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

by

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TITLE

Ellipsometric Study of Cleaning Silicon by

Ion Bombardment and Heating in Ultra High Vacuum

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

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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 Δ 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 Å thick oxide film were found to agree favorably with the measured values for a nearly-clean silicon surface (4 Å 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° C) and ion-bombardment with 400 eV argon ions, at an ion current density of 2 $\mu A/cm^2$ remove about 15 Å 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° C.

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TABLE OF SYMBOLS

Symbol		Definition
A		analyzer null azimuth
B		vector representing parameters of interface
D		film thickness
D_D		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_S		substrate extinction coefficient
K_D		extinction coefficient of damaged layer
K	(1)	Boltzmann constant
	(2)	number of unknown parameters
m	(1)	number of angles-of-incidence
	(2)	slope of Δ-time plot
N_D		refractive index of damaged layer
N_S		refractive index of substrate
N_F		refractive index of surface-film
N_O		Avogadro's number
n_O		surface-layer density
n_g		number of reactive atoms striking a unit surface per second

Symbol		Definition
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)
α	(1)	first derivative of Δ with respect to film thickness
	(2)	tilt of specimen surface
Δ		relative change in phase
∂		partial differential operator
δ		total differential operator
δ_c		compensator relative retardation
λ		wavelength

Symbol	Definition
ρ	ratio of complex reflection coefficient
Φ	angle of incidence
Ψ	angle whose tangent is the relative amplitude attenuation

LIST OF FIGURES

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 Δ with cumulative ion-bombardment time, at 6328 Å, 70° angle of incidence, 800° C specimen temperature, ion voltage and current 400 ev and 2 $\mu A/cm^2$ respectively. + - S95, ⊙ - S100, x - S118, ▢ - S125.

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

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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 $\Phi = 70^o$, of ion bombardment of 0.1 Ω-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 Δ is decreasing to the right.

Fig. 13 The change in Δ 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 4×10^{-8} and 6×10^{-8} torr, respectively.

Fig. 14 The increase in Ψ, induced in silicon by ion-bombardment at 4×10^{15} ions/cm^2 (2 μA/cm^2). Each point was obtained after 5 minutes bombardment 6328 Å and 70^o angle of incidence. + - S95 (30 Ω-cm). Θ - S100 (8 Ω-cm), x - S118 (0.1 Ω-cm), $\square$ - S125 (0.01 Ω-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 0.1Ω-cm silicon, S27, due to 350 ev ion bombardment at 5×10^{16} ions/cm^2. Broken and solid lines are for the optical constants before and after bombardment, respectively.

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CHAPTER I

INTRODUCTION

1.1 Ellipsometry

The fundamental physical process of ellipsometry[1] 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[2a] have derived simplified equations for the changes in the ellipticity of polarized light upon reflection from a surface. Azzam and Bashara[2b] 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[3] 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[3] found satisfactory MAI solutions for film properties at a specific thickness only. Burge and Bennett[4] showed that MAI could not be used to determine whether a film is present on a substrate. Schueler[5] 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 ψ and Δ. Oldham[6] discusses the problem of a film on a known substrate at one and two angles of incidence. Johnson and Bashara[7] 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 $Si-SiO_2$ 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[8,9] transistors (MOST) are critically dependent on the properties of an insulating SiO_2 layer on the silicon and the properties of the silicon-insulator interface. Also, an important factor in making nearly ideal metal-semi-conductor contacts[10] 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[11,12] 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_2 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

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

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 ψ and Δ (relative phase difference) are determined from azimuthal angle measurements of the polarizer, analyzer and compensator. For a compensator azimuth of $+45^{o}$, there are two pairs of