Effective-substrate theory for optical reflection from a layered substrate

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We show that reflection of a monochromatic light from a semi-infinite medium covered with a stack of layered media is equivalent to that from an effective "semi-infinite medium" characterized by two distinct optical dielectric constants for the *s*- and *p*-polarized components, respectively. Such an effective-substrate approach simplifies the analysis of ellipsometry measurements of a wide range of surface-bound processes including thin-film growth and surface-bound reactions. © 2008 Optical Society of America

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1. INTRODUCTION

Optical reflection techniques such as ellipsometry [1–6], surface plasmon polariton wave excitation [7–11], spectral interferometry [12–14], reflection anisotropy spectroscopy [15,16], and surface photoabsorption [17] are widely used to monitor processes at surfaces and interfaces of solids. They are desirable for their versatility, noninvasiveness, and ease of implementation. There exist extensive theoretical studies that link optical reflection to physical and chemical characteristics of solid surfaces and thin films [18–24]. Though optical wavelengths are much larger than the atomic scale, optical reflection contains a remarkable amount of information on atomic-scale structures and compositions of a surface (or a thin film) in directions parallel as well as perpendicular to the surface [23]. As a result optical reflection measurements have been used for both qualitative and quantitative studies of surface processes such as surface-bound reactions and epitaxial growths of thin films [1–32].

A surface-bound process causes changes in structure such as thickness or composition of structural components (e.g., terraces, step edges, mounds) and chemical makeup. These changes alter optical reflection through the dielectric responses of altered constituents of the surface. Often one is interested in changes in the topmost layer of a surface or a thin film. Such a layer of atomic scale may reside on top of a semi-infinite substrate or a stack of films (multilayers) on a semi-infinite substrate. It is desirable to relate changes in the topmost layer to suitably performed optical reflection measurements in a form that enables convenient analysis and exploration of how a stack of multilayers may enhance the optical response of the topmost layer.

In this paper we show that optical reflection of a monochromatic light from a stack of multilayer films on top of a semi-infinite medium is equivalent to that of another semi-infinite medium characterized by two effective optical constants, $\varepsilon_{s,\mathrm{eff}}^{(s)}$ and $\varepsilon_{s,\mathrm{eff}}^{(p)}$, for *s*- and *p*-polarized components, respectively. The effective optical constants are relatively simple functions of optical and structural properties of the multilayers and the original semi-infinite medium, and of the incidence angle. Such an effective-substrate approach simplifies the analysis of optical reflection from multilayer systems often encountered in studies of surface reactions and thin-film growth [23,24].

2. BACKGROUND ON OPTICAL REFLECTION FROM A SURFACE

As shown in Fig. 1, let $r^{(p)}=|r^{(p)}|\exp(i\Phi^{(p)})$ and $r^{(s)}=|r^{(s)}|\exp(i\Phi^{(s)})$ be the reflectivity (reflection coefficient) for *p*- and *s*-polarized components of a monochromatic light off a substrate covered with an ultrathin layer with thickness d and optical constant ε_d, and $r^{(p0)}=|r^{(p0)}|\exp(i\Phi^{(p0)})$ and $r^{(s0)}=|r^{(s0)}|\exp(i\Phi^{(s0)})$ be the reflectivity from the bare substrate. One can define the oblique-incidence reflectivity difference (OI-RD) as [6,19,23]

$$\Delta_p-\Delta_s\equiv\delta Ln\left(\frac{r^{(p)}}{r^{(s)}}\right)=\frac{|r^{(p)}|-|r^{(p0)}|}{|r^{(p0)}|}-\frac{(|r^{(s)}|-|r^{(s0)}|)}{|r^{(s0)}|}+i[(\Phi^{(p)}-\Phi^{(p0)})-(\Phi^{(s)}-\Phi^{(s0)})]. \tag{1}$$

Such a difference vanishes at normal incidence. In the present paper, except for the notation of the OI-RD, $\Delta_p-\Delta_s$, we will use subscripts to keep track of the media in the order of their appearance and use superscripts to indicate polarizations. When the substrate is a semi-infinite homogeneous medium with optical constant ε_s, the OI-RD can be expressed as [6,23]

$$\Delta_p-\Delta_s\cong\left[(-i)\frac{4\pi\cos\phi_0\sin^2\phi_0\sqrt{\varepsilon_0}\varepsilon_s}{\lambda(\varepsilon_s-\varepsilon_0)(\varepsilon_s\cos^2\phi_0-\varepsilon_0\sin^2\phi_0)}\right]\times\frac{(\varepsilon_d-\varepsilon_0)(\varepsilon_d-\varepsilon_s)}{\varepsilon_d}d. \tag{2}$$

Zhu and coworkers extended Eq. (2) to allow the substrate to consist of a uniform layer with optical constant

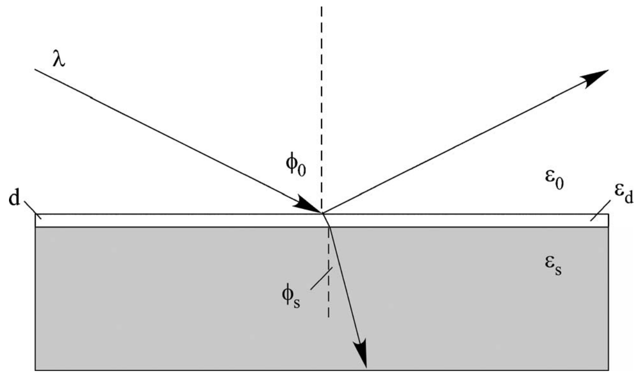

Fig. 1. Reflection of a monochromatic light at vacuum wavelength λ from the surface of a semi-infinite substrate (ε_s) covered with an ultrathin layer (ε_d) with a thickness of $d \ll \lambda$. The beam travels in a semi-infinite ambient (ε_0) before reflection.

ε_2 and arbitrary thickness d_2 on top of the semi-infinite medium with ε_s [24]. They found that the optical response of such a "composite" substrate could be represented by that of an effective semi-infinite medium characterized by a *single* effective optical constant $\varepsilon_{s,\text{eff}}$ such that Eq. (2) remains essentially intact,

$$\Delta_p - \Delta_s \cong \alpha_{\text{eff}} \frac{(\varepsilon_d - \varepsilon_0)(\varepsilon_d - \varepsilon_{s,\text{eff}})}{\varepsilon_d} d. \tag{3}$$

The effective optical constant $\varepsilon_{s,\text{eff}}$ depends on ε_0, ε_2, d_2, ε_s, and the incidence angle ϕ_0 (see Eq. (A5) in [24]). The prefactor α_{eff} in Eq. (3), given by Eq. (A6) in [24], has a much more complex dependence on ε_0 ε_2, d_2, ε_s, and ϕ_0 than that in Eq. (2). This extension made by Zhu and coworkers [24] is most useful when analyzing the topmost surface of a thin film during epitaxial growth, particularly when d_2 is no longer small compared to optical wavelengths.

Though a significant step forward, it is difficult to extend the approach of Zhu *et al.* [24] to optical reflection from an ultrathin layer on top of a stack of multilayers on a semi-infinite medium. It is also difficult to see how α_{eff} physically depends on the effective optical constant of the effective semi-infinite medium and particularly whether there exists incidence angles that enhance α_{eff} as the Brewster angle does on a semi-infinite medium.

By using a different algebraic approach, we intend to show that (1) reflection of a monochromatic light from a stack of more than one layer on a semi-infinite medium can be represented by that of an effective semi-infinite medium characterized by two effective optical constants: $\varepsilon^{(s)}_{s,\text{eff}}$ for the s-polarized component and $\varepsilon^{(p)}_{s,\text{eff}}$ for the p-polarized component; (2) Eq. (2) remains valid for an ultrathin surface layer added on top of such an effective medium except that $\varepsilon_{s,\text{eff}}$ is now an algebraic function of $\varepsilon^{(s)}_{s,\text{eff}}$ and $\varepsilon^{(p)}_{s,\text{eff}}$; (3) there exists an effective Brewster angle (polarizing angle) at which the magnitude of α_{eff} is maximally enhanced. This approach greatly simplifies the analysis of optical reflection for useful information on the topmost layer and how the information can be optimally extracted.

3. EFFECTIVE-SUBSTRATE APPROACH TO OPTICAL REFLECTION FROM A STACK OF MULTILAYERS ON A SEMI-INFINITE MEDIUM

Although one can resort to numerical computation of optical reflection from a topmost surface layer on an arbitrary multilayer stack over a semi-infinite medium using software packages, the numerical approach lacks the transparency of physical insight into the effect of the topmost layer on optical reflection and how a composite substrate instead of a simple homogenous semi-infinite substrate alters such an effect in a controllable fashion.

The goals of our algebraic approach are twofold: (1) to explore whether the reflection from a stack of more than one layer on a homogenous semi-infinite medium can be made equivalent to that from an effective homogenous medium if suitable effective optical constants are introduced; (2) to further explore whether the OI-RD can still be expressed by Eq. (3), and if so, whether α_{eff} contains a similar dependence on incidence angle as in Eq. (2).

We begin with a two-medium model consisting of a semi-infinite ambient with $\varepsilon_0 = n_0^2$ and a semi-infinite substrate with $\varepsilon_s = n_s^2$ as illustrated in Fig. 2(a). A monochromatic light at vacuum wavelength λ is incident from the ambient onto the surface of the substrate at angle ϕ_0. We first consider the reflection of the s-polarized component. The reflectivity is given by

$$r^{(s)}_{0s} = \frac{n_0 \cos \phi_0 - n_s \cos \phi_s}{n_0 \cos \phi_0 + n_s \cos \phi_s}, \tag{4}$$

where ϕ_s is determined from Snell's law $n_s \sin \phi_s = n_0 \sin \phi_0$. When a uniform layer with $\varepsilon_1 = n_1^2$ and an arbitrary thickness d_1 is added between the two semi-infinite media [Fig. 2(b)], the reflectivity for the s-polarized light is altered and can be calculated as follows:

$$r^{(s)}_{01s} = \frac{r^{(s)}_{01} + r^{(s)}_{1s} e^{i\Psi_1}}{1 + r^{(s)}_{01} r^{(s)}_{1s} e^{i\Psi_1}}, \tag{5}$$

where

$$r^{(s)}_{ab} = \frac{n_a \cos \phi_a - n_b \cos \phi_b}{n_a \cos \phi_a + n_b \cos \phi_b}, \tag{6}$$

$$\Psi_1 = \frac{4\pi n_1 d_1 \cos \phi_1}{\lambda}, \tag{7}$$

ϕ_1 is determined from $n_1 \sin \phi_1 = n_0 \sin \phi_0$. We now introduce an effective optical constant for the s-polarized light, $\varepsilon^{(s)}_{s,\text{eff}}(1,s) = (n^{(s)}_{s,\text{eff}}(1,s))^2$, such that

$$n^{(s)}_{s,\text{eff}}(1,s) \sin \phi^{(s)}_{s,\text{eff}}(1,s) = n_0 \sin \phi_0, \tag{8}$$

$$r^{(s)}_{01s} \equiv r^{(s)}_{0s,\text{eff}}(1,s) \equiv \frac{n_0 \cos \phi_0 - n^{(s)}_{s,\text{eff}}(1,s) \cos \phi^{(s)}_{s,\text{eff}}(1,s)}{n_0 \cos \phi_0 + n^{(s)}_{s,\text{eff}}(1,s) \cos \phi^{(s)}_{s,\text{eff}}(1,s)}. \tag{9}$$

We use a set of numbers and letters in parentheses to indicate the added layer and the substrate and the order of

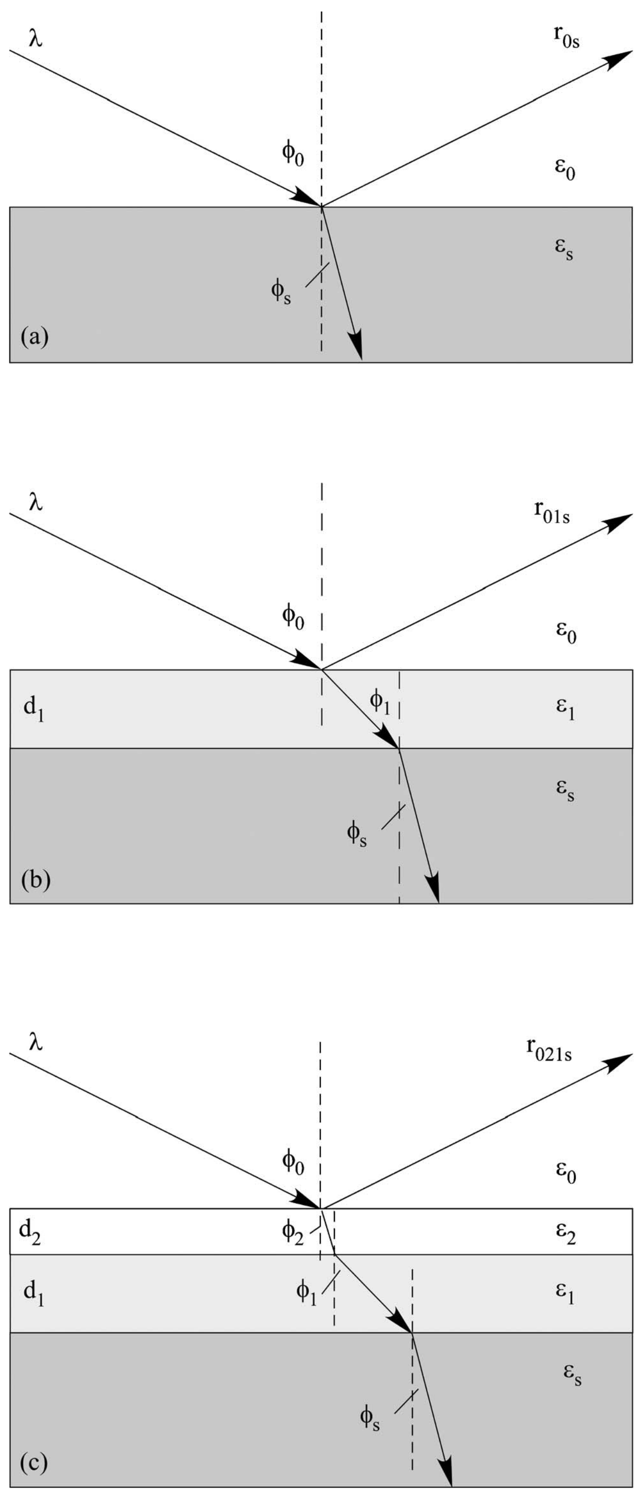

Fig. 2. (a) Reflection of a monochromatic light at vacuum wavelength λ from the bare surface of a semi-infinite substrate (ε_s); (b) reflection from the surface of a semi-infinite substrate (ε_s) covered with a uniform dielectric layer (ε_1) with arbitrary thickness d_1; (c) reflection from the surface of a semi-infinite substrate covered with two uniform dielectric layers (ε_1 and ε_2) with arbitrary thicknesses d_1 and d_2.

their appearance for which the effective optical constants and the corresponding angles of transmission are defined. We solve Eq. (9) for $\varepsilon^{(s)}_{s,\mathrm{eff}}(1,s)$ with Eqs. (5) and (8),

$$\varepsilon^{(s)}_{s,\mathrm{eff}}(1,s) = n_0^2 \sin^2 \phi_0 + n_1^2 \cos^2 \phi_1 \left(\frac{1 - r^{(s)}_{1s} e^{i\Psi_1}}{1 + r^{(s)}_{1s} e^{i\Psi_1}} \right)^2 . \quad (10)$$

It is clear from Eq. (10) that $\varepsilon^{(s)}_{s,\mathrm{eff}}(1,s)$ depends on properties of the added layer and the original substrate as expected. $\varepsilon^{(s)}_{s,\mathrm{eff}}(1,s)$ also depends on the property of the ambient but only through Snell's law or $n_0 \sin \phi_0$. The latter does not change as more layers are subsequently added to the substrate. Equations (8)–(10) confirm that the reflection of the s-polarized light from a system of ambient(0)–layer(1)–substrate (s) is equivalent to the reflection from a system of ambient(0)–effective substrate(s,eff) characterized by $\varepsilon^{(s)}_{s,\mathrm{eff}}(1,s)$.

This algebraic strategy can be readily extended to a system with m layers covering the substrate so that the reflection from such a stack of multilayers on a semi-infinite substrate can be replaced by the reflection from an effective substrate characterized by $\varepsilon^{(s)}_{s,\mathrm{eff}}$ $(m,m-1,\ldots,1,s)$. For example, for a system of ambient(0)–layer(2)–layer(1)–substrate(s) as illustrated in Fig. 2(c), we define $\varepsilon^{(s)}_{s,\mathrm{eff}}(2,1,s) \equiv (n^{(s)}_{s,\mathrm{eff}}(2,1,s))^2$ such that the Snell's law remains valid and the reflectivity has the familiar form,

$$n^{(s)}_{s,\mathrm{eff}}(2,1,s) \sin \phi^{(s)}_{s,\mathrm{eff}}(2,1,s) = n_0 \sin \phi_0, \quad (11)$$

$$r^{(s)}_{0s,\mathrm{eff}}(2,1,s) = \frac{n_0 \cos \phi_0 - n^{(s)}_{s,\mathrm{eff}}(2,1,s) \cos \phi^{(s)}_{s,\mathrm{eff}}(2,1,s)}{n_0 \cos \phi_0 + n^{(s)}_{s,\mathrm{eff}}(2,1,s) \cos \phi^{(s)}_{s,\mathrm{eff}}(2,1,s)}. \quad (12)$$

Solving Eqs. (11) and (12), we find

$$\varepsilon^{(s)}_{s,\mathrm{eff}}(2,1,s) = n_0^2 \sin^2 \phi_0 + n_2^2 \cos^2 \phi_2 \left(\frac{1 - r^{(s)}_{21s} e^{i\Psi_2}}{1 + r^{(s)}_{21s} e^{i\Psi_2}} \right)^2$$
$$= n_0^2 \sin^2 \phi_0 + n_2^2 \cos^2 \phi_2 \left(\frac{1 - r^{(s)}_{2s,\mathrm{eff}}(1,s) e^{i\Psi_2}}{1 + r^{(s)}_{2s,\mathrm{eff}}(1,s) e^{i\Psi_2}} \right)^2, \quad (13)$$

with

$$r^{(s)}_{21s} \equiv r^{(s)}_{2s,\mathrm{eff}}(1,s) \equiv \frac{n_2 \cos \phi_2 - n^{(s)}_{s,\mathrm{eff}}(1,s) \cos \phi^{(s)}_{s,\mathrm{eff}}(1,s)}{n_2 \cos \phi_2 + n^{(s)}_{s,\mathrm{eff}}(1,s) \cos \phi^{(s)}_{s,\mathrm{eff}}(1,s)}, \quad (14)$$

with $n^{(s)}_{s,\mathrm{eff}}(1,s)$ and $\phi^{(s)}_{s,\mathrm{eff}}(1,s)$ are given by Eqs. (10) and (8).

For a system of ambient(0)–layer(m)-layer($m-1$)-⋯-layer(1)–substrate, we can generally define and find an effective optical dielectric constant for the s-polarized light, $\varepsilon^{(s)}_{s,\mathrm{eff}}(m,m-1,\ldots,1,s) \equiv \varepsilon^{(s)}_{s,\mathrm{eff}} = (n^{(s)}_{s,\mathrm{eff}})^2$, such that the reflection from such a system is given by

$$r_{0s,\mathrm{eff}}^{(s)}(m,m-1,\ldots,1,s)=\frac{n_0\cos\phi_0-n_{s,\mathrm{eff}}^{(s)}\cos\phi_{s,\mathrm{eff}}^{(s)}}{n_0\cos\phi_0+n_{s,\mathrm{eff}}^{(s)}\cos\phi_{s,\mathrm{eff}}^{(s)}},\tag{15}$$

$$n_{s,\mathrm{eff}}^{(s)}\sin\phi_{s,\mathrm{eff}}^{(s)}=n_0\sin\phi_0.\tag{16}$$

Here $\varepsilon_{s,\mathrm{eff}}^{(s)}(m,m-1,\ldots,1,s)$ is found iteratively using the following equations:

$$\varepsilon_{s,\mathrm{eff}}^{(s)}(m,m-1,\ldots,1,s)=n_0^2\sin^2\phi_0+n_m^2\cos^2\phi_m\left(\frac{1-r_{ms,\mathrm{eff}}^{(s)}(m-1,\ldots,1,s)e^{i\Psi_m}}{1+r_{ms,\mathrm{eff}}^{(s)}(m-1,\ldots,1,s)e^{i\Psi_m}}\right)^2,\tag{17}$$

$$r_{ms,\mathrm{eff}}^{(s)}(m-1,\ldots,1,s)=\frac{n_m\cos\phi_m-n_{s,\mathrm{eff}}^{(s)}(m-1,\ldots,1,s)\cos\phi_{s,\mathrm{eff}}^{(s)}(m-1,\ldots,1,s)}{n_m\cos\phi_m+n_{s,\mathrm{eff}}^{(s)}(m-1,\ldots,1,s)\cos\phi_{s,\mathrm{eff}}^{(s)}(m-1,\ldots,1,s)}.\tag{18}$$

This process is repeated until Eq. (17) is reduced to Eq. (10).

We now apply a similar procedure for the p-polarized component. For a two-medium system as illustrated in Fig. 2(a), the reflectivity for the p-polarized light is given by

$$r_{0s}^{(p)}=\frac{n_0\cos\phi_s-n_s\cos\phi_0}{n_0\cos\phi_s+n_s\cos\phi_0},\tag{19}$$

where $n_s\sin\phi_s=n_0\sin\phi_0$. When a uniform layer with $\varepsilon_1=n_1^2$ and an arbitrary thickness d_1 is added between the two semi-infinite media [Fig. 2(b)], the reflectivity for the p-polarized light is altered to

$$r_{01s}^{(p)}=\frac{r_{01}^{(p)}+r_{1s}^{(p)}e^{i\Psi_1}}{1+r_{01}^{(p)}r_{1s}^{(p)}e^{i\Psi_1}},\tag{20}$$

where Ψ_1 is given by Eq. (7),

$$r_{ab}^{(p)}=\frac{n_a\cos\phi_b-n_b\cos\phi_a}{n_a\cos\phi_b+n_b\cos\phi_a},\tag{21}$$

and $n_1\sin\phi_1=n_0\sin\phi_0$. We now introduce an effective optical constant for the p-polarized light, $\varepsilon_{s,\mathrm{eff}}^{(p)}(1,s)=(n_{s,\mathrm{eff}}^{(p)}\times(1,s))^2$, such that

$$n_{s,\mathrm{eff}}^{(p)}(1,s)\sin\phi_{s,\mathrm{eff}}^{(p)}(1,s)=n_0\sin\phi_0,\tag{22}$$

$$r_{01s}^{(p)}\equiv r_{0s,\mathrm{eff}}^{(p)}\equiv\frac{n_0\cos\phi_{s,\mathrm{eff}}^{(p)}(1,s)-n_{s,\mathrm{eff}}^{(p)}(1,s)\cos\phi_0}{n_0\cos\phi_{s,\mathrm{eff}}^{(p)}(1,s)+n_{s,\mathrm{eff}}^{(p)}(1,s)\cos\phi_0}.\tag{23}$$

Solving Eq. (23) for $\varepsilon_{s,\mathrm{eff}}^{(p)}(1,s)$ together with Eqs. (20) and (22), we arrive at

$$\frac{\varepsilon_{s,\mathrm{eff}}^{(p)}(1,s)}{\left(\dfrac{n_1^2}{\cos^2\phi_1}\right)\left(\dfrac{1-r_{1s}^{(p)}e^{i\Psi_1}}{1+r_{1s}^{(p)}e^{i\Psi_1}}\right)^2}+\frac{n_0^2\sin^2\phi_0}{\varepsilon_{s,\mathrm{eff}}^{(p)}(1,s)}=1.\tag{24}$$

$\varepsilon_{s,\mathrm{eff}}^{(p)}(1,s)$ is a function of properties of the added layer and the original semi-infinite substrate and only depends on the property of the ambient through $n_0\sin\phi_0$. As a result the reflection for p-polarized light from a system of ambient(0)–layer(1)–substrate(s) is equivalently replaced by the reflection from a system of ambient(0)–effective substrate(s, eff) characterized by $\varepsilon_{s,\mathrm{eff}}^{(p)}(1,s)$.

Such a strategy is easily extended to the reflection from a system of ambient(0)–layer(m)–layer($m-1$)-⋯-layer(1)–substrate by repeating the aforementioned steps to define and find an effective optical constant for p-polarized light $\varepsilon_{s,\mathrm{eff}}^{(p)}(m,m-1,\ldots,1,s)\equiv\varepsilon_{s,\mathrm{eff}}^{(p)}=(n_{s,\mathrm{eff}}^{(p)})^2$ so that the reflection from such a system is given by

$$r_{0s,\mathrm{eff}}^{(p)}(m,m-1,\ldots,1,s)=\frac{n_0\cos\phi_{s,\mathrm{eff}}^{(s)}-n_{s,\mathrm{eff}}^{(s)}\cos\phi_0}{n_0\cos\phi_{s,\mathrm{eff}}^{(s)}+n_{s,\mathrm{eff}}^{(s)}\cos\phi_0},\tag{25}$$

$$n_{s,ff}^{(p)}\sin\phi_{s,ff}^{(p)}=n_0\sin\phi_0.\tag{26}$$

Here $\varepsilon_{s,\mathrm{eff}}^{(p)}(m,m-1,\ldots,1,s)$ is given by

$$\frac{\varepsilon_{s,\mathrm{eff}}^{(p)}(m,m-1,\ldots,1,s)}{\left(\dfrac{n_m^2}{\cos^2\phi_m}\right)\left(\dfrac{1-r_{ms,\mathrm{eff}}^{(p)}(m-1,\ldots,1,s)e^{i\Psi_m}}{1+r_{ms,\mathrm{eff}}^{(p)}(m-1,\ldots,1,s)e^{i\Psi_m}}\right)^2}+\frac{n_0^2\sin^2\phi_0}{\varepsilon_{s,\mathrm{eff}}^{(p)}(m,m-1,\ldots,1,s)}=1,\tag{27}$$

$$r_{ms,\mathrm{eff}}^{(p)}(m-1,\ldots,1,s)\equiv\frac{n_m\cos\phi_{s,\mathrm{eff}}^{(p)}(m-1,\ldots,1,s)-n_{s,\mathrm{eff}}^{(p)}(m-1,\ldots,1,s)\cos\phi_m}{n_m\cos\phi_{s,\mathrm{eff}}^{(p)}(m-1,\ldots,1,s)+n_{s,\mathrm{eff}}^{(p)}(m-1,\ldots,1,s)\cos\phi_m}.\tag{28}$$

Again this process is repeated until Eq. (27) is reduced to Eq. (24).

To briefly summarize, we have shown that optical reflection for a monochromatic light beam from a stack of multilayers on top of a semi-infinite substrate can be reduced to reflection of the same beam from an effective semi-infinite substrate with two distinct optical constants for s- and p-polarized components. The two optical constants depend on the incidence angle in the ambient through Snell's law and can be found iteratively. One can easily show that when the thicknesses of the multilayers are taken to zero, the effective optical constants for both s- and p-polarized components are reduced to ε_s.

4. OBLIQUE-INCIDENCE REFLECTIVITY DIFFERENCE DUE TO AN ULTRATHIN SURFACE LAYER ON TOP OF A STACK OF MULTILAYERS ON A HOMOGENEOUS SEMI-INFINITE SUBSTRATE

We compute the fractional change in reflectivity for both polarizations when an ultrathin layer with thickness $d \ll \lambda$ and optical constant ε_d is added between the ambient with ε_0 and the effective substrate with $\varepsilon_{s,\text{eff}}^{(p)}$ and $\varepsilon_{s,\text{eff}}^{(s)}$, as illustrated in Fig. 3.

For the s-polarized component of the incident light the reflectivities before and after the addition of the extra layer are

$$r_{0s,\text{eff}}^{(s)} = \frac{n_0 \cos\phi_0 - n_{s,\text{eff}}^{(s)} \cos\phi_{s,\text{eff}}^{(s)}}{n_0 \cos\phi_0 + n_{s,\text{eff}}^{(s)} \cos\phi_{s,\text{eff}}^{(s)}}, \tag{29}$$

$$r_{0ds,\text{eff}}^{(s)} = \frac{r_{0d}^{(s)} + r_{ds,\text{eff}}^{(s)} e^{i\Psi_d}}{1 + r_{0d}^{(s)} r_{ds,\text{eff}}^{(s)} e^{i\Psi_d}}, \tag{30}$$

with $n_d \sin\phi_d = n_0 \sin\phi_0$ and

$$r_{ds,\text{eff}}^{(s)} = \frac{n_d \cos\phi_d - n_{s,\text{eff}}^{(s)} \cos\phi_{s,\text{eff}}^{(s)}}{n_d \cos\phi_d + n_{s,\text{eff}}^{(s)} \cos\phi_{s,\text{eff}}^{(s)}}, \tag{31}$$

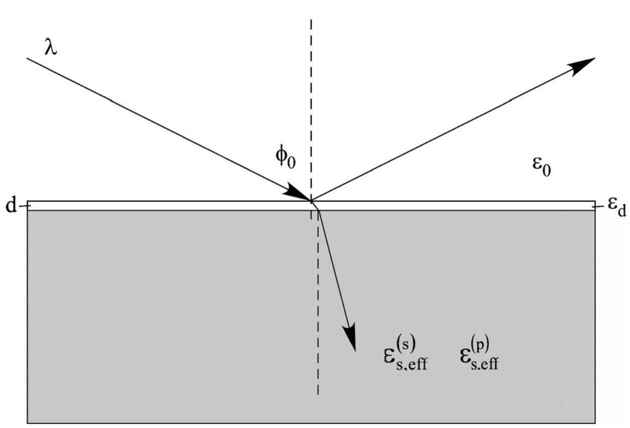

Fig. 3. Reflection from the surface of an effective substrate covered with an ultrathin layer (ε_d) with thickness $d \ll \lambda$. The effective substrate is characterized by two optical constants, $\varepsilon_{s,\text{eff}}^{(p)}$ and $\varepsilon_{s,\text{eff}}^{(s)}$, for the s and p-polarized components of the incident light.

$$r_{0d}^{(s)} = \frac{n_0 \cos\phi_0 - n_d \cos\phi_d}{n_0 \cos\phi_0 + n_d \cos\phi_d}, \tag{32}$$

$$\Psi_d = \frac{4\pi n_d d \cos\phi_d}{\lambda}. \tag{33}$$

The differential reflectivity for the s-polarized component can be derived from Eq. (29) through Eq. (33) and is given by

$$\Delta_s \equiv \frac{r_{0ds,\text{eff}}^{(s)} - r_{0s,\text{eff}}^{(s)}}{r_{0s,\text{eff}}^{(s)}} \cong \frac{(\varepsilon_d - \varepsilon_{s,\text{eff}}^{(s)})}{(\varepsilon_0 - \varepsilon_{s,\text{eff}}^{(s)})} \left(\frac{i4\pi n_0 \cos\phi_0}{\lambda} \right) d, \tag{34}$$

where we only keep the term that varies linearly with d/λ.

For the p-polarized component of the incident light, the reflectivities before and after adding the extra layer are given by the following expressions:

$$r_{0s,\text{eff}}^{(p)} = \frac{n_0 \cos\phi_{s,\text{eff}}^{(p)} - n_{s,\text{eff}}^{(p)} \cos\phi_0}{n_0 \cos\phi_{s,\text{eff}}^{(p)} + n_{s,\text{eff}}^{(p)} \cos\phi_0}, \tag{35}$$

$$r_{0ds,\text{eff}}^{(p)} = \frac{r_{0d}^{(p)} + r_{ds,\text{eff}}^{(p)} e^{i\Psi_d}}{1 + r_{0d}^{(p)} r_{ds,\text{eff}}^{(p)} e^{i\Psi_d}}, \tag{36}$$

with Ψ_d given by Eq. (33) and

$$r_{ds,\text{eff}}^{(p)} = \frac{n_d \cos\phi_{s,\text{eff}}^{(p)} - n_{s,\text{eff}}^{(p)} \cos\phi_d}{n_d \cos\phi_{s,\text{eff}}^{(p)} + n_{s,\text{eff}}^{(p)} \cos\phi_d}, \tag{37}$$

$$r_{0d}^{(p)} = \frac{n_0 \cos\phi_d - n_d \cos\phi_0}{n_0 \cos\phi_d + n_d \cos\phi_0}. \tag{38}$$

From Eq. (35) through Eq. (38), we find the differential reflectivity for the p-polarized component,

$$\Delta_p \equiv \frac{r_{0ds,\text{eff}}^{(p)} - r_{0s,\text{eff}}^{(p)}}{r_{0s,\text{eff}}^{(p)}} \cong \left[\frac{((\varepsilon_d + \varepsilon_{s,\text{eff}}^{(p)})\varepsilon_0 \sin^2\phi_0 - \varepsilon_d \varepsilon_{s,\text{eff}}^{(p)})(\varepsilon_d - \varepsilon_{s,\text{eff}}^{(p)})}{\varepsilon_d(\varepsilon_0 \sin^2\phi_0 - \varepsilon_{s,\text{eff}}^{(p)} \cos^2\phi_0)(\varepsilon_0 - \varepsilon_{s,\text{eff}}^{(p)})} \right] \times \left(\frac{i4\pi n_0 \cos\phi_0}{\lambda} \right) d. \tag{39}$$

The OI-RD as defined by Eq. (1) then takes on the same form as Eq. (3):

$$\Delta_p - \Delta_s \cong \alpha_{\text{eff}} \frac{(\varepsilon_d - \varepsilon_0)(\varepsilon_d - \varepsilon_{s,\text{eff}})}{\varepsilon_d} d, \tag{40}$$

with

$$\alpha_{\text{eff}} \cong -\left(\frac{i4\pi n_0 \cos \phi_0}{\lambda}\right) \times \frac{\varepsilon_0 \varepsilon_{s,\text{eff}}^{(s)} \sin^2 \phi_0 + (\varepsilon_{s,\text{eff}}^{(p)})^2 \cos^2 \phi_0 - \varepsilon_{s,\text{eff}}^{(s)} \varepsilon_{s,\text{eff}}^{(p)}}{(\varepsilon_0 - \varepsilon_{s,\text{eff}}^{(p)})(\varepsilon_0 - \varepsilon_{s,\text{eff}}^{(s)})(\varepsilon_{s,\text{eff}}^{(p)} \cos^2 \phi_0 - \varepsilon_0 \sin^2 \phi_0)}, \tag{41}$$

$$\varepsilon_{s,\text{eff}} \cong \frac{(\varepsilon_{s,\text{eff}}^{(p)})^2 (\varepsilon_0 - \varepsilon_{s,\text{eff}}^{(s)}) \sin^2 \phi_0}{\varepsilon_0 \varepsilon_{s,\text{eff}}^{(s)} \sin^2 \phi_0 - \varepsilon_{s,\text{eff}}^{(p)} (\varepsilon_{s,\text{eff}}^{(s)} - \varepsilon_{s,\text{eff}}^{(p)} \cos^2 \phi_0)}. \tag{42}$$

It is easily verified that when the thickness of the stack of multilayers goes to zero, $\varepsilon_{s,\text{eff}}$ is reduced to ε_s and we regain Eq. (2).

To see that the general results expressed by Eqs. (40)–(42) are reduced to the results reported by Zhu and co-workers [24] for a system of ambient(0)–surface layer(d)–layer(1)-substrate(s) as illustrated in Fig. 4, we can rewrite Eqs. (41) and (42) into the following forms with the help of Eqs. (10) and (24):

$$\alpha_{\text{eff}} \cong -\left(\frac{i4\pi n_0 \cos \phi_0}{\lambda}\right)\left(\frac{1}{\varepsilon_{s,\text{eff}}^{(s)}(1,s) - \varepsilon_0}\right) \times \left(\frac{\cos^2 \phi_0 - \varepsilon_{s,\text{eff}}^{(s)}(1,s)\left(\frac{\cos \phi_1}{n_1}\right)^2 \left(\frac{1 + r_{1s}^{(p)} e^{i\Psi_1}}{1 - r_{1s}^{(p)} e^{i\Psi_1}}\right)^2}{\cos^2 \phi_0 - \varepsilon_0 \left(\frac{\cos \phi_1}{n_1}\right)^2 \left(\frac{1 + r_{1s}^{(p)} e^{i\Psi_1}}{1 - r_{1s}^{(p)} e^{i\Psi_1}}\right)^2} \right), \tag{43}$$

$$\varepsilon_{s,\text{eff}} \cong \frac{(\varepsilon_0 - \varepsilon_{s,\text{eff}}^{(s)}(1,s)) \sin^2 \phi_0}{\cos^2 \phi_0 - \varepsilon_{s,\text{eff}}^{(s)}(1,s)\left(\frac{\cos \phi_1}{n_1}\right)^2 \left(\frac{1 + r_{1s}^{(p)} e^{i\Psi_1}}{1 - r_{1s}^{(p)} e^{i\Psi_1}}\right)^2}. \tag{44}$$

Equation (43) is the same as Eq. (A6) of [24] except for the difference in notation. Equation (44) is the same as Eq. (A7) of [24] except for notation.

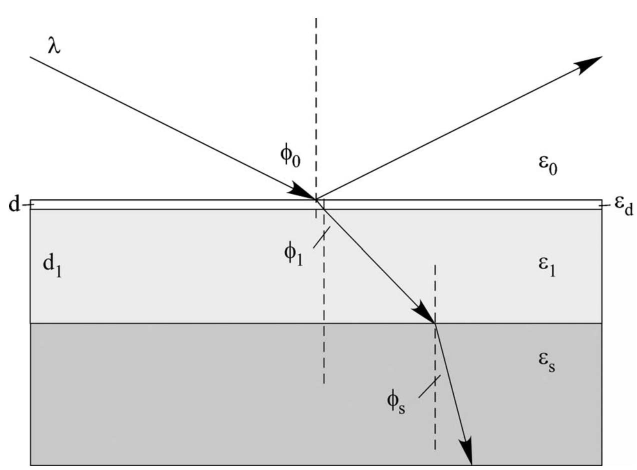

Fig. 4. Reflection from the surface of a semi-infinite substrate covered with an ultrathin film (ε_d) with a thickness of $d \ll \lambda$ and a uniform dielectric layer (ε_1) with arbitrary thickness d_1.

Equations (40)–(44) together with Eqs. (10) and (24) are the main results of this paper. We emphasize that optical constants $\varepsilon_{s,\text{eff}}^{(p)}$ and $\varepsilon_{s,\text{eff}}^{(s)}$ of the effective substrate are functions of the incidence angle ϕ_0 as well as the properties of its constituents. As ϕ_0 changes, $\varepsilon_{s,\text{eff}}^{(p)}$ and $\varepsilon_{s,\text{eff}}^{(s)}$ need to be computed again.

5. DISCUSSION

We discuss the key features of the present effective-substrate model and the significance of such a general approach to optical reflection from a multilayer stack on a semi-infinite substrate. It is remarkable that given the incidence angle from an ambient, the reflectivity from an arbitrary stack of multilayers on top of a semi-infinite substrate can always be represented by the reflectivity from an effective substrate characterized by two complex optical constants, one for the s-polarized component and the other for the p-polarized component.

It is equally remarkable that the OI-RD due to the presence or addition of an ultrathin layer on top of the effective substrate has the same form as that for the ultrathin layer on top of a homogeneous semi-infinite substrate. Only in this case the effective optical constant $\varepsilon_{s,\text{eff}}$ is an algebraic function of $\varepsilon_{s,\text{eff}}^{(p)}$ and $\varepsilon_{s,\text{eff}}^{(s)}$ [prescribed by Eqs. (42) or (44)], and the prefactor α_{eff} is also an algebraic function of $\varepsilon_{s,\text{eff}}^{(p)}$ and $\varepsilon_{s,\text{eff}}^{(s)}$ [prescribed by Eqs. (41) or (43)]. Compared to the theory reported by Zhu and co-workers [24], we have now generalized Eq. (40) to an ultrathin film on top of an arbitrary stack of multilayers on a homogeneous, semi-infinite substrate. This makes the present model applicable to practically all cases of thin-films growth and surface reactions when the light is incident from the ambient.

The factorized form of Eq. (41) reveals explicitly how the prefactor α^{eff} in Eq. (40) varies with the incidence angle and the dielectric properties of the ambient and the effective substrate. α_{eff} has three poles: $\varepsilon_{s,\text{eff}}^{(p)}=\varepsilon_0$, $\varepsilon_{s,\text{eff}}^{(s)}=\varepsilon_0$, and $\varepsilon_{s,\text{eff}}^{(p)}=\varepsilon_0 \tan^2 \phi_0$. The latter is equivalent to the pole in Eq. (2) associated with the Brewster angle (the polarizing angle). Since the Brewster angle is only associated with the p-polarized component of an incident light, it is physically sensible and reassuring that an effective Brewster angle for the effective substrate exists and is determined only by the effective optical constant for the p-polarized component, $\varepsilon_{s,\text{eff}}^{(p)} \cos^2 \phi_0 = \varepsilon_0 \sin^2 \phi_0$. The poles in α_{eff} are useful in practice because the magnitude of $\Delta_p - \Delta_s$ in response to the ultrathin surface layer can be enhanced at or near these poles, as pointed out by Landry and co-workers [33]. At the interface between two semi-infinite homogeneous media the only practical pole is the Brewster angle determined by $\varepsilon_s \cos^2 \phi_{0B} = \varepsilon_0 \sin^2 \phi_{0B}$. At the interface between a homogeneous ambient and an effective substrate consisting of a multilayer stack on a semi-infinite homogeneous medium, we have three usable poles if suitable choices of thickness and optical dielectric properties of the multilayers are made.

The present theory of oblique-incidence optical reflectivity difference is significant as it covers essentially all systems encountered in thin-film growths and surface reactions. During a film growth or surface reactions on functionalized or modified substrates, one often deals with a topmost surface layer on top of another layer (on a homogeneous substrate) whose structural and electronic properties may vary along the surface normal, either by design or as a result of the kinetic process. When the thickness of the intervening layer is no longer small compared to the optical wavelength and the optical dielectric response of the layer cannot be adequately described by averaging the optical constant along the surface normal, one needs to treat the layer as a stack of multilayers each of which has its distinct optical constant and thickness [24,34–36]. The present theory offers an analytical way to treat such an intervening layer by introducing an effective substrate and thus simplifies the physical analysis of OI-RD. Since one of the objectives of optical reflection measurement is to determine the property of the topmost surface layer during a surface-bound process, an intervening layer may be utilized to enhance the net optical response of the surface layer by making α_{eff} close to one of the poles or to enhance the contrast of the ellipsometric detection by making $\varepsilon_{s,\text{eff}}$ [given by Eqs. (42) or (44)] close to ε_d so that minute changes in ε_d during the subsequent kinetic process are readily observable.

6. CONCLUSION

We developed an effective-substrate theory to treat optical reflection from a stack of multilayers on a homogeneous semi-infinite substrate. Such a theory simplifies the physical analysis of optical reflection from such a system and the change of it when an ultrathin film (i.e., the surface layer) is added or changed on top of the stack. Within the framework of the effective-substrate theory, the oblique-incidence reflectivity difference (OI-RD) (ubiquitously measured in various forms of ellipsometry) maintains a simple, factorized form. There exists a great potential for enhancing the optical response of an ultrathin surface layer with suitably chosen effective substrates.

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