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# **Spectroscopic Ellipsometry Data Analysis: Measured vs. Calculated Quantities**

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## **Abstract**

Spectroscopic ellipsometry is a very powerful technique for optical characterization of thin-film and bulk materials, but the technique measures functions of complex reflection coefficients, which are usually not of interest per se. The interesting characteristics such as film thickness, surface roughness thickness, and optical functions can be determined only by modeling the near-surface region of the sample. However, the measured quantities are not equivalent to those determined from the modeling. Ellipsometry measurements determine elements of the sample Mueller matrix, but the usual result of modeling calculations are elements of the sample. Often this difference is academic, but if the sample depolarizes the light, it is not. Ellipsometry calculations also include methods for determining the optical functions of materials. Data for bulk materials are usually accurate for substrates, but are not appropriate for most thin films. Therefore, reasonable parameterizations are quite useful in performing spectroscopic ellipsometry data analysis. Recently, there has been an increased interest in anisotropic materials, both in thin-film and bulk form. A generalized procedure will be presented for calculating the

elements of the Jones matrix for any number of layers, any one of which may or may not be uniaxial.

## I. Introduction

Spectroscopic ellipsometry (SE) is a powerful optical characterization technique for a variety of needs,<sup>1,2</sup> including the monitoring of film growth and the determination of the optical properties of thin film and bulk materials. However, the data obtained from a SE measurement is not useful by itself. If one is interested in film or roughness thickness, or the optical functions of bulk or thin film materials, one must first model the near-surface region of the sample and obtain the complex reflection coefficients (CRC) from the model.<sup>3,4</sup> The CRCs must then be compared with the ellipsometric data, which involves some assumptions concerning the nature of the light interaction with the surface.

Another problem associated with the interpretation of SE measurements taken on thin film systems is that often the optical properties of thin-film material are quite different from those of the bulk material; moreover, these optical properties will often be a very strong function of the deposition process. This is at once an advantage and a curse. A major advantage of SE is that it is sensitive to the details of the deposition process and can therefore be used to monitor and control the process. However, this sensitivity of the optical functions means that we begin the modeling having only a rough idea of the values of the thin-film optical functions, which must then either be measured or parameterized.

Recently, work on SE and its interpretation has been extended from isotropic to anisotropic materials. This is a challenge both from an experimental and a theoretical

point of view, in that traditional ellipsometers cannot measure all the relevant parameters in one configuration and methods of calculation must be developed to determine the additional parameters resulting from the sample anisotropy.

In this paper, the procedure used to compare calculations with SE data will be examined. First, the differences between measured and inferred quantities will be discussed. Secondly, the three steps involved in comparing SE data with a model of the near-surface region of a sample will be briefly outlined. Some of the recent model parameterizations used to deal with thin film and bulk materials will then be discussed. Finally, the steps involved in calculating the CRCs from models where one or more of the constituents is anisotropic will be outlined.

## **II. Measured and Calculated Quantities**

### **A. Measured Quantities**

In a generalized ellipsometry experiment, the light from the source passes through the polarization state generator (PSG), interacts with the sample (reflects from or transmits through), and then passes through more polarization optics and is detected [the polarization state detector (PSD)]. The light that has passed through the PSG is described by its Stokes vector,<sup>5,6</sup> where

$$\mathbf{S}_{\text{PSG}} = \begin{pmatrix} I_o \\ Q \\ U \\ V \end{pmatrix} = \begin{pmatrix} I_o \\ I_0 - I_{90} \\ I_{45} - I_{-45} \\ I_{rc} - I_{lc} \end{pmatrix} \quad (1)$$

The elements of the Stokes vector are all intensities and are therefore real. The quantity  $I_o$  is the total intensity and  $I_{-45}$ ,  $I_0$ ,  $I_{45}$ , and  $I_{90}$  are the intensities of light polarized at  $-45^\circ$ ,  $0^\circ$ ,  $45^\circ$ , and  $90^\circ$  with respect to the plane of incidence of the sample. The quantities  $I_{rc}$  and  $I_{lc}$  denote the intensities of right-circularly and left-circularly polarized light. The Stokes representation contains all possible polarizations of the light beam, including partial polarization. In general,

$$I_o \geq (Q^2 + U^2 + V^2)^{1/2}, \quad (2)$$

where the equal sign holds for totally polarized light. The PSD can be represented by the transpose of Eq. 1. Therefore, one requires a 4X4 Mueller matrix  $\mathbf{M}$  to describe the interaction of the light beam with the sample, given by

$$\mathbf{M} = \begin{pmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{pmatrix} \quad (3)$$

Of course, not all of these elements are independent in that any polarization system

cannot “overpolarize” the light, nor can the output energy exceed the input energy; this leads to several necessary constraints on the elements of  $\mathbf{M}$ .<sup>7</sup> The intensity of the light incident upon the detector is a linear combination of the elements of  $\mathbf{M}$ :

$$I = \mathbf{S}_{\text{PSD}} \mathbf{M} \mathbf{S}_{\text{PSG}}. \quad (4)$$

Usually, ellipsometers measure 2 to 4 independent linear combinations of the Mueller matrix elements. If the PSG (PSD) does not contain a compensating element, then the 4<sup>th</sup> element of  $\mathbf{S}_{\text{PSG}}$  ( $\mathbf{S}_{\text{PSD}}$ ) will be 0 and the ellipsometer is not sensitive to elements of the 4<sup>th</sup> row (4<sup>th</sup> column) of  $\mathbf{M}$ .

## B. Calculated Parameters

Optical calculations for a reflection ellipsometry experiment determine the elements of the complex Jones reflection matrix, given by

$$\mathbf{J} = \begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} = r_{ss} \begin{pmatrix} \rho_{pp} & \rho_{ps} \\ \rho_{sp} & 1 \end{pmatrix} = r_{ss} \begin{pmatrix} \gamma_{pp} e^{i\Delta_{pp}} & \gamma_{ps} e^{i\Delta_{ps}} \\ \gamma_{sp} e^{i\Delta_{sp}} & 1 \end{pmatrix}, \quad (5)$$

where the elements are the polarization-dependent complex reflection coefficients. The elements of this Jones matrix will depend upon the angle of incidence and the details of the near-surface region of the sample, including the number and thicknesses of the thin films, as well as their refractive indices ( $n$ ) and extinction coefficients ( $k$ ). For



transmission experiments, the  $r$  terms are replaced with complex transmission coefficients  $t$ . The normalized Jones matrix has 6 independent quantities. If the sample is isotropic, then the off-diagonal elements are zero and only 2 parameters are independent.

To compare the calculated Jones matrix with experimentally measured quantities (elements of the sample Mueller matrix), one can calculate an equivalent Mueller-Jones matrix given by<sup>8</sup>

$$\mathbf{M} = \mathbf{A} ( \mathbf{J} \otimes \mathbf{J}^* ) \mathbf{A}^{-1} \quad (6)$$

where

$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & -i & i & 0 \end{pmatrix} \quad (7)$$

There are constraints on the elements of  $\mathbf{M}$  for it to be a realizable Mueller matrix<sup>7</sup> and additional constraints for  $\mathbf{M}$  to be a Mueller-Jones matrix.<sup>9,10</sup> If the normalized representations of the sample Jones matrix and Mueller matrix are used, then only the 6 elements of  $\mathbf{M}$  are linearly independent.

For an isotropic sample in a reflection ellipsometry configuration, the normalized sample Mueller matrix is given by<sup>1</sup>

$$\mathbf{M} = \begin{pmatrix} 1 & -N & 0 & 0 \\ -N & 1 & 0 & 0 \\ 0 & 0 & C & S \\ 0 & 0 & -S & C \end{pmatrix} \quad (8)$$

where  $N = \cos(2\psi)$ ,  $S = \sin(2\psi) \sin(\Delta)$ , and  $C = \sin(2\psi) \cos(\Delta)$ . If an ellipsometer contains a compensating element, and measures at least 3 independent parameters, then it is possible to totally characterize  $\mathbf{M}$  (such as with the two-channel spectroscopic polarization modulation ellipsometer<sup>11</sup>). If no compensating elements are used (as with the simple rotating element ellipsometer<sup>12</sup>), then it is impossible to measure  $S$ . The addition of a static compensating element in a rotating element ellipsometer<sup>13</sup> makes it possible to measure a linear combination of the  $C$  and the  $S$  component.

If the sample is not isotropic, or if there are strained windows between the PSG and the sample, or between the sample and the PSD, then there are additional non-zero and independent elements in the Mueller matrix for the sample and windows. The Mueller matrix for an isotropic sample between input and output strained windows is given by<sup>14</sup>:

$$\mathbf{M} = \begin{pmatrix} 1 & -N & 0 & N\delta_{Sw0} \\ -N & 1 & S\delta_{Sw1} & -\delta_{Sw0} - C\delta_{Sw1} \\ 0 & S\delta_{Sw0} & C - S\delta_W & S + C\delta_W \\ -N\delta_{Sw1} & \delta_{Sw1} + C\delta_{Sw0} & -S - C\delta_W & C - S\delta_W \end{pmatrix}, \quad (8)$$

where

$$\delta_{Sw0} = \delta_0 \sin(2 \theta_{w0}) \quad , \quad (9a)$$

$$\delta_{Sw1} = \delta_1 \sin(2 \theta_{w1}) \quad , \quad (9b)$$

$$\text{and} \quad \delta_w = \delta_0 \cos(2 \theta_{w0}) + \delta_1 \cos(2 \theta_{w1}) \quad . \quad (9c)$$

The quantity  $\delta_0$  ( $\delta_1$ ) is the static strain retardation of the window between the PSG (PSD) and the sample and  $\theta_{w0}$  ( $\theta_{w1}$ ) is the azimuthal angle of the fast axis of the window with respect to the plane of incidence. Therefore, the use of windows introduces three additional independent parameters into the Mueller matrix. If either the upper right or lower left 2X2 block of the sample Mueller matrix is measured, then the parameters  $\delta_{Sw0}$  and  $\delta_{Sw1}$  can be determined. The measurement of  $\delta_w$  requires the use of a known sample. Once these three parameters are known, then corrected values of N, S, and C can be obtained.

If the sample is anisotropic, then the off-diagonal elements of the sample Jones matrix may be non-zero and the resulting sample Mueller-Jones matrix (from Eq. 6) is<sup>4,14</sup>

$$\mathbf{M} = \begin{pmatrix} 1 & -N - \alpha_{ps} & C_{sp} + \zeta_1 & S_{sp} + \zeta_2 \\ -N - \alpha_{sp} & 1 - \alpha_{sp} - \alpha_{ps} & -C_{sp} + \zeta_1 & -S_{sp} + \zeta_2 \\ C_{ps} + \xi_1 & -C_{ps} + \xi_1 & C + \beta_1 & S + \beta_2 \\ -S_{ps} + \xi_2 & S_{ps} + \xi_2 & -S + \beta_2 & C - \beta_1 \end{pmatrix}, \quad (10)$$

where

$$N = (1 - \gamma_{pp}^2 - \gamma_{sp}^2 - \gamma_{ps}^2) / D \quad D = (1 + \gamma_{pp}^2 + \gamma_{sp}^2 + \gamma_{ps}^2) = 2/(1+N) \quad (11a, b)$$

$$S = 2 \gamma_{pp} \sin(\Delta_{pp}) / D \quad C = 2 \gamma_{pp} \cos(\Delta_{pp}) / D \quad (11c, d)$$

$$S_{sp} = 2 \gamma_{sp} \sin(\Delta_{sp}) / D \quad C_{sp} = 2 \gamma_{sp} \cos(\Delta_{sp}) / D \quad (11e, f)$$

$$S_{ps} = 2 \gamma_{ps} \sin(\Delta_{ps}) / D \quad C_{ps} = 2 \gamma_{ps} \cos(\Delta_{ps}) / D \quad (11g, h)$$

$$\alpha_{sp} = 2 \gamma_{sp}^2 / D \quad \alpha_{ps} = 2 \gamma_{ps}^2 / D \quad (11i, j)$$

$$\beta_l = (D/2) (C_{sp} C_{ps} + S_{sp} S_{ps}) \quad \beta_2 = (D/2) (C_{sp} S_{ps} - S_{sp} C_{ps}) \quad (11k, l)$$

$$\zeta_l = (D/2) (C C_{ps} + S S_{ps}) \quad \zeta_2 = (D/2) (C S_{ps} - S C_{ps}) \quad (11m, n)$$

$$\xi_l = (D/2) (C C_{sp} + S S_{sp}) \quad \xi_2 = (D/2) (C S_{sp} - S C_{sp}) \quad (11o, p)$$

Thus, the measurement of 7 parameters ( $N, S, C, S_{sp}, C_{sp}, S_{ps}, C_{ps}$ ) completely determines the sample Mueller-Jones matrix. In this approximation, the measurement of either the upper right or the lower left 2X2 submatrix and one element of  $\mathbf{M}$  corresponding to each of the N, S, and C parameters is sufficient to completely determine  $\mathbf{M}$ . The normalization condition can be written as

$$N^2 + S^2 + C^2 + S_{sp}^2 + C_{sp}^2 + S_{ps}^2 + C_{ps}^2 = p^2. \quad (12)$$

If the sample is non-depolarizing, then  $p=1$  and we have only 6 independent parameters. However, if the sample does depolarize the light beam, then the NSC parameters so measured will normalize to  $p<1$  and  $p$  becomes a measure of this depolarization. Most samples do not measurably depolarize the incoming light, but there are many real

situations where the sample does depolarize the incoming light beam: 1) If the input light beam illuminates an area of the sample where the film thickness(es) are not uniform, quasi-depolarization can occur<sup>11</sup>, and  $p < 1$ . 2) If the sample substrate is transparent then light reflecting from the back surface will contribute an intensity component to the light entering the PSD that is not phase-related to the light reflected from the front face and the light beam will be partially quasi-depolarized.<sup>16</sup>

It must be emphasized that one can always associate a Jones matrix with a Mueller matrix, but the converse is not true. Rough surfaces, for example, depolarize the incident light beam,<sup>17,18</sup> both in the sense that some of the light reaching the PSD has no identifiable polarization state, and in the sense that cross polarization occurs in nominally isotropic systems (s-polarized light goes to p-polarized light and visa versa). Some depolarization effects can be monitored with the  $p$ -parameter of Eq. 12, but the cross-polarization effects cannot.

### III. Calculation Procedure

If it can be assumed that the light reflecting from or transmitted through a sample can be represented by a modified Mueller-Jones matrix, the fitting of ellipsometric data is a three-part procedure<sup>3</sup>:

1. Assume a model, including the number of layers and layer type (isotropic, anisotropic, or graded).
2. Determine or parameterize the optical functions of each layer

3. Fit the data with a suitable algorithm and figure of merit to obtain the unspecified parameters.

As was pointed out in refs. 3, 19 and 20, step 3 is critical. If there is no measure of the figure of merit, one does not know whether the model fits the data. One MUST use an error-based figure of merit, such as the reduced  $\chi^2$ , which is given by

$$\chi^2 = \frac{1}{NM - m - 1} \sum_{j=1}^M \sum_{i=1}^N \frac{(\rho_{j,\text{exp}}(\lambda_i) - \rho_{j,\text{calc}}(\lambda_i, \mathbf{z}))^2}{\delta\rho_j(\lambda_i)^2} \quad (13)$$

In Eq. 13,  $\rho_{j,\text{exp}}(\lambda_i)$ ,  $\rho_{j,\text{calc}}(\lambda_i)$ , and  $\delta\rho_j(\lambda_i)$  represent the experimental, calculated, and error quantities at wavelength  $\lambda_i$ , and data set  $j$ , while  $N$  is the total number of data points,  $m$  is the number of fitted parameters, and  $M$  is the number of data sets. Furthermore, realistic measurements of the error limits of the fitted parameters must be calculated as well as cross correlation coefficients. To ignore this step invites drastic errors in the interpretation of spectroscopic ellipsometry data.

## IV. Parameterization of Optical Functions

One of the critical steps involved in fitting spectroscopic ellipsometry data to a given model is that one often must use existing knowledge of the optical functions for each of the layers in order to make the problem tractable. Unfortunately, the optical functions of thin films are often quite different from the optical functions of nominally

equivalent bulk materials,<sup>21</sup> even for epitaxial films.<sup>22</sup> Furthermore, the optical functions of crystalline thin films can change with composition<sup>23,24</sup> or with temperature.<sup>25</sup> The problem is even more severe for amorphous films, since even single-element films can have widely different deposition-dependent optical functions.<sup>26-30</sup>

One of the first attempts to deal with this complexity<sup>31,32</sup> was to model the layer using a Bruggeman<sup>33</sup> effective medium approximation, where the complex dielectric function  $\epsilon$  of the composite film was given by solving the equation

$$0 = \sum_j f_j \frac{\epsilon_j - \epsilon}{\epsilon_j + 2\epsilon}; \quad 1 = \sum_j f_j, \quad (14)$$

where the sum goes over  $j$  constituents. (see Roussel et al.<sup>34</sup> for an elegant method for performing this calculation with two constituents, thereby avoiding problems associated with the selection of the proper branch from a multivalued inverse of a complex function.) Generally, the early work did not use a reliable measure of the figure of merit, so it is not possible to know whether the data actually fit the model. Recent experience has shown that this model is not generally useable, but can be reliable in certain circumstances.

Although amorphous materials often have optical functions that depend upon deposition conditions, the optical functions usually have no sharp features, and so it is possible to model them using only a few parameters. One of the first attempts to parameterize the optical functions of amorphous materials is due to Forouhi and Bloomer.<sup>35</sup> In this formulation, the extinction coefficient  $k(E)$  was

$$k(E) = \frac{A(E - E_g)^2}{E^2 - BE + C} \quad (15)$$

and the refractive index  $n(E)$  was determined using Kramers-Kronig integration, where an additional fitting parameter  $n(\infty)$  was included. This formalism approximately fitted some data in the literature, but again a realistic figure of merit to quantify the goodness of fit was not used.

There are several fundamental errors in the Forouhi and Bloomer parameterization:<sup>30</sup>

- 1)  $k(E) > 0$  for  $E < E_g$ . This is clearly unphysical for interband transitions.
- 2)  $k(E) \rightarrow \text{constant}$  as  $E \rightarrow \infty$ .  $k(E)$  should go to 0 as  $1/E^3$  or faster.
- 3) In performing the Kramers-Kronig analysis, Forouhi and Bloomer did not use the time-reversal requirement that  $k(-E) = -k(E)$ .

Recently, Jellison and Modine<sup>30</sup> derived a model for the optical functions of amorphous materials that does not violate the problems listed above. This formulation uses a combination of the Tauc band edge and the Lorentz formulation for a collection of uncoupled atoms to determine the imaginary part of the complex dielectric function  $\epsilon_2(E)$ , which is given by

$$\epsilon_{2TL} = \frac{AE_o C (E - E_g)^2}{(E^2 - E_o^2)^2 + C^2 E^2} \frac{1}{E} \quad E > E_g \quad (16)$$

$$= 0 \quad E \leq E_g$$



The real part of the dielectric function is determined from  $\epsilon_2(E)$  using Kramers-Kronig integration from 0 to  $\infty$ , so time-reversal symmetry need not be considered. The model employs at least 4 fitting parameters: the band gap  $E_g$ , the Lorentz resonant energy  $E_o$ , the Lorentz broadening parameter  $C$ , and the transition matrix element, which is proportional to  $A$ . In some cases, one can include  $\epsilon_i(\infty)$  as a 5<sup>th</sup> parameter, although this is not always necessary (often<sup>37</sup> it can be set directly to 1). Several data sets found in the literature were fit to this Tauc-Lorentz (TL) model, and the fits were far better than when the Forouhi and Bloomer<sup>35</sup> model was used.

Recently, the TL model has been used by Fujiwara et al.<sup>36</sup> to analyze spectroscopic ellipsometry data from graded amorphous silicon-carbon alloys. Jellison et al.<sup>37</sup> have also used the TL model to characterize a series of SiN films grown on silicon using plasma-assisted chemical vapor deposition. In both cases, the fits obtained from the TL model were far better. In the case of the SiN work,  $\epsilon_i(\infty)$  was set to 1, and the resulting  $\chi^2$ s were all near 1, verifying that the model fits the data.

An alternate empirical model, using 7 parameters, has been proposed by Yamaguchi et. al.<sup>29</sup> which consists of a sum of damped harmonic oscillator terms (Lorentz oscillators), whose square root amplitudes are distributed according to a hyperbolic function of photon energy connected to an exponential function. Reasonable fits to a-Si and a-SiN data sets (from Ref. 38) were obtained over a very wide energy range, although no attempt was made to determine a goodness of fit.

Crystalline materials present even more of a challenge to parameterize the optical functions, where critical points exist in the optical spectrum that often result in sharp features in the dielectric response functions. A realistic model becomes even more important when one wishes to simulate spectra from alloys, such as  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  or  $\text{Si}_x\text{Ge}_{1-x}$ , which contain critical points in the optical spectrum that vary continuously with composition  $x$ . Snyder et al.<sup>23</sup> compared 3 models for the dielectric functions of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  and found that the best fits were obtained when the critical points were modeled using one or more Lorentz oscillators. For each oscillator, the peak energy, width, and amplitude is fit as a function of  $x$ , allowing the composite dielectric function to be calculated as a function of  $x$ . This approach works reasonably well near the critical points, but breaks down at small photon energies where the absorption coefficient becomes small. Susuki and Adachi<sup>28</sup> used a similar approach to fit the spectroscopic ellipsometry data from microcrystalline silicon films. One of the main problems with this approach is that often 15 or more parameters are required to fit crystalline spectra, and correlations between parameters can become significant.

## V. Calculations involving Anisotropic Materials

Until very recently, very little spectroscopic ellipsometry work has been done on anisotropic materials. The problem is both experimental and theoretical. In general, the off-diagonal elements of the sample Jones matrix (Eq. 5) are non-zero, so additional measurements must be made to determine all the components. Using a rotating element ellipsometer at multiple polarizer azimuths, Schubert et al.<sup>39</sup> measured the 6 independent

elements for rutile (TiO<sub>2</sub>), which is a uniaxial material. Using 2-modulator generalized ellipsometry<sup>14</sup>, Jellison et al.<sup>40</sup> simultaneously measured 7 components (in the NSC representation) with a single measurement. (The measurement of the S parameters means that the surface roughness can be taken into account; this is not possible with the measurements of Schubert et al.<sup>39</sup>)

Theoretically, the analysis of spectroscopic ellipsometry data where one or more of the components is anisotropic is considerably more involved than for isotropic media.<sup>41-53</sup> The approach which we have used in our laboratory is based primarily on the paper by Berriman<sup>42</sup> and the modifications of Lin-Chung.<sup>43,53</sup> There are significant parallels between this calculation and that of Schubert.<sup>49</sup>

The Berriman equation is given by

$$\frac{d\Psi}{dz} = i\Delta\Psi \quad (17)$$

where  $\Psi^T = (E_x, H_y, E_y, -H_x)$ , and  $\Delta$  is the 4X4 complex Berriman matrix. The components of the  $\Psi$  matrix are just the instantaneous electric and magnetic fields in the x-and y- directions, where the z-direction is defined as perpendicular to the plane of stratification. *This is just a re-formulation of Maxwell's equation.* For a uniaxial crystal, the Berriman matrix becomes<sup>45</sup>

$$\Delta = \begin{pmatrix} \Delta_{11} & \Delta_{12} & \Delta_{13} & 0 \\ \Delta_{21} & \Delta_{11} & \Delta_{23} & 0 \\ 0 & 0 & 0 & 1 \\ \Delta_{23} & \Delta_{13} & \Delta_{43} & 0 \end{pmatrix} \quad (18)$$

where the elements are given in Ref. 45. If it is assumed that the  $\Delta$  matrix is independent of  $z$  over a short interval  $\delta z$ , then the solution to Eq. 17 is given by

$$\psi(z + \delta z) = \chi \mathbf{K}(\delta z) \chi^{-1} \psi(z) = \mathbf{P}(\delta z) \psi(z),$$

where the  $\mathbf{K}(\delta z)$  matrix is given by

$$\mathbf{K}(\delta z) = \begin{pmatrix} e^{iq_1 \delta z} & 0 & 0 & 0 \\ 0 & e^{iq_2 \delta z} & 0 & 0 \\ 0 & 0 & e^{iq_3 \delta z} & 0 \\ 0 & 0 & 0 & e^{iq_4 \delta z} \end{pmatrix}. \quad (19)$$

The  $q_i$  are the 4 eigenvalues of the  $\Delta$  matrix (Eq. 18), and the  $\chi$  matrix is a 4X4 matrix where the  $i^{\text{th}}$  column is the  $i^{\text{th}}$  eigenvector associated with  $q_i$ .

If the near-surface region consists of several layers, then

$$\psi(0) = \mathbf{P}^{-1}(d_1) \mathbf{P}^{-1}(d_2) \dots \mathbf{P}^{-1}(d_n) \psi(d_1 + d_2 + \dots + d_n). \quad (20)$$

This expression gives the solution in terms of the electric and magnetic field components.

However, we observe elements of the modal matrix<sup>43</sup>,  $\Phi^T = (E_x, R_x, E_y, R_y)$

$$\Phi = \begin{pmatrix} E_x \\ R_x \\ E_y \\ R_y \end{pmatrix} = \chi_0 \Psi(0) = \frac{1}{2} \begin{pmatrix} 1 & \frac{\cos(\phi)}{n_a} & 0 & 0 \\ -1 & \frac{\cos(\phi)}{n_a} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{n_a \cos(\phi)} \\ 0 & 0 & 1 & \frac{1}{n_a \cos(\phi)} \end{pmatrix} \Psi(0) \quad (21)$$

where  $E_x, E_y$  are the x-and y-components of the electric field for the input light, and  $R_x, R_y$  are the x-and y-components of the electric field for the reflected or output light. The solution in the substrate must also be transformed to the modal solution, which yields

$$\Phi = \chi_0 \mathbf{P}^{-1}(d_1) \mathbf{P}^{-1}(d_2) \dots \mathbf{P}^{-1}(d_n) \chi_s \Phi_s = \mathbf{M} \Phi_s, \quad (22)$$

where  $\chi_s$  is the column-wise set of eigenvectors for the  $\Delta$  matrix associated with the substrate and  $\Phi_s^T = (A_1, 0, A_3, 0)$ . The 0 elements of  $\Phi_s^T$  arise because it is assumed that any light propagating away from the layer stack will either be absorbed or transmitted out the back of the sample and lost. Therefore, two of the eigenvalues ( $q_1$  and  $q_3$ ) must be selected such that they are the two physically realizable solutions (that is, the modes that are propagating back to the layer stack).

The complex components of the reflection Jones matrix can be calculated:

$$r_{pp} = \frac{m_{12}m_{20} - m_{10}m_{22}}{m_{02}m_{20} - m_{00}m_{22}} \quad (23a)$$

$$r_{ps} = \frac{m_{32}m_{20} - m_{30}m_{22}}{m_{02}m_{20} - m_{00}m_{22}} \quad (23b)$$

$$r_{sp} = \frac{m_{10}m_{02} - m_{12}m_{00}}{m_{02}m_{20} - m_{00}m_{22}} \quad (23c)$$

$$r_{ss} = \frac{m_{30}m_{02} - m_{32}m_{00}}{m_{02}m_{20} - m_{00}m_{22}} \quad (23d)$$

Note that the  $A_1$  and  $A_3$  parameters are not involved in the expressions of Eqs. 23

This formalism assumes that the  $\Delta$  matrix is non-singular. If the layer is isotropic, or if the layer is uniaxial with its optical axis in the plane of incidence or perpendicular to the plane of incidence, then the  $\Delta$  matrix becomes block-diagonal<sup>50</sup>. If this is the case, then the resulting eigenvectors have two zero components and the  $\mathbf{P}$  matrix is also block-diagonal. For isotropic layers, the  $\mathbf{P}$  matrix reduce to two Abelés matrices,<sup>51, 54</sup> the one for the p-component in the upper left block, and the one for the s-component in the lower right block with all elements of the upper right and lower left blocks being 0. Bearing this in mind, this formalism can be used for any layer structure.

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## References

1. R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, North Holland, Amsterdam, 1977.
2. P. S. Hauge, *Surf. Sci.*, 96 (1980) 108.
3. G. E. Jellison, Jr., *Thin Solid Films*, 234 (1993) 416.
4. G. E. Jellison, Jr. *Thin Solid Films*, 290-291 (1996) 40-45.
5. R. A. Chipman, *Handbook of Optics*, Vol. II, 2<sup>nd</sup> edition, McGraw-Hill, New York, 1995, Ch. 22.
6. D. S. Kliger, J. W. Lewis, and C. E. Randall, *Polarized light in optics and spectroscopy*, Academic, New York, 1990.
7. A. B. Kostinski, C. R. Givens, and J. M. Kwiatkowski, *Appl. Opt.*, 32, (1993) 1646.
8. R. Barakat, *Opt. Commun.*, 38, (1981) 159.
9. D. G. M. Anderson and R. Barakat, *J. Opt. Soc. Am.*, A11, (1994) 2305.
10. C. Brosseau, C. R. Givens and A. B. Kostinski, *J. Opt. Soc. Am.*, A10, (1993) 2248.
11. G. E. Jellison, Jr. and F. A. Modine, *Appl. Opt.*, 29, (1990) 959.
12. D. E. Aspnes and A. A. Studna, *Appl. Opt.*, 14, (1975) 220.



13. P. Chindaudom and K. Vedam, *Appl. Opt.*, **32**, (1993) 6391.
14. G. E. Jellison, Jr. and F. A. Modine, "Two Modulator Ellipsometry: Theory", submitted to *Appl. Opt.*
15. G. E. Jellison, Jr. and J. W. McCamy, *Appl. Phys. Lett.*, **61**, (1992) 512.
16. R. Joerger, K. Forcht, A. Gombert, M. Köhl, and W. Graf, *Appl. Opt.*, **36**, (1997) 319.
17. S. Krishnan and P. C. Nordine, *Appl. Opt.*, **33**, (1994) 4184.
18. D. A. Ramsey and K. C. Luderna, *Rev. Sci. Instrum.*, **65**, (1994) 2874.
19. G. E. Jellison, Jr., *Appl. Opt.*, **30**, (1991) 3354
20. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes*, 2<sup>nd</sup> edition Cambridge, New York, 1992,.
21. G. E. Jellison, Jr., M. F. Chisholm, and S. M. Gorbalkin, *Appl. Phys. Lett.*, **62**, (1993) 3348.
22. G. E. Jellison, Jr., L. A. Boatner, D. H. Lowndes, R. A. McKee, and M. Godbole, *Appl. Opt.*, **33**, (1994) 6053
23. P. G. Snyder, J. A. Woollam, S. A. Alterovitz, and B. Johs, *J. Appl. Phys.*, **68**, (1990) 5925
24. D. E. Aspnes, W. E. Quinn, and S. Gregory, *Appl. Phys. Lett.*, **57**, (1990) 2707.
25. D. E. Aspnes, W. E. Quinn, and S. Gregory, *Appl. Phys. Lett.*, **56**, (1990) 2569.

26. S. A. Alterovitz, N. Savvides, F. W. Smith, and J. A. Woollam, *Handbook of optical constants of solids II* E. D. Palik, editor, Academic, New York, 1991, p. 837.
27. W. A. McGahan, T. Makovicka, J. Hale, and J. A. Woollam, *Thin Solid Films*, 253, (1994) 57.
28. T. Suzuki and S. Adachi, *Jpn. J. Appl. Phys.*, 32, (1993) 4900
29. T. Yamaguchi, Y. Kaneko, A. H. Jayatissa, M. Aoyama, A. V. Zotov, and V. G. Lifshits, *J. Appl. Phys.*, 77, (1995) 4673.
30. G. E. Jellison, Jr. and F. A. Modine, *Appl. Phys. Lett.*, 69, (1996) 371; *ibid.*, 69, (1996) 2137.
31. B. G. Bagley, D. E. Aspnes, A. C. Adams, and C. J. Mogab, *Appl. Phys. Lett.*, 38, (1981) 56.
32. K. Vedam, P. J. McMarr, and J. Narayan, *Appl. Phys. Lett.*, 47, (1985) 339.
33. D. A. G. Bruggeman, *Ann. Phys. (Leipzig)*, 24, (1935) 636.
34. Ph. J. Roussel, J. Vanhellemont, and H. E. Maes, *Thin Solid Films*, 234, (1993) 423.
35. A. R. Forouhi and I. Bloomer, *Phys. Rev. B* 34, (1986) 7018.
36. H. Fujiwara, J. Koh, C. R. Wronski, and R. W. Collins, "Application of real time spectroscopic ellipsometry for high resolution depth-profiling of compositionally-graded amorphous silicon alloy thin films," *Appl. Phys. Lett.* 70, xxx-xxx (1997).

37. G. E. Jellison, Jr., F. A. Modine, P. Doshi, and A. Rohatgi, Thin Solid Films (this volume) (1997).
38. E. D. Palik, ed., *Handbook of Optical Constants* Academic, New York, 1985.
39. Mathias Schubert, B. Rheinländer, J. A. Woollam, B. Johs, and C. M. Herzinger, *J. Opt. Soc. Am.*, A13, (1996) 875.
40. G. E. Jellison, Jr., F. A. Modine, and L. A. Boatner, "The measurement of the optical functions of uniaxial materials using two-modulator generalized ellipsometry: Rutile ( $\text{TiO}_2$ ), Submitted to Opt. Lett. (1997).
41. S. Teitler and B. Henvis, *J. Opt. Soc. Am.*, 60, (1970) 830.
42. D. W. Berriman, *J. Opt. Soc. Am.*, 62, (1972) 502.
43. P. J. Lin-Chung and S. Teitler, *J. Opt. Soc. Am.* A1, (1984) 703.
44. P. Yeh, "Optical Waves in Layered Media," (Wiley, New York, 1988).
45. H. Wöhler, G. Hass, M. Fritsch, and D. A. Mlynski, *J. Opt. Soc. Am.* A5, (1988) 1554.
46. K. Eidner, *J. Opt. Soc. Am.* A6, (1990) 1657.
47. J. Lekner, *J. Phys: Condens. Matter*, 3, (1991) 6121.
48. V. V. Filippov, A. Yu. Tronin, and A. F. Konstantinova, *Crystallography Reports*, 39, (1994) 313.
49. Mathias Schubert, *Phys. Rev. B* 53, (1996) 4265.

- 50. H. Wöhler, M. Fritsch, G. Hass, and D. A. Mlynski, *J. Opt. Soc. Am.*, A8, (1991) 536.
- 51. H. L. Ong, *J. Opt. Soc. Am.*, A8, (1991) 303.
- 52. D. J. De Smet, *J. Appl. Phys.* 76, (1994) 2571.
- 53. P. J. Lin-Chung, *Superlattices and microstructures*, 13, (1992) 93.
- 54. F. Abelés, *Ann. de Physique*, 5 (1950) 596.