

UNAMBIGUOUS DETERMINATION OF THICKNESS AND DIELECTRIC FUNCTION OF THIN FILMS BY SPECTROSCOPIC ELLIPSOMETRY

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We present a spectroscopic method of determining both thicknesses and dielectric functions of thin films on previously characterized substrates. The method requires that spectroscopic ellipsometric data be taken over an energy range where the substrate has a sharp optical structure, *e.g.* a critical point. These data are used to determine a "pseudodielectric" function for the film, which necessarily depends on the assumed film thickness. We develop a general first-order theory which shows that the correct thickness and dielectric function of the film are those for which the substrate feature vanishes in the calculated pseudodielectric function. The theory is also used to investigate sensitivity and applicability. We show that sensitivity can be enhanced by differentiating the pseudodielectric function with respect to energy. The method is demonstrated with several numerical and experimental examples, which illustrate that monolayer thickness accuracy can be achieved.

1. INTRODUCTION

A major difficulty in determining the dielectric response $\epsilon_0 = \epsilon_{o1} + i\epsilon_{o2}$ of thin films from ellipsometric data is the three unknowns at any wavelength, *i.e.* ϵ_{o1} , ϵ_{o2} and the film thickness d ¹. If the film is transparent, only two unknowns are involved, but for very thin films the quantities determined are not ϵ_{o1} and d but the optical thickness $n_0 d$ where n_0 is the index of refraction².

One approach to resolving this problem is to obtain further data by varying a system parameter. For example, the sample can be measured in different ambients³⁻⁵, the film can be deposited in different thicknesses^{4,6} or on different substrates or additional known films can be deposited on the sample⁷. However, the dielectric properties of the film are not necessarily independent of such manipulations. Alternatively, the angle of incidence ϕ may be varied^{3,4,8-12}. However, in addition to complicating the design of sample chambers, the variable ϕ method suffers from a lack of sensitivity for materials with large dielectric functions because Snell's law shows that propagation within the film is nearly normal to the surface

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regardless of the value of ϕ . More seriously, if the film is very thin, the angle of incidence enters the appropriate ellipsometric equations only trivially and no independent conditions can be obtained from it¹³.

Reflectance data have also been used to provide the missing information. Paik and coworkers^{14,15} and Cahan and coworkers^{16,17} showed that a simultaneous measurement of the change $\Delta R/R$ in reflectance resulting from the growth of a film on a previously bare substrate could be combined with ellipsometric data to yield all three unknowns. Alternatively, in some cases the reflectance was simply assumed to be independent of the film thickness ($\Delta R/R = 0$) to yield the necessary third condition^{3,18-20}. However, this is a somewhat dangerous assumption and, in any case, computations involving reflectance do not always converge or lead to physical solutions²¹. If convergence does not occur, it is not clear whether the model or the data are inadequate. Also, at present thin films must be grown *in situ* to obtain the necessary accuracy in $\Delta R/R$. Problems in precision can also arise if the dielectric properties of the film are very similar to those of the substrate²².

Another approach is to vary the wavelength. If the film is known to be transparent in a certain region of the spectrum, d can be determined there and used as a system invariant to calculate the dielectric properties of the film in the region where the film is absorbing^{23,24}. While this can also be done at single wavelengths, the advantage of spectroscopic measurements is that the assumptions about the validity of the model and the value determined for the thickness can be checked by looking for interference- or interface-related structure in the calculated dielectric response of the film^{25,26}. If the film is sufficiently thick, the simple models can be extended to obtain information about interface regions^{25,26}.

The purpose of this paper is to show that spectroscopic ellipsometry can also provide accurate values of film thicknesses by requiring that *substrate*-related optical structure in the calculated dielectric properties of films also vanish. This approach has several advantages over previous methods. Much thinner films can be investigated than is possible with interference-oscillation-dependent methods. No special thicknesses or ambients are necessary. The method can also be used with absorbing films. Finally, it yields some insight about the widths of film interfaces. The principle and theory are given in Section 2 and several representative examples are discussed in Section 3.

2. THEORY

2.1. General formulation

We suppose a three-phase system consisting of a substrate, film and ambient whose dielectric functions are given by ϵ , ϵ_0 and ϵ_a respectively. We assume for simplicity that the substrate and film are isotropic so that ϵ and ϵ_0 are scalar quantities. The complex reflectance ratio of the system can be calculated by taking the ratio of the Fresnel reflectance expressions for p- and s-polarized light¹. Assuming an ideal system, the complex reflectance ratio can be expressed formally as

$$\rho_{\text{exp}} = \rho(\epsilon, \epsilon_0, \epsilon_a, d, \lambda, \phi) \quad (1)$$

where d is the film thickness, λ is the wavelength of the light and ρ_{exp} is the quantity measured by the instrument. We assume that everything is known but ϵ_0 and d .

The objective is to find ϵ_0 without knowing *a priori* the value of d . If $\langle d \rangle$

represents a guess approximately equal to the true value d , eqn. (1) still can be solved numerically for ϵ_0 , but the value obtained will be a pseudodielectric function $\langle \epsilon_0 \rangle$. This quantity can be related to the exact solution ϵ_0 by expanding eqn. (1) to first order in $\langle d \rangle - d$, assuming this quantity to be small. We find that

$$\langle \epsilon_0 \rangle = \epsilon_0 - (\langle d \rangle - d) \frac{\partial \rho / \partial d}{\partial \rho / \partial \epsilon_0} \quad (2)$$

which shows how an error in $\langle d \rangle$ affects the calculated spectrum $\langle \epsilon_0 \rangle$.

Now, although d is not known, its value can in principle be inferred because ϵ_0 must satisfy some rather general criteria. Obviously ϵ_0 cannot be a function of the angle of incidence or other physical dimensions of the system or of the substrate or ambient dielectric functions, and its dependence on energy is presumably different from that of the other parameters of the system. From the form of eqn. (2) it is clear that $\langle \epsilon_0 \rangle$ will be generally independent of these parameters only when $\langle d \rangle = d$. Only then does the correction term, which in principle is a function of all the parameters of the system, vanish completely. The problem is therefore solved, because if $\langle d \rangle = d$, then $\langle \epsilon_0 \rangle = \epsilon_0$.

Equation (2) is the formal first-order representation of the statement that a correct solution to ϵ_0 will show no system-related artifacts such as interference oscillations^{23,26} or, as will be developed here, optical structure originating from the dielectric response of the substrate. The above approach can clearly be generalized to n -phase laminar systems, systems containing inhomogeneous media or any physical system where measurable quantities can be modeled in terms of a few parameters.

Precisely because it is simple, eqn. (2) provides new insight into the practical aspects of determining both the thickness and the dielectric response of a film. The most favorable cases obviously occur when the derivative ratio is large. If the ratio is small, then the data may not be sufficiently accurate to allow a unique solution of d and ϵ_0 to be obtained. A special case of this type occurs if d and ϵ_0 appear as a separately factorable function $f(d, \epsilon_0)$ within ρ . Then eqn. (2) can be written

$$\langle \epsilon_0 \rangle = \epsilon - (\langle d \rangle - d) \frac{\partial f / \partial d}{\partial f / \partial \epsilon_0} \quad (3)$$

and the remaining system parameters disappear regardless of the form of ρ . The solution for d and ϵ_0 must then depend on second-order effects. We shall show that this is the situation for thin relatively unpolarizable films on highly polarizable substrates but not for similar films on relatively unpolarizable substrates.

Finally, if substrate- or interference-related artifacts cannot be made to vanish for any $\langle d \rangle$, this indicates that the term called ϵ_0 in eqn. (2) must itself be a function of the system parameters. This will occur if the film is not a completely independent phase but contains some substrate material. This can also occur if the solution for ϵ_0 represented by eqn. (2) is not exact because the actual sample configuration is more complicated than that assumed in the model. Examples of the latter situation include the assumption of the isotropic three-phase model to describe a sample where the interfaces are microscopically rough or otherwise graded or where the film is anisotropic. The proper approach here is to use the more complicated model that more accurately represents the sample when solving for ϵ_0 .

2.2. Special cases

The mathematical formulation of the three-phase model¹ is too complicated to treat analytically. Therefore in this section we shall illustrate the above theory in the special case where the film is thin enough for the first-order expansion in d/λ to apply. In addition to providing physical insight, the model is also of practical importance in many systems. Thicker films will be discussed in Section 3, where other applications of the above theory will be illustrated by numerical calculations.

Because spectroscopic ellipsometric data are generally represented in the thin film limit in pseudodielectric function form, we use the first-order expansion²⁷

$$\langle \varepsilon \rangle = \varepsilon + \frac{4\pi i d n_a}{\lambda} \frac{\varepsilon(\varepsilon - \varepsilon_o)(\varepsilon_o - \varepsilon_a)}{\varepsilon_o(\varepsilon - \varepsilon_a)} \left(\frac{\varepsilon}{\varepsilon_a} - \sin^2 \phi \right)^{1/2} \quad (4)$$

where $\langle \varepsilon \rangle$ is the experimentally determined quantity. Using eqn. (2) (it should be noted that $\partial \rho / \partial d = (\partial \rho / \partial \langle \varepsilon \rangle) \partial \langle \varepsilon \rangle / \partial d$ etc.), we obtain

$$\langle \varepsilon_o \rangle = \varepsilon_o - \frac{\langle d \rangle - d}{d} \frac{\varepsilon_o(\varepsilon_o - \varepsilon_a)(\varepsilon - \varepsilon_o)}{\varepsilon_a \varepsilon - \varepsilon_o^2} \quad (5)$$

We see that the sensitivity is low if ε_o is nearly equal to ε_a or ε but that it can be very large if ε_o is near $(\varepsilon_a \varepsilon)^{1/2}$. If $|\varepsilon|, |\varepsilon_o| \gg \varepsilon_a$ then eqn. (5) simplifies to

$$\langle \varepsilon_o \rangle = \varepsilon_o + (\langle d \rangle - d) \frac{\varepsilon - \varepsilon_o}{d} \quad (6)$$

In this limit the substrate dielectric properties appear explicitly in the calculated pseudodielectric function of the overlayer. The sensitivity can be enhanced by taking the κ th derivative of eqn. (6) with respect to the energy E :

$$\frac{\partial^\kappa \langle \varepsilon_o \rangle}{\partial E^\kappa} \approx \frac{\langle d \rangle - d}{d} \frac{\partial^\kappa \varepsilon}{\partial E^\kappa} \quad (7)$$

where we have used the assumption that ε_o varies slowly with E . Therefore only when $\langle d \rangle = d$ do the substrate features $\partial^\kappa \varepsilon / \partial E^\kappa$ vanish in $\partial^\kappa \langle \varepsilon_o \rangle / \partial E^\kappa$.

If $|\varepsilon| \gg |\varepsilon_o|, |\varepsilon_a|$ then eqn. (4) simplifies to

$$\langle \varepsilon \rangle = \varepsilon + \frac{4\pi i d}{\lambda} \varepsilon^{3/2} \left(1 - \frac{\varepsilon_a}{\varepsilon_o} \right) \quad (8)$$

Here d and ε_o now factor as the function $f(d, \varepsilon_o) = d(1 - \varepsilon_a/\varepsilon_o)$. By evaluating eqn. (2) explicitly we obtain

$$\langle \varepsilon_o \rangle = \varepsilon_o - (\langle d \rangle - d) \frac{\varepsilon_o(\varepsilon_o - \varepsilon_a)}{d \varepsilon_a} \quad (9)$$

Equation (9) is a specific manifestation of eqn. (3): there is no substrate dependence in $\langle \varepsilon_o \rangle$, and consequently the correct thickness cannot be found by minimizing substrate features in $\langle \varepsilon_o \rangle$. We conclude, as earlier researchers have also done², that the thickness and dielectric function of the film cannot be separated in first order if the film is very thin and the substrate is highly polarizable. However, the above derivation shows that this restriction is only limited to situations where $|\varepsilon| \gg |\varepsilon_o|$. For many overlayer-substrate systems, both optical properties and film thickness can be obtained.

3. APPLICATIONS

Since the sensitivity and ultimately the limits of the method depend on the magnitude of the derivatives in eqn. (2), we give several examples showing the level of accuracy attainable. We begin with three numerical examples covering both transparent and absorbing overlayers as well as a four-phase system with an intermediate rough region between the substrate and the film. We finish with two experimental applications: amorphous tellurium (a-Te) on HgCdTe and polypyrrole on gold.

All calculations were done in three- or four-phase models using the exact Fresnel expressions for the complex reflectance ratio $\rho = \tan \psi \exp(i\Delta)$ ¹. When the dielectric function of a film was calculated for an assumed film thickness, the exact Fresnel expressions were solved by iterative numerical inversion. Thus no mathematical approximations were used in any of the calculations. The film(s), substrate and interfaces were all assumed to be ideal.

Dielectric function data used in the numerical computations were obtained from the following sources. Crystalline silicon (c-Si) and a-Si data are from refs. 28 and 26 respectively, the SiO₂ data are from work by Malitson²⁹ and the Hg_{1-x}Cd_xTe data for a nominal composition $x = 0.29$ are from ref. 24. Measurements on thin films were done with a spectroscopic ellipsometer^{30,31} with an energy range of 1.5–6.0 eV. The samples were cleaned and maintained in a dry N₂ ambient in a windowless cell. An angle of incidence of 1.171 rad was used in all examples. The polypyrrole films were formed by electropolymerization on evaporated gold films³². Fabrication details and further results on polypyrrole will be presented in a future publication.

3.1. Numerical examples

3.1.1. SiO₂ on c-Si

The complex reflectance ratio ρ was calculated from 1.5 to 6.0 eV for a 2 nm SiO₂ overlayer on a c-Si substrate. Using these values of ρ as "experimental" data, we solved the three-phase model numerically for the pseudodielectric function of the overlayer with different estimates of $\langle d \rangle$. The second derivatives of $\langle \epsilon_o \rangle$ with respect to energy were then calculated to enhance the sensitivity to substrate-related structure. In Fig. 1 we show some examples of derivative spectra near the 3.4 eV E₁ critical point of c-Si.

This numerical example represents a severe test of sensitivity since it falls nearly within the scope of eqn. (9). The main sources of uncertainty are the statistical fluctuations in the data for c-Si, which generate noise in the higher derivative spectra of $\langle \epsilon_o \rangle$. Nevertheless, the thickness can be determined to within 0.02 nm. Since the film is transparent, we can also use the commonly applied criterion that the correct film thickness is that for which the imaginary part of ϵ_o vanishes. Using this we also find the correct value of d to within 0.02 nm.

3.1.2. a-Si on c-Si

In this example we study an overlayer which is everywhere absorbing in the experimental energy range. Thus the criterion of finding a value of $\langle d \rangle$ for which $\langle \epsilon_o \rangle$ is purely real is not applicable. In the same manner as before we calculate an experimental ρ spectrum for a 5 nm layer of a-Si on a c-Si substrate and then

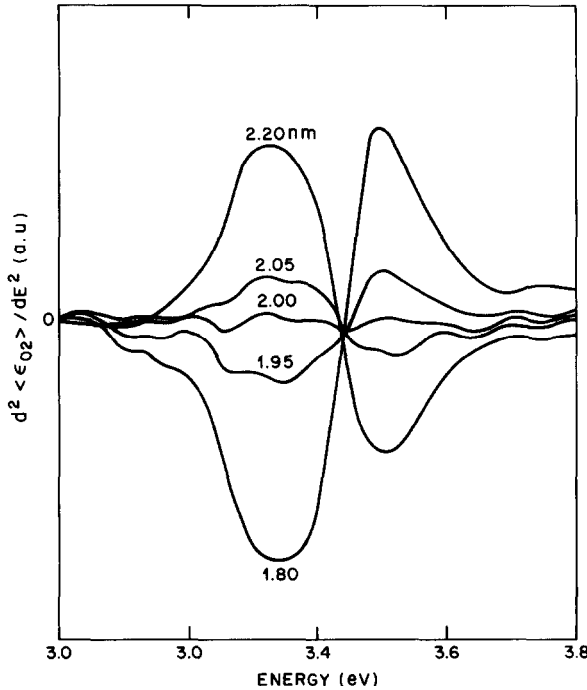


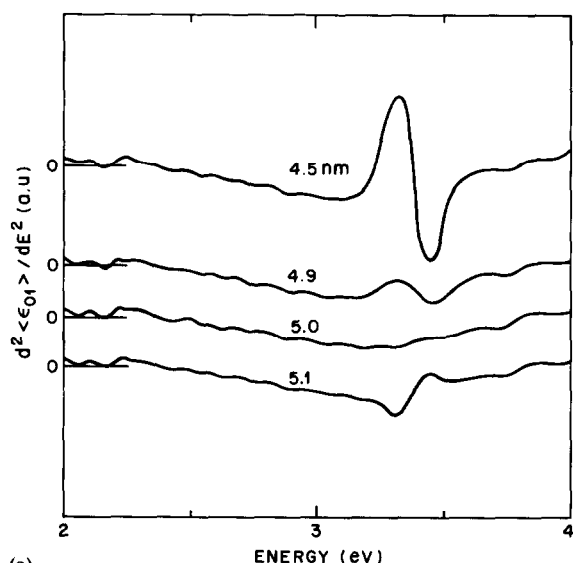
Fig. 1. Second energy derivative of the imaginary part of $\langle \epsilon_o \rangle$ for different estimates of the film thickness $\langle d \rangle$ for data numerically calculated for 2 nm of SiO_2 on c-Si near the E_1 critical point of c-Si.

evaluate the film thickness from computations of $\langle \epsilon_o \rangle$. In Fig. 2(a) we see that the second derivative of $\langle \epsilon_{o1} \rangle$ for a-Si has a broad spectral dependence owing to its dispersive properties. However, the sharp structure at 3.4 eV due to the c-Si substrate is clearly distinguishable if a wrong thickness estimate is used in the calculation. The correct thickness can readily be determined to well within atomic dimensions. In Fig. 2(b) we show that attempts to determine the correct value of d by direct observation of $\langle \epsilon_o \rangle$ are at least one order of magnitude less sensitive and are also subject to judgment as to which spectrum is best. The differentiation method is more accurate because it accentuates the structure due to the substrate.

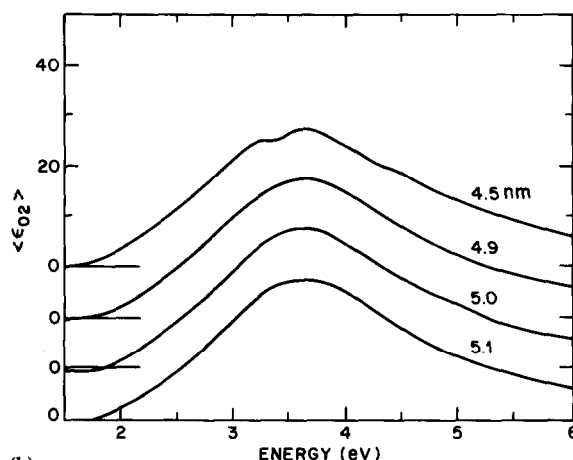
3.1.3. a-Si/finite interface/c-Si

Here we discuss a five-phase sample consisting of a c-Si substrate covered with three layers. The first is a 1 nm film consisting of equal volume fractions of c-Si and SiO_2 . The second is a 1 nm film consisting of equal volume fractions of SiO_2 and a-Si. The third is a 3 nm film of a-Si. The dielectric functions of the mixtures were calculated in the effective medium approximation³³. The structure is intended to simulate a microscopically rough oxidized substrate upon which an a-Si film is deposited. Assuming that we are not aware that the roughness and oxide are present, we analyze the experimental ρ spectrum, calculated correctly with the five-phase model, as if the three-phase model were applicable.

Spectra calculated for three different values of $\langle d \rangle$ are shown together with a reference spectrum of a-Si in Fig. 3. In no case is it possible to eliminate either the E_1 or the 4.2 eV E_2 spectral features of the substrate from $\langle \epsilon_o \rangle$. (As usual, this is much



(a)



(b)

 Fig. 2. (a) As Fig. 1 but for 5 nm of a-Si on c-Si; (b) imaginary part of $\langle \epsilon_o \rangle$ for the same thicknesses.

more apparent in numerically calculated derivatives.) Therefore we can conclude that the term ϵ_o in eqn. (2), as calculated in the three-phase model, is still dependent on the system parameters. That is, the three-phase model does not adequately represent the sample. The substrate structure can be minimized for $\langle d \rangle = 4.5$ nm, but this thickness does not correspond to any combination of thicknesses used in the model calculation. The results indicate also that finite interface widths may be detected from this analysis.

Despite these complications, the gross behavior of $\langle \epsilon_o \rangle$ shows surprisingly little dependence on $\langle d \rangle$: the overlayer would be correctly identified from the spectral dependence of $\langle \epsilon_o \rangle$ as a-Si although the apparent magnitudes are reduced by about 15%. If the warnings provided by the inability to eliminate artifacts in $\langle \epsilon_o \rangle$ were

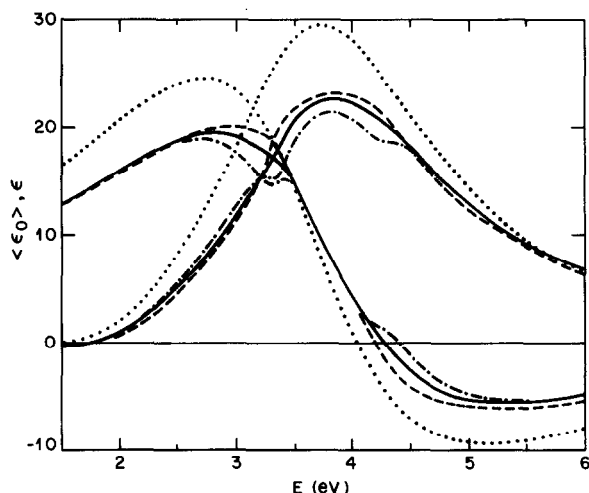


Fig. 3. As Fig. 2(b) but for 3 nm of a-Si on c-Si with an intermediate rough layer: ·····, a-Si; —, $\langle d \rangle = 4.0$ nm; — — —, $\langle d \rangle = 4.5$ nm; - - -, $\langle d \rangle = 5.0$ nm. Details are given in the text.

ignored and the data were analyzed in the effective medium approximation, the film density would be incorrectly underestimated by about 10%.

3.2. Experimental examples

3.2.1. a-Te on HgCdTe

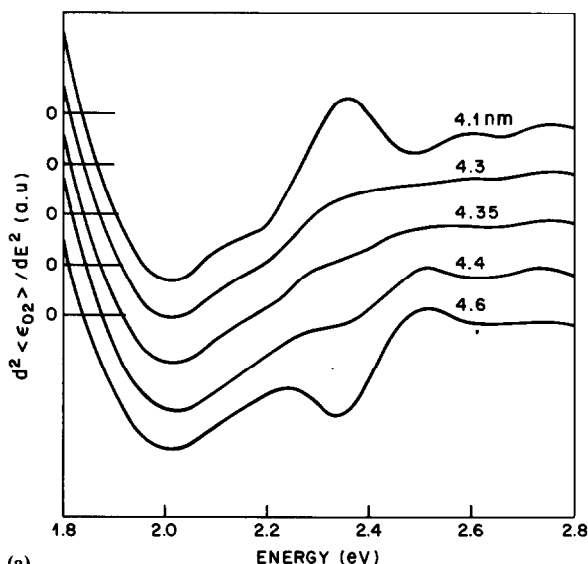
If anodic oxides on HgCdTe are stripped with hydrochloric acid, a residue precipitates on the surface²⁴. This residue has tellurium-like optical and chemical properties and its thickness is in the range of 5%–10% of that of the original oxide. If we simply calculate the second derivative of $\langle \epsilon_0 \rangle$ in the region of the E_1 transition of $\text{Hg}_{0.71}\text{Cd}_{0.29}\text{Te}$ at 2.37 eV for various $\langle d \rangle$, then d can be determined to about ± 0.1 nm. This is sufficiently accurate for most purposes because most interfaces cannot be assumed to be definable to less than 0.1 nm. However, if we smooth the derivatives by reducing the high frequency noise, d can be determined to within a few hundredths of a nanometer. This case is shown in Fig. 4(a) for a film 43.5 nm thick. The distortion in the derivative spectra introduced by filtering is of no importance as long as the main features are not completely smoothed out. Figure 4(b) shows that the overlayer spectrum calculated for this film is absorbing everywhere in the experimental energy range. Application of this approach to precipitated a-Te films of thicknesses ranging from 1 to 5 nm has shown that the ϵ spectra are the same except for density effects.

3.2.2. Polypyrrole on gold

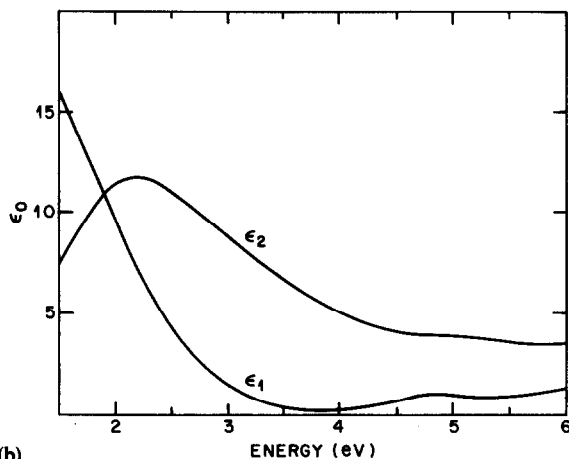
Polypyrrole is a conducting polymer^{32,34} which, like most other organic materials, has a low polarizability in the visible and UV wavelength region. Furthermore, it has broad adsorption bands in this energy range. The actual dielectric response of polypyrrole depends strongly on its oxidation state which readily can be changed by charge injection^{34–36}.

We have applied our method to a thin polypyrrole film on a gold substrate. This system represents a class of applications in which the dielectric functions of both substrate and film are not significantly higher than that of the ambient. Gold has two

suitable critical points in the energy range 1.5–6.0 eV: the d band to Fermi level transition near 2.5 eV and the L transition near 3.6 eV. Depending on the type of polymer or its oxidation state, either or both of these critical points may be used. Our measurements were done on an air-exposed polypyrrole film.



(a)



(b)

Fig. 4. (a) Second energy derivative of the imaginary part of $\langle \epsilon_0 \rangle$ for different estimates of the film thickness $\langle d \rangle$ for ellipsometric data taken on a-Te on $\text{Hg}_{0.71}\text{Cd}_{0.29}\text{Te}$ near the E_1 critical point of the substrate; (b) dielectric function of a-Te calculated for $\langle d \rangle = 4.35$ nm.

In the optical spectrum of this particular film, the tail of the free carrier absorption extended above the gold critical point at 2.5 eV. In Fig. 5(a) we show the second derivative of $\langle \epsilon_0 \rangle$ with respect to E for the pyrrole film for different values of $\langle d \rangle$. We see immediately that the gold-derived spectral feature at 2.5 eV can be minimized but cannot be completely removed. The most appropriate thickness is

22.0 ± 0.5 nm. According to the previous section, these results suggest that the sample configuration is more complicated than the model used to calculate $\langle \epsilon_0 \rangle$. It is likely that the interface between the substrate and the film was roughened by the polymerization process. We have verified this hypothesis by measuring gold surfaces which were processed in the same way but with no pyrrole monomer in the solution. If we ignore the roughness as a minor perturbation, we obtain the refractive index $N = n + ik = \epsilon_0^{1/2}$ shown in Fig. 5(b) for the pyrrole film. The results are in good qualitative agreement with literature data^{34,35}.

We also attempted a similar analysis on data from a poly(*N*-methyl pyrrole) film that showed very little absorption below 3 eV. We could not find the thickness

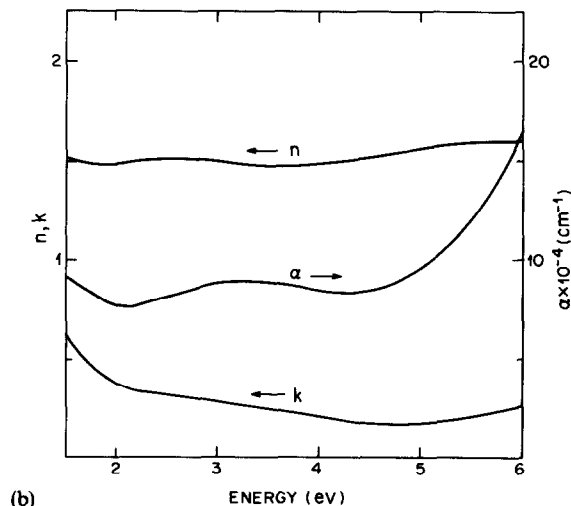
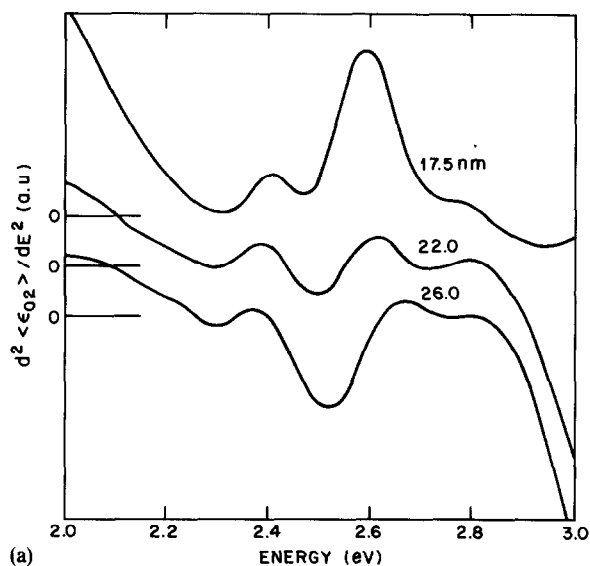


Fig. 5. (a) As Fig. 4(a) but for polypyrrole on gold; (b) refractive index and absorption coefficient for polypyrrole calculated for $\langle d \rangle = 22.0$ nm.

by analyzing derivatives near 2.5 eV. However, at the L transition near 3.6 eV the thickness could be determined to within 0.2 nm.

4. DISCUSSION

We have described a spectroscopic method for determining the thickness and dielectric function of a thin film on a substrate. The method can be applied directly to existing data and does not require special ambients, deposition conditions or sample configurations. However, it does require that the substrate have a distinct optical feature somewhere in the experimentally accessible energy range. This requirement is fulfilled by many semiconductors and metals. The method loses sensitivity for very thin films on highly polarizable substrates, but this effect can be entirely understood from the general theoretical formulation that we have developed and verified with numerical calculations. In this case the first-order effect vanishes and the sensitivity must come from second-order terms in the expansion.

The method is ultimately limited by the sample complexity and the accuracy with which optical data can be measured. If there is a graded interface between the film and the substrate, it may or may not be possible to reduce the amplitudes of the substrate features in $\langle \epsilon_o \rangle$ below that of the intrinsic uncertainty due to noise. Thus the ability of the data to show whether the assumptions of the model used to represent the sample are actually satisfied by the sample reduces ultimately to the question of experimental sensitivity. It is usually true that the inability to eliminate artifacts completely in a film spectrum is an indication that the model is too simple. In the thin film configurations discussed here, such failures can be traced to finite interface widths or to film inhomogeneities or anisotropies. For example, uniaxial films have been treated to first order in d/λ in ref. 13, and the improper assumption of isotropy leads to an equation for the film dielectric function where those of both substrate and ambient appear explicitly (see ref. 13, eqn. (4.2): the term $\epsilon_t \epsilon_1 \epsilon_3 / \alpha_3 \epsilon_t$ in this expression should be $\epsilon_t + \epsilon_1 \epsilon_3 / \alpha_3 \epsilon_t$).

The numerical example consisting of an a-Si layer on a thin SiO₂ film on a rough c-Si substrate illustrates a situation where the three-phase model is too simple and the substrate structure in $\langle \epsilon_o \rangle$ cannot be made to vanish for any $\langle d \rangle$. However, model calculations for the c-Si/SiO₂/a-Si system show that the substrate structure in $\langle \epsilon_o \rangle$ can be made nearly to vanish in a three-phase model if the interfaces are assumed to be planar. Therefore, while the inability to eliminate artifacts shows that an assumed model is too simple, the ability to eliminate artifacts to within experimental accuracy may *not* be conclusive evidence that this model is adequate. Of course, if independent measurements show that a sample is more complex, difficulties can be avoided by using the more complicated model that better represents the sample.

We have also found that the sensitivity to variations in $\langle d \rangle$ can be quite dependent on specific values of d , ϵ and ϵ_o , as indicated in the example of poly(*N*-methyl pyrrole) on gold where analysis at 3.6 eV gave much better results than analysis at 2.5 eV. These low sensitivity combinations may be due to a small numerator in eqn. (2) or to an effective factoring of the derivative ratio as in eqn. (3). Owing to the complexity of the reflectance equations, these low sensitivity combinations are best found by numerical calculations and best eliminated by

changing wavelength, film thickness or substrate material in situations where this can be done. Another difficulty can arise if the dielectric function of the overlayer has sharp structure which overlaps that of the substrate. This is generally not a problem as many films are amorphous and have optical parameters that vary slowly with energy. However, some organic films, such as phthalocyanine³⁷ may have sharp threshold energies. Here the calculated derivative spectra may be dominated by the intrinsic optical properties of the film. The method was not applicable to an absorbing 1,4,5,8-naphthalenetetracarboxylic dianhydride film on a silicon substrate³⁸, although other substrates could have been used.

To utilize the method fully, it is also desirable to perform some type of noise filtering either by smoothing the calculated derivatives or by Fourier filtering³⁹. From Fig. 2 it is obvious that differentiating $\langle \epsilon_o \rangle$ with respect to energy enhances sensitivity. We have found empirically that a second-order derivative is generally sufficient. Third derivatives require more smoothing of the data, which can be done as long as the optical features of the substrate are not completely removed.

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