

Overlayer effects in the critical-point analysis of ellipsometric spectra: Application to $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys

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We investigate the effect of incomplete removal of semiconductor overlayers on critical-point (CP) parameters determined from the analysis of ellipsometric spectra. An approximate analytic expression shows that CP energies and broadening parameters should be relatively unaffected for isolated CPs if the dielectric response of the overlayer varies slowly with energy. The results are confirmed by model calculations for InAs, which show that the energies of the E_1 and $E_1 + \Delta_1$ CP structures that are commonly used for compositional analysis of semiconductor alloys are relatively unaffected. We also analyze overlayer-removal data for a series of $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloy samples. Consistent with the above, the amplitudes and phases are affected significantly for all CPs, while the energies of the well-separated E_1 and $E_1 + \Delta_1$ transitions are relatively invariant. The results show that accurate values of composition can be obtained from the analysis of the E_1 and $E_1 + \Delta_1$ CP structures, even if complete removal of overlayers is not achieved. © 2008 American Institute of Physics. [DOI: 10.1063/1.2902502]

I. INTRODUCTION

Critical-point (CP) analysis of dielectric-function data obtained by spectroscopic ellipsometry (SE) has been widely used to obtain the compositions of semiconductor alloys through critical-point energies determined from these data.^{1–7} The strong dependence of these data on overlayers also makes SE an important tool in determining film thicknesses. However, this same sensitivity complicates efforts to extract CP parameters that are characteristics of the associated excitations. If the thickness d and dielectric function ϵ_0 of a given overlayer are known, the SE data can be corrected for its presence. However, since this information is not generally available, a widely used procedure that is generally considered to yield the most accurate results is the removal of overlayers by chemical etching assessed in real time.^{8,9} A challenge in practice is that complete removal of overlayers cannot generally be expected.

The question then arises as to what extent CP parameters are affected by these overlayers, and, in particular, whether any of these parameters are relatively insensitive to their presence. We recently reported a theoretical analysis addressing these issues.¹⁰ Here, we extend our earlier treatment and consider the $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys for testing the validity of the proposed theory.

II. EXPERIMENTAL

$\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys films were grown on (001)InP substrates by solid-source molecular beam epitaxy.¹¹ $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers 1 μm thick were grown at 510 °C at a rate of 0.6 $\mu\text{m}/\text{h}$. These thicknesses were well beyond those required for lattice relaxation, so the measured dielectric re-

sponses can be considered to represent those of unstrained material. The compositions of the layers were determined by high-resolution x-ray diffraction. Details of the growth are provided in Ref. 11.

SE data from 1.5 to 6.0 eV were obtained with the previously described ellipsometer¹² converted to rotating-compensator operation. Complex-reflectance-ratio spectra ρ were calculated from the measured Fourier coefficients by curve fitting. The ρ spectra were then converted by the two-phase (substrate/ambient) model to pseudodielectric function $\langle\epsilon\rangle = \langle\epsilon_1\rangle + i\langle\epsilon_2\rangle$ form, which is the dielectric response of a hypothetical substrate where roughness is absent. The samples were at room temperature. Overlayers were removed by flowing appropriate etchants over the vertical surfaces of the samples while maintaining them in a dry N_2 ambient to avoid atmospheric contamination. Processing was repeated until the $\langle\epsilon\rangle$ spectra showed no further changes. This occurred at the highest value of the E_2 peak of $\langle\epsilon_2\rangle$, thereby indicating that the most abrupt interface had been achieved with the given combination of chemicals.⁸ To obtain information on overlayer effects, spectra were obtained before, during, and after processing.

III. RESULTS AND DISCUSSION

A. Chemical etching

Figure 1 shows the change of $\langle\epsilon(\omega)\rangle$ during overlayer removal for $\text{In}_x\text{Ga}_{1-x}\text{As}$ samples with $x=0.00, 0.17, 0.34, 0.49$, and 0.66 . Overlayers were removed through successive applications of a 1:5 mixture of NH_4OH and methanol, a 0.05% solution of bromine in methanol, de-ionized water, and methanol. Chemical processing was repeated until the $\langle\epsilon\rangle$ spectra showed no further change. The initial, one intermediate, and the final “best” spectra are shown for $\langle\epsilon_2\rangle$ for

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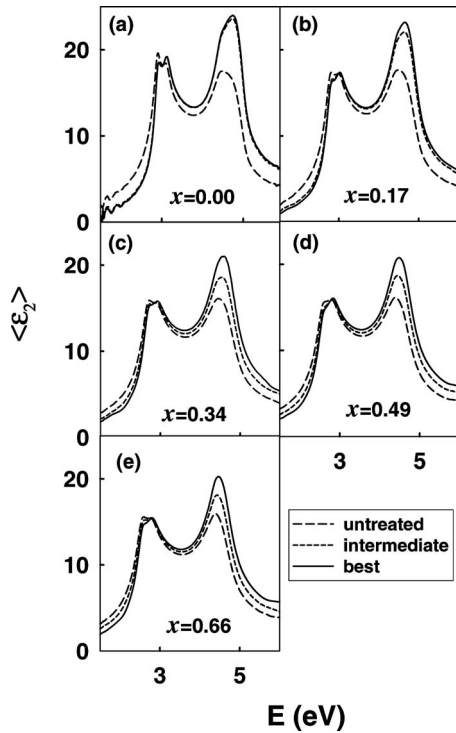


FIG. 1. $\langle \epsilon_2 \rangle$ data obtained before (long dashed), during (short dashed), and after (solid) overlayer removal for a series of $\text{In}_x\text{Ga}_{1-x}\text{As}$ films. The compositions x are indicated in the panels.

the different alloys in Fig. 1. The increase of $\langle \epsilon_2 \rangle$ at the E_2 peak and decrease below the E_1 structure as the overlayers are removed are consistent with the expectation.

Surface roughness is always a possible by-product of chemical etching, although only that on the nanometer scale is relevant for $\langle \epsilon \rangle$. To investigate the effect of such roughness on $\langle \epsilon \rangle$, we performed model calculations of $\langle \epsilon \rangle$ assuming that the spectra with the highest value of the E_2 peak of $\langle \epsilon_2 \rangle$ is the substrate dielectric function ϵ , and that the substrate is covered with a rough surface of thickness d whose dielectric response is given by a Bruggeman effective-medium mixture of 50% air and 50% ϵ .^{13,14} The results for InAs for several thicknesses are shown in Fig. 2, where the identification of the CP structures is that given in Ref. 11. It is clear that the

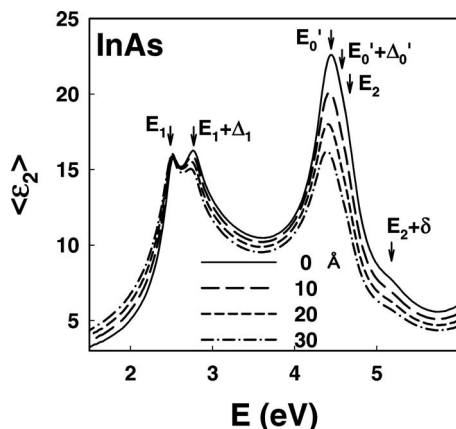


FIG. 2. $\langle \epsilon_2 \rangle$ spectra of InAs calculated for different thicknesses of an assumed overlayer representing roughness on the nanoscopic scale. The identification of the CP structures is that of Ref. 11.

existence of surface roughness of an equivalent thickness of even 1 nm would cause a strong decrease of the E_2 peak at the $\langle \epsilon \rangle$ spectrum of InAs. While we have no way of being certain, the fact that the same E_2 peak height of $\langle \epsilon_2 \rangle$ is obtained through several sequences of chemicals suggests that surface roughness is probably unimportant for samples for which the best spectra are obtained.

B. Theory

With overlayers present, the complex-reflectance ratio ρ of the sample measured by SE is described by the three-phase (substrate/overlayer/ambient) model. Results are usually presented in as pseudodielectric functions $\langle \epsilon \rangle$ form, where $\langle \epsilon \rangle$ is the dielectric function calculated from ρ in the two-phase (substrate/ambient) model, i.e., ignoring the possible existence of overlayers. If the overlayer thickness d is much less than the wavelength λ , the three-phase (substrate/overlayer/ambient) model can be expanded to first order in d/λ to give¹⁵

$$\langle \epsilon \rangle \approx \epsilon_s + \frac{4\pi id}{\lambda} \epsilon_s^{3/2}, \quad (1)$$

which is valid when $|\epsilon_a| \ll |\epsilon_o| \ll |\epsilon_s|$, where ϵ_a and ϵ_s are the dielectric functions of the ambient and substrate, respectively. Under these conditions, ϵ_o does not appear in the expression. If ϵ_o and ϵ_a are comparable, then the first-order term must be multiplied by $(1 - \epsilon_a/\epsilon_o)$, but to reduce the complexity of the resulting expressions we ignore this factor here. We obtain useful information about the effect of overlayers on CP parameters by considering a model substrate dielectric function consisting of a single oscillator on a uniform background ϵ_{so} :

$$\epsilon_s = \epsilon_{so} + \frac{Ae^{i\phi}}{(E - E_g + i\Gamma)^n}. \quad (2)$$

If the second term is much smaller than the first, we can expand $\epsilon_s^{3/2}$ as

$$\epsilon_s^{3/2} \approx \epsilon_{so}^{3/2} + \frac{3}{2} \frac{Ae^{i\phi}}{(E - E_g + i\Gamma)^n} \epsilon_{so}^{1/2}. \quad (3)$$

If $|\epsilon_a|, |\epsilon_o| \ll |\epsilon_s|$, we obtain

$$\langle \epsilon \rangle \approx \epsilon_s + \frac{4\pi id}{\lambda} \left(1 - \frac{\epsilon_a}{\epsilon_o} \right) \epsilon_s^{3/2} \quad (4a)$$

$$= \left[1 + \frac{4\pi id}{\lambda} \left(1 - \frac{\epsilon_a}{\epsilon_o} \right) \epsilon_{so}^{1/2} \right] \epsilon_{so} + \left[1 + \frac{6\pi id}{\lambda} \left(1 - \frac{\epsilon_a}{\epsilon_o} \right) \epsilon_{so}^{1/2} \right] \frac{Ae^{i\phi}}{(E - E_g + i\Gamma)^n}. \quad (4b)$$

This result shows that for small d/λ the singularity is simply multiplied by a complex constant, so the presence of the overlayer has negligible effect on either E_g or Γ . On the other hand, A and ϕ are obviously modified. This treatment is clearly a simplification, but it does provide insight as to which CP parameters are likely to be the most strongly affected by the overlayers. The result is promising because it suggests that the CP energies, the quantities usually of most

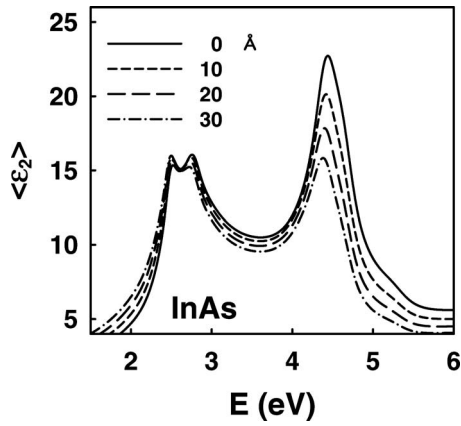


FIG. 3. As Fig. 2, but for an assumed oxide overlayer.

interest, are somewhat independent of the presence of overlayers.

To assess the validity of these conclusions, we generated model data for InAs for oxide coverages of 0, 10, 20, and 30 Å, using literature dielectric-function spectra for InAs (Ref. 9) and its oxide.¹⁶ Results for $\langle \epsilon_2 \rangle$ are shown in Fig. 3. These spectra show typical behavior, with a strong reduction of the amplitude of the E_2 peak of $\langle \epsilon_2 \rangle$ near 4.8 eV with increasing oxide thickness. CP parameters were extracted from these spectra by calculating second energy derivatives numerically and performing least-squares fits to the results using standard analytic expressions:^{17,18}

$$d^2\epsilon/d\omega^2 = n(n-1)Ae^{i\phi}(E_g - E + i\Gamma)^{n-2}, \quad n \neq 0, \quad (5a)$$

$$= Ae^{i\phi}(E_g - E + i\Gamma)^{-2}, \quad n = 0, \quad (5b)$$

where the CP is described by an amplitude A , threshold energy E , broadening Γ , phase ϕ , and order n . Second derivatives calculated for oxide coverages of 0 (open circles) and 30 Å (solid squares) along with best fits are shown in Fig. 4. Extracted CP parameters are shown in Fig. 5(a) for ϕ , 5(b) for E_g , and 5(c) for Γ . Consistent with theory, the E_1 and $E_1 + \Delta_1$ CP energies and broadening parameters show virtu-

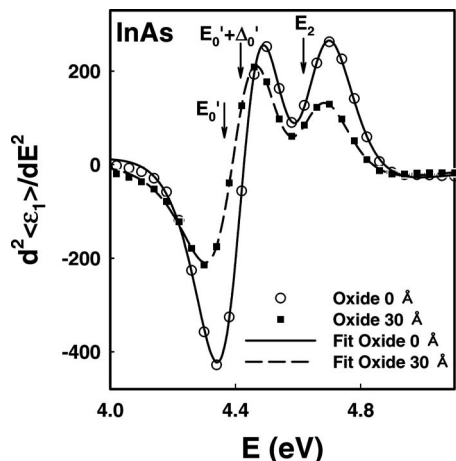
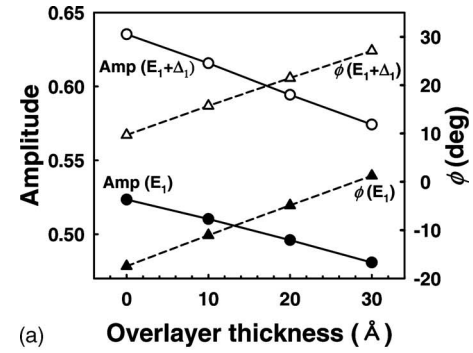
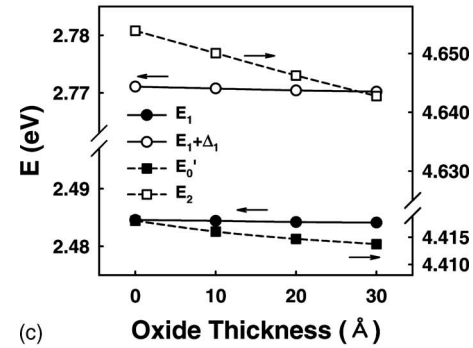


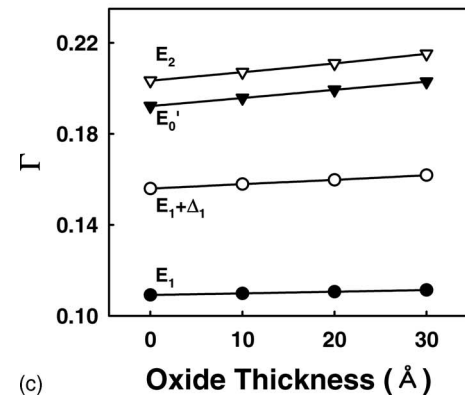
FIG. 4. Numerically calculated second derivatives of the $\langle \epsilon_2 \rangle$ spectra of InAs for oxide coverages of 0 (open circles) and 30 Å (solid squares). Best fits in the E_2 region for 0 and 30 Å coverages using standard analytic expressions are shown as the solid and dashed lines, respectively.



(a) Overlayer thickness (Å)



(c) Oxide Thickness (Å)



(c) Oxide Thickness (Å)

FIG. 5. Dependence of amplitude and phase (a), energy (b), and broadening (c) of the parameters of the E_1 , $E_1 + \Delta_1$, E_0' , and E_2 CPs vs d , obtained by analyzing the false-data spectra of Fig. 3.

ally no change with overlayer thickness, although dependences are seen in the E_2 region. The E_2 variations are probably not surprising, because the spectra here are complicated, containing contributions from several closely spaced CPs, and the oxide exhibits substantial spectral dependence there as well. On the other hand, Fig. 5(a) shows that the amplitude for both peaks changes significantly with overlayer thickness. Therefore, we conclude that where CP structures do not overlap and ϵ_0 varies relatively slowly with energy, the CP energies are basically unaffected by the presence of overlayers.

The same conclusions apply to the roughness effects shown in Fig. 2. This is particularly important because oxide removal can be followed relatively easily in real time, but roughness is much more difficult to detect and eliminate.

C. $\text{In}_x\text{Ga}_{1-x}\text{As}$ data

We now consider the $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys as a critical test, using the overlayer-removal data of Fig. 1. These data were

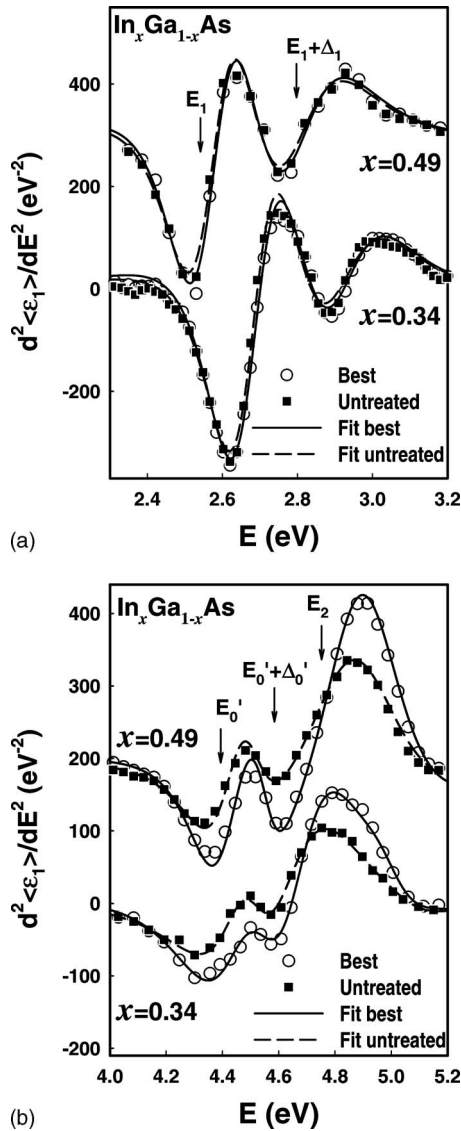


FIG. 6. Numerically calculated second derivatives of the $\langle \epsilon_2 \rangle$ spectra of $\text{In}_x\text{Ga}_{1-x}\text{As}$ in the E_1 (a) and E_2 (b) spectral regions for $x=0.34$ and 0.49 for untreated (solid squares) and best (open circles) conditions. The dashed and solid lines are the best fits of the standard analytic expression to these data. The $x=0.49$ spectra are offset by 300 eV^{-2} (a) and 200 eV^{-2} (b).

differentiated numerically to second order with respect to energy by the same procedure described in previous section. Some of the results obtained by fitting standard analytic expression are shown in Fig. 6. As expected, in the E_1 and $E_1 + \Delta_1$ peak regions [Fig. 6(a)], the difference of derivative spectra with and without an overlayer present is negligible, whereas that in the E_2 peak region is significant [Fig. 6(b)]. The resulting CP energies of the E_1 transitions are shown in Fig. 7(a) on the scale of Fig. 5(b) for easy comparison, while those for E_2 are shown in Fig. 7(b). To reduce complexity in the display, the energies of the $E_1 + \Delta_1$ CPs were not shown. However, the results are the same as for the E_1 CPs. Even if the variations of CP energies with thickness of the data [Fig. 7(a)] are slightly larger than those of the theory [Fig. 5(b)], we can conclude that the experimentally determined E_1 (and $E_1 + \Delta_1$) CP energies are almost independent of overlayer thickness, exhibiting less than a 10 meV difference from start to finish. However, the amplitude and phase are very

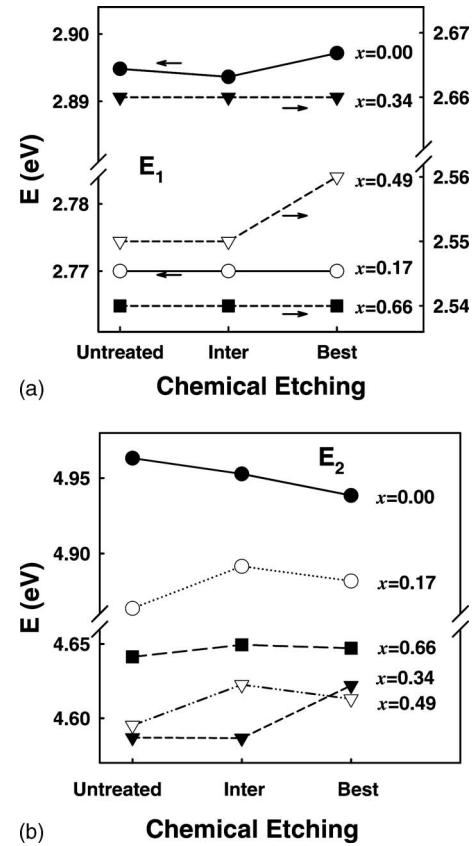


FIG. 7. Variations of the E_1 (a) and E_2 (b) CP energies at different stages of overlayer removal for the data of Fig. 1.

sensitive to overlayers, which can be expected from the noticeable shape changes seen in Fig. 1. In contrast, Fig. 7(b) shows that the changes of the CP parameters in the E_2 region are unacceptably large. This is not surprising, because the E'_0 , $E'_0 + \Delta'_0$, and E_2 CPs that occur in this energy range lead to a single broad peak, as seen in Fig. 1. Therefore, as is well known, this region is not suitable for compositional analysis.

IV. CONCLUSION

We present an analytic approximation, false-data calculations, and real-time etching data of InGaAs alloys as an example to show that the energies of the well-separated E_1 and $E_1 + \Delta_1$ CPs are relatively independent of overlayer thicknesses, in contrast to the fairly large changes seen in their amplitudes and phases and in the energies of the E_2 peak. Because the E_1 and $E_1 + \Delta_1$ structures are the ones commonly used for compositional analysis, we conclude that accurate compositional results can be obtained even if complete overlayer removal cannot be achieved. However, we emphasize that for accurate determination of CP parameters, overlayers should be removed as much as possible since the line shape distortions caused by overlayers influence the remaining CP parameters.

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- ¹S. M. Kelso, D. E. Aspnes, M. A. Pollack, and R. E. Nahory, *Phys. Rev. B* **26**, 6669 (1982).
- ²J. Humlicek, M. Garriga, M. I. Alonso, and M. Cardona, *J. Appl. Phys.* **65**, 2827 (1989).
- ³P. G. Snyder, J. A. Woollam, S. A. Alterovitz, and B. Johs, *J. Appl. Phys.* **68**, 5925 (1990).
- ⁴R. Lange, K. E. Junge, S. Zollner, S. S. Iyer, A. P. Powell, and K. Eberl, *J. Appl. Phys.* **80**, 4578 (1996).
- ⁵S. G. Choi, Y. D. Kim, S. D. Yoo, D. E. Aspnes, D. H. Woo, and S. H. Kim, *J. Appl. Phys.* **87**, 1287 (2000).
- ⁶H. Kanazawa, S. Adachi, T. Yamaguchi, S. Murashige, and K. Murakami, *J. Appl. Phys.* **86**, 2611 (1999).
- ⁷C. M. Herzinger, H. Yao, P. G. Snyder, F. G. Celii, Y. C. Kao, B. Johs, and J. A. Woollam, *J. Appl. Phys.* **77**, 4677 (1995).
- ⁸D. E. Aspnes and A. A. Studna, *Appl. Phys. Lett.* **39**, 316 (1981).
- ⁹D. E. Aspnes and A. A. Studna, *Phys. Rev. B* **27**, 985 (1983).
- ¹⁰Y. W. Jung, T. H. Ghong, Y. D. Kim, and D. E. Aspnes, *Appl. Phys. Lett.* **91**, 121903 (2007).
- ¹¹T. J. Kim, T. H. Ghong, Y. D. Kim, S. J. Kim, D. E. Aspnes, T. Mori, T. Yao, and B. H. Koo, *Phys. Rev. B* **68**, 115323 (2003).
- ¹²D. E. Aspnes and A. A. Studna, *Appl. Opt.* **14**, 220 (1975).
- ¹³D. E. Aspnes, *Thin Solid Films* **89**, 249 (1982).
- ¹⁴J. L. Freeouf, *Appl. Phys. Lett.* **53**, 2426 (1988).
- ¹⁵J. D. E. McIntyre and D. E. Aspnes, *Surf. Sci.* **24**, 417 (1971).
- ¹⁶S. Zollner, *Appl. Phys. Lett.* **63**, 2523 (1993).
- ¹⁷M. Cardona, in *Modulation Spectroscopy*, Solid state Physics, Supplement No. 11, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969).
- ¹⁸D. E. Aspnes, in *Handbook on Semiconductors*, edited by M. Balkanski (North-Holland, Amsterdam, 1980), Vol. 2, p. 109.