  is the mean energy required for the generation of one electron-hole pair in CuInSe<sub>2</sub>. Further assume the electron beam of current density  $J_B$  suffers a mean energy loss of dE in penetrating a layer of material dX. The number of electron-hole pairs created per unit time per unit volume within dX of CuInSe<sub>2</sub>, g(x), is

$$g(X) = \frac{J_B}{eE_A} \frac{dE}{dX}$$
(10.3)

The rate of excess carrier generation is proportional to the rate of energy loss by the incident electrons. From the differential energy loss of the electrons versus depth results (Figure 10.3), for incident energies of 12 and 15 KeV, it is expected that most of the excess carrier generation will occur within 0.5  $\mu$ m of the surface. Therefore, the excess carriers have a bell-shaped distribution with distance below the surface. The volume occupied by the excess carriers is very small compared to the total volume in the Bethe range because the diameter of the electron beam can be adjusted to about 100 Å. A schematic diagram showing the volume containing the excess carriers is illustrated in Figure 8.4. More than 90% of the excess carrier generation occurred before the differential energy loss reached 1/e of the peak value. For an electron beam with an incident energy of 15 KeV, the depth below the surface of 1/e generation

volume is about 0.66 µm which is about 30% of the Bethe range.

10.2.4 Determination of Diffusion Length From EBIC Measurements

When an electron beam is incident on a p-n junction, the excess carriers created in the neutral region of the p-n junction diffuse toward the junction. Some of these carriers reach the depletion region before recombining. These excess carriers will be separated by the electric field and produce a short circuit current. Detailed treatment of diffusion length measurements with the EBIC method has been reported in literature [10.14][10.15]. The current induced is an exponential function of distance between the electron beam and the depletion edge, x:

$$I = I_{SC}(0) \exp(-x/L)$$
(10.4)

where L is the diffusion length and  $I_{sc}(0)$  is the short circuit current created when the electron beam strikes the junction plane at x=0. A plot of induced current (logarithmic scale) versus distance (x) should yield a straight line. From the slope of this straight line (-1/L), the diffusion length, L, can be determined. The excess carrier life-time  $\tau$  in turn can be calculated from the diffusion length:

$$\tau = \frac{L^2}{D} = \left(\frac{q}{kT\mu}\right)L^2$$
 (10.5)

Here, D is the diffusion coefficient and  $\mu$  is the mobility of minority carrier (electrons in p-type CuInSe<sub>2</sub>).

The validity of the Equation (10.4) has to be examined because the excess carriers are subject not only to bulk recombination but also to surface recombination. As stated before, the electron beam used can be approximated by a steady state point source located at a depth,  $\xi$ , below the surface. The carrier generation rate of the point source is equal to  $G\delta(x,y,z-\xi)$ , where G is constant and  $\delta(x,y,z-\xi)$  is a distribution function. The steady state concentration of excess carriers,  $\Delta p(x,y,z)$ , can be obtained from the continuity equation:

$$D_{n} \operatorname{div} \left[\operatorname{grad} \Delta p(x, y, z)\right] - \Delta p(x, y, z) / \tau_{n} + G \delta(x, y, z - \xi) = 0$$
(10.6)

Here  $D_n$ , and  $\tau_n$  are the diffusion coefficient and life-time of minority carriers, respectively. The boundary condition at surface (z=0) is:

$$D_{R} \frac{\partial \Delta p}{\partial x} \Big|_{z=0} = S \Delta p \Big|_{z=0}$$
(10.7)

S is the surface recombination velocity of electrons at the plane Z = 0. Assuming that the depth,  $\xi$ , of the point source from the surface is much smaller than the thickness of the CuInSe<sub>2</sub>, t, then the total steady state excess electron concentration can be expressed as:

$$\Delta p(\xi) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{0}^{\infty} dz \Delta p(x, y, z)$$
(10.8)

From Hachett's treatment [10.2],  $\Delta p(\xi)$  can be expressed as:

$$\Delta p(\xi) = \left(\frac{GL^2}{D}\right) \left[1 - \left(\frac{s}{s+1}\right) \exp\left(-\frac{\xi}{L}\right)\right]$$
(10.9)

where L is the bulk diffusion length of the electrons and s is the reduced surface recombination velocity given by the relation:

$$s = \frac{S\tau_{eff}}{L_{eff}}$$
(10.10)

Here  $\tau_{eff}$  and  $L_{eff}$  are the effective lifetime and diffusion length, respectively, of electrons in the CuInSe<sub>2</sub>.

Under steady state conditions,  $\Delta p(\xi)$  can be related to the effective lifetime,  $\tau_{eff}$ , as follows ( $\tau_{eff}$  can further be related to the measured effective diffusion length,  $L_{eff}$ ):

$$\Delta p(\xi) = G\tau_{\text{eff}}, \qquad (10.1^{\circ})$$

The effective diffusion length is related to  $\tau_{eff}$  through the following equation:

$$L_{cff} = \sqrt{D_n \tau_{cff}}$$
(10.12)

Combining Equations (10.10), (10.11) and (10.12), the effective diffusion length can be obtained.

$$L_{eff}^{2} = L^{2} \left[ 1 - \left( \frac{s}{s+1} \right) \exp\left( -\frac{\xi}{L} \right) \right]$$
(10.13)

It is evident that if  $\xi \leq L$ , the effective diffusion length,  $L_{eff}$ , will be much smaller than the bulk diffusion length due to surface recombination. Hence, special precautions should be taken when the EBIC method is used to determine the diffusion length of minority carriers in a semiconductor.

#### **10.3 DETAILS OF THE MEASUREMENTS**

Several solar cells with an Al/ZnO/CuInSe<sub>2</sub>/Mo structure were selected for the determination of electron diffusion length by the EBIC method. The EBIC measurements were carried out in the JOEL model JSM-6100 scanning electron microscope. A schematic diagram of the experimental setup used for the experiments is shown in Figure 10.1. The sample was mounted on a brass holder by tightening a screw. The brass holder was directly attached to a stage located in the vacuum chamber of the SEM. The electrical contact to the n-type ZnO was made by soldering a copper wire and connecting it to a GW specimen current amplifier (Model

No. Type E 103B). From the sample stage, the common ground was connected to the p-type  $CuInSe_2$ . In this experiment, the sample to be examined was mounted with the surface perpendicular to the electron beam.

After a fine adjustment of the sample position, the edge of the ZnO window was located and the SEM was switched to a line scan mode. The electron beam was swept across the edge separating the ZnO and CuInSe. The incident electron beam induced a current in the cell which was collected and amplified by the current amplifier. The amplitude of the current was superimposed on the scanning image of the cell. A picture was taken and variation of the induced current amplitude with the electron beam position was then obtained. The variation of current with position was finally used to determine the diffusion length of minority carriers.

### 10.4 RESULTS AND DISCUSSION

Figure 10.5 shows a SEM photograph taken from a cell (sample Y12) with an electron energy of 15 KeV at 5000×. The curve superimposed on it is the EBIC scan showing a current peak. The material on the left-hand side of the current peak is ZnO on CuInSe<sub>2</sub>. The material on the right-hand side of the peak is bare CuInSe<sub>2</sub>. In the left-hand region, the carrier generation took place mostly in the ZnO (thickness was 1  $\mu$ m). The diffusion length of the holes in the ZnO is very short due to the high concentration (10<sup>20</sup> cm<sup>-3</sup>) and low mobility. Therefore, only the EBIC current generated in the bare CuInSe<sub>2</sub> side is useful for determination the diffusion length of electrons.

From the SEM picture with the EBIC scan, the logarithm of the current on the CuInSe<sub>2</sub> side of the junction was plotted as a function of the location of the electron beam. The results

are shown in Figure 10.6. From the slope of the plot, the effective minority carrier diffusion length of the CuInSe<sub>2</sub> was found to be 1.07  $\mu$ m.

Figure 10.7 shows two SEM photographs with EBIC scans magnified at 4000× for sample X33. The measurements were taken at two incident electron energies of 12 and 15 KeV. From the EBIC scans, the current on the CuInSe<sub>2</sub> side of the junction was taken and plotted against the distance between the electron beam and the metallurgical junction in a semi-logarithmic scale in Figure 10.8. The electron diffusion lengths of sample X33 were 1.55 and 1.60  $\mu$ m at incident energies of 12 and 15 KeV, respectively. Without considering the effects of surface recombination, the diffusion length of electrons in the CuInSe<sub>2</sub> of this sample was at least 1.5  $\mu$ m for the sample X33.

It should be noted that the diffusion length of electrons obtained was the effective value, which depended strongly on the surface recombination of the electrons. From experiments carried out by Everhart and Hoff [10.12], it was found that the effective diffusion length of electrons in CuInSe<sub>2</sub> increased with the increase of energy of incident electrons. In Section 10.3, it was shown that the penetration depth of the electron beam into the substrate increased with the increase of the electron energy. Therefore, the carriers generated by electrons of higher energy were at a larger distance from the surface. The influence of surface recombination on these carriers was less significant than that on carriers generated by electrons with a lower energy.

In this work, the thickness of the CuInSe<sub>2</sub> films used was small (about 1  $\mu$ m), and incident electron beam was perpendicular to the CuInSe<sub>2</sub> surface. It was thus very important to ensure that the location of the point source was not too close to the back surface of the CuInSe<sub>2</sub>. This was achieved by keeping the value  $\xi$  to be smaller than 1/e of the thickness. Hence, for CuInSe<sub>2</sub>, the energy of electrons in the incident beam used was smaller than 25 KeV. In the present work, the energies were kept at 12 KeV and 15 KeV and the corresponding values of  $\xi$  were 0.14 and 0.2  $\mu$ m, respectively. Therefore, the condition  $\xi \ll t$  was well met for all of the EBIC measurements carried out in this work.

After the effective diffusion lengths at different incident electron energies was calculated from Equation (10.13), the bulk diffusion lengths could be obtained. In addition to the bulk diffusion length (L), there was another unknown, namely the reduced surface recombination velocity (s). The two unknowns were obtained from results taken using at least two primary electron beam energies. The calculated bulk diffusion length of sample X33 was 3.36 µm and the reduced surface recombination velocity, s, was 2.98.

In order to estimate the surface recombination velocity and the effective carrier lifetime, it is necessary to know the electron mobility of the electrodeposited CuInSe<sub>2</sub>. Because the CuInSe<sub>2</sub> films used were electrodeposited on conducting substrates, it was difficult to determine the mobility of the electrons by Hall effect measurements. In this work, a value of 250 cm<sup>2</sup>/Vsec was taken for the mobility of the electrons [9.12]. The effective carrier lifetime,  $\tau_{eff}$ , and the surface recombination velocity, S, were obtained from Equations (10.10) and (10.12) at room temperature. The effective carrier lifetime,  $\tau_{eff}$ , was 0.17×10<sup>-9</sup> sec and the surface recombination velocity, was 5.75×10<sup>5</sup> cm/sec for sample X33.

The bulk electron diffusion length of 3.36 µm obtained in this work on electrodeposited CuInSe<sub>2</sub> films was very close to the value obtained by Piekozewski and coworkers [9.12] from monocrystalline CuInSe<sub>2</sub>. This diffusion length value was larger than the values obtained by Piekozewski from CuInSe<sub>2</sub> thin films [9.13]. However, the surface recombination velocity of

5.75×10<sup>5</sup> cm/sec was very close to that reported for a vacuum deposited CuInSe<sub>2</sub> cell.

#### **10.5 CONCLUSIONS**

Minority carrier diffusion length in an electrodeposited  $CuInSe_2$  thin film was measured using the EBIC method. During the measurements, the electron beam was scanned along the surface of the cells and the induced current recorded. Using this planar configuration, the distance between the electron beam and the depletion edge was larger than if the electron beam was directed onto cleaved junction (thickness of CuInSe<sub>2</sub> was 1.5 µm). In the present work, it was assumed that the excess carriers generated by a point source located at a depth,  $\xi$ , below the surface. The  $\xi$  values at the two different energies of incident electrons used in the CuInSe<sub>2</sub> were estimated as 0.14 and 0.2 µm. These values were smaller than the thickness of the CuInSe<sub>2</sub> can be neglected.

From the present experiments, it was found that the electron diffusion length was at least 1.4  $\mu$ m for the sample X33 and 1  $\mu$ m for the sample Y12. Considering surface recombination, the electron diffusion length of the CuInSe<sub>2</sub> was found to be 2.42  $\mu$ m. This large electron diffusion length was consistent with the large short circuit current density found in most of photovoltaic cells fabricated on the electrodeposited CuInSe<sub>2</sub> thin films. This was because the electrodeposition used was a slow process which did not involve bombardment of the substrate by high energy particles as in evaporation and sputtering. Therefore, a lower density of trap centers in the electrodeposited films was resulted. This was believed to be the main reason for the larger electron diffusion length observed in electrodeposited CuInSe<sub>2</sub>.

The surface recombination velocity and lifetime of electrons in  $CuInSe_2$  were estimated. It was found that the surface recombination velocity of the  $CuInSe_2$  in the order of 10<sup>6</sup> cm/sec. In the future, more research is needed to develop process for the fabrication of  $CuInSe_2$  thin films with a low surface recombination velocity.









Figure 10.2 The percentage of back scattered electron energy from the target plotted versus the atomic number.



Figure 10.3 Differential energy loss of the incident electrons plotted versus depth below the surface of CuInSe<sub>2</sub>.



Figure 10.4 A schematic profile showing the generation of excess carriers by an electron beam.



Figure 10.5 An SEM photograph with the superimposed EBIC scan of cell Y-12.



Figure 10.6 Electron beam induced current plotted versus the distance between the electron beam and the junction in semi-logarithmic scale.



Figure 10.7 An SEM photograph with the EBIC scans of cell X33 at two different electron voltages, (a) 12 KeV and (b) 15 KeV.



Figure 10.8 Electron beam induced current plotted versus the distance between the electron beam and the junction.

# CHAPTER 11 CONCLUSIONS

In the final chapter of the thesis, the main conclusions of the research work are summarized. This is done firstly on the CBD CdS thin films and then on the rf sputtered ZnO. Main results on the fabrication of solar cells and EBIC measurements are also summarized. Some suggestions for future work to improve the ZnO/CdS/CuInSe<sub>2</sub> cells are finally given.

## 11.1 CdS THIN FILMS PREPARED BY THE CBD METHOD [8.4][8.5]

From the present work, conditions for the preparation of high quality, high resistivity CdS thin films by the CBD method have been established (thickness about 500 Å). From the work carried out on monocrystalline Si substrates, it was observed that the growth rate and quality of the CdS films were affected by the solution temperature and concentration of NH<sub>4</sub>OH. An optimum temperature of 60°C was found to prepare uniform CdS films with good adhesion to the Si substrates. From results of electrical measurements obtained on CdS/Si heterojunctions, it was concluded that the solution containing 0.48 M of NH<sub>4</sub>OH was the best to prepare high quality CdS films. The room temperature electrical resistivity of the CBD CdS films deposited under the optimum conditions on glass substrates was about  $5 \times 10^4 \Omega$ -cm. In addition to the thin films cells described in this thesis, the conditions developed for the CBD CdS thin films have been successfully used in research work on monocrystalline CuInSe<sub>2</sub>. Recently, photovoltaic cells of the form ZnO/CdS/CuInSe<sub>2</sub> with an efficiency greater than 10% have been obtained in our laboratory [5.9].

## 11.2 LOW RESISTIVITY ZnO THIN FILMS BY RF SPUTTERING [6.7-6.9]

Using the rf sputtering method, conditions for the deposition of low resistivity and highly transparent ZnO films with a thickness of 1  $\mu$ m have been established. Good quality films have been deposited on glass substrates from ZnO targets containing In and Al. The deposited films were single phase with a preferred (002) orientation. Both electrical and optical transmission measurements were carried out. From these measurements, the optimum In (or Al) concentration for the deposition of low resistivity and transparent ZnO films, was found to be 2%. The resistivity of the best films was  $9\times10^{-4} \Omega$ -cm. The cut-off wavelength was about 0.38  $\mu$ m and transmission values in the wavelength range from 0.5 to 0.8  $\mu$ m were about 90% for ZnO films was affected by the position of the substrates. For samples deposited on horizontal substrates, the resistivity was further affected by the distance from the projection of the target centre. The resistivity values were found to decrease by 2 orders of magnitude at a distance 2 cm away from the projection of the target center.

The doped low resistivity ZnO films were observed to be more stable thermally than undoped low resistivity ZnO films (which were obtained by controlling the stoichiometry). The thermal stability improved as the doping concentration was increased. For the undoped ZnO, a drastic increase of resistivity was observed after the first treatment step at 200°C. This was consistent with what had been reported in the literature. The increase in resistivity is due to the diffusion of oxygen atoms. The diffused oxygen atoms compensated the donor level created by oxygen vacancies in ZnO. For ZnO film with 2 wt.% In, on horizontal substrate, only a slight increase was observed after heat treatment for 2 hours in air at a temperature of 200°C. However,
at a temperature of 350°C, the resistivity of the increased more than three orders of magnitude after a period of 2 hours. Therefore, during the fabrication of semiconductor devices involving the doped low resistivity ZnO, the processing temperatures must be limited to below 250°C.

## 11.3 ZnO/CdS/CuInSe, PHOTOVOLTAIC CELLS [8.4-8.5]

Using the conditions developed in this work for high resistivity CdS and low resistivity ZnO, photovoltaic cells of the form ZnO/CdS/CuInSe<sub>2</sub> have been fabricated on CuInSe<sub>2</sub> thin films prepared by the electrodeposition method. The properties of the ZnO/CdS/CuInSe<sub>2</sub> heterojunction cells with an active area of 0.078 cm<sup>2</sup> were studied. For those cells fabricated on vacuum treated CuInSe<sub>2</sub> films, the junctions were usually poor and an air heat treatment at 180°C was need to improve their properties. After the air heat treatment, however, the open circuit voltage and conversion efficiency of the cell fabricated on vacuum treated CuInSe<sub>2</sub> were still low (the efficiency was 2%). The low open circuit voltage and conversion efficiency were found from capacitance-voltage measurements to be due to a high acceptor concentration on the surface of the vacuum treated CuInSe<sub>2</sub> films (10<sup>17</sup> cm<sup>-3</sup>).

For the cells fabricated with both In-doped CdS and Al-doped ZnO on the CuInSe<sub>2</sub> films treated in Ar, strong photovoltaic effects were present even before the air heat treatment. For the best cell with the ZnO/CS/CuInSe<sub>2</sub> structure, (sample O51), an open circuit voltage of 0.35 V and a conversion efficiency of 6.3% have been obtained. From one of the best cells with In-doped CdS window, sample J8-4 an open circuit voltage of 0.35 V and an efficiency of 6.84% have been observed under simulated solar radiation. The acceptor concentration of the best cells was about  $10^{16}$  cm<sup>-3</sup>, which was one order of magnitude lower than that of CuInSe<sub>2</sub> films treated in

204

vacuum.

From the results obtained in this work, it is clear that conditions developed for high resistivity CdS and low resistivity ZnO are useful for the fabrication of good quality photovoltaic cells on the electrodeposited CuInSe<sub>2</sub> thin films. Attempts have been made to find the reason why the efficiency of the best cells in the present work is still less than that for the all-vacuum deposited ZnO/CdS/CuInSe<sub>2</sub> cells. The results obtained will be summarized in the next section.

## 11.4 MINORITY CARRIER DIFFUSION LENGTH IN CuInSe, [7.3][8.4][8.5]

The diffusion length of minority carrier (electrons) in p-type of CuInSe<sub>2</sub> was first measured using the PC and the DPC methods. For the vacuum treated CuInSe<sub>2</sub> films, the electron diffusion length was less than 0.1  $\mu$ m. The short diffusion length has resulted in a small short circuit current density and low energy conversion efficient in the final cells. For the films treated in Ar, the electron diffusion length values were about 0.5  $\mu$ m. The values are close to those reported by other researchers on vacuum evaporated CuInSe<sub>2</sub> thin films. In addition, the diffusion lengths obtained using the DPC method were smaller than those from the PC method, due to the difference in the assumption used.

In the present work, it was also found that the diffusion lengths measured from the CdS/CuInSe<sub>2</sub> cells were close to that from ZnO/CdS/CuInSe<sub>2</sub> cells. Hence, the electronic quality of the CuInSe<sub>2</sub> films were not affected strongly by the CBD process used for high resistivity CdS and the rf deposition process for ZnO. Furthermore, it was found that the diffusion lengths of the CuInSe<sub>2</sub> with acceptor concentrations less than  $2 \times 10^{16}$  cm<sup>-3</sup> was not dependent on the concentration. However, for the cells with acceptor concentrations greater than  $2 \times 10^{16}$  cm<sup>-3</sup>, the

diffusion lengths were smaller.

In order to obtain more reliable diffusion length results on the electrodeposited CuInSe<sub>2</sub>, measurements were also made using the EBIC method. During the measurements, an electron beam was scanned along the surface of the cells. To obtain the diffusion length from the EBIC measurements, it was assumed that excess carriers were generated by a point source lay a depth,  $\xi$ , below the surface. The  $\xi$  values at two incident beams with different electron energies in the CuInSe<sub>2</sub> were estimated as 0.14 and 0.2 µm (at 12 and 15 keV). These values were much smaller than the thickness of the CuInSe<sub>2</sub> films used (1.5 µm). Thus, surface recombination of carriers in the back surface of the CuInSe<sub>2</sub> films can be neglected. From the above experiments, the effective diffusion length was obtained. The values was 1.51 µm for Sample X33 and 1.07 µm for Sample Y12. The electron diffusion length were calculated by excluding surface recombination at the junction (on the front surface of CuInSe<sub>2</sub>). The true electron diffusion length of the CuInSe<sub>2</sub> was found to be 2.4 µm. This large electron diffusion length was consistent with the high short circuit current densities found in the electrodeposited CuInSe<sub>2</sub> cells.

From the above analysis, the surface recombination velocity and electron lifetime were also estimated. A surface recombination velocity as high as  $5.75 \times 10^6$  cm/sec was found for the present ZnO/CdS/CuInSe<sub>2</sub> cells. The large surface recombination velocity value, which is about 10 times greater than that from a high efficiency ZnO/CdS/CuInSe<sub>2</sub> cells, is the main cause for the low open circuit voltage observed. When the surface recombination velocity in a solar cell is high, the resulting leakage current will be large and the open circuit voltage under a constant illumination will be small. The electron life time obtained in this work was 17.4 psec.

From the results obtained in the present work, it is clear that polycrystalline CuInSe<sub>2</sub> thin

films prepared by the novel electrodeposition method developed in our laboratory are suitable for the fabrication of  $ZnO/CdS/CuInSe_2$  thin film cells. The deposition of the  $CuInSe_2$  thin films is carried out at a low temperature with a relative high deposition rate. In addition, the material utilization rate is high and the equipment required is simple. Hence, the method developed in our laboratory is specially important and has potential for photovoltaic cell production in the future.

Several suggestion to improve the performance of the CuInSe<sub>2</sub>-based cells are given bellow. (1) Carry out CBD deposition of CdS from source with different purity and determine the dark electrical resistivity. (2) Study heterojunction cells with the CBD CdS and examine effects of impurities on the density of interface states. (3) Design and construct a rotating jig for low resistivity ZnO in order to improve the thickness and resistivity uniformities. (4) Carry out detailed EBIC measurements on CuInSe<sub>2</sub> films treated under different conditions in order to establish a procedure for high efficiency thin film solar cells.

 $\sim$ 

## Appendix 1 Photolithographic Process for Patterning of ZnO

- 1. Place the sample on the spinner.
- 2. Apply 2 to 3 drops of Shipley onto the samples.
- 3. Spin the sample at 5000 rpm for 20 seconds.
- 4. Place the sample in a Pyrex glass dish and pre-bake at 90°C for 15 minutes.
- 5. Place the sample under a photomask in a mask aligner.
- 6. Expose the sample under UV light for 90 seconds.
- 7. Develop with Shipley developer (1:1 diluted) for 50 seconds.
- 8. Rinse with D.I. water.
- 9. Dry sample in air
- 10. Examine the sample under microscope to ensure that developing process is completed.
- 11. Post-bake the sample at 120°C for 20 minuets.
- 12. Immerse the sample in diluted HCl for 10 seconds.
- 13. Examine the sample under microscope to ensure that etching process is completed.
- 14. Immerse the sample in ACE for 1 minute to remove the Shipley.
- 15. Examine the sample under microscope to ensure that the Shipley is removed completely.
- 16 Dry the sample in air.

## REFERENCES

- [1.1] T.J. Coutts and J.D. Meakin, Current Topics in Photovoltaic, Chapter 2, Academic Press, (1985).
- [1.2] L.L. Kazmerski, Ternary Compounds, 35, p.217, Inst Phys., London, (1977).
- [1.3] K.J. Backmann, E. Buehler, J.L. Shay, and S. Wagner, Appl. Phys. Lett. 29, p.121 (1976).
- [1.4] L.L. Kazmerski, P.J. Ireland, F.R. White, and R.B. Cooper, IEEE Photovoltaic Spec. Conf. 13, p.620, (1978)
- [1.5] C.X. Qiu, and I. Shih, Canadian J. of Phys., 65, p.1011, (1987).
- [1.6] I. Shih and C.X. Qiu, Proc. 19th IEEE Photovoltaic Specialist Conference, p.1291, (1987).
  [1.7] C.X. Qiu, S.N. Qiu and I. Shih, Proceeding of the 6th international Photovoltaic Science and Engineering Conference, 1021, New Delhi, (1992).
- [1.8] C.X. Qiu, S.N. Qiu and I. Shih, Proceeding of 4th International Photovoltaic Science and Engineering Conference, February 14-17, Sydney, (1989).
- [2.1] S. Wagner, J.L. Shay, P. Migliorato, and H.M. Kasper, Appl. Phys. Lett., 25, p.434, (1974).
- [2.2] J.L. Shay, S. Wagner, and H.M. Kasper, Appl. Phys. Lett., 27, p.89, (1975).
- [2.3] Y. Kokuban and M. Wada, Jpn. J. Appl. Phys. 16, p.879, (1977).
- [2.4] E. Elliott, R.D. Tomlinson, J. Parkes and M.J. Hampshire, Thin Solid Films, 20, p.525, (1974).
- [2.5] L.L. Kazmerski, M.S. Ayyagiri and G.A. Sanborn, Bull. Am. Phys. Soc. 20, p.391, (1975).
- [2.6] L.L. Kazmerski, F.R. White, and G.K. Morgen, Appl. Phys. Lett. 29, p.268 (1976).
- [2.7] W.E. Devaney, R.A. Michelsen, and W.S. Chen, Proc. 18th IEEE Photovoltaic Spec. Conf., p.1733, (1985).
- [2.8] R. Noufi, R.C. Powell, V. Ramanathan, R.J. Matson, Proc. 7th Internat. Conf. on Ternary and Multinary Compounds, p.453, (1986).
- [2.9] W.H. Bloss, H.W. Schock, Proc. 8th European PV Solar Energy Conf., p.1571, (1988).
- [2.10] V.K. Kapur, B.M. Basol, E.S. Tseng, Solar Cells, 21, p.65, (1987).
- [2.11] A. Rockett, A. Argarwal, L. C. Yang, E. Banda, G. Kenshole, C.J. Kiely and T. Talieh Proc. 21th IEEE Photovoltaic Spec. Conf., 764, (1990).

- [2.12] C.X. Qiu, and I. Shih, Proc. 8th European PV Solar Energy Conf., p.1051, (1988).
- [2.13] S.N. Qiu, C.X. Qiu, and I. Shih, Solar Energy Mater., 15, p.261, (1987).
- [2.14] S.N. Qiu, C.X. Qiu, and I. Shih, Material Lett. 5, p.263, (1987).

[2.15] R.R. Potter, C. Eberspacher, L.B. Fabrick, Proc. 18th IEEE Photovoltaic Specialist Conference, Las Vegas, p.1659, (1985).

- [2.16] K.W. Mitchell, C. Eberspacher, J. Eemer, D. Pier, Proc. 20th IEEE Photovoltaic Spec. Conf., p.1384, (1988).
- [2.17] B.M. Basol and V.K. Kapur, IEEE Transactions on Electron Devices, 37, p.546, (1990).

[2.18] L. Stolt, J. Hedström, J. Kessler, M. Ruckh, K.-O. Velthaus, and W.-H. Schok, Appl. Phys. Lett. 62, p.597 (1993).

[2.19] J. Hedström, H. Ohlsén, M. Bodegård, A. Kylner, L. Stolt, M. Ruckh, and W.-H. Schok, Proc. 23th IEEE Photovoltaic Spec. Conf., p.364, (1993).

[2.20] W.S. Chen, J.M. Stewart, B.J. Stanbery, W.E. Devaney, and R.A. Mickelsen, Proc. 19th IEEE Photovoltaic Specialist Conference, p.1445, (1987).

[2.21] W.E. Devaney, W.S. Chen, J.M. Stewart, and R.A. Mickelsen, IEEE Transactions on Electron Devices, 37, p.428, (1990).

[2.22] W.S. Chen, J.M. Stewart, W.E. Devaney, R.A. Mickelsen, and B.J. Stanbery, Proc. 23th IEEE Photovoltaic Specialist Conference, p.422, (1993).

[2.23] M.S. Tomar and F.J. Garcia, Thin Solid Films, 90, p.419, (1982).

- [2.24] V.K. Kapur, B.M. Basol, E.S. Tseng, Proc. 18th IEEE Photovoltaic Specialist Conference, p.1429, (1985).
- [3.1] H.J. Hovel, Semicondutors and Semimetal, Volume 11, Solar cell, Academic Press, (1975).

[3.2] S.J. Fonash, Solar Cell Physics, Academic Press, (1981).

[3.3]K.L. Chopra and S.R. Das, Thin Film Solar Cells, Plenum Press, (1983).

[4.1] P.J. Grundy and G.A. Jone, Electron Microscopy in the Study of Materials, The Structures and Properties of Solid, Vol. &, Edward Arnold Ltd. (1976).

[4.2] M.K. Mukerjee, F. Pfisterer, G.H. Hewig, H.W. Shock, and W.H. Bloss, J. Appl. Phys. 48, 1538 (1977).



[4.3] L. Eckerlova, Physics Of Thin films, Plenum Press, (1977).

[4.4] A. Segmuller and M. Murakami, Thin Films From Free Atoms And Particles, Academic Press Inc., (1985).

[4.5] S.M. Semiconductor Devices, John Wiley & Sons, (1985).

[4.6] P.J. Chen, S.C. Pao, A Neugroschel and F.A. Lindholm, IEEE Trans. Electron Dev., ED-25, 386 (1978).

[5.1] G.A. Kitaev, A.A. Uritskaya and S.G. Mokrushin, Russian Journal of Physical Chemistry, 39, 1101, (1965).

[5.2] R.H. Mauch, J. Hedstrom, D. Lincot, M. Ruckh, J. Kessler, R. Klinger, L. Stolt, J. Vedel and H.W. Schock, 22nd IEEE Photovoltaic Specialist Conference, Las Vegas, 898, (1991).

[5.3] G.K. Padam, S.U.M. Rao and G.L. Malhotra, Proc. of 20th IEEE Photovoltaic Specialist Conference, 1591, (1988).

[5.4] Y.F. Nicolau and J.C. Menard, Journal of Crystal Growth, 92, 128, (1988).

[5.5] I. Kaur, K.D. Pandya, and K.L. Chopra, J. Electrochem. Soc., 127, 943, (1980).[6.2] N.R. Pavaskar, C.A. Menzes, and A.P.B. Sinha, J. Electrochem. Soc., 124, 743, (1977).

[5.6] N.G. Dhere, D.L. Waterhouse, K.B. Sundaram, O. Melendez, N.R. Parikh and B.K. Patnaik, Proc. of 23rd Photovoltaic Specialists Conference, 466, (1993).

[5.7] T.L. Chu, S.S. Chu, N. Schultz, C. Wong, and C.Q. Wu, J.Electrochem. Soc. 139, 2443, (1992).

[5.8] N.R. Pavaskar, C.A. Menzes, and A.P.B. Sinha, J. Electrochem. Soc. 124, 743, (1977).

[5.9] L.S. Yip, and I Shih, Proceedings of the First World Conference on Photovoltaic Energy Conversion, 210, (1994)

[6.1] J.H. Morgan, D.E. Brodie, Can. J. Phys. 60, 1387, (1982).

[6.2] J.B. Webb, D.F. Williams and M. Buchman, Appl. Phys. Lett., 39, 640, (1981).

[6.3] J. Aranovich, A. Ortiz, R.H. Bube, J. Vac. Sci. Technol., 16, 994, (1979).

[6.4] K. Ito, and T. Nakazawa, Jpn. J. Appl. Phys., 22, L245, (1983).

[6.5] T. Minami, H. Nanto and S. Takata, Appl. Phys. Lett., 41, 985, (1982).

[6.6] T. Minami, H. Nanto, S. Shooji and S. Takata, Thin Solid Films, III, 167, (1984).

[6.7] S.N. Qiu, C.X. Qiu and I. Shih, Canadian Patent No. 1,272,107, July, (1990).
[6.8] S.N. Qiu, C.X. Qiu and I. Shih, Solar Energy Materials, 15, 261, (1987).
[6.9] S.N. Qiu, C.X. Qiu and I. Shih, Material Letters, 5, 263, (1987).

[6.10] S.N. Qiu, C.X. Qiu and I. Shih, Journal of Applied Physics, 63, 2787, (1988).
[6.11] S.N. Qiu, C.X. Qiu and I. Shih, Canadian Journal of Physics, 67, 435, (1989).
[6.12] S.N. Qiu, C.X. Qiu and I. Shih, Solar Energy Materials, 16, 471, (1987).
[6.13] R.V. Stuart, Vacuum technology, thin films, and sputtering, Academic Press Inc., (1983).

[7.1] C.X. Qiu and I. Shih, Canadian Patent application, Pending.

[7.2] I. Shih and C.X. Qiu, Proceeding of the 19th IEEE Photovoltaic Specialist Conference, 1291, New Orleans, (1987).

[7.3] I. Shih, C.X. Qiu, S.N. Qiu and J.F. Huang, Journal of Applied Physics, 63, 439, (1987).
[7.4] S.N. Qiu, C.X. Qiu, I. Shih and C.H. Champness, Solar Energy Materials and Solar Cells, 37, 389, (1995).

[7.5] I. Shih, C.X. Qiu, S.N. Qiu and W.L. Choi, Journal of Canadian Ceramic Society, 56, 67, (1987).

[8.1] C.X. Qiu, McGill University Ph.D Thesis, (1991)

[8.2] R. Noufi, R. Axton, D. Cahen and S.K. Deb, Proceeding of 17th IEEE Photovoltaic Specialist Conference, 927, (1984).

[8.3] S.N. Qiu, C.X. Qiu and I. Shih, Materials Letters, 17, 190, (1993).

[8.4] S.N. Qiu, L. Li, C.X. Qiu and I. Shih, Proceeding of 12th European Photovoltaic Solar Energ Conference, Paper 9A.11, Amsterdam, (1994).

[8.5] S.N. Qiu, C.X. Qiu and I. Shih, Accepted for Applied Surface Science, (1995)

- [8.6] D. Wilett and S. Kuriyagawa, 23th IEEE Photovoltaic Specialist Conference, 495, (1993).
- [9.1] A.M. Goodman, J. Appl. Phys., 32, p.2550, 1961.
- [9.2] S.S. Li, Appl. Phys. Lett., 29, p.126, 1976.
- [9.3] W.Y. Wang, C.R. Baraona and H.W. Brandhorst, Jr., J.Electrochem. Soc., 121, p.973, 1974.

[9.4] J. Vilms and W.E. Spicer, J. Appl. Phys., 36, 2815, 1965.

[9.5] C.J. Wang, J. Appl. Phys., 40, p.3731, 1969.

[9.6] P.D. Dapkus, W.H. Hackett, Jr., O.G. Loromor, G.W. Kammlott and S.E. Haszko, Appl. Phys. Lett., 22, p.227, 1973.

[9.7] R.J. Lender, S. Tiwari, J.M. Borrego and S.K. Ghandhi, Solid-State Electronics, 22, p.213, 1979.

[9.8] M.L. Young and D.R. Wight, J. Phys. D: Appl. Phys., 7, p.1824, 1974.

[9.9] E.H. Stupp and A. Milch, J. Appl. Phys., 48, p.282, 1976.

[9.10] J.J. Oakes, I.G. Greenfield and L.D. Partain, J. Appl. Phys., 48, p.2548, 1977.

[9.11] C.J. Wu and D.B. Wittry, J. Appl. Phys., 49, p.2827, 1978.

[9.12] J. Piekosewki, L. Castaner, J.J. Loferski, J. Beall and W. Giriat, J. Appl. Phys., 51, p.5375, 1980.

[9.13] A. Bouazzi, J.J. Loferrski, M. Kwietniak, R.R. Arya and M. Sosnowski, J. Power sources, 12, p.167, 1983.

[9.14] B.L. Smith and M. Abbott, Solid-State Electronics, 15, p.361, 1971.

[9.15] A. Lastras-Martinez, P.M. Raccah and R. Triboulet, Appl. Phys. Lett., 36, p.469, 1980.

[9.16] J. Dorantes-Davila, A. Lastras-Martinez and P.M. Raccah, Appl. Phys. Lett., 38, p.442, 1980.

[9.17] C.H. Champness, Z.A. Shukri and C.H. Chan, Can. J. Phys., 69, p.538, 1990.

[9.18] T. Sukegawa, T.Watanabe, T. Mizuki and A. Tanaka, IEEE Transaction on Electron Devices, 27, p.1251, 1980.

[10.1] W.H. Hacheet, Jr., J. Appl., Phys., 42, 3249, (1971).

[10.2] W.H. Hacheet, Jr., J. Appl. Phys., 43, 1649, (1972).

[10.3] J. Jastrzebski, J. Lagowski, and H.C. Gatos, Appl. Phys. Lett., 27, 537, (1975).

[10.4] D.B. Wittry and D.F. Kyser, J. Appl. Phys., 36, 1378, (1964).

[10.5] R.D. Rayn and J.E. Eberhardt, Solid-State Electronics, 15, 865, (1971).

[10.6] D.B. Wittry and D.F. Kyser, J. Appl. Phys., 38, 375, (1966).

[10.7] T.S. Rao-Sahib and D.B. Wittry, J. Appl. Phys., 40, 3745, (1969).

[10.8] D.B. Wittry, J. Appl. Phys., 29, 1543, (1958).

- [10.9] V.E. Cosslett and R.N. Thomas, Brit. J. Appl. Phys., 15, 1283, (1964).
- [10.10] C.A. Klein, Applied Optics, 5, 1922, (1966).
- [10.11] H.E. Bishop, Brit. J. Appl. Phys., 18, 703, (1967).
- [10.12] T.E. Everhart and P.H. Hoff, J. Appl. Phys., 42, 5837, (1971).
- [10.13] R.F. Herzog, J.S. Greeneich, T.E. Everhart, and T. Van Duzer, IEEE Trans. Electron devices, ED-19, 635, (1972).
- [10.14] W.V. Roosbroeck, J. Appl. Phys., 26, 380, (1954).
- [10.15] F. Berz and H.K. Kuiken, Solid-State Electronics, 19, 437, (1975).