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# Extended spectroscopy with high-resolution scanning ellipsometry

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The extrapolation of dielectric-function data taken over the near ir-uv spectral region by high-resolution wavelength-scanning ellipsometry is investigated. The possibility of determining the amplitudes of a number of oscillators outside the measurement interval by application of the Kramers-Kronig integral allows spectroscopic information to be determined in experimentally inaccessable spectral regions. Several examples are given.

The analytic continuation theorem of complex variables states that any holomorphic (analytic) function whose real and imaginary parts are known along any line segment may be calculated over the entire complex plane.[1] Since the complex dielectric function $\epsilon(E)=\epsilon_1(E)+i\epsilon_2(E)$ is analytic in the upper half-plane,[2] and since its real and imaginary parts can be measured directly over a part of the real energy axis by ellipsometry,[3] the problem of obtaining the detailed behavior of $\epsilon$ at all energies from finite-range ellipsometric data reduces essentially to one of experimental accuracy. Here, we investigate the possibility of extrapolating $\epsilon_2$ beyond experimentally accessible energy ranges. Using representative data obtained with a high-precision wavelength-scanning ellipsometer recently developed by us,[4] we show that the possibility of determining the amplitudes of up to six oscillators by a suitable application of the Kramers-Kronig integral[5] allows useful information to be determined outside of experimentally accessible ranges.

The idea of using the measured dispersion of the index of refraction in regions of transparency to characterize absorption properties at higher energies is well known. In its simplest form, it provides the basis of the Phillips–Van Vechten theory of chemical bonding[6] and has been used in other applications in solids[7] as well. Oscillator strengths of atoms and molecules in the gas phase have been calculated by fitting one or more Sellmeyer oscillators,[8] calculating moment integrals,[9] evaluating Padé approximants,[10] or generating continued-factorization series[11] from dispersion data.

Dispersion applications are a special limiting situation for which $\epsilon_2$ is known to be zero and the measurement of $n^2=\epsilon_1$ is sufficient to entirely determine $\epsilon$. If $\epsilon_2\neq 0$, the situation is not as straightforward. Nevertheless, information can still be obtained beyond experimental limits. Beaglehole[12] has used the observed discrepancies between the measured and calculated values of $\epsilon_1$ for Cu and Au to estimate the limiting values of $\epsilon_2$ at low and high energies. Methods have also been developed to fit oscillator functions to the reflectivity alone of absorbing systems over a finite energy range.[13] But reflectivity fitting is not suitable for continuation purposes, since the reflectivity is only the real part of an analytic function, and to calculate the imaginary part (by a Kramers-Kronig transformation) one needs the information desired.

Here, we show that it is possible to determine systematically the amplitudes of a number of oscillators from ellipsometric data and thus to obtain more detailed information about spectral response in experimentally inaccessible regions. To do this, we exploit the connection between $\epsilon_1$ and $\epsilon_2$, expressed by the Kramers-Kronig integral, to reduce the absorbing-system case to a dispersion-type situation as follows.

The Kramers-Kronig integral can be written

$$\epsilon_1(E)=1+\frac{2}{\pi}\mathcal{P}\int_0^\infty \frac{E'dE'}{E'^2-E^2}\epsilon_2(E'), \tag{1}$$

where $\mathcal{P}$ indicates that the principal part is taken. If $\epsilon_1$ and $\epsilon_2$ are known over a finite energy range $E_i\leq E\leq E_f$, then Eq. (1) can be written

$$\frac{2}{\pi}\int_0^{E_i}\frac{E'dE'}{E'^2-E^2}\epsilon_2(E')+\frac{2}{\pi}\int_{E_f}^\infty \frac{E'dE'}{E'^2-E^2}\epsilon_2(E')$$

$$=\epsilon_1(E)-1-\frac{2}{\pi}\mathcal{P}\int_{E_i}^{E_f}\frac{E'dE'}{E'^2-E^2}\epsilon_2(E'), \tag{2a}$$

$$=\epsilon_1'(E),\quad E_i<E<E_f. \tag{2b}$$

Equations (2) represent a constraint upon $\epsilon_2$ outside the experimentally accessible energy range. The integral in the right-hand side of Eq. (2a) simply extracts from $\epsilon_1(E)$ the effect of the absorption processes occurring in the measurement interval. This enables us to define the effective real part $\epsilon_1'(E)$ which arises entirely from absorption processes outside the measurement interval. The right-hand side of Eq. (2a) can be calculated from ellipsometric data, or can be obtained directly from refractive index data if $\epsilon_2(E)\equiv 0$ over this range. It is clear that any extrapolation method[8–11] can be applied to Eq. (2b) since $\epsilon_1'(E)$ has been corrected by the finite-range transformation for the effect of $\epsilon_2$.

For our purposes here, we shall extrapolate $\epsilon_2$ by means of an oscillator-fitting procedure.[8] We represent $\epsilon_2$ outside the accessible range by a series of finite-width constant-amplitude oscillators such that for any $n=1,2,\ldots,N$,

$$\epsilon_{2,n}(E)=\begin{cases}A_n & \text{for } E_n\le E\le E_n' ,\\ 0 & \text{elsewhere.}\end{cases}\qquad(3)$$

We choose the limits $E_n$ and $E_n'$ of the $n$th oscillator and seek to determine the values of $A_n$ that best represent $\epsilon_1(E)$ in the accessible range. Although the limits $E_n$ and $E_n'$ can be chosen arbitrarily, the most physical approach is to set $E_n'=E_{n+1}$, except for excluding the accessible range. Substituting Eq. (3) into Eqs. (2) gives

$$\epsilon_1'(E)=\left(\epsilon_1(E)-1-\frac{2}{\pi}\mathcal{P}\int_{E_i}^{E_f}\frac{E'dE'}{E'^2-E^2}\,\epsilon_2(E')\right)=\sum_{n=1}^{N}A_n\frac{1}{\pi}\ln\left|\frac{E_n'^2-E^2}{E^2-E_n^2}\right| .\qquad(4)$$

For simplicity, we calculate the $A_n$ by evaluating Eq. (4) for $N$ values $E=E_j$, equally spaced within the interval ($E_i+0.01$ eV) to ($E_f-0.01$ eV). The 0.01 eV shifts are included to eliminate singularities in the logarithm for the two terms in Eq. (4) adjacent to the measurement interval. Equation (4) then leads to $N$ simultaneous linear equations in $N$ unknowns, which can be solved for the coefficients $A_n$.

The oscillator-fitting procedure attempts to represent the functional dependence of $\epsilon_1'(E)$ from $E_i\le E\le E_f$ by an expansion of dispersion curves of the functional form given by the right-hand side of Eq. (4). If any two of the trial oscillators have dispersion curves that are too similar, then it is not possible to clearly distinguish between them. In practical terms, the coefficient matrix defined by the right-hand side of Eq. (4) then becomes nearly singular, and the coefficients $A_n$ are determined by small differences between large numbers. This occurs for example if two oscillators are chosen to represent absorption at energies $E_n\gtrsim 3E_f$, for which the dispersion curves are nearly constant over the measurement interval, or if too many oscillators are chosen too close together. Under these conditions, it is possible to obtain nonphysical solutions for which some of the $A_n$ are negative. We have found that this effect currently leads to practical limits of $E_{n=1}=0$, $E_{n=N}'\cong 2E_f$, and $N=6$.

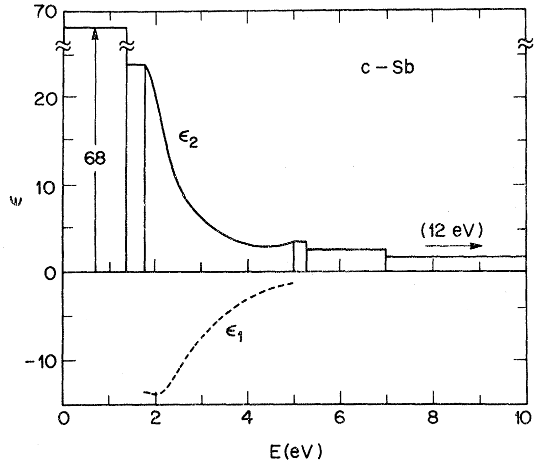

FIG. 2. Five-oscillator extension of $\epsilon_2(E)$ for an optically thick polycrystalline Sb film, based on extrapolation of ellipsometric data over the range 1.8–5.0 eV.

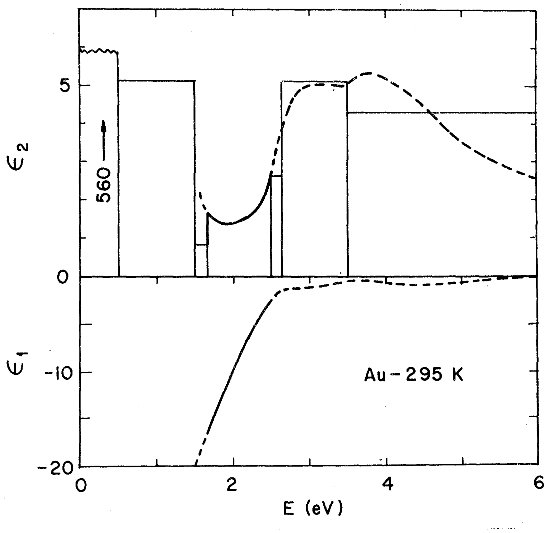

FIG. 1. Six-oscillator extension of $\epsilon_2(E)$ for Au, based on extrapolation of ellipsometric data over the range 1.65–2.50 eV as the heavy solid lines. For comparison purposes, the measured data from 1.5 to 6.0 eV are shown as the dashed lines.

The oscillator-fitting procedure also places relatively stringent requirements on the accuracy of the values of $\epsilon_1'(E_j)$ in Eq. (4). We found that a large source of inaccuracy in evaluating Eq. (4) when $\epsilon_2\neq 0$ occurs in calculating the Kramers-Kronig integral. The usual method of direct application of Simpson's rule is inaccurate by as much as several percent. This is beyond acceptable tolerences of about 0.1%, a limit which we have observed by applying the method to theoretical exact lineshapes. Simpson's rule in effect integrates in closed form the best-fit parabola to the *integrand* taken three points at a time. We eliminated the inaccuracy by fitting the parabola to the *data*, $\epsilon_2$, instead of the entire integrand, before performing the closed-form integration.[14–16]

As a test of the extrapolation procedure, we show in Fig. 1 the energy dependence of the extension of $\epsilon_2$ calculated by fitting the measured dielectric function of a thick Au film over the relatively nar-

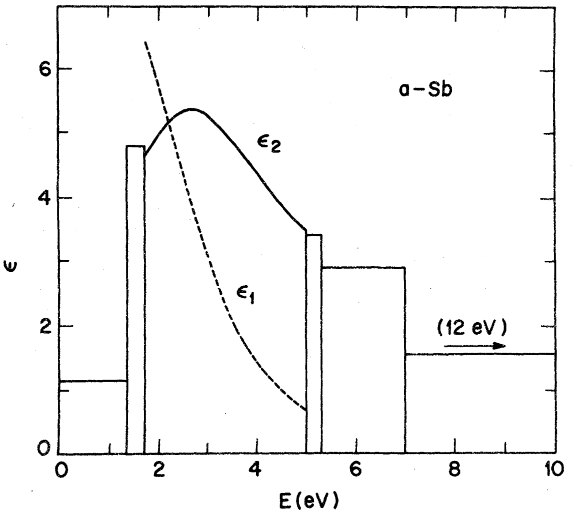

FIG. 3. Five-oscillator extension of $\epsilon_2(E)$ for an optically thick amorphous Sb film, based on extrapolation of ellipsometric data over the range 1.8–5.0 eV.

row energy range 1.65–2.50 eV, indicated by the solid lines. The data were actually taken from 1.5 to 6.0 eV, as indicated by the dashed lines. $\epsilon_1$ shows a rapid increase over the narrow range. Thus, $\epsilon_1$ shows the onset of the strong absorption edge at 2.5 eV, due to *d*-band Fermi-level transitions,[17] well before its actual appearance in $\epsilon_2$. A useful extrapolation procedure should be able to extract not only the approximate location, but also the magnitude of this edge in $\epsilon_2$ from the $\epsilon_1$ data below 2.5 eV. As can be seen from Fig. 1, the general behavior of $\epsilon_2$ above 2.5 eV is indeed given quite well by the extrapolation procedure. The extended dielectric function shows a decrease at higher energies, in agreement with the data measured over the wider interval.

We consider next the extrapolation of the spectra shown in Figs. 2 and 3 for polycrystalline and amorphous Sb films, respectively.[18] Ellipsometric data were taken from 1.8 to 5.0 eV, and $\epsilon_2$ was extended with 5 oscillators to cover the range 0 to 12 eV. The negative but rising variation of $\epsilon_1$ with $E$ from 1.8 to 5.0 eV in Fig. 2 indicates qualitatively that the polycrystalline Sb film is metallic (actually semimetallic), so that most of the oscillator strength should occur below 1.8 eV. The quantitative extrapolation demonstrates this clearly. The extended part of $\epsilon_2$ rises to very large values as $E \rightarrow 0$, and little oscillator strength remains above 5 eV. The general features of this spectrum are in very good agreement with the *n*, *k* data of Cardona and Greenaway,[19] who obtained the optical functions of crystalline Sb from a Kramers-Kronig analysis of reflectance data from 1 to 20 eV.

By contrast, the positive but falling variation of $\epsilon_1$ with $E$ from 1.8 to 5.0 eV for the amorphous Sb film in Fig. 3 indicates qualitatively that this film is a semiconductor, with a substantially greater amount of oscillator strength remaining above 5 eV than for the polycrystalline film. Quantitative verification is obtained by the extrapolation procedure, which shows in addition that the peak in $\epsilon_2$ seen in the measurement interval near 2.7 eV is in fact the absolute maximum of the $\epsilon_2$ spectrum. The oscillator strength is seen to drop off sharply below 1.4 eV, a conclusion not obvious from a visual inspection of $\epsilon_1$. This result is consistent with transmission measurements, which show an absorption threshold for this material in the near ir.[18]

We have used the extrapolation procedure to extend ellipsometrically measured dielectric function data for thin films, such as native oxides, as well as for bulk samples as discussed here. We are currently investigating other calculation methods to extrapolate dielectric function data in greater detail. It is clear that extrapolation techniques cannot hope to achieve resolution attainable with direct measurements. But these methods should be useful for the many physical systems, such as liquid-solid or gas-solid interfaces, which have a window only in the visible or near-uv spectral region, or which are not compatible with the high-vacuum environment needed for vacuum-uv measurements.

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