

72-15,992

IBRAHIM, Magdi Mahmoud M., 1944-  
ELLIPSOMETRIC STUDY OF CLEANING SILICON BY  
ION BOMBARDMENT AND HEATING IN ULTRA HIGH  
VACUUM.

The University of Nebraska, Ph.D., 1971  
Engineering, electrical

University Microfilms, A XEROX Company , Ann Arbor, Michigan

ELLIPSOMETRIC STUDY OF CLEANING SILICON  
BY ION BOMBARDMENT AND HEATING IN  
ULTRA HIGH VACUUM

by

Magdi Mahmoud M. Ibrahim

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

December, 1971

**TITLE**

Ellipsometric Study of Cleaning Silicon by

Ion Bombardment and Heating in Ultra High Vacuum

**BY**

Magdi Mahmoud M. Ibrahim

**APPROVED**

**DATE**

N. M. Bashara

Nov. 29, 1971

John J. Scholz

"

A. Bruce Buckman

"

Frank G. Ullman

"

A. L. Jain

"

**SUPERVISORY COMMITTEE**

**GRADUATE COLLEGE**

**UNIVERSITY OF NEBRASKA**

PLEASE NOTE:

Some pages may have

indistinct print.

Filmed as received.

University Microfilms, A Xerox Education Company

## Acknowledgment

The author wishes to express his sincere thanks and gratitude to Professor N. M. Bashara, for his valuable guidance as well as his continuous encouragement and support. Thanks are also given to the members of the supervisory committee. Financial support by the National Science Foundation and the U. S. Office of Naval Research is deeply appreciated. Special thanks to Mrs. Eunice Everett for typing the manuscript.

ELLIPSOMETRIC STUDY OF CLEANING SILICON BY ION  
BOMBARDMENT AND HEATING IN ULTRA HIGH VACUUM

Magdi Mahmoud M. Ibrahim, Ph.D.

University of Nebraska, 1971

Adviser: N. M. Bashara

Multiple-angle-of-incidence ellipsometry reduces the effects of experimental errors when estimating the optical constants of filmed surfaces using least squares. A test for correlation between parameters is developed which does not require exact values of the parameters so that approximate values can be used to test for correlation. Correlation between two parameters is present when the normalized ratio of the derivatives of  $\Delta$  with respect to each of the parameters is constant with angle-of-incidence. To solve for the uncorrelated parameters independent estimates of the correlated parameters are needed. A common problem is correlation between the refractive index and thickness of the film when a very thin film covers a substrate. Experimentally, the optical constants of silicon in the presence of  $20 \text{ \AA}$  thick oxide film were found to agree favorably with the measured values for a nearly-clean silicon surface ( $4 \text{ \AA}$  contamination), using multiple-angle measurements. Simultaneous heating and ion-bombardment is more effective in cleaning silicon surfaces than

either heating only at elevated temperatures, ion-bombardment at room temperature or sequential heating ( $800^{\circ}\text{C}$ ) and ion-bombardment with 400 eV argon ions, at an ion current density of  $2\text{ }\mu\text{A}/\text{cm}^2$  remove about  $15\text{ }\text{\AA}$  of silicon oxide in 30 minutes. For the first time ellipsometry is used to measure quantitatively the damage of silicon by low-energy ions. There is an increase in absorption in the infrared, a decrease of reflectivity in the ultraviolet and the absorption peak is broadened. The optical constants return to their original value on annealing at  $800^{\circ}\text{C}$ .

## Table of Contents

	Page
Acknowledgment . . . . .	ii
Abstract . . . . .	iii
Table of Symbols . . . . .	vii
List of Figures . . . . .	x
List of Tables . . . . .	xiv
Chapter I Introduction . . . . .	1
1.1 Ellipsometry . . . . .	1
1.2 Silicon-interface in ultra-high vacuum. . . . .	4
1.3 Arrangement of the dissertation . . . . .	5
Chapter II Ellipsometric Theory . . . . .	6
2.1 Ellipsometric technique in U.H.V. . . . .	6
2.2 Ellipsometric equations for a filmed surface . . . . .	12
Chapter III Parameter-Correlation Test . . . . .	16
3.1 Multiple-angle ellipsometric equations. . . . .	17
3.2 Correlation between the parameters for SiO <sub>2</sub> -Si . . . . .	22
3.3 Parameter accuracy for cross-correlation . . . . .	26
Chapter IV Computational Considerations in Multiple-angle Ellipsometry . . . . .	28
4.1 Reducing experimental errors in by MAI. . . . .	29
4.2 The diagonal elements of the Hessian Matrix . . . . .	32



	Page
4.3 Results and discussion . . . . .	36
A. Initial estimates for SiO <sub>2</sub> on Si . . .	36
B. Thickness effects. . . . .	37
C. Errors . . . . .	39
D. Comparison of error estimation . . .	40
E. Angle of incidence . . . . .	42
Chapter V Experimental Procedure and Results . . . . .	43
5.1 Test equipment and arrangement . . . . .	44
5.2 Cleaning by simultaneous heating and ion bombardment . . . . .	46
5.3 Heating in ultra-high vacuum . . . . .	48
5.4 Ion bombardment at room temperature. . . . .	51
5.5 Sputtering yield and sticking probability. . . . .	54
5.6 Surface damage . . . . .	56
Chapter VI Conclusions. . . . .	60
6.1 Computational . . . . .	60
6.2 Experimental . . . . .	62
References . . . . .	64
Tables . . . . .	68
Figures . . . . .	82
Appendix A Correction for the birefringence of the vacuum-chamber windows . . . . .	99
Appendix B Alignment of a specimen surface inside the vacuum chamber . . . . .	103
Appendix C Heater calibration . . . . .	105
Appendix D Computer programs . . . . .	108

## TABLE OF SYMBOLS

<u>Symbol</u>	<u>Definition</u>
A	analyzer null azimuth
B	vector representing parameters of interface
D	film thickness
D <sub>D</sub>	thickness of damaged-layer caused by ion-bombardment
E	electric field
F	residual of reflection coefficient
G	sum-of-squares of residuals
i	$\sqrt{-1}$
J	ion-current density
K <sub>S</sub>	substrate extinction coefficient
K <sub>D</sub>	extinction coefficient of damaged layer
K	(1) Boltzmann constant (2) number of unknown parameters
m	(1) number of angles-of-incidence (2) slope of $\Delta$ -time plot
N <sub>D</sub>	refractive index of damaged layer
N <sub>S</sub>	refractive index of substrate
N <sub>F</sub>	refractive index of surface-film
N <sub>O</sub>	Avogadro's number
n <sub>O</sub>	surface-layer density
n <sub>g</sub>	number of reactive atoms striking a unit surface per second

<u>Symbol</u>	<u>Definition</u>
$n_i$	ion-beam density (J/e)
$n_v$	density of atoms in silicon
P	(1) polarizer null azimuth (2) pressure (3) subscript denoting quantities pertaining to the plane-of-incidence
Q	compensator azimuth
R	(1) reflection coefficient (2) relative error in estimating refractive indexes
S	(1) sticking probability (2) subscript denoting quantities pertaining to the normal to the plane-of-incidence
T	(1) compensator transmission ratio (2) temperature
t	time of bombardment
y	sputtering yield (atoms/ion)
$\alpha$	(1) first derivative of $\Delta$ with respect to film thickness (2) tilt of specimen surface
$\Delta$	relative change in phase
$\partial$	partial differential operator
$\delta$	total differential operator
$\delta_c$	compensator relative retardation
$\lambda$	wavelength

<u>Symbol</u>	<u>Definition</u>
$\rho$	ratio of complex reflection coefficient
$\phi$	angle of incidence
$\psi$	angle whose tangent is the relative amplitude attenuation

## LIST OF FIGURES

Fig. 1 The basic arrangement for ellipsometric measurements and cleaning in ultra-high vacuum. LS-3 mw laser ( $6328 \text{ \AA}$ ) with quarter-wave plate at the output, P Glan-Prism polarizer (air gap), IG Varian (UHV-12 KF) Ionization gauge, SP Varian titanium sublimation pump, IP Vacion pump (500 liter/sec), MS Varian quadruple mass spectrometer, W Window, TC Test chamber, S Specimen holder on manipulator, A Glan-Prism analyzer (air gap), PM Photomultiplier (RCA 1P28) connected to a Keithley model 153 micro-volt-ammeter, LV Variable--leak valve, model 951-5100, B Varian ion-bombardment gun, C Soleil-Babinet compensator.

Fig. 2 Dependence of compensator-retardation  $\delta_c$  on specimen tilt  $\alpha$ , at  $5461 \text{ \AA}$  and  $70^\circ$  angle of incidence.

Fig. 3 Illustrates the errors in estimating the refractive index and thickness of a film due to a small error in  $\psi$  when measurements are made at one angle of incidence.

Fig. 4 Cross sections of the error function G. Curve 1 is for a thick film and 2 for a thin film.

Fig. 5 The relative error  $R = \delta N_S / \delta N_F$  in estimating the substrate refractive index compared to the film refractive index as a function of film thickness.

Fig. 6 The increase in  $\Delta$  with cumulative ion-bombardment time, at 6328 Å, 70° angle of incidence, 800° C specimen temperature, ion voltage and current 400 ev and 2 mA/cm<sup>2</sup> respectively. + - S95, ● - S100, x - S118, □ - S125.

Fig. 7 The normalized increase in  $\Delta$  as a function of the ion current density. Same conditions as for Fig. 6.

Fig. 8 The change in the refractive index of silicon with temperature, assuming a two-layer model: silicon oxide film and substrate. Specimen S95 at 6328 Å.

Fig. 9 The changes in  $\Delta$  and  $\Psi$  with the duration of the heat treatment.  $\Delta$  -solid lines,  $\Psi$  -dashed lines. Specimen S95, at 6328 Å and 70° angle of incidence. Starting background pressure 10<sup>-9</sup> torr.

Fig. 10 The spectrum of the residual gases in the vacuum system. Partial pressures at 1200°C are given in Fig. 11.

Fig. 11 The changes of the partial pressures of the residual gases in the vacuum system during heating at 1200° C, S95.

Fig. 12  $\Psi - \Delta$  Plot of the experimental results at  $\phi = 70^\circ$ , of ion bombardment of 0.1  $\Omega$ -cm silicon at room temperature, S-27. Curve A is for the surface before bombardment, B, C, D and E after a 30-minute bombardment period. Specimen S39 showed similar behavior. Note  $\Delta$  is decreasing to the right.

Fig. 13 The change in  $\Delta$  and film thickness with bombardment time of S27 and S39 at room temperature. The origin is taken after the first bombardment cycle. Lines 1 and 2 correspond to base pressures of  $4 \times 10^{-8}$  and  $6 \times 10^{-8}$  torr, respectively.

Fig. 14 The increase in  $\Psi$ , induced in silicon by ion-bombardment at  $4 \times 10^{15}$  ions/cm<sup>2</sup> ( $2 \mu\text{A}/\text{cm}^2$ ). Each point was obtained after 5 minutes bombardment 6328 Å and  $70^\circ$  angle of incidence. + - S95 (30  $\Omega$ -cm).  
 ○ - S100 (8  $\Omega$ -cm), x - S118 (0.1  $\Omega$ -cm),  
 □ - S125 (0.01  $\Omega$ -cm).

Fig. 15 (A) represents a typical range-distribution of the trapped particles in an amorphous target, (B) a three-layer model, (C) a two-layer model to represent the silicon interface.

Fig. 16 The changes in the optical constants of 0.1 $\Omega$ -cm silicon, S27, due to 350 ev ion bombardment at  $5 \times 10^{16}$  ions/cm<sup>2</sup>. Broken and solid lines are for the optical constants before and after bombardment, respectively.



## List of Tables

- I. The variation with angle-of-incidence of the normalized derivatives of  $\Delta$  and  $\Psi$  for Si-SiO<sub>2</sub> system at a wavelength of 5461 Å and film thickness of 20 Å.
- II. The variation with angle-of-incidence of the derivatives of  $\Psi$  and the relative derivatives of  $\Delta$  for Si-SiO<sub>2</sub> and film thickness of 20 Å.
- III. Correlation between parameters for SiO<sub>2</sub>-Si.
- IV. First derivatives of  $\Delta$  and  $\Psi$  with respect to  $N_F$  for a thin oxide film on silicon at an angle of incidence of 70°.
- V. MAI determination of optical constants of boron-doped silicon ( 0.1 ohm-cm) covered with a natural oxide.
- VI. DEHM values for Si-SiO<sub>2</sub> at a wavelength of 4358 Å.
- VII. Effect of initial guesses and experimental errors on the final solutions for the Si-SiO<sub>2</sub> system.
- VIII. Simulated angle-of-incidence effects in error analysis.

- IX. Dopant, resistivity and crystal orientation of silicon specimens used.
- X. The changes in the optical constants of silicon, after cleaning, ion bombardment and annealing, at  $6328 \text{ \AA}$ , from multiple-angle measurements,  $70^\circ$ ,  $74^\circ$ , and  $76^\circ$ .
- XI. The changes in the optical constants of silicon due to 400 e.v. ion bombardment at room temperature.
- XII. The changes in  $\Psi$  and  $\Delta$  caused by ion bombardment at  $20^\circ \text{ C}$ , a wavelength of  $6328 \text{ \AA}$  and  $70^\circ$  angle-of-incidence, and after temperature annealing.
- XIII. The variation with angle-of-incidence of the normalized derivative of  $\Delta$  for three-layer model, Si-SiO<sub>2</sub> system.

## CHAPTER I

### INTRODUCTION

#### 1.1 Ellipsometry

The fundamental physical process of ellipsometry<sup>1</sup> is the interaction between polarized radiation and the array of molecules that constitute the surface. To extract useful information, two basic problems are involved:

- (1) To carry out accurate measurements of the polarization change induced by the interaction process. In the visible and near visible regions of the electromagnetic wave spectrum, optical techniques are very convenient for making these measurements because of the availability of high quality components.
- (2) To relate the ellipsometric measurements with the optical and geometrical parameters of the surface.

Johnson and Bashara<sup>2a</sup> have derived simplified equations for the changes in the ellipticity of polarized light upon reflection from a surface. Azzam and Bashara<sup>2b</sup> have studied in detail the effect of the imperfections in the optical components on the accuracy of ellipsometric measurements.

In the case of a thin film on an absorbing substrate, it is necessary to carry out and interpret a number of independent experimental measurements, because a single set of ellipsometric measurements at given angle of incidence and wavelength is only able to determine two unknowns whereas there may be as many as five unknowns; namely, the complex indices of substrate and film and film thickness. McCrackin and Colson<sup>3</sup> investigated four methods for increasing the available data; (1) measurements on films of different thickness, (2) measurements on a single film with different surrounding media, (3) measurements on a single film using various substrates and (4) measurements on a single film at various angles of incidence.

The variation of angle of incidence is convenient experimentally and avoids the complications of introducing new physical factors.

Multiple-angle-of-incidence (MAI) ellipsometry has found only limited use because of unresolved questions in various studies. Using a chrome substrate, McCrackin and Colson<sup>3</sup> found satisfactory MAI solutions for film properties at a specific thickness only. Burge and Bennett<sup>4</sup> showed that MAI could not be used to determine whether a film is present on a substrate. Schueler<sup>5</sup> examined the relation of MAI measurements to experimental error for a film-covered substrate and proposed a feasibility test for such

measurements in the presence of experimental errors. His method involves first derivatives of the ellipsometer parameters  $\psi$  and  $\Delta$ . Oldham<sup>6</sup> discusses the problem of a film on a known substrate at one and two angles of incidence. Johnson and Bashara<sup>7</sup> studied contamination films on silver using MAI and found that their solutions were sensitive to starting estimates of the unknowns.

A primary objective of this study is to clarify the theoretical aspects of the computational problem of MAI ellipsometry. To this end two useful tests (the parameter-correlation test and the convergence-second-derivative test) are developed and applied to the Si-SiO<sub>2</sub> interface.

## 1.2 Silicon Interface in Ultra-high Vacuum

Further development and refinement of surface-sensitive semi-conductor devices depends critically on understanding and controlling the silicon surface interface. For example, the characteristics of metal-oxide-semi-conductor<sup>8,9</sup> transistors (MOST) are critically dependent on the properties of an insulating SiO<sub>2</sub> layer on the silicon and the properties of the silicon-insulator interface. Also, an important factor in making nearly ideal metal-semi-conductor contacts<sup>10</sup> is to minimize the thickness of the interfacial layer between the metal and the semi-conductor.

An important step in controlling the silicon surface is to study the problems associated with obtaining an atomically clean silicon surface. Such a surface is defined<sup>11,12</sup> as "a surface free of all but a few percent of a single monolayer of foreign atoms, either adsorbed on or substitutionally replacing surface atoms of the parent lattice." Because of the known interactions of atmospheric gases with a silicon surface, it follows that clean-surface investigations must be performed in ultrahigh vacuum with a low residual pressure.

### 1.3 Arrangement of the Dissertation

Chapter II is devoted to analyzing the ellipsometric theory where we will consider the effect of a small tilt in the specimen on the ellipsometric measurements. Also, the matrix approach of relating the ellipsometric measurements to the optical parameters of filmed surfaces will be discussed. Chapters III and IV deal with computational problems of multiple-angle ellipsometry. In Chapter III, a parameter-correlation test is introduced and applied to the Si-SiO<sub>2</sub> system. The conditions for minimizing parameter correlation are developed. The effect of experimental errors on the accuracy of estimating the optical parameters of a filmed surface is considered in Chapter IV. Also another useful computational test is developed using the second derivatives of least-square residuals. Chapter V is devoted to experimental studies on cleaning silicon surfaces using argon-ion bombardment, heating in ultra-high vacuum, and a combination of the two. The summary and conclusions are included in Chapter VI. Finally, details of the essential computer programs are given in Appendix D.

## CHAPTER II

### ELLIPSOMETRIC THEORY

#### 2.1 Ellipsometric Technique in U.H.V.

The basic ellipsometric arrangement is shown in Fig. 1. The ellipsometer consists of polarizer, compensator (Soleil-Babinet), the surface under investigation and analyzer. Linearly polarized light becomes, in general, elliptically polarized upon passing through the compensator. Reflection from the specimen introduces changes in the relative magnitudes and phases of the electric field components of the light. The ratio of the parallel to the perpendicular reflection coefficients,  $R_p$  and  $R_s$  respectively is defined as

$$\rho = R_p / R_s = \tan \psi \exp(j\Delta) \quad , \quad (2.1)$$

where the subscripts p and s refer to those components parallel and perpendicular to the plane of incidence, which in turn is determined by the direction of the light ray and the normal to the test specimen surface. The parameters  $\psi$  and  $\Delta$  (relative phase difference) are determined from azimuthal angle measurements of the polarizer, analyzer and compensator. For a compensator azimuth of  $+45^\circ$ , there are two pairs of