

AIN SHAMS UNIVERSITY
FACULTY OF ENGINEERING

PREPARATION AND CHARACTERIZATION
OF $Zn_x Cd_{1-x}S/ZnTe$ HETEROJUNCTIONS
AND THEIR APPLICATIONS

BY

Eng. Moustafa M. Abd Elnaby

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SUPERVISED BY

Prof. Dr. Mohamed Nabil Saleh
Dr. Mohamed Fikri El Akkad
Dr. Abd Elhalim Zekry

621.380 414
M. M.

2772

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Examiners Committee

Signature

1. Prof. Dr. Elsayed A. Talkhan
Head of Electronic and communication
Department-Faculty of Engineering
Cairo University.

2. Prof. Dr. Mohamed Nabil Saleh
Professor of Electronics,
Vice Dean, Faculty of Engineering
Ain Shams University.

3. Dr. Abdelhalim Zekry,
Assistant professor, Electronic
and Computer Department
Faculty of Engineering, Ain Shams University.


Date : / /1988.



STATEMENT

This dissertation is submitted to Ain Shams University for the degree of Doctor of Philosophy in Electrical Engineering.

The work included in this thesis was carried out by the author in the Department of Electronic and Computer Engineering, Ain Shams University, from April 1985 to July 1988.

No part of this thesis has been submitted for a degree or a qualification at any other university or institution.

Date : 1 / 9 / 1988

Signature: *Mustafa*

Name: Moustafe M. Abd Elnaby

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TO MY PARENTS AND WIFE

A B S T R A C T

In this thesis $\text{Zn}_{1-x}\text{Cd}_x\text{S}/\text{ZnTe}$ heterojunctions were intensively investigated. Our aim was to relate the terminal electrical and optoelectronic characteristics with the internal physical and technological parameters of the device. The efforts were devoted to work out the optimum performance of this heterojunction as a solar cell, as well as to explore the physical mechanisms responsible for the observed low solar energy conversion efficiency of such heterojunctions.

In this way one can propose methods for enhancing the device performance regarding its application as a solar cell.

The substrate was single crystalline ZnTe while a new method has been utilized to deposit the required Cd Zn S films. This method is the r.f. sputtering technique.

The electrical, photoelectrical and structural characteristics of these films were studied as a function of the technological parameters, namely, film thickness, substrate temperature, and postpreparation annealing. It was found that the resistivity values of the CdS films can be controlled within a certain range by controlling the substrate temperature and film thickness. Also the resistivity of the films decreased after annealing in H_2 , and no aging effect after 12 months was observed. The activation energies for the temperature dependence of electrical conductivity for Cd S films are in the same order of magnitude for

Cd S films prepared by other methods. Appreciable photosensitivity was obtained for low deposition temperatures and larger thicknesses of the films. Therefore, for solar cell applications where smaller sheet resistance is required, moderate deposition temperature and relatively small thickness are preferable.

The effect of increasing Zn concentration x of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ films resistivity was studied. The resistivity values obtained are lower than those of films prepared by other techniques. They fall within the range of solar cell quality films.

The composition dependence of the optical band gap agrees with that represented for $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ single crystals up to $x = 0.6$. Improvement in the C-axis preferential orientation was observed after annealing and the grain size increased.

The electrical and optical properties of undoped and phosphorous doped Zn Te crystals were measured. It was found that doping Zn Te with phosphorous reduces the room temperature electrical resistivity from $55 \Omega \text{ cm}$ (for undoped Zn Te) to $0.16 \Omega \text{ cm}$ (for P doped ZnTe). Also a broad absorption peak at about 1.06 eV was observed for the P doped Zn Te with the increase of hole concentration.

The effect of alloying ZnTe with Mg was also examined to explore the origin of the infrared band absorption that emerges in the absorption spectra of doped crystals. The results show that the absorption coefficient is directly related to the number of vacant states near the top of the valence bands.

A self consistent electrical and opto-electrical characterization of $\text{Zn Cd}_{1-x}\text{S}/\text{ZnTe}$ junction as a solar cell was carried out. It was generally observed that the properties of the $\text{Zn Cd}_{1-x}\text{S}/\text{ZnTe}$ junctions depends largely on the technological parameters.

Heat treatment was found necessary to improve the cells efficiency, while heat treatment for longer times (>3 h) deteriorates both V_{oc} and J_{sc} .

To determine the properties of the space charge region formed at the interface of the two materials C-V and G-V measurements was carried out at different frequencies from 10 KHz to 1 MHz. For some samples, the measured junction capacitance was reduced appreciably by increasing the frequency. To account for this behaviour we developed a small signal model taking into account the series resistance of the junction and the shunting effect of the conductance on the measured value of the transition capacitance. It has been found that the junction capacitance decreases with the composition x of Zn concentration. Consequently the width of the space charge increases with the composition x of zinc in the film. The effect of heat treatment on capacitance voltage characteristics was also studied.

After excluding the effects of the series and shunt resistances from the measured dark I-V characteristics, it was found that the conduction in the junctions is dominated by recombinations inside the space charge region.

The reverse saturation current J_0 increases firstly with Zn content in the film then decreases. This behaviour of J_0 was explained for the first time. It was also generally noticed that the absolute value of J_0 are relatively large for solar cell applications. This large value is due to the very small lifetime of minority carriers in the film because of traps at boundaries of the very small grains of the films.

It has been found that photocurrent decreases monotonically with Zn concentration in the film. Its maximum measured value is about 1 mA/cm^2 which is less than that estimated under AM1 illumination (3.5 mA/cm^2). This difference is due to the very small lifetime of minority carriers in the film and substrate as well as the reduction in the collection efficiency of the photogenerated carriers in the space charge region. The variation of short circuit current J_{sc} , open circuit voltage V_{oc} , efficiency and fill factor FF as a function of composition x of the $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ ZnTe ($0 \leq x \leq 0.2$) cells showed high open circuit voltage of 0.55 V for the composition $x = 0.2$ and short circuit current of 1 mA/cm^2 for $x = 0.05$. It should be noted that the maximum measured value of 0.55 V for open circuit voltage is practical for solar cell applications.

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CHAPTER I

GENERAL INTRODUCTION

The importance of energy in our society has become too apparent in recent years. Today, the demand for electrical energy is increasing at the rate of 5 to 10 percent a year. Of the various energy alternatives, solar energy has the very desirable property of being essentially limitless clean and non-hazardous.

Solar cells are devices which convert sunlight directly into electricity. They have been an important part of the space program for decades. The advantages of solar cells over conventional electricity generators lie in their ability to provide permanent power at no operating cost. They also have a high power per weight ratio compared to other power sources. Their chief disadvantages lie in the low power per unit area of sunlight, their relatively low efficiency, and the degradation that takes place in hostile high energy particle environments. Today, however, the realization that oil and gas supplies can only last a relatively few decades and the freedom of solar energy from pollution, have led to closer looks at solar energy as an alternative to present day fossil - fuel systems.

Silicon solar cells are presently the most economically feasible and widely used cells. However, the solar electricity produced by such cells is still too expensive to be competitive

with conventional electricity in densely populated zones. To be competitive, the cost of solar electricity must be reduced by at least, a factor of 10. For reasons related to the fundamental properties of Si and to its growth technology, single crystal Si-cells are unable to achieve this goal. Therefore, the development of alternative cells (e.g. poly- and amorphous Si, CdS cells, GaAs ... etc.) for large scale application of photovoltaic electricity has been an active research area over the last decade. Two categories of cells are currently under investigation by many research groups; namely, low cost cells and high efficiency cells (e.g. GaAs). Apart from Si (poly- or amorphous) the most promising candidates for low cost solar cells are believed to be thin film heterojunctions with CdS or CdZnS windows; for example CdS/CdTe, CdZnS/CuInSe₂, and tandem cells. Consequently, CdS and CdZnS thin films have been prepared using different techniques and their properties studied closely in relation to their application as window layers in solar cells. However few articles in the literature were devoted to the properties of CdS films prepared using r.f. sputtering technique, and still fewer on CdZnS. Sputtering is known to allow a relatively easy access to the control of stoichiometry and doping of binary compounds and to the control of composition for ternary alloys as compared with other techniques. It is also known to be adapted for the production of low cost and large area films as required for the terrestrial application of solar cells. Although the preparation of r.f. sputtered CdS thin films with solar cell quality has already been reported by Martil et al ^[1-2], still further efforts have to be made in order to clarify the role of