IMPROVED SENSITIVITY IN ELLIPSOMETRY OF THIN BIOCHEMICAL FILMS BY EMPLOYING SUBLAYERS

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Abstract

Ellipsometry is widely used for investigating the optical properties of thin films on planar substrates, including films of adsorbed proteins or polymers. The average thickness and effective refractive index of the adsorbed layer are calculated by measuring the Δ and Ψ ellipsometry parameters. Unfortunately the thickness of the adsorbed protein layers is often too thin to significantly affect the Δ and Ψ parameters. However, using a substructure consisting of an additional sublayer placed between the substrate and the adsorbed layer, we can improve the sensitivities of both Δ and Ψ to changes in the adsorbed layer, provided that the thickness of the sublayer is optimized. We show that for a SiO2 layer on a Si wafer, the optimum SiO2 thickness is about 1350 Å when the incident angle is 70 degrees and the wavelength is 6328 Å. The materials of the sublayer can be metal, semiconductor and/or dielectric.

1 Introduction

Ellipsometry is currently employed to investigate the optical properties of solids and thin films at interfaces. In biochemical applications, ellipsometry has been used for studying physical and chemical adsorption.

De Feijter, et al. [1] and Kawaguchi, et al. [2] [3] mentioned the applicability of ellipsometry for investigating the adsorption behavior of macromolecules at the air-water interface. The properties of adsorbed macromolecular films depend not only on the amount adsorbed, but also on the conformation of the adsorbed molecules. The advantage of ellipsometry is that it provides information on both aspects. Cuypers, et al. [4] used ellipsometry as a tool to study protein films at liquid-solid interfaces. They suggested that an automatic ellipsometer for biochemical work should have a sensitivity of about 0.005 degree, corresponding to a layer thickness sensitivity of 5 Å. With this sensitivity, the resolution of the instrument permits monomolecular layers of biomolecules to be observed. Arwin, et al. [5] and Nygren et al [6] studied protein adsorption and antibody and antigen reactions. They measured the optical properties of protein films at air-solid interfaces with ellipsometry.

We know the sensitivity of ellipsometry increases with increasing difference between the refractive indices of the substrate and the adsorbed layer. This is the reason why most publications on the subject deal with macromolecules adsorbed on to semiconductor or metal surfaces.

Arwin [5] pointed out that if the substrate is absorbing and its polarizability is relatively low, then both the refractive index and the thickness of the adsorbed layer can be separately obtained. The problem therefore reduces to one of selecting a suitable substrate. But unfortunately, the substrates applied in biochemical studies may not have the proper refractive index values. From optical thin film theory [7], we know that a substrate and a sublayer can form a substructure which has an effective refractive index. Changing the thickness or/and the refractive index of the sublayer means changing the effective refractive index of the substructure. In this way, we can deduce a substructure which fits our requirements. In this paper we give the analysis, calculation, and experiment for selecting a suitable substructure.

2 Theoretical Analysis

A light beam incident on a nominally specular surface will undergo reflection and refraction [8] [9] [10]. The electric fields of the incident and reflected light beams are described by the complex amplitudes Ei and Er. Each of these can be resolved into two components parallel (p) and perpendicular (s) to the plane of incidence, where the plane of incidence is defined by the incident beam and the normal of the surface. The complex reflection coefficients are defined by

$$r_p = \frac{E_{rp}}{E_{ip}} \qquad (1)$$

$$r_s = \frac{E_{rs}}{E_{is}} \qquad (2)$$

and the ratio of these two coefficients gives the fundamental equation of ellipsometry.

$$\rho = \frac{r_p}{r_s} = \tan\psi\, e^{j\Delta} \qquad (3)$$

The two parameters Δ and ψ relate to the relative phase and amplitude change upon reflection, respectively.

A film covered substrate, three media system, is shown as Fig. 1. N_0, N_1 and N_2 are the refractive indices of the ambient, the film and the substrate, respectively; d is the thickness of the film; and ϕ is the angle of incidence. Assuming that the layer is planar, homogeneous and infinite in extent, we know

$$r_p = \frac{r_{01p} + r_{12p}x}{1 + r_{01p}r_{12p}x} \qquad (4)$$

$$r_s = \frac{r_{01s} + r_{12s}x}{1 + r_{01s}r_{12s}x} \qquad (5)$$

where

$$x = \exp(-j4\pi d_1 (N_1^2 - N_0^2 \sin^2\phi)^{0.5}/\lambda) \qquad (6)$$

and r_{ij} is Fresnel reflection coefficient of the ij interface and written as

$$r_{ij} = \frac{\eta_i - \eta_{i+1}}{\eta_i + \eta_{i+1}} \qquad (7)$$

where η_i is the optical admittance, $\eta = \cos\phi/n$ for p-wave, $\eta = n\cos\phi$ for s-wave.

The fundamental equation of ellipsometry can be represented as a function of the refractive indices N_0, N_1 and N_2 of the ambient, the film and the substrate, respectively; the thickness, d_1, of the film; the angle of incidence, ϕ; and the wavelength, λ, of the light. We can write formally

$$\rho_{exp} = \rho\ (N_0, N_1, N_2, d_1, \lambda, \phi) \qquad (8)$$

where ρ_{exp} is the quantity determined experimentally. We assume that ρ_{exp}, N_0, N_2, λ and ϕ are known, and then solve equation (8) implicitly for the optical parameters of the film, which are concerned with material properties such as the microstrcture, the composition and void fraction.

The adsorbed organic layer usually is transparent, k_1 is zero, and there are only two unknown optical parameters, d_1 and n_1 of the film. We can get two real equations from equation (8), which is complex. In principle, d_1 and n_1 can be determined by

$$\rho_{exp} = \tan\psi\ \exp(i\Delta) \qquad (9)$$

For adsorbed layers which are too thin to significantly affect ψ, only Δ changes with adsorption. This can be seen directly from the first-order approximation for ρ for very thin films, which can be written as [9]

$$\frac{\delta\rho}{\rho}=\frac{\delta\tan\psi}{\tan\psi}+j\,\delta\Delta=\frac{j\,4\,\pi\,n_0 d_1\cos\phi}{\lambda}\,\frac{n_2^2\left(n_1^2-n_0^2\right)\left(n_2^2-n_1^2\right)}{n_1^2\left(n_2^2-n_0^2\right)\left(n_2^2\cot^2\phi-n_0^2\right)} \quad (10)$$

where $\delta\rho$, $\delta\tan\psi$ and $\delta\Delta$ represent the first-order changes in the respective ellipsometric parameters. From equation (10), we understand that $\delta\Delta=0$, when $n_2=n_1$ or $n_1=n_0$, that is, if the refractive index of the adsorbed layer is equal to the ambient or to the substrate, the right-hand side of equation (10) is zero; this means the sensitivity of ellipsometry is very low. On the other hand, when $n_2\cot\phi=n_0$ or $n_2=n_0$ for a symmetric system, $\delta\Delta$=infinity, and we get the highest sensitivity. The refractive index of the dielectric substrate is real in the visible range, then the right-hand side of equation (10) is purely imaginary and consequently

$$\delta\psi=0 \quad (11)$$

and only one datum $\delta\Delta$ can be measured.

One way for solving this difficulty is to choose a substrate with complex refractive index at the wavelength employed. In this case, the right-hand side of equation (10) is complex and both Δ and ψ change in different ways with n_1 and d_1. This is why so many authors prefer semiconductor or metal substrates to dielectric ones. In the case of the semiconductor substrate, $k_2<<n_2$, (for silicon substrate, $N_2=3.85 - j\ 0.02$ at wavelength of 633 nm), so the right-hand side of equation (10) is nearly imaginary. Thus the measurement yields a negligible change in ψ for small d_1. In contrast, $\delta\Delta$ can be very large. In an individual situation, we can have $\delta\Delta/\delta d=0.5$ degree per nm. As one can easily measure $\delta\Delta$ with a precision of 0.01 degree or better, it is clear that the detection limit is well below atomic dimensions. However, even though the detection sensitivity for non-absorbing films on silicon substrates is high, one of the two unknowns, n_1 or d_1, must be guessed or determined independently.

Now we consider the metal substrate, where the imaginary part of refractive index is much larger than the real part, $|N_2|>>n_1$. Another difficulty arises, and equation (10) can be approximated as [5]

$$\frac{\delta\rho}{\rho}=\frac{j\,4\,\pi\,n_0 d_1\sin\phi\tan\phi}{\lambda}\,\frac{n_1^2-n_0^2}{n_1^2} \quad (12)$$

Once again we find that the right-hand side of equation (10) or (12) is purely imaginary, so we are still left with a situation of having one datum and two unknowns, although the scaling factor for the thickness d_1 is now different. For some metals, the real and imaginary parts of its refractive index are of the same order in magnitude, and is suitable for obtaining two ellipsometric quantities.

Using a substructure which consists of an additional sublayer placed between the substrate and the adsorbed layer may be another way for overcoming this difficulty. It is suitable for dielectric, semiconductor and metal materials. Of course, the thickness and the refractive index of the sublayer should be optimized.

Now we consider a four media system, shown as Fig. 2. N_0, N_1, N_2, and N_3 of the ambient, the adsorbed layer, the sublayer and the substrate respectively; d_1 and d_2 are the thicknesses of the adsorbed layer and the sublayer. From optical thin film theory the characteristic matrix of one single layer can be written as

$$M_i=\begin{bmatrix}\cos\delta_i & j/\eta_i\sin\delta_i\\ j\eta_i\sin\delta_i & \cos\delta_i\end{bmatrix} \quad (13)$$

where $\delta_i=2\,\pi\,n_i d_i\cos\phi_i/\lambda$.

The characteristic matrix of the substructure can be written as

$$\begin{bmatrix}B\\ C\end{bmatrix}=\begin{bmatrix}\cos\delta_2 & j/\eta_2\sin\delta_2\\ j\eta_2\sin\delta_2 & \cos\delta_2\end{bmatrix}\begin{bmatrix}1\\ \eta_3\end{bmatrix} \quad (14)$$

The effective optical admittance of the substructure is

$$Y = \frac{C}{B} \qquad (15)$$

Usually Y is complex and a function of ϕ, λ and the optical parameters of the substrate and the sublayer.

We analysis the problem using the concept of effective refractive index and effective admittance of the substructure. Substituting equation (14) into equation (15) we have

$$Y_s = \frac{\eta_{3s}\cos\delta_2 + j\,\eta_{2s}\sin\delta_2}{\cos\delta_2 + j\,\eta_{3s}/\eta_{2s}\sin\delta_2} \qquad (16)$$

for s-wave and

$$Y_p = \frac{\eta_{3p}\cos\delta_2 + j\,\eta_{2p}\sin\delta_2}{\cos\delta_2 + j\,\eta_{3p}/\eta_{2p}\sin\delta_2} \qquad (17)$$

for p-wave.

Assuming the substructure has an effective refractive index G, we can write the effective admittance as

$$Y_s = G\cos\Phi \qquad (18)$$

$$Y_p = \cos\Phi/G \qquad (19)$$

G and $\cos\Phi$ are functions of N_3, n_2, d_2, ϕ and λ.

From equations (16), (17), (18) and (19) we have

$$G\cos\Phi = \frac{\eta_{3s}\cos\delta_2 + j\,\eta_{2s}\sin\delta_2}{\cos\delta_2 + j\,\eta_{3s}/\eta_{2s}\sin\delta_2} \qquad (20)$$

and

$$\cos\Phi/G = \frac{\eta_{3p}\cos\delta_2 + j\,\eta_{2p}\sin\delta_2}{\cos\delta_2 + j\,\eta_{3p}/\eta_{2p}\sin\delta_2} \qquad (21)$$

From two complex equations, (20) and (21), we can evaluate two complex unknowns. If we know N_3, ϕ and λ, changing n_2 and d_2 we can get different G. This means that we may have any refractive index value of the substructure. Substituting G for n_2 in equation (10) we have

$$\frac{\delta\rho}{\rho} = \frac{\delta\tan\psi}{\tan\psi} + j\,\delta\Delta = \frac{j\,4\pi n_0 d_1\cos\phi}{\lambda}\,\frac{G^2\left(n_1^2-n_0^2\right)\left(G^2-n_1^2\right)}{n_1^2\left(G^2-n_0^2\right)\left(G^2\cot^2\phi-n_0^2\right)} \qquad (22)$$

We can optimize the thickness and the refractive index of the sublayer with equation (22). The optimum values of n_2 and d_2 make both $\delta\tan\psi/\tan\psi$ and $\delta\Delta$ large enough for much higher sensitivity of ellipsometry.

3 Numerical Calculation and Experimental Result

It is usually more convenient to deal with the corresponding changes $\delta\psi$ and $\delta\Delta$ of the ellipsometric angles ψ and Δ. From equation (3) we have

$$\delta\psi = \frac{1}{2}\sin 2\psi\,\mathrm{Re}\left\{\delta\rho/\rho\right\} \qquad \delta\Delta = \mathrm{Im}\left\{\delta\rho/\rho\right\} \qquad (23)$$

For simplification, we assume that $\delta\rho/\rho$ is caused by a fractional change of film thickness $\delta d/d$ and rewrite equation (23) as

$$\delta\psi = \frac{1}{2}\sin 2\psi\,\mathrm{Re}(K)\,\delta d/d \qquad \delta\Delta = \mathrm{Im}(K)\,\delta d/d \qquad (24)$$

where

$$K=\frac{4\pi n_2 d_2 \cos\phi_2}{j\lambda}X\left(\frac{r_{23p}}{r_{12p}+r_{23p}X}-\frac{r_{12p}r_{23p}}{1+r_{12p}r_{23p}X}-\frac{r_{23s}}{r_{12s}+r_{23s}X}+\frac{r_{12s}r_{23s}}{1+r_{12s}r_{23s}X}\right) \quad (25)$$

and

$$X=\exp(-j4\pi n_2 d_2 \cos\phi_2/\lambda)$$

In a difference way, $\delta\psi$ and $\delta\Delta$ can be written as

$$\psi=\psi_0+S_\psi\delta d_2 \qquad \Delta=\Delta_0+S_\Delta\delta d_2 \quad (26)$$

where

$$S_\psi(d_2)=\delta\psi/\delta d_2=180/\pi\,\frac{1}{2}\sin2\psi\,\mathrm{Re}(K)/d_2 \quad (27a)$$

$$S_\Delta(d_2)=\delta\Delta/\delta d_2=180/\pi\,\mathrm{Im}(K)/d_2 \quad (27b)$$

respectively, in units of degree per angstrom.

$S\psi$ and $S\Delta$ are ψ and Δ sensitivity factors that determine the extent to which small changes of thickness of the film phase influence the ellipse of polarization of the reflected light beam. Using equations (27), we can calculate $S\psi$ and S_Δ as functions of d_2. The calculation results are shown as Fig. 3(a), for a Si substrate and SiO_2 sublayer. From the results it is clear that S_Δ is large when d_2 is very small, but $S\psi$ is approximately equal to zero. If the substrate is a Si wafer with natural oxidized SiO_2 sublayer, only one datum, Δ, can be obtained for protein absorption. If the thickness of the sublayer is about 1350 Å, both $S\psi$ and $S\Delta$ are much larger, when the incident angle is 70 degrees and the wavelength of the light employed is 6328 Å. Fig. 3(b) shows Δ and ψ plot for different refractive indices and thickness of adsorbed layer on the substructure consisting of 1300Å SiO2 sublayer on Si wafer.

A series of experiments with different sublayer thickness values were done. The SiO_2 films of high quality on Si wafers were supplied by the HEDCO Microelectronics Lab, University of Utah. A chemical vapor deposition process was used for coating SiO_2 sublayers. Different concentrations of human IgG were used in the experiments. The experimental results, shown in Fig. 4, are fully supportive of the concept that a substrcture, consisting of an additional sublayer placed between the substrate and the adsorbed layer, can be used for improving the sensitivities of both Δ and ψ to changes in the adsorbed layer.

The material of the sublayer can be metal, semiconductor, and /or dielectric. The optimized thickness can be evaluated provided that the materials of sublayer, substrate and environment are chosen.

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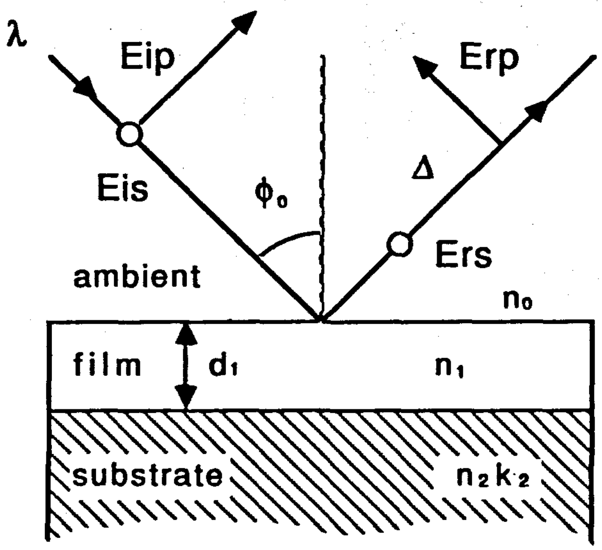

Fig. 1 The incident and reflected light and film covered substrate.

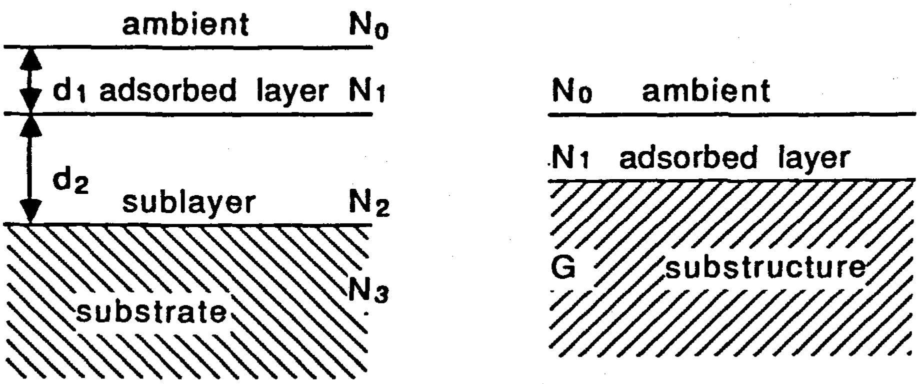

Fig. 2 Four medium system and diagram of substructure consisting of a sublayer placed between substrate and adsorbed layer.

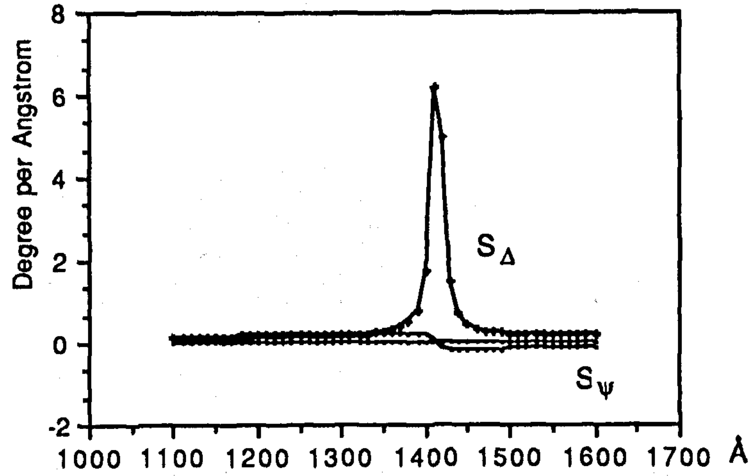

Fig. 3(a) Sensitivity Factor of Ellipsometry

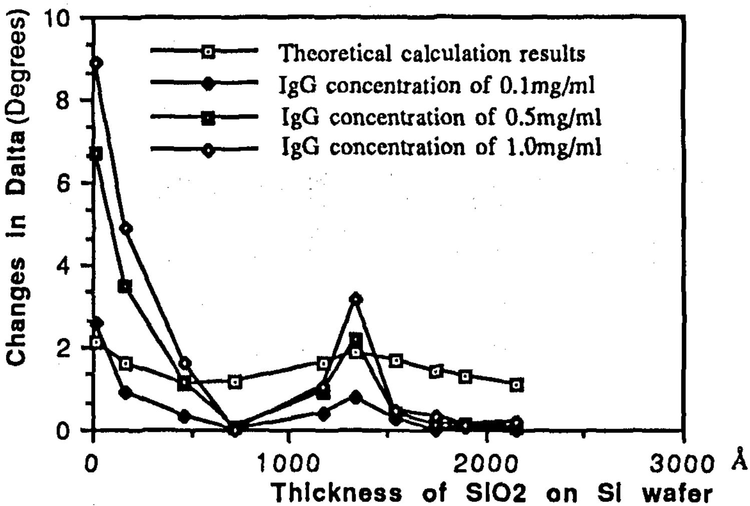

Fig. 4 (a) Sensitivity of Delta changes with the thickness of SiO2 layer on Si wafer.

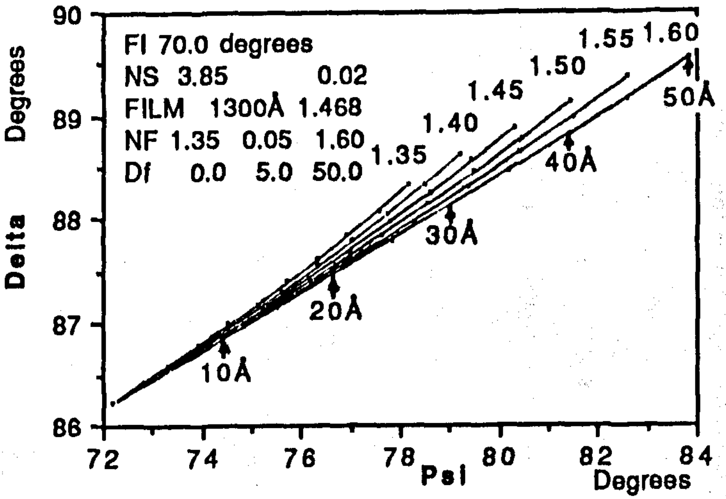

Fig. 3(b) Delta and Psi for different refractive indices and thickness of adsorbed layer on the substructure consisting of SiO2 sublayer on Si wafer.

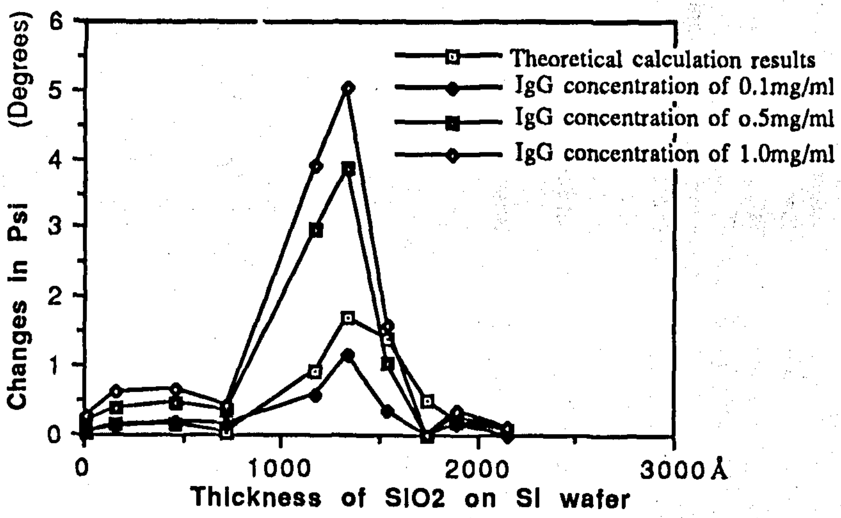

Fig. 4 (b) Sensitivity of Psi changes with the thickness of SiO2 layer on Si wafer.