Effect of overlayers on critical-point parameters in the analysis of ellipsometric spectra

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As the complete removal of overlayers may not be possible in general, the authors investigate the effect of incomplete removal on critical-point parameters in the analysis of ellipsometric data. Using an approximate analytic expression, they show that energies and broadening parameters are much less affected by overlayers than amplitudes and phases. These conclusions are confirmed by false-data calculations for GaAs and overlayer-removal data for CdTe. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2784187]

Spectroscopic ellipsometry (SE) has been widely applied to study dielectric responses of semiconductors, and, in particular, the critical-point energies used to assess alloy compositions.[1–6] SE is sufficiently surface sensitive to determine overlayer thicknesses in the picometer range.[7] Unfortunately, this sensitivity becomes a disadvantage when the objective is to obtain the intrinsic dielectric response of a material and may also be a disadvantage in determining the critical-point (CP) energies E_g on which compositional analysis of semiconductor alloys depends. The two basic methods of dealing with overlayer effects are the direct approach of removing them as far as possible by chemical processing[7,8] and the indirect method of correcting for their effects mathematically when the thickness and dielectric function of the overlayer are known. Since complete removal is not expected to occur even in the most favorable circumstances, it is important to assess the effects of overlayers on CP parameters, particularly the CP energies that are commonly used for compositional analysis of semiconductor alloys.

As the influence of overlayers on CP parameters appears not to have been investigated previously, we examine the topic here in three ways: first, by a general analytic approximation, second, by false-data calculations for GaAs, and third, by the analysis of overlayer-removal data for CdTe. We find that the CP energies E_g and broadening parameters Γ are relatively unaffected, at least for the E_1 and $E_1+\Delta_1$ transitions that are usually used for compositional analysis, whereas the amplitudes A and phases ϕ are affected to a much larger extent. The results indicate that it is possible to obtain accurate values of E_g even when complete removal cannot be demonstrated or achieved.

To provide an analytic assessment, we take advantage of the fact that the thicknesses d of the overlayers are typically much less than the accessible wavelengths λ to approximate the exact three-phase-model equations to first order in d/λ. In this approximation $\langle\varepsilon\rangle$ can be written as[9]

$$\langle\varepsilon\rangle \approx \varepsilon_s + \frac{4\pi i d}{\lambda}\varepsilon_s^{3/2}, \tag{1}$$

where $\varepsilon_a \ll \varepsilon_o \ll \varepsilon_s$. Here, ε_a, ε_o, and ε_s are the dielectric functions of the air ambient, overlayer, and substrate, respectively. If $\varepsilon_o \sim \varepsilon_a$, then the first-order term must be multiplied by $(1-\varepsilon_a/\varepsilon_o)$, but we ignore this factor here in the interest of reducing the apparent complexity of the resulting expressions. To obtain insight as to how overlayers might affect CP parameters, we use for the substrate a model dielectric function consisting of a single oscillator on a uniform background ε_{so},

$$\varepsilon_s = \varepsilon_{so} + \frac{Ae^{i\phi}}{(E-E_g+i\Gamma)^n}. \tag{2}$$

Making the assumption that the second term in Eq. (2) is much smaller than the first, we can expand $\varepsilon_s^{3/2}$, obtaining

$$\langle\varepsilon\rangle \approx \left[\varepsilon_{so} + \frac{4\pi i d}{\lambda}\varepsilon_{so}^{3/2}\right] + \frac{Ae^{i\phi}}{(E-E_g+i\Gamma)^n}\left[1 + \frac{6\pi i d}{\lambda}\varepsilon_{so}^{1/2}\right]. \tag{3}$$

The result shows that the singularity is simply multiplied by a complex constant; hence, with these approximations, the presence of the overlayer has no effect on either E_g or Γ. On the other hand, A and ϕ are affected directly. The above model is obviously a simplification, but it does provide insight as to which CP parameters are likely to be the most strongly affected.

To assess the validity of these conclusions, we first analyze false data for GaAs for oxide coverages of 0, 10, 20, and 30 Å. The data were generated using literature dielectric-function spectra for GaAs (Ref. 8) and its oxide.[10] The $\langle\varepsilon_2\rangle$ results are shown in Fig. 1. These spectra show typical behavior, with a strong reduction occurring in the amplitude of the E_2 peak of $\langle\varepsilon_2\rangle$ near 4.8 eV with increasing overlayer thickness. We extracted CP parameters from these spectra by calculating their second energy derivatives and performing least-squares fits to model dielectric functions containing CP structures of the form given above. The results are shown in Fig. 2(a) for the amplitude and phase and in Fig. 2(b) for E_g and Γ. Consistent with the theory, the amplitude and phase show strong overlayer dependences, whereas the E_1 and E_1

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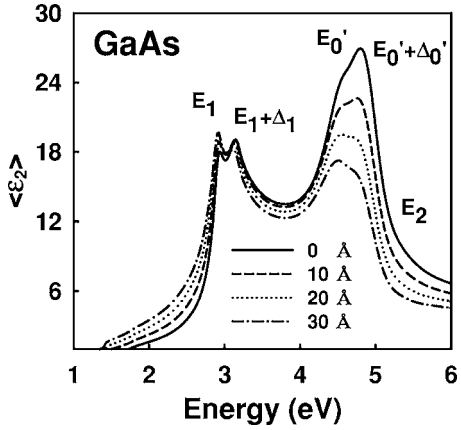

FIG. 1. $\langle \varepsilon_2 \rangle$ spectra for GaAs with oxide overlayers of different thicknesses. The overlayer spectra were calculated in the three-phase model.

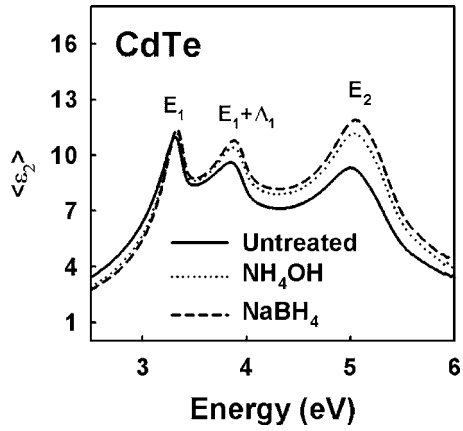

FIG. 3. $\langle \varepsilon_2 \rangle$ data for CdTe at three different stages during overlayer removal.

$+\Delta_1$ CP energies and broadening parameters show virtually no change with overlayer thickness, although a dependence is seen at the E_0' and $E_0'+\Delta_0'$ structures in the E_2 peak region. This is probably not surprising because spectra in the E_2 region are rather complicated and also correspond to the absorption edge of the oxide overlayer. However, for the simple case of nonoverlapping CPs in the spectral range where the oxide dielectric function is relatively independent of energy, the approximation is seen to be quite good.

As a second test, we investigate the critical-point energies of CdTe using data obtained before, during, and after overlayer removal. The $\langle \varepsilon \rangle$ spectra of molecular-beam-epitaxy-grown CdTe were obtained from 1.5 to 6.0 eV using an automatic spectroscopic rotating-compensator ellipsometer operating at an angle of incidence of 67.08°.[11] The CdTe sample was mounted vertically, and overlayers were removed by flowing NH_4OH and $NaBH_4$ solutions over the surface followed by water rinses. Processing was done at room temperature, and surfaces were maintained in a filtered N_2 ambient to minimize the possibility of atmospheric contamination. Treatments continued until the $\langle \varepsilon \rangle$ spectra showed no further changes, which also corresponded to the highest values of $\langle \varepsilon_2 \rangle$ in the region of the E_2 peak, thereby indicating that overlayers had been removed to the extent possible with the chemical etching procedure whose result is shown in Fig. 3. The critical-point energies calculated as described above are shown in Fig. 4 and are entirely consistent with the conclusions drawn from the approximate expression and the false-data calculations involving GaAs. Judging from the significant increase of the E_2 peak in Fig. 3, roughness caused by overlayer removal is probably negligible. A detailed treatment will be given elsewhere.[12]

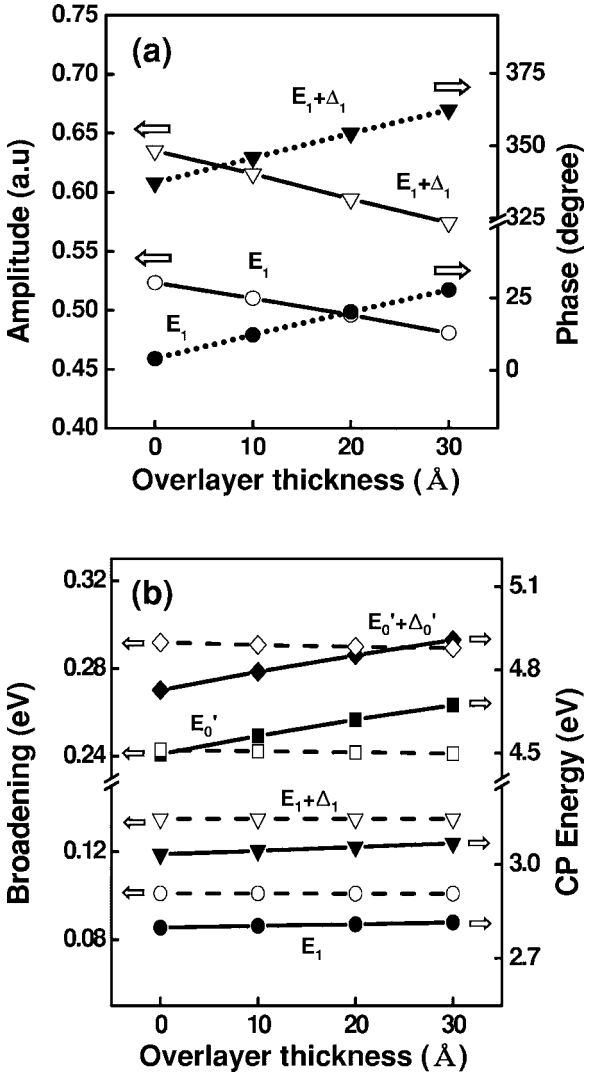

FIG. 2. (a) Dependence on overlayer thickness of the amplitudes A and phases ϕ of the E_1 and $E_1+\Delta_1$ transitions evaluated from the false data of Fig. 1. (b) Same for the critical-point energies E_g and broadening parameters Γ of the E_1, $E_1+\Delta_1$, and E_2-region (E_0' and $E_0'+\Delta_0'$) peaks.

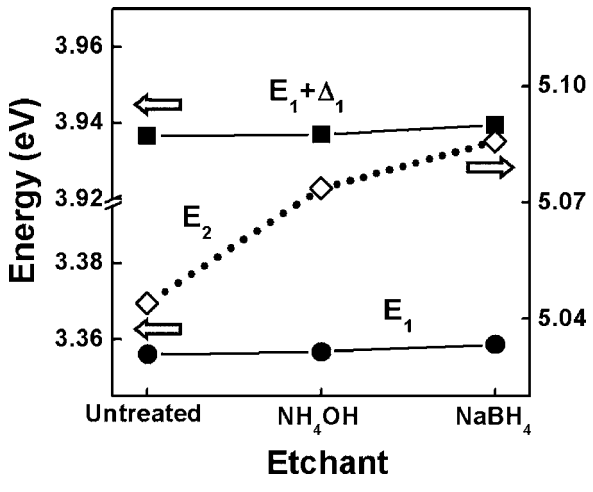

FIG. 4. As Fig. 2 for the data of Fig. 3.

In conclusion, an analytic approximation, false-data calculations, and the analysis of overlayer-removal data show that the CP energies for the E_1 and $E_1+\Delta_1$ transitions are essentially unaffected by overlayers, whereas the energies obtained in the E_2 spectral range show dependences. Because the E_1 and $E_1+\Delta_1$ structures are those commonly used for compositional analysis, the results indicate that accurate critical-point energies can be obtained even if complete overlayer removal is unattainable. However, we emphasize that for accurate determination of CP parameters, overlayers should still be removed to the extent possible because the lineshape changes caused by overlayers affect the remaining CP parameters.

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