Ain Shams University
Faculty of Girls for Arts,
Science and Education
Physics Department

Investigation of Some Physical Properties of SnS Thin Films Using Electrical and Optical Measurements

53018
A-F

THESIS

Submitted for the Degree

of Ph. D. in Physics

52221

By

AMAL FAWZY SHAFIK EL-DEEB

M.Sc. (1984)

Supervised By

Prof. Dr. MANSOUR MOHAMED HASSAB EL-NABI

Prof. Dr. HILMY TAHA EL-SHAIR

Ass. Prof. Dr. HODA SHEHATA SOLIMAN

September 1995

Central Library - Ain Shams University

Ain Shams University
Facutly of Girls for Arts,
Science and Education
Physics Department

Name of Student: **AMAL FAWZY SHAFIK EL-DEEB**

Title of Thesis:

Investigation of Some Physical Properties of SnS Thin Films Using Electrical and Optical Measurements

Supervised By	Approved
Prof. Dr. **MANSOUR MOHAMED HASSAB EL-NABI**	Mansour H. El Na
Prof. Dr. **HILMY TAHA EL-SHAIR**	Helmi T. El Shair
Ass. Prof.Dr. **HODA SHEHATA SOLIMAN**	Hoda Shehata

Central Library - Ain Shams University

بسم الله الرحمن الرحيم

Central Library - Ain Shams University

بسم الله الرحمن الرحيم

·قالوا سبحانك لا علم لنا إلا ما علمتنا
إنك أنت العليم الحكيم·

صدق الله العظيم

(سورة البقرة– آية – ٣٢)

Central Library - Ain Shams University

إهـــــــداء

أهدى هزا العمل المتواضع
إلى كل أهلي وعشيرتي
الزين تمنوا ودعوا لي بالكثير
وتحملوا وعانوا معي الكثير

Central Library - Ain Shams University

Acknowledgement

It gives me a great pleasure to express my sincere thanks and appreciations to Prof. M.M.H. El-Nabi, Prof. of Phys., Fac. of Girls, Ain Shams U., for his guidance, valuable continuous supervision and fruitful comments.

My gratitude and thanks to Prof. H.T.El-Shair, Prof. of Phys., Fac. of Educ., Ain Shams U., for his fruitful supervision and also for his advice and assistance.

Deep thanks to Dr. H.S. Soliman, Ass. Prof. of Phys., Fac. of Educ., Ain Shams U., for her encouragement and assistance.

Sincere thanks and appreciations are offered to prof. A.B. El-Bialy, Head of phys. Dep., Fac. of Girls, and are also offered to prof. M.Abd El-Hady, Head of phys. Dep., Fac. of Educ., Ain Shams U., for providing the necessary facilitate needed to carry out this work.

Deep thanks to Prof. B.A.Khalifa, Prof. of Phys., fac. of Science, Ain Shams U., for her sincere help, valuable suggestions and discussions.

Sincere thanks to Prof. M.M.El-Nahass, Prof. of Phys., Fac. of Edu., and Dr. D. Abd el-Hady, Ass. Prof. of phys., Fac. of eng., Ain Shams U., for their help and support during the experimental work.

Finally, I would like to thank all the staff members of the research groups in the phys. Dep. in the Fac. of Educ., Ain Shams U., for their friendship, encouragement and for their kind Co-operation in various ways.

Central Library - Ain Shams University

Contents

Page

List of Plates and figures i

List of Tables ii

ABSTRACT iii

SUMMARY iv

INTRODUCTION 1

CHAPTER I : LITERATURE REVIEW AND THEORITICAL BACKGROUND 2

I.1 Structural properties of Tin Sulphide Material 2

I.2 The Electronic Band Structure of SnS 11

I.3 Transport Properties of SnS 13

I.4 Optical Properties of SnS 24

CHAPTER II : EXPERIMENTAL TECHNIQUES 43

II.1 Material Under Investigation 43

II.2 Preparation of SnS Thin Films 43

  II.2.a) Cleaning of the Glass and Quartz Substrates 43

  II.2.b) Evaporation Technique 44

II.3 Methods for Film Thickness Measurements.................46

  II.3.a) Quartz Crystal Thickness Monitor Technique.46

  II.3.b) Interferometric Technique 47

II.4 Structural Identification of the Investigated Samples ..52

  II.4.a) X-ray Diffraction 53

  II.4.a.1) Correction and Normalizatin of the x-ray Intensities 53

    i) Correction 53

    ii) Normalization of the x-ray Intensities to Absolute Units 55

  II.4.a.2) Minimization process, Evaluation of the Background Scattering and the Resolution of the overlapped peaks 55

Central Library - Ain Shams University

II.4.a.3) Crystallite Sizes and Lattice Distortion 56
II.4.a.4) Determination of the Ideal crystallite Sizes..57
II.4.b) Transmission Electron Microscopy 58
II.4.b.1) Electron Diffraction 58
II.4.b.2) Preparation of SnS Thin Films for Microscopic observation 60
II.5) Transport Properties Measurements 64
II.5.a) Electrical Resistivity Measurements 64
II.5.b) Thermoelectric Power Measurements 65
II.5.c) Current-Voltage Characteristics Measurements 71
II.6) Determination of the Optical constants of SnS Thin Films 71
II.6.a) The Transmittance T(λ) at Normal Light Incidence 73
II.6.b) The Reflectance R(λ) at Normal incidence...76
II.6.c) A computational Technique for Determining the Optical Constant n(λ) and k(λ) of thin Films...77

CHAPTER III: STRUCTURAL PROPERTIES OF SnS MATERIAL...84
III.1 X-ray Diffraction Analysis of SnS in Powder Form 84
III.2 The Structural Dependence on Film Thicknesses of SnS Thin Films...84
III.3 Structural Dependence on the Annealing Temperature for the SnS thin films...89
III.4 Crystallite Sizes and Lattice Straines of SnS Thin Films...89
III.5 Electron Diffraction Studies of SnS Thin Films 101

CHAPTER IV: OPTICAL PROPERTIES OF SnS THIN FILMS 105

Central Library - Ain Shams University

IV.1 The Spectral Distribution of the TransmissionT (λ) and Reflection R (λ) of SnS Thin Films 106
IV.2 The Spectral Distribution of both the Refractive Index n (λ) and the Absorption Index k(λ) of SnS Thin Films 106
IV.3 The Lattice Dielectric Constant ε_L of SnS Thin Films 109
IV.4 The Spectral Distribution of the Absorption Coefficient (α) of SnS Thin Films 113
IV.5 The Allowed Optical Transitions in SnS Thin Films .. 113

CHAPTER V: ELECTRICAL TRANSPORT PROPERTIES OF SnS THIN FILMS 122
V.1 Dark Electrical Resistivity of SnS Thin Film 123
  V.1.a) Dark Electrical Resistivity Dependence of the SnS Film Thickness 123
  V.1.b) Dark Electrical Resistivity Dependence of the SnS Film Temperature 127
  V.1.c) Dark Electrical Resistvity Dependence of the Annealing Temperature 135
V.2. Thermoelectric Power (Seebeck Coefficient S) of SnS Thin Films 135
  V.2.a) Seebeck Coefficient Dependence of the SnS Film Thickness 135
  V.2.b) Seebeck Coefficient Dependence of the Annealing Temperature 142
V.3. The Current-Voltage Characteristics of p-SnS/n-Si Heterojunction 152
  V.3.a) Static I-V charateristics of a p-SnS/n-Si Heterojunction 152
  V.3.a.i) Determination of the Base Resistance R_b ... 155
  V.3.a.ii) Forward Current Activation Energy 157
  V.3.a.iii) Reverse Current Activation Energy 159
  V.3.a.iv) Rectification Ratio 162

Central Library - Ain Shams University

V.3.a.v) The Conduction Mechanism 162
V.3.b) Capacitance-Voltage (C-V) Characteristics of p-SnS/n-Si Heterojunction 170
CONCLUSIONS 171
REFERENCES 175
ARABIC SUMMARY

***

Central Library - Ain Shams University

List of Plates and Figures

Page

Plate (1) : A photograph of the coating unit
(type E 306 A Edwards, England)................ 45

Plate (2) : A photograph of the Thickness Monitor
(Model FTM4, Edwards, England)............... 48

Plate (3) : The x-ray Diffractometer (type PW 1373, Philips). 54

Plate (4) : Electron Diffraction pattern of thin
polycrystalline vacuum deposited gold film
At 60 kV.. 62

Plate (5) : A photograph of the Double Beam
Spectrophotometer (CARY 2390, Varian Co.). 74

Plate (6) : The electron diffraction pattern of SnS thin film
(30 nm thick) deposited onto glass substrate... 102

Plate (7) : The electron diffraction pattern of SnS thin
film (60nm thick) deposited onto glass substrate. 102

Fig.(1) : Crystal structure of SnS according to Hofmann... 3

Fig.(2) : Transformation of SnS from orthorhombic
crystal to cubic.. 5

Fig. (3) : The Brillouin Zone appropriate to SnS................ 12

Fig. (4) : A plane monochromatic light at normal incident
on an absorbing film between the two dielectric
media air and quartz... 41

Fig. (5) : Schematic diagram of the interferometer
used for thickness measurement................. 50

Fig. (6) : The optical set-up for producing multiple
beam Fizeau fringes at reflection.............. 50

Fig. (7) : The Multiple-beam Fizeau fringes with step.. 51

Fig. (8) : Relation between the ring radii and $(h^2+k^2+\ell^2)^{1/2}$
of allowed reflecting planes of f.c.c.gold........ 63

Fig. (9) : A Schematic diagram of the film electrode system. 66

Central Library - Ain Shams University

Fig. (10): Cryostat used for resistivity measurements. 67
Fig. (11): Holder used for thermoelectric power measurements.70
Fig. (12): Electric circuit for current-voltage characteristics of p-n heterojunction.. 72
Fig. (13): Simplified optical, schematic (A) in the V case and (B) in the W case. 75
Fig. (14): Flow chart diagram of program used for n and k calculation.. 79
Fig. (15): Plot of n versus variance for different values of k, $t/\lambda = 0.1$, $T_{exp} = 0.484$ and $R_{exp} = 0.327$....... 80
Fig. (16): Flow chart diagram of step-length optimisation technique... 82
Fig. (17): X-ray diffraction pattern of original SnS powder. 85
Fig. (18): X-ray diffraction patterns of SnS thin films with different thickness.................................... 88
Fig. (19) : X-ray diffraction patterns of SnS thin films (400 nm thick) deposited at room temperature then annealed at the temperatures marked on the curves... 90
Fig. (20): The profiles of SnS powder annealed at 300°C for five hours... 93
Fig. (21): The profiles of the resolved (111,130) reflection planes of SnS thin film (400 nm thick) as deposited.94
Fig. (22): The profiles of the resolved (111,130) reflection planes of SnS thin film (400 nm thick) annealed at 60°C.. 95
Fig. (23): The profiles of the resolved (111,130) reflection planes of SnS thin film (400nm thick) annealed at 100°C... 96
Fig. (24): The profiles of the resolved (111,130) reflection planes of SnS thin film (400nm thick) annealed at 150°C... 97

Central Library - Ain Shams University

Fig. (25): The profiles of the resolved (111,130) reflection planes of SnS thin film (400 nm thick) annealed at 200°C.......... 98
Fig. (26): The spectral distribution of the transmission T(λ) for SnS thin films with different thicknesses....... 107
Fig. (27): The spectral distribution of reflection R (λ) for SnS thin films with different thicknesses........... 108
Fig. (28): Dispersion curves of both n and k for the as-deposited SnS thin films.......... 110
Fig. (29): The real dielectric constant ε_r as a function of λ^2 for SnS thin films.......... 112
Fig. (30): The absorption coefficient (α) of SnS thin films as a function of the photon energy (hν).......... 115
Fig. (31): Dependence of $(\alpha h\nu)^{1/2}$ on the photon energy (hν) for SnS thin films.......... 119
Fig. (32): Dependence of $(\alpha h\nu)^2$ on the photon energy ((hν) for SnS thin films.......... 120
Fig. (33): The relation between log ((αhν) and log $(\frac{1}{\lambda})$ for SnS thin films.......... 121
Fig. (34): I-V relation for SnS thin film with Al electrodes. 124
Fig. (35): I-V relation for SnS thin film with Ag electrodes. 125
Fig. (36): The dark electrical resistivity (*P*) of SnS films versus the film thickness (t).......... 126
Fig. (37): Temperature dependence of the electrical resistivity of SnS thin film of thickness (60nm). 128
Fig. (38): Temperature dependence of the electrical resistivity of SnS thin film of thickness (100nm). 129
Fig. (39): Temperature dependence of the electrical resistivity of SnS thin film of thickness (130nm).......... 130
Fig. (40): Temperature depndence of the electrical resistivity of SnS thin film of thickness (140nm).......... 131

Central Library - Ain Shams University

Fig. (41): Temperature dependence of the electrical resistivity of SnS thin films of thickness (180nm)............ 132
Fig. (42): Temperature dependence of the electrical resistivity of SnS thin film of thickness (230nm)............... 133
Fig. (43): Temperature dependence of the electircal resistivity of SnS thin film (120nm thick) as deposited........ 136
Fig. (44): Temperature dependence of the electrical resistivity of SnS thin film (120nm thick) annealed at 100°C for two hours.. 137
Fig. (45): Temperature dependence of the electrical resistivity of SnS thin film (120nm thick) annealed at 125°C for two hours..138
Fig. (46): Temperature dependence of the electrical resistivity of SnS thin film (120nm thick) annealed at 150°C for two hours.. 139
Fig. (47): Temperature dependence of the electrical resistivity of SnS thin film (120nm thick) annealed at 175°C for two hours.............................. 140
Fig. (48): Seebeck coefficient (S) versus temperature (T) for SnS thin film (160nm thick) as deposited...... 143
Fig. (49): Seebeck coefficient (S) versus temperature (T) for SnS thin film (300nm thick) as deposited..... 144
Fig. (50): Seebeck coefficient (S) versus temperature (T) for SnS thin film (330nm thick) as deposited..... 145
Fig. (51): Seebeck coefficient (S) versus temperature (T) for SnS thin film (417.6nm thick) as deposited... 146
Fig. (52): Seebeck coefficient (S) versus temperature (T) for SnS thin film (160nm thick) annealed at 100°C for two hours.. 147
Fig. (53): Seebeck coefficient (S) versus temperature (T) for SnS thin film (417.6nm thick) annealed at 100°C for two hours... 148

Central Library - Ain Shams University

Fig. (54): Seebeck coefficient (S) versus temperature (T) for SnS thin film (160nm thick) annealed at 170°C for two hours 149
Fig. (55): Seebeck coefficient (S) versus temperature (T) for SnS thin film (417.6nm thick) annealed at 170°C for two hours 150
Fig. (56): I-V characteristics for pre-annealed P-SnS/n-Si heterojunction at different ambient temperatures.. 154
Fig. (57): Ln (Base resistance R_b) versus $\frac{1000}{T}K^{-1}$ 156
Fig. (58): Ln (forward current I_f) versus $\frac{1000}{T}K^{-1}$ 158
Fig. (59): Forward current activation energy ΔE_f as a function of the applied forward voltage V_f 158
Fig. (60): Ln (reverse current I_r) versus $\frac{1000}{T}K^{-1}$ 160
Fig. (61): Reverse current activation energy ΔE_r as a function of the applied reverse voltage 161
Fig. (62): The rectification ratio (RR) versus voltage 163
Fig. (63-67): LogI versus the applied voltage at a given temperature 164-168
Fig. (68): Log I_o versus T k 169

Central Library - Ain Shams University