

**This dissertation has been
microfilmed exactly as received**

70-4673

**SCHUELER, Donald George, 1940-
ELECTROREFLECTANCE STUDIES OF
SEMICONDUCTING FILMS BY ELLIPSOMETRY.**

**The University of Nebraska, Ph.D., 1969
Engineering, electrical**

University Microfilms, Inc., Ann Arbor, Michigan

**ELECTROREFLECTANCE STUDIES OF SEMICONDUCTING
FILMS BY ELLIPSOMETRY**

by

Donald G. Schueler

A THESIS

Presented to the Faculty of

The Graduate College in the University of Nebraska

in Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Department of Electrical Engineering

Under the Supervision of Professor N. M. Bashara

Lincoln, Nebraska

June, 1969

TITLE

ELECTROREFLECTANCE STUDIES OF SEMICONDUCTING

FILMS BY ELLIPSOMETRY

BY

Donald George Schueler

APPROVED

DATE

Nicolas M. Bashara

June 30, 1969

Allen R. Edison

June 30, 1969

Frank G. Ullman

June 30, 1969

John J. Scholz

June 30, 1969

K. Krishna Rao

June 30, 1969

SUPERVISORY COMMITTEE

GRADUATE COLLEGE

UNIVERSITY OF NEBRASKA

ACKNOWLEDGEMENTS

The author expresses his deepest appreciation to Professor N. M. Bashara for his advice and continual encouragement. Professor F. G. Ullman has offered valuable suggestions on the preparation of the manuscript. Sandia Laboratories of Albuquerque, New Mexico, under sponsorship of the United States Atomic Energy Commission, has provided financial support and the use of equipment and facilities under the Doctoral Study Program. Dr. F. L. English of Sandia Laboratories assisted in preparation of the field effect samples.

PREVIEW

ABSTRACT

This dissertation is concerned with the study of electric field modulation of the optical properties of semiconducting films, employing ellipsometry as the basic spectroscopic method. The theoretical and experimental aspects of modulated reflectance ellipsometry are presented within the general framework of electroreflectance theory. The ellipsometric method provides additional experimental information about the optical modulation not obtained by electroreflectance measurements using linearly polarized light. In this study, the added information is used to calculate the penetration depth of the optical modulation in semiconducting SnO_2 films. Based on a perturbation having an exponential profile, the effective penetration depth is of the order of 75 \AA . This is approximately twice the effective penetration depth of the electric field, as determined from field-effect conductivity measurements. The static optical properties of the SnO_2 film indicate an indirect-transition edge near 2.6 eV and a direct-transition edge near 4.0 eV . The electroreflectance spectra of the SnO_2 film have a broad background typical of high carrier concentration semiconductors, but generally indicate the expected lineshape and spectral position of the absorption thresholds. The use of a ferroelectric ceramic for the substrate of the semiconducting film represents a significant departure from previous experimental methods and overcomes some of the limitations of previous sample configurations.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	ii
ABSTRACT	iii
TABLE OF SYMBOLS	vii
LIST OF FIGURES	xi
LIST OF TABLES	xv
CHAPTER 1: INTRODUCTION	1
1.1 Historical Survey and General Considerations	2
1.2 Purpose	6
1.3 Organization of Dissertation	9
CHAPTER 2: THEORETICAL CONSIDERATIONS	10
2.1 Modulated Reflectance at Oblique Incidence	10
2.2 Derivation of Modulated Ellipsometry Relationships	17
2.3 Reflection Coefficients of Optically Inhomogeneous Films	27
2.3.1 The Macroscopic Wave Equations	28
2.3.2 The Characteristic Matrix Formulation	33
2.3.3 Approximate Methods	36
2.4 Optical Properties and Energy Band Structure	42
2.5 Electromagnetic Theory	47

TABLE OF CONTENTS (CONT'D)

	<u>Page</u>
CHAPTER 3: ANALYTICAL METHODS	50
3.1 Optical Properties of a Substrate	51
3.2 Optical Properties and Thickness of a Film	52
3.3 Modulated Reflectance Parameters	55
3.4 Fractional Coefficients	58
3.5 Perturbation Depth	59
CHAPTER 4: EXPERIMENTAL TECHNIQUE AND RESULTS	61
4.1 Experimental Apparatus	61
4.1.1 Optical System	61
4.1.2 Electronics	62
4.1.3 Alignment and Calibration	63
4.2 Substrate Material and Properties	65
4.2.1 Substrate Preparation	65
4.2.2 Electrical Properties	66
4.2.3 Optical Properties	67
4.3 Preparation and Properties of the SnO ₂ Films	69
4.3.1 Film Deposition and Sample Configuration	69
4.3.2 Electrical Properties	70
4.3.3 Static Optical Properties	71
4.4 Electromodulated Spectra	74

TABLE OF CONTENTS (CONT'D)

	<u>Page</u>
CHAPTER 5: SUMMARY	79
5.1 Theoretical Aspects	79
5.2 Experimental Aspects	81
REFERENCES	83
FIGURES	89
APPENDIXES	122
A. Sensitivity Considerations for Modulated Reflectance Studies	122
A. Computer Code Listings	127

TABLE OF SYMBOLS

<u>Symbol</u>	<u>Definition</u>
A	analyzer null azimuth
a	analyzer azimuth
a_f	fundamental frequency component of modulation voltage
B	(1) band structure constant for direct-transitions (2) signal-to-noise ratio coefficient
C_1, C_2	modulated ellipsometry coefficients
c	(1) velocity of light (2) compensator azimuth
D	electric displacement
d	film thickness
E	electric field
\mathcal{E}	energy
e	electronic charge
F	(1) modulation parameter (2) electro-optic function
f	frequency
Δf	frequency bandwidth
G	(1) electro-optic function (2) photomultiplier gain
H	magnetic displacement
$H(x)$	unit step function
\hbar	Planck's constant/ 2π
I	radiation intensity

TABLE OF SYMBOLS (CONT'D)

<u>Symbol</u>	<u>Definition</u>
$I_m \{ \}$	imaginary part of complex number
i	$\sqrt{-1}$
J	joint density of states
K	absorption coefficient
k	propagation constant
L	electric field penetration depth
l	optical modulation depth
M	(1) characteristic matrix (2) critical point designation
m	modulation index
m_{ij}	element of characteristic matrix
m_e	electron mass
N	(1) number of interfaces in a stratified medium (2) number of unknown parameters
n	index of refraction
P	(1) polarization (2) polarizer null azimuth
\hat{p}	unit vector in the plane of incidence
p	(1) plane of incidence (2) polarizer azimuth
Q	band structure constant for indirect-transitions
q	normalized wave admittance
R	complex reflection coefficient

TABLE OF SYMBOLS (CONT'D)

<u>Symbol</u>	<u>Definition</u>
R	reflectance
$\text{Re}\{ \}$	real part of complex number
r	Fresnel coefficient
S	Snell's constant
g	unitary transformation
\hat{s}	unit vector normal to the plane of incidence
s	plane of the surface
T_c	compensator transmission ratio
$T(\lambda)$	spectral sensitivity of photomultiplier
t	time
$u(z)$	z -dependence of wave equation solution
$v(z)$	z -dependence of wave equation solution
x_a	analyzer off-null angle
x_p	polarizer off-null angle
Z	wave impedance
z	coordinate of film surface normal
α	fractional reflection coefficient
β	fractional reflection coefficient
Γ	lifetime broadening parameter
γ	(1) complex optical phase (2) excess noise factor
Δ	ellipsometric parameter
Δ_c	compensator phase shift

TABLE OF SYMBOLS (CONT'D)

<u>Symbol</u>	<u>Definition</u>
δ	total differential operator
∂	partial differential operator
ϵ	complex relative dielectric function
ϵ_0	permittivity of free space
ϵ_1	real part of ϵ
ϵ_2	imaginary part of ϵ
$\Delta\epsilon$	perturbation in ϵ
θ	(1) polar coordinate angle (2) electroreflectance parameter
κ	extinction coefficient
λ	vacuum wavelength of light
μ	reduced effective mass
μ_0	permeability of free space
ξ	complex optical phase
ρ	ratio of complex reflection coefficients
σ	polarization state of a plane wave
τ	time constant
ϕ	angle of incidence
χ	matrix of fractional coefficients and modulated reflectance parameters
ψ	ellipsometric parameter
ω	angular frequency
∇	del operator

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.2-1	Region of absorption — film thickness space accessible to electroreflectance measurements for the sample configuration of this study.	89
2.2-1	Symbolic representation of the optical components of the ellipsometer in terms of polarization-state operators.	90
2.2-2	Definition of the ellipsometer reference frames and azimuth angles looking into the reflected light beam.	91
2.3-1	(a) Definition of the coordinate system and plane of incidence for a film-covered surface. (b) Schematic profiles of the real and imaginary parts of the dielectric function for an inhomogeneous film on an absorbing substrate.	92
2.3-2	(a) Sublayer and interface notation for the stratified media problem. (b) Approximation of an inhomogeneous film with a number of homogeneous sublayers.	93
2.3-3	Comparison of βp calculated according to the WKB approximation and the Rouard method as a function of the effective penetration depth of $\Delta\epsilon$ for an exponential profile.	94

LIST OF FIGURES (CONT'D)

<u>Figure</u>		<u>Page</u>
2.5-1	Electric field-induced profile of ϵ_2 , according to the Franz-Keldysh theory, at (a) an indirect edge, and (b) a direct (Mo) edge.	95
4.1-1	Schematic diagram of the optical and electronic equipment used for modulated reflectance ellipsometry.	96
4.2-1	Real and imaginary parts of the dielectric function vs photon energy for the ferroelectric ceramic substrate.	97
4.2-2	Refractive index and extinction coefficient vs photon energy for the ferroelectric ceramic substrate.	98
4.2-3	Plot of $(K\alpha)^2$ vs photon energy in the vicinity of the fundamental absorption edge for the ferroelectric ceramic substrate.	99
4.3-1	Schematic view of the thin film field-effect sample configuration and plane of incidence of the light beam.	100
4.3-2	Real and imaginary parts of the dielectric function for a 310 Å thick SnO_2 film vs photon energy.	101

LIST OF FIGURES (CONT'D)

<u>Figure</u>		<u>Page</u>
4.3-3	Refractive index and extinction coefficient for a 310 Å thick SnO_2 film vs photon energy.	102
4.3-4	$(K\alpha)^{\frac{1}{2}}$ for a 310 Å thick SnO_2 film vs photon energy. Extrapolated indirect edge is at 2.64 eV.	103
4.3-5	$(K\alpha)^2$ for a 310 Å thick SnO_2 film vs photon energy, corrected for absorption due to indirect-transitions. Extrapolated direct edge is at 4.0 eV.	104
4.4-1	Spectral profile of $\delta R_s/R_s$ for a 310 Å thick SnO_2 film at various angles of incidence.	105
4.4-2	Spectral profile of $\delta R_p/R_p$ for a 310 Å thick SnO_2 film at various angles of incidence.	106
4.4-3	Spectral profile of $2\delta\Delta$ for a 310 Å thick SnO_2 film at various angles of incidence.	107
4.4-4	Relative sum of squares of the residuals of $2\delta\Delta$ vs the penetration depth for various interfacial polarizations.	108
4.4-5	Percent change in SnO_2 film resistivity vs the interfacial polarization.	109
4.4-6	Optical modulation depth, l , and electrical modulation depth, L , vs the interfacial polarization.	110
4.4-7	α_s and β_s vs angle of incidence for an SnO_2 film.	111

LIST OF FIGURES (CONT'D)

<u>Figure</u>		<u>Page</u>
4.4-8	α_p and β_p vs angle of incidence for an SnO_2 film.	112
4.4-9	α_p and β_p vs angle of incidence for an SnO_2 film.	113
4.4-10	Spectral dependence of the fractional coefficients for an SnO_2 film.	114
4.4-11	Spectral profile of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ for a 310 Å thick SnO_2 film.	115
4.4-12	Theoretical profile of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ in the vicinity of an Mo edge in the presence of lifetime broadening (from Reference 12).	116
4.4-13	Spectral profile of $\delta R_s/R_s$ for various polarization states of the ferroelectric substrate.	117
4.4-14	Spectral profile of $\delta R_p/R_p$ for various polarization states of the ferroelectric substrate.	118
4.4-15	Spectral profile of $2\delta\Delta$ for various polarization states of the ferroelectric substrate.	119
A-1	Modulation index vs photomultiplier anode current at various signal-to-noise ratios.	120
A-2	Allowable noise bandwidth of coupling network as a function of modulation index for various photomultiplier anode currents.	121

LIST OF TABLES

<u>Table</u>		<u>Page</u>
2.2.1	The coefficients, C_1 and C_2 , and the modulation index, m , for various analyzer and polarizer azimuths.	26
B.1	Input requirements for program INVERT for various types of problems.	129

CHAPTER 1

INTRODUCTION

The interaction of electromagnetic radiation with materials has long been recognized as a valuable means of acquiring information about their basic properties. In this connection, optical studies of crystalline solids have provided much information about their energy band structure and the role of fundamental electronic excitations. In recent years there has been an increased activity in the measurement of the optical properties of insulators, metals, and semiconductors in the visible and near-visible regions of the electromagnetic spectrum. The stimulus for this activity has come mainly from the development of theoretical methods for calculating the energy band structure and optical constants of crystalline solids and the development of a quantum mechanical description of the effect of an electric field on the optical properties of crystalline solids, along with the simultaneous development of sensitive experimental techniques for detecting the extremely small changes in the optical properties induced by various perturbations. It is the purpose of this dissertation to investigate the theoretical and experimental aspects of electric field modulation of the optical properties of semiconducting films, employing ellipsometry as the basic spectroscopic method.

1.1 Historical Survey and General Considerations

Ellipsometry, or polarimetric spectroscopy, is the measurement of the change in the polarization state of light caused by reflection from a planar surface. The ellipsometer has proved to be a versatile instrument for investigation of the optical properties of surfaces, interfaces, and thin films.¹ Hall² has recently surveyed the historical development of ellipsometry, whose theoretical foundations extend back to the nineteenth century and the fundamental works of Fresnel, Rayleigh, and Drude. Throughout its development, the most serious limitation of the ellipsometric method has been the complexity of the Drude equations, which relate the reflection coefficients to the optical properties of a film-covered surface. It is generally not possible to obtain closed-form analytical expressions for the optical properties in terms of experimentally measured quantities, and considerable effort has been expended in developing various linear approximations to the exact Drude equations.³ The approximate equations, however, are limited to films, generally non-absorbing, which are very thin in comparison to the wavelength of the light. Unfortunately, these approximations have often been extended to situations which may result in considerable inaccuracy in the results. The widespread availability of high-speed electronic computers with complex number capability is making the use of the exact Drude equations routine. Ellipsometric determination of the optical properties and thickness of films is no longer restricted to regions of the electromagnetic spectrum where the film is non-absorbing and is becoming extremely useful in studying fundamental absorption thresholds of thin films.

The theoretical relation between the energy band structure and the optical properties of a solid was well established by the middle 1950's.⁴ Experimentally observed spectra, however, seldom resembled the predicted profiles and unambiguous identification of structural features met with limited success. The first calculations of the effect of an electric field on the optical properties of crystalline solids were published in 1958 by Franz⁵ and Keldysh.⁶ The Franz-Keldysh theory predicts a field-induced shift of the fundamental absorption edge toward lower photon energies, due to field-assisted interband excitation of electrons. Phillips⁷ and others later extended the Franz-Keldysh theory to higher energy interband transitions.

Experimental observations of the Franz-Keldysh effect were first demonstrated by electroabsorption measurements of semiconductors.⁸ It was soon realized that optical modulation could be observed in reflectance as well as in transmittance and in 1965 the first electroreflectance experiments were performed.⁹ Electroreflectance measurements allow observation of optical modulation at the higher energy parabolic and saddle-point edges not accessible to electroabsorption measurements. The diagnostic value of electroreflectance measurements comes from the differential nature of the technique which allows separation of slope discontinuities in the optical dielectric function from the continuous background. Identification of the spectral position and type of slope discontinuity, which occur at points of high symmetry in the Brillouin zone, are essential to properly adjust theoretical energy band structure calculations.

The theory of electric field effects on the optical dielectric properties of solids has progressed sufficiently to allow inclusion of such important effects as phonon scattering, exciton transitions, lifetime broadening, impurity scattering, etc.¹⁰⁻¹² Quantitative interpretation of experimental results has been much less successful. The theoretical understanding of electric field effects in real solids, however, is showing the need for further refinement of experimental investigations. The existing experimental results are being re-examined with these improved analytic methods.

Further refinement of the interpretation of the electroreflectance spectra of semiconductors seems to depend on a better definition of the effective electric field, both with respect to the actual field at the surface of the semiconductor and its spatial dependence over the region of the penetration of the light. In this connection, the effect of spatially nonuniform changes in the optical dielectric function are just beginning to receive attention.^{13,29,30} Quantitative interpretation of electroreflectance spectra requires determination of the functional dependence of the optical modulation on the electric field. Theoretical considerations, such as the inclusion of lifetime broadening effects, can only indicate the general nature of this dependence.

Sample configurations for electroreflectance experiments have been of two basic types: electrolytic cells²⁸ in which the external modulating field is applied to the sample surface through the semiconductor-electrolyte surface barrier, and the field-effect configuration¹⁴ in which a thin, transparent dielectric serves to space a transparent field electrode from the surface. Both types have undesirable features.

Because of the complex potential distribution in the electrolytic cell and chemical processes at the semiconductor-electrolyte interface, the actual modulating field is not well known. The field-effect configuration can have a limited spectral range due to the fundamental absorption edges of the transparent dielectric and field electrode.

Two comprehensive review articles on optical modulation theory and experiments have recently been written. Aspnes and Bottka¹² review the recent advances in the theoretical description of electric field effects on the optical dielectric function of insulators and semiconductors, and Seraphin¹⁵ reviews the experimental methods and results in electroreflectance.

The advantages of combined electroreflectance and ellipsometric measurements were first realized by Buckman and Bashara,^{16,17} who studied the electroreflectance spectra of gold and silver films in an electrolytic cell. However, their phenomenological interpretation of the optical modulation parameters does not utilize the conventional formulation of oblique incidence electroreflectance. Also, the recent derivations of modulated reflectance by Schmidt and Knausenberger,¹⁸ which are concerned with determining spatially uniform changes in the optical properties of a homogeneous material, do not realize the full potential of the ellipsometric method. A more rigorous development of modulated reflectance ellipsometry in the general framework of electroreflectance theory is presented in this dissertation.

1.2 Purpose

The purpose of this work is to present the important theoretical and experimental aspects of modulated reflectance ellipsometry and to propose an improved sample configuration for thin-film semiconductor electroreflectance studies.

The ellipsometric method allows determination of the perturbation in the polarization state of the reflected light due to optical modulation of the sample, as well as the perturbation in the oblique reflectances. This added information may be used to establish a better understanding of the optical modulation process. In order to connect the experimentally observed changes in reflectance to the changes in the optical dielectric function, the static optical properties of the sample must be accurately known. Modulated reflectance ellipsometry combines the static and dynamic measurements and, in addition, allows separation of the changes in the real and imaginary parts of the complex dielectric function. This is especially important if the measurements are restricted to a narrow spectral range, making a dispersion analysis difficult, if not impossible.

A primary objective of the experimental measurements is to demonstrate the analytical potential of the ellipsometric method in characterizing the spatial extent of the optical modulation. To accomplish this, a unique sample configuration was used to vary the surface potential of the semiconductor film. The sample configuration is essentially that of an insulated-gate thin film field-effect device, with one important distinction; the insulator is a ferroelectric ceramic which also serves as the substrate for the semiconductor film.¹⁹ The electric field is applied to the thin film at the semiconductor-ferroelectric interface by

a voltage impressed across the substrate. The light impinges obliquely on the free surface of the semiconducting film and is multiply reflected from the free surface and the film-substrate interface. Since the optical modulation occurs in the space-charge region at the film-substrate interface, rather than at the free surface, as in the case of the previous sample configurations, the penetration depth of the light in the semiconductor film must be large enough to allow a significant portion of the incident intensity to reach the film-substrate interface. Figure 1.2-1 illustrates the approximate range of applicability of this sample configuration, in terms of the film thickness and film absorption. The division between the accessible and inaccessible areas represents the region in which the absorption coefficient-thickness product is unity.

A ferroelectric ceramic makes an ideal substrate for this sample configuration. These materials typically have a high static dielectric constant which results in electric field amplification at the film-substrate interface, a high index of refraction which makes them a good reflector, and, perhaps most important, the remanent ferroelectric polarization may be used to vary the charge carrier density of the semiconductor over a larger range than is possible with a linear dielectric. Also, the interfacial polarization is easily established by measuring the electrical charge supplied to the field electrode of the sample. This sample configuration does not have the spectral limitations of the electrolytic cell and field-effect sandwich, and may be used in vacuum and at low temperatures.