

Fabrication and Characterization of Nano-Semiconductor/Tetrahedral Semiconductor Heterostructures

Thesis

Submitted for the degree of Doctor of Philosophy

In

Physics

To

Physics Department Faculty of Science Ain Shams University

By

Jumana Zamel Sattam El-Waheidi

B. Sc. & M. Sc. (Physics)

Supervised by

Prof. D. Sc. M. F. Kotkata Head of Semiconductor Technology Lab.

Faculty of Science-Ain Shams University

Dr. M. S. Al-Kotb Semiconductor Technology Lab.

Faculty of Science-Ain Shams University

2018



Degree: Doctor of Philosophy in Physics

Title: Fabrication and Characterization of Nano-

Semiconductor/Tetrahedral Semiconductor

Heterostructures

Name: Jumana Zamel Sattam El-Waheidi

Thesis Supervisors	<u>Approved</u>	
1. Prof. Dr. Sc. M. F. Kotkata	••••••	
Professor of Material Sciences		
Physics Department, Faculty of Science,		
Ain Shams University		
2. Dr. M. S.Al-Kotb	••• •••	
Associate professor of Material Sciences		
Physics Department, Faculty of Science,		
Ain Shams University		

Fabrication and Characterization of Nano-

Semiconductor/Tetrahedral Semiconductor Heterostructures»

Jumana Zamel Sattam El-Waheidi
(B. Sc. & M. Sc.)
Semiconductors Technology Lab., Physics Department, Faculty of Science
Ain Shams University
2018

Abstract

In this work, nano-crystallite CdSe thin films were deposited by thermal evaporation technique from CdSe nano-powders on glass substrates. The structural features of the deposited films have been characterized by using optical transmission measurements, The X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The X-ray line profile analysis revealed that the CdSe films are nano-crystallite and have a wurtzite (hexagonal) structure. These nano-crsytallite CdSe films are preferentially oriented along the (002) plane with a *c*-axis perpendicular to the substrate surface. The crystallite size for these films lies in the range 16 - 36 nm as measured from X-ray line broadening. It has been found that the variation of film thickness has a great influence on the microstructural parameters, such as micro-strain, the stacking-fault probabilities, dislocation densities as well as the crystallite size. In this respect, the micro-strain, dislocation density and

stacking fault probabilities demonstrate a decrease by increasing the film thickness. The refractive indices (n) and absorption coefficients (α) of the investigated films were obtained from transmission spectra. Here, the Sellmeier dispersion relationship quite agrees with the estimated values of n over a spectral range of 200 nm to 2500 nm. Various optical parameters of the investigated nano-crystallite CdSe films have been interpreted in the frame of Wemple-DiDomenico single oscillator model. Such evaluated parameters provide valuable physical insights; such as, the relationship between the ionicity of the CdSe films and microstructural parameters.

Furthermore, the temperature dependent electrical properties of Au Schottky contacts to a-plane CdSe thin films growing on p-Si (001) that investigated over the temperature range of 160–360 K, showed a rectification behavior. Nevertheless, the magnitude of the peak broadening (β_c) of the films grown on p-Si (100) substrates is narrower than that of the films grown on glass substrates; this is, due to a 21% lattice mismatch between CdSe and Si substrate. The respective barrier height (φ_b) and ideality factor (p) values were found to be 0.863 eV at 360 K to 0.451 eV at 160 K, and 2.48 \pm 0.11 at 360 K to 5.18 \pm 0.19 at 160 K. The increasing of φ_b while decreasing p with the increase of temperature has been described by a double Gaussian distribution with two different temperature regions: 240–360 and 160–240 K. Also, it was observed that the Au/CdSe/Si/Al heterostructure exhibits space charge limited

current (SCLC) at all temperatures investigated. The transition voltage (V_x) from ohmic to SCLC, is found to be quite dependent on temperature. The defect levels were estimated from the slope of ln J versus 1/T plots, that yield two values of activation energies $\Delta E_{d1} = 0.227 \pm 0.011$ eV in the 240–360 K range and $\Delta E_{d2} = 0.128 \pm 0.003$ eV in the 160–240 K range. Moreover, the characteristic parameters of the considered Ni/CdSe/p-Si/Al structure, demonstrates a deviation from the pure thermionic emission—diffusion theory. In conclusion, the increase of series resistance R_s as the temperature decreases, is believed to be resulted due to an amorphous layer between CdSe/Si that responsible for increasing n and/or lack of free-charge carriers at low temperatures.

Acknowledgments

The five years spent pursuing this thesis have truly been a wonderful experience, although there were times in those five years when I might not have fully appreciated that fact. It is factually a challenge, as well as a pleasure, to attempt to recall all of the many friends and colleagues who have supported me over the course of those years. I hope no offense is taken by those contributions I have inadvertently omitted.

The person primarily responsible for ensuring the existence of this work is my supervisor, *Prof. D.Sc. M. F. Kotkata* and for welcoming me as a member in his group, for sharing his knowledge and wisdom, His persistence, encouragement and finding the representation of the data of the thesis. I could not have asked for a better mentor.

I wish to express my sincere thanks to *Associate Prof. M. S. Al-Kotb* for interesting advice and scientific guidance in the course of the work. His participation has certainly improved the quality of my work. He has always supported me and encouraged my efforts.

I would like to thank *Prof. Dr. S. Bakry*, Head of physics department, Faculty of Science, Ain Shams University, for his encouragement and providing the necessary facilities.

I wish to express my special thanks to all members of the Semiconductor Technology Lab, Faculty of Science, Ain Shams University, for helping me to complete the experimental work and for kind cooperation in various ways.

Last but not least, my heartfelt appreciation goes out to my family for their encouragement. I am grateful to *my dear mother*, for her unwavering love and supporting me in so many ways throughout the whole process. Finally, I dedicate my thesis to my lovely son *Mohamed*.

Contents

Acknowledgmen	nts	6
List of Figures		9
List of Tables		16
Introduction		17
CHAPTER 1:	A Comprehensive Theoretical Considerations	25
CHAPTER 2:	Device Preparation and Experimental Technique	57
2.1.	Preparation of Nanocrystalline CdSe	57
2.2.	Preparation of Nanocrystalle CdSe Thin Films	57
2.3.	Compositional and structural Techniques	59
2.4.	DC conductivity measurements	65
2.5.	Optical measurements	66
2.6.	Photoluminescence measurements	69
CHAPTER 3:	Characterizations of CdSe quantum dots	71
3.1	Characterizations of CdSe quantum dots	71
3.2	X-ray profile line analysis	73
3.3	Photoluminescence and UV-Vis measurements	76
CHAPTER 4:	Microstructural and Optical Properties of Nano-Cryst	allite
	CdSe Thin Films	79
4.1	X-ray full profile line analysis	80
4.2	Determination of microstructure parameters	84
4.3	Determination of optical constants	87
4.3.1	Determination of film thickness	87
4.3.2	The refractive index dispersion	87
4.3.3	Dispersion energy parameters	91
4.4	Determination of the optical band gap	94
4.5	Photoluminescence analysis	98
CHAPTER 5:	Nano-structure M/CdSe film/Si(001) heterostructures	102
5.1	The surface morphology of CdSe/Si	104
5.2	Au/CdSe/Si heterostructure diodes	106
5.2.1	Current-Voltage- Temperature analysis	106
5.2.2	Inhomogeneities barrier analysis	112
5.2.3	Richardson plot	116
5.2.4	Space charge limited current model	117
5.3	Ni/CdSe/p-Si heterostructure diodes	121
Conclusions		127

List of Figures

Figure 1.1: Polymorphism in CdSe. Ball-and-stick model of (a) the
zinc blende structure in the [111] direction, showing the sequence of
monoatomic stacking planes "cAaBbCc" and (b) the wurtzite structure in the
[001] direction with stacking plane sequence "bAaBb"
Figure 1.2: Energy gaps at the Γ point of the zinc-blende (cubic) and
wurtzite (hexagonal) structure
Figure 1.3: Band mixing under the action of crystal-field and spin orbit
interactions in wurtzite crystals. To the left, splitting induced only by the
crystal field; to the right, splitting induced only by the spin-orbit interaction.
The combined case is given in the middle (Voon, Willatzen et al. 1996) 31
Figure 1.4: Ideal energy-band diagram before contact and after contact
(b) for a metal-n-type semiconductor junction for $\varphi_{\rm m} < \varphi_{\rm s}$
Figure 1.5: Ideal energy-band diagram of a metal-n-type
semiconductor ohmic contact with a positive voltage applied to the metal (a)
and with a positive voltage applied to the semiconductor (b)
Figure 1.6: Energy-band diagram of a heavily doped n-semiconductor-
to-metal junction
Figure 1.7: Theoretical and experimental specific contact resistance as
a function of doping (Sze & Ng, 2006)

Figure 1.8: Electron energy band diagrams of metal contact to n-type
semiconductor for (a) neutral materials separated from each other and (b)
thermal equilibrium state after the contact has been made
Figure 1.9: Electron energy band diagram of Schottky junction in a
reverse bias (a), and a forward bias (b). Where, $J_{m \to s} is$ the current from the
metal to the semiconductor, $J_{s \rightarrow m}$ is the current from the semiconductor to the
metal
Figure 1.10: The energy ranges for various rectification theories
relative to the Schottky barrier height (Rideout 1978)
Figure 1.11: Values of E _{oo} and kT as a function of doping density for
Si with $mtun * = 0.3$, T = 300 K and schematic band energy diagram of a
metal/n-semiconductor contact showing the three major current transport
mechanisms
Figure 1.12: Schematic representations of atomic layers making up
metal-interlayer-semiconductor (MIS) interfaces and the formation of
interface dipole; (a) intimate MS interface; (b) interlayer bonded to both sides;
interface dipole; (a) intimate MS interface; (b) interlayer bonded to both sides; (c) interlayer preferentially bonded to the semiconductor (Li, Long et al. 2011).
(c) interlayer preferentially bonded to the semiconductor (Li, Long et al. 2011).
(c) interlayer preferentially bonded to the semiconductor (Li, Long et al. 2011).
(c) interlayer preferentially bonded to the semiconductor (Li, Long et al. 2011). 56 Figure 2.1: the schematic diagram of the Ni/CdSe/Si configuration.
(c) interlayer preferentially bonded to the semiconductor (Li, Long et al. 2011).

Figure 2.3: Schematic diagram of the DC conductivity measurement
setup
Figure 2.4: Recorded plots of optical transmittance and reflectance
versus wavelength plots of CdSe films investegated
Figure 2.5: Recorded optical transmission versus wavelength for the
investigated CdSe film. The solid curves are the envelope functions of
minimum (T_{m}) and maximum (T_{M}) transmittance. The horizontal straight line
represents the measured transmittance of the used glass substrates (Ts) of the
investigated sample
Figure 2.6: Hypothetical PL spectrum and band picture, assuming n-
type material (Sites and Hollingsworth 1987)
Figure 3.1: HR-TEM image of a colloidal CdSe nanocrystals72
Figure 3.2: Particle size distribution of a colloidal CdSe
Figure 3.3: SAED pattern of CdSe QDs with a ring pattern and the
scale bar is 5 1/nm
Figure 3.4: Rietveld refinement of the experimental XRD of CdSe
QDs
Figure 3.5: Williamson-Hall plot for CdSe QDs76
Figure 3.6: Absorption and photoluminescence spectra for CdSe QDs
78

Figure 4.1: XRD patterns of <i>nc</i> -CdSe films in the thickness range 246-
1061 nm, with a preferred orientation perpendicular to c -axis and the inset
displays the unit cell and atomic positions
Figure 4.2: The (002) peak is shifted towards lower diffraction angle
with increasing the film thickness due to a combination effect of changes in
lattice parameter, residual stress, and the presence of stacking fault81
Figure 4.3: The final Rietveld refinement results of CS02 by applying
the FULLPROF software, observed (x), calculated (red line), and differential
(blue line). The tick marks give the positions of all possible Bragg reflections.
Figure 4.4 : The variation of crystallite size (D) and strain (ε) against
the film thickness
Figure 4.5: The variation of dislocation density and stacking fault
probability against crystallite size
Figure 4.6: The plot of $1/2$ versus n/λ to determine the order number
and thickness
Figure 4.7: The refractive index as a function of wavelength and the
color solid line represents the curve fitting via Sellmeier form and the inset
shows the fitting of the data of Terekhova, Onishchenko et al. (1985) 89
Figure 4.8: The plot of $(n^2-1)^{-1}$ vs. λ^{-2} and the colored straight lines
represent the best fit line91

Figure 4.9: The plot of $(n^2-1)^{-1}$ vs. hv^2 and the colored straight lines
represent the best-fit line. 92
Figure 4.10: $(\alpha h v)^2$ vs hv plots for (a) 1061 nm, (b) 960 nm, (c) 561
nm, and (d) 248 nm CdSe nano-crystalline thin films deposited at room
temperature. 95
Figure 4.11: Tauc plot for a typical film of thickness 550 nm on glass
substrate. The inset shows the band gap, E_{g} and E_{o} transitions [c.f.(Ninomiya
and Adachi 1995)]
Figure 4.12: The photoluminescence spectra of <i>nc</i> -CdSe thin films. 98
Figure 4.13: Deconvolution of the PL spectrum for CS03 thin film. 99
Figure 5.1: FESEM micrographs of CdSe surface grown on p-Si (001),
and the inset displays the dislocation network
Figure 5.2: XRD scans for CdSe/Si (100) with CdSe(002) reflection
peak at $2\theta = 25.425^{\circ}$ and Si (400) at $2\theta = 69.285^{\circ}$
Figure 5.3: XRD scans for CdSe with (002) reflection peak at $2\theta =$
25.415. The inset shows profile fitting results for CdSe (002) peak 106
Figure 5.4: I–V-T characteristic curves of Au/n-CdSe/p-Si/Al at three
different temperatures
Figure 5.5: Semi-logarithmic plots of I–V characteristic for
Au/CdSe/p-Si heterostructure diodes at different temperatures

Figure 5.6: Temperature dependence of barrier height (ϕ_b) and ideality
factor (<u>n</u>) of Au/CdSe/p-Si heterostructure diodes
Figure 5.7: Plot of the experimental values of φb and 1/n versus 1/T
for Au/CdSe/p-Si diode. 113
Figure 5.8: Least-squares fit of ϕ_b versus n in the temperature ranges
of 160-240 and 240-360 K
Figure 5.9: Estimated schematic band diagram formed by Au/CdSe/p-
Si configuration. 116
Figure 5.10: The typical Richardson plot: ln(I _s /AT ²) versus 1000/T for
the Au/CdSe/p-Si in the temperature range 160–360 K
Figure 5.11: Plots of ln (I) vs ln (V) of the Au/CdSe/p-Si
heterostructure at various temperatures
Figure 5.12: Variation of V _X values with temperature for Au/CdSe/p-
Si heterostructure, and the inset shows the variation of m against the
temperature. 120
Figure 5.13: Arrhenius plots of ln(J) versus 1000/T for Au/CdSe/p-Si
heterostructure
Figure 5.14: I-V-T characteristic curves of Ni/CdSe/p-Si
heterostructure diodes
Figure 5.15: Temperature dependence of barrier height (φ_b) and
ideality factor (<u>n</u>) of Ni/CdSe/p-Si heterostructure diodes

Figure 5.16: The typical Richardson plot: $ln(I_s/AT^2)$ versus 1000/7	Γ for
the Ni/CdSe/p-Si in the temperature range 160–360 K	. 124