AIN SHAMS UNIVERSITY
FACULTY OF GIRLS
FOR LITERATURE
SCIENCE AND PEDAGOGY
DEPARTMENT OF PHYSICS

THESIS

SUBMITTED FOR DEGREE OF

DOCTOR OF PHILOSOPHY

(SOLID STATE - PHYSICS)

Name Of Student

Magda Mohamed Sayed Mohamed

SOME STUDIES ON CADMIUM SELENIDE (CdSe) THIN FILMS

Supervising Committee

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Date of Research: / /1995

Approval Stamp: **Date of Approval: / /1995**

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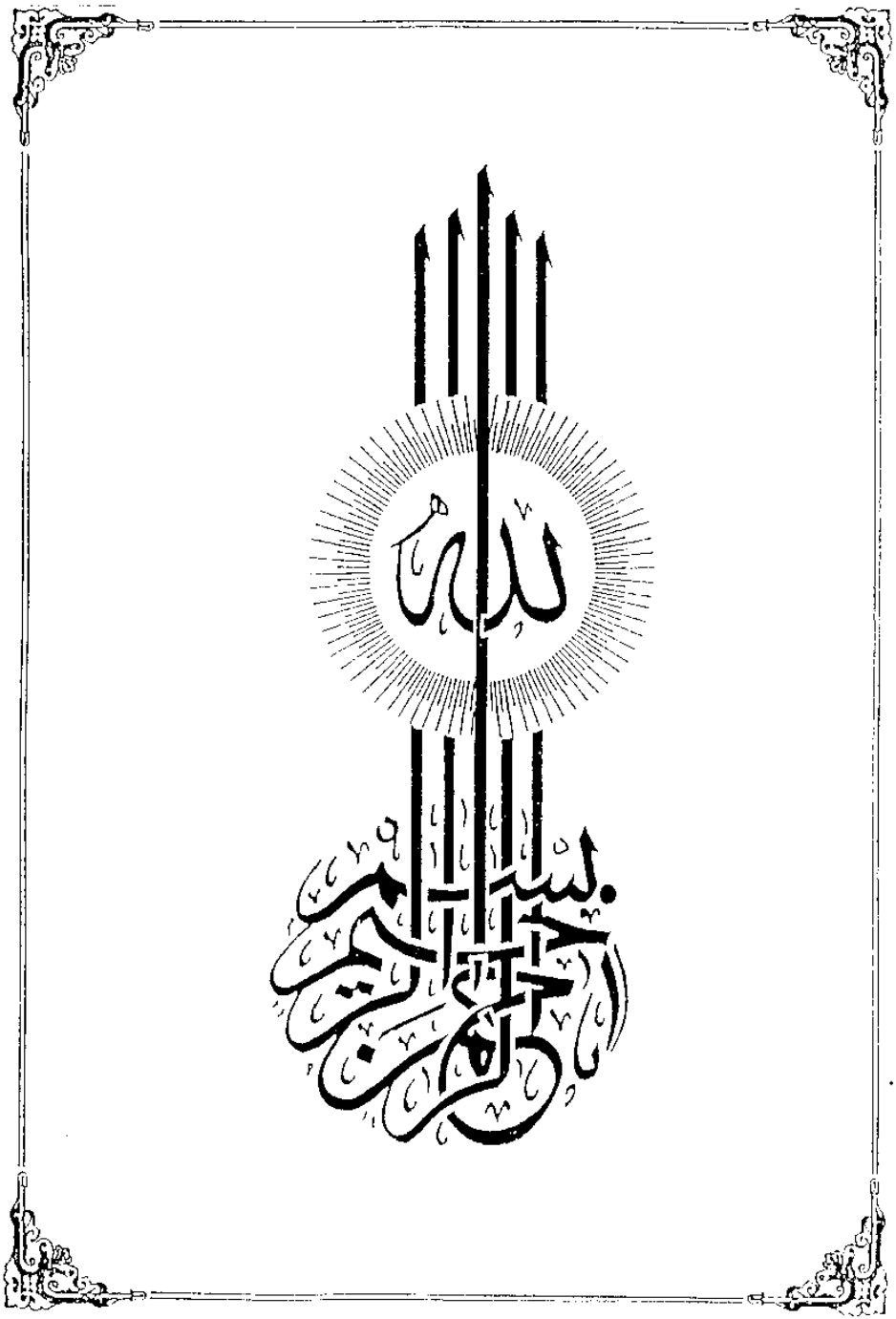

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Name Of Student : *Magda Mohamed Sayed Mohamed*

Scientific Degree : Doctor of Philosophy in Physics

Department : Physics

Name Of Faculty : Faculty of Girls

University : Ain Shams

Graduation Date : September 1979

CONTENTS

SUMMARY

The aim of the present work mainly describes and discusses an investigation on the microstructure, optical and electrical properties of thin cadmium selenide films obtained by two different techniques namely vacuum evaporation and chemical bath deposition. Also, it is to investigate some effects such as thermal treatment on the structure, optical and electrical properties of the various films. The films were heat-treated for 15 min at 773 K. All the deposits are examined before and after their thermal treatment, by scanning electron microscopy and by X-ray diffraction. The thickness of the film was measured by weighting and by an interference methods.

The essential results could be concluded as :

1. The microstructure of the thin films was studied by transmission electron microscopy, electron diffraction and X-ray diffraction. The rate of deposition was estimated interferomctrically to about 10 nm/sec and 20 nm/sec for films deposited at room-temperature. All the films deposited onto glass substrates at room-temperature were found to be polycrystalline. They indicated a hexagonal structure with preferential orientation of the crystallites along the (002) plane parallel to the surface of the films. The formation of the hexagonal phase is perhaps due to the non-stoichiometric ratio of Cd and Se in the films. The

excess of Cd has caused the deviation of the "c/a" value from the ideal 1.63 value due to a deviation of "u" and increased the probability of appearance of hexagonal phase.

To study the degree of crystallinity and the crystallite size, X-ray diffraction spectra of the freshly deposited CdSe film of different thicknesses and rates are obtained. The crystallite size was estimated using the Scherrer formula. The crystallite size and degree of orientation increase with thickness and the films are polycrystalline with the hexagonal structure. The increasing crystallite size with thickness may be due to recrystallization caused by the compressive stress in the film due to differences in expansion coefficients of film and substrate.

The chemically deposited samples under different conditions were studied by means of X-ray diffraction and scanning electron microscopy. Analyzing the film structure in detail by X-ray analysis, it was found that the crystallites in the deposited layers are of polycrystalline type and the films are stoichiometric CdSe alloy. Also, the Table (3.2) show that all the CdSe grown samples have wurtzite structure. The electron micrographs of the heated and non-heated layers demonstrated the increase in the grain size with increase of dipping time. The rate of deposition and the terminal thickness depend sensitively on the pH value of the bath, concentration of the reactants, and the temperature of the deposition.

2. For optical measurements, the thicker layers were obtained by chemical bath method and by vacuum sublimation of high quality CdSe powder onto quartz slides. The refractive index "n", and the extinction coefficient "K", of CdSe films were determined from the transmission spectra. It is found that, the values of the extinction coefficient "K" are small and ranges between .01 to 0.41 for the evaporated films and between 0.08 to 0.75 for the chemicaly deposited layers. The value of the refractive index "n" is about 2.6 and varies slowly with the photon energy. For further analysis of the refractive index data, the high frequency dielectric constant, "ε_∞", the average oscillator strength, "S_o", the refractive-index dispersion parameter, "E_o/S_o" and the average oscillator position, "λ_o", can be calculated [section (4.7)- Table (4.2)]. According to the optical absorption "α" sharp rise in the absorption spectra is observed for all the samples. The square of the absorption coefficients "α" is plotted against $\hbar\omega$ to obtain the values of the band gaps. The values of the optical band gap "Eg" are estimated from the intercepts of the straight lines. It is observed that the band gap in the evaporated CdSe layers varies continuously with film thickness from 1.813 eV to 1.78 eV at rate of deposition of ~ 10 nm/sec from 1.79 eV to 1.703 eV at rate of deposition ~ 20 nm/sec. Also, the values of "Eg" are calculated for the selected chemical deposited specimens, under different conditions.

3. A group of thin films of cadmium selenide were grown by thermal evaporation and chemical bath deposition techniques on glass substrates The results are obtained to study the changes in resistivity due to stoichiometric variations in the source material during the process of evaporation. The results indicate that, for a fixed source temperature, when the thickness is increased, there is a definite decrease in resistivity. The activation energies for the two parts regions are calculated from the relation of log R vs. 1/T for the different thicknesses and conditions. The first section [Table (5.1)] can be due to the ionization of excess cadmium levels into the conduction band. The second section of activation energy (1.75-1.72) is an intrinsic activated process.

In case cadmium acetate solution, the curves revealed that the activation energy of the heated samples under different conditions is constant (1.76 eV). But, the activation energy of the non-heated samples is varied with thickness from about 1.72 eV to 1.75 eV. In case cadmium nitrate solution, the curves illustrated that the activation energy is dependent of thickness. Also, the activation energies calculated from the slopes of the curves during the heating and cooling cycle for the different thicknesses, are nearly the same as can also be seen from the near parallelism of the plots [Fig. 5.13-a,b].

GENERAL

INTRODUCTION

GENERAL INTRODUCTION

Metal chalcogenides are important materials for such applications as photoconducting cells, photovoltaic cells, and other electro-optical devices. These materials can be obtained in thin film form by evaporation, sputtering, pyrolysis, and chemical deposition techniques[1]. Of all these techniques, chemical solution growth is relatively inexpensive, simple, and convenient for large area deposition of II-VI and IV-VI compounds. By this technique, films can be deposited on a variety of substrates by allowing them to remain in an aqueous solution of the appropriate chemicals for a predetermined time[2-5].

Thin film cadmium selenide has been prepared by a new electrochemical process in which the film is deposited at the cathodes from a nonaqueous solution containing tri-n-butylphosphine selenide as the selenium source. The films are found to be less dense than those prepared using selenosulfite ion. The as-deposited films appear free of cracks and pinholes when deposited on titanium, but cracks develop when the films are annealed. A stoichiometric composition is obtained for the film over a 0.4 V potential range[6]. Also, Zhou *et al.*[7] studied thin films of CdSe, CdS and CdTe prepared by the electrochemical deposition. The morphology of thin-films changed from amorphous to polycrystalline as the annealying temperature (AT) was increased from 523

to 723 K. A CdSe film annealed at T < 553 K has a higher concentration of Se and is of p-type; when T is ≥ 553 K, the Cd concentration is greater than the Se concentration and the film is of n-type[7]. The band gap of the material deposited by this method was calculated and was found to be lower than the band gap reported earlier by various workers. The photoresponse is relatively constant over a wide range of wavelengths and it does not decrease at shorter wavelengths. There is an increase in the stability when the CdSe electrode is coated with a thin film of indium[8].

The n-CdSe single crystals (carrier concentration 10^{17} cm^{-3} and electron mobility ~ 500 cm^2/V Sec) were obtained by vertical zone melting. The experimental points in the $\{\alpha,\hbar\omega\}$ coordinates, at 295 K with α ranging from 10 to 2×10^4 cm^{-1}, followed Urbach's rule. The spectral dependence of the absorption coefficient determined experimentally at 85 K agreed with the inter-band-transition theory developed by Segal for the direct exciton absorption with accounting for the single longitudinal optical phonon. The oscillator strength was[9] 1.3×10^{-3}.

Calculation of the optical constants

The optical behaviour of thin films may be considered from two of points view. From studies of the structure of the films formed by most available methods, it is found that film generally consist of aggregates of crystallites of variable size and orientation

and with differing extents of voids. Description of the optical behaviour of such a system is essentially a scattering problem and this approach is often used in studying the effects of a transition layer on the surface of a solid. The mathematical problems involved are difficult generally but become tractable for layers whose thickness is of the order of molecular spacings[10].

It proves convenient to treat problems involving thicker layers by describing the layer by a refractive index and for absorbing materials, by an extinction coefficient. The optical properties of the layer can then be calculated using the classical electromagnetic theory. The reflectance and transmittance can be calculated explicitly in terms of the optical constants and film thicknesses[10].

Expressions for the reflection and transmission coefficients of a surface covered with a single homogeneous isotropic film are conveniently expressed in terms of the Fresnel reflection and transmission coefficients for the two interfaces. The Fresnel coefficients (ratio of reflected or transmitted to incident amplitude) depend on the plane of polarization considered. For light incident from a medium of refractive index n_m on the boundary with a medium of index n_{m-1} we have (Figure 1) for the p-component.

$$r_{mp} = \frac{n_m \cos\phi_{m-1} - n_{m-1}\cos\phi_m}{n_m \cos\phi_{m-1} + n_{m-1}\cos\phi_m} \quad \text{(reflection)} \qquad \ldots.1$$

$$t_{mp} = \frac{2n_m \cos\phi_m}{n_m \cos\phi_{m-1} + n_{m-1}\cos\phi_m} \quad \text{(transmission)} \qquad \ldots.2$$

For the S-component

$$r_{ms} = \frac{n_m \cos\phi_m - n_{m-1}\cos\phi_{m-1}}{n_m \cos\phi_m + n_{m-1}\cos\phi_{m-1}} \qquad \ldots.3$$

$$t_{ms} = \frac{2n_m \cos\phi_m}{n_m \cos\phi_m + n_{m-1}\cos\phi_{m-1}} \qquad \ldots.4$$

The ϕ's are related by Snell's law :

$$n_m \sin\phi_m = n_{m-1}\sin\phi_{m-1} \qquad \ldots\ldots.5$$

In order to simplify the equations, Fresnel coefficients will generally be written simply as r_m, t_m, with the understanding that when equations (1) and (2) are used, the result gives the p-component, and with equations (3) and (4), the S-component.

For a single film of index n_1 and thickness d_1 on a substrate of index n_0 (Figure 2), the amplitude of the reflection and transmission coefficients are given by[10] :

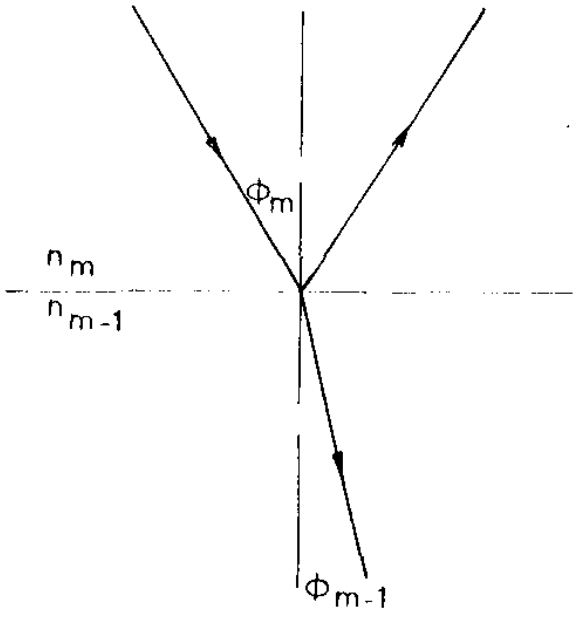

Figure (1)

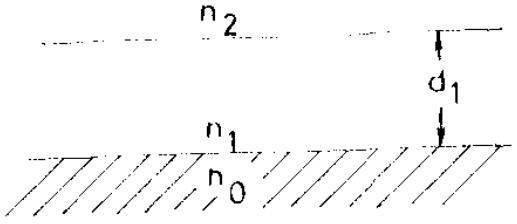

Figure (2)