Comparative Study of Defects in Semiconductors by Electrolyte Electroreflectance and Spectroscopic Ellipsometry

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It is shown that, because of the electrostriction and polarization of defects by the modulating electric field, electroreflectance spectra are more affected by defects than are third-derivative spectra from ellipsometry data. The theory of electroreflectance is generalized to include these effects. Plasticity and long-range strains are shown to lead to a first-derivative line shape and polarizable defects to a second-derivative line shape. For defect-rich samples these new terms dominate the usual third-derivative line shape.

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Low-field electrolyte electroreflectance (EER) has been used primarily to determine accurately the interband transition energies, E_j, in semiconductors. According to the existing theory[1,2] the EER spectrum is proportional to a linear combination of the third derivatives of the real and imaginary parts, ϵ_1 and ϵ_2, of the complex dielectric function, $\epsilon(E)$, with respect to energy. This third-derivative expression leads to an approximate parameterized functional form,[2] the third-derivative functional form (TDFF), which fits remarkably well[3] the EER spectra obtained from defect-free semiconducting surfaces. The fits yield values for the critical energy E_j, the linewidth Γ_j, and the phase θ_j associated with the jth transition. Because $\epsilon_1(E)$ and $\epsilon_2(E)$ can be measured by automatic spectroscopic ellipsometry (ASE), it is also possible to compute numerically from the independently measured ASE data the third-derivative line shape (TDL) which, according to this theory, should be proportional to the EER line shape.

However, our EER data for mercury cadmium telluride ($Hg_{1-x}Cd_xTe$) cannot be well fitted by the TDFF and are in serious disagreement with the TDLs obtained from ASE data. In particular, we have studied the effects of different surface treatments on EER spectra[4,5] and have reported[4] that chemical or chemomechanical treatment of the surface of $Hg_{1-x}Cd_xTe$ samples substantially changes the linewidth and overall shape of their EER spectra. In contrast, Arwin, Aspnes, and Righer[6,7] have recently presented ASE results which show that similar surface treatments performed on comparable samples do not measurably affect the linewidth of the TDL. This contrast between EER and ASE results led us to suspect[5] the possibility of an interaction between the EER modulating electric field and the defects. This idea was further supported by the failure of the conventional TDFF to fit most $Hg_{1-x}Cd_xTe$ EER spectra except over a narrow range around each critical-point energy.

These results have led us to formulate a new, more general theory of EER which incorporates the effect of defects on the electroreflectance line shape and thus allows us to obtain quantitatively information about defects in near-surface regions of defectuous semiconductors such as $Hg_{1-x}Cd_xTe$. This treatment includes two new terms resulting primarily from the electrostriction and polarization of defects by the EER modulating electric field, and extends the applicability of the attractively simple EER technique to the study of defects in semiconductors.

In a systematic study we have obtained and analyzed the EER and ASE spectra of over 100 samples. For materials with a low defect density ($\leq 10^5$ etch pits per cm^2)[8] the agreement between EER and the ASE-derived TDL was excellent. On the other hand, for materials with a high defect density the agreement was poor, with the EER spectra being much broader than the TDL. However, provided the range of the fit of the TDFF to the EER data was limited to the vicinity of the critical energy, the values of E_j determined from EER and ASE data were the same. The parameter most affected by defects was the value of the linewidth Γ_j determined from the EER spectra; it approximately doubled for defectuous materials. Representative examples are given in Fig. 1, in which the depth-profile EER results for E_1 and Γ_1 are compared to the values obtained from ASE data on the same sample. The agreement on E_1 is excellent, whereas the values of Γ_1 differ by a factor of 2.

In previous theoretical treatments of the EER line shape the primary effect of the modulating electric $\vec{E}$ field has been assumed to be the accel-

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eration of the excited electrons and the resultant breakdown of translational symmetry.[1,2] The effects of $\vec{E}$ on the E_j and on the defect scattering strengths have been assumed to be negligible. We have generalized the low-field theory in the simplest way consistent with our observations. To this end we introduce the quantity σ^2 of Lukes and Somaratna,[9] which is the mean square defect-induced deviation from the crystal potential. We then abandon the usual assumption of the field independence of the E_j and σ^2 and introduce new parameters ΔE_j and $\Delta\sigma$.[2,10] The small increments ΔE_j can arise from piezoelectric strain in nonelemental semiconductors, in which case it is linear in $\vec{E}$,[11] or from the electrostriction of defects, in which case both linear and quadratic terms in $\vec{E}$ can be important. The increment $\Delta\sigma^2$ results from the polarization of defects by the modulating field $\vec{E}$.

Upon allowing σ^2 and the E_j to depend on $\vec{E}$, we find that the field-induced change in that part of the dielectric function which results from the jth critical point is

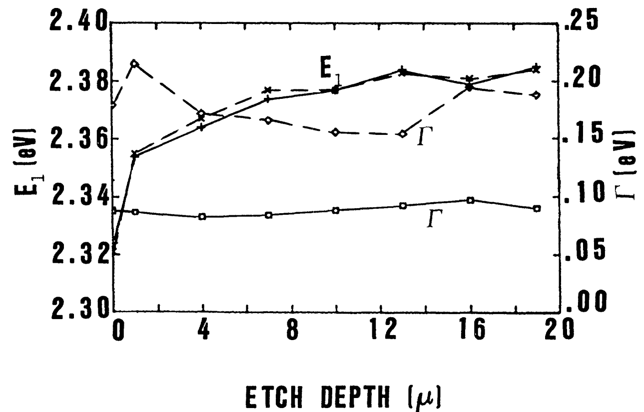

FIG. 1. Values of the energy E_1 and the linewidth Γ_1 from ASE (solid lines) and EER (dashed lines) data as a function of etch depth from a representative $Hg_{1-x}Cd_xTe$ depth profile. The EER values were found by fitting with the third-derivative functional form (TDFF) of Aspnes.

$$\Delta\epsilon_j(E_+,\vec{E}) = i(C_{0j}/E_+)^2\int_{\rm loc} d^3k\int_0^\infty ds\,\exp\{is[E_+ - E_j(\vec{k})] - 2\sigma_0^2 s^2\} \times [\exp\{-is\Delta E_j - 2s^2\Delta\sigma^2 - \tfrac{1}{3}i(s\hbar\Omega_j)^3\} - 1]. \quad (1)$$

Here $E_+ \equiv E + i\Gamma_j$, C_{0j} is a real constant, the subscript "loc" on the first integral denotes an integral over only that region of $\vec{k}$ space close to the E_j critical point, $E_j(k)$ is the interband transition energy at $\vec{k}$ points in that region, σ_0 is the value of σ for $\vec{E}=0$,

$$\Delta E_j = E_j(\vec{E}) - E_j(\vec{E}=0),$$

$$\Delta\sigma^2 = \sigma^2(\vec{E}) - \sigma_0^2,$$

$$\hbar\Omega_j \equiv (e^2E^2\hbar^2/8\mu_j)^{1/3},$$

and μ_j is the appropriate interband reduced mass.

Equation (1) reduces to Eq. (2.3b) of Ref. 2 in the case $\Delta E_j = \sigma_0^2 = \Delta\sigma^2 = 0$. The terms proportional to σ_0^2, ΔE_j, and $\Delta\sigma^2$, *a priori*, should all be retained. However, we have shown[12] that even for extremely defectuous semiconductors the term proportional to σ_0^2 can be neglected; the only additional terms left are those proportional to ΔE_j and $\Delta\sigma^2$. Following the same procedure as was used in deriving the original TDFF, one now finds from Eq. (1) the generalized functional form (GFF)

$$L(E) = C_jE^{-2}[(\hbar\Omega_j)^3L(E,\tfrac{5}{2}) - 4\Delta\sigma^2L(E,\tfrac{3}{2}) - 4\Delta E_jL(E,\tfrac{1}{2})] \quad (2)$$

for the EER line shape, where

$$L(E,n/2) = \cos(\theta_j - n\Phi_j/2)[(E-E_j)^2 + \Gamma_j^2]^{-n/4} \equiv L_n, \quad (3)$$

with

$$\Phi_j = \tan^{-1}[\Gamma_j/(E-E_j)].$$

Here, C_j and θ_j have a weak dependence on energy, which is easily taken into account by the introduction of Seraphin coefficients.[13] That energy dependence is, however, usually ignored because the evaluation of the Seraphin coefficients requires an independent knowledge of the real and imaginary parts of the dielectric function and because neglecting it only affects the determination of the parameter θ_j, leaving E_j and Γ_j essentially unaffected.

It is apparent that the GFF reduces to the conventional TDFF upon setting ΔE_j and $\Delta\sigma^2$ equal to zero, with L_5 being proportional to the TDFF. For $n=1$ and $n=3$, L_n is proportional to the first and second derivatives, respectively, of the same linear combination of ϵ_1 and ϵ_2 as occur in the TDFF. It is clear that L_3 and L_1 have qualitatively different

shapes from the TDFF and from one another.

We have compared the fits given by the GFF with those given by the TDFF. Figure 2 shows the result of a typical fitting of the TDFF and the GFF to a $Hg_{1-x}Cd_xTe$ sample with a comparatively low defect density; the TDFF fits were even worse for more defectuous samples. Both fits were performed simultaneously at E_1 and at $E_1+\Delta_1$. We have found that the use of the TDFF with defectuous materials yields the correct values for the critical energies but presents the following difficulties: (a) The fit is accurate only over the limited range $|E-E_j|<\Gamma_j$ and, in effect, behaves as an elaborate three-points method.[2] (b) The value obtained for the linewidth Γ_j is much larger than the value obtained from ASE data using the TDL. (c) It requires a parametrized constant or linearly varying background, which is outside the theory, the physical meaning of which is obscure, and which often is too large to be physically reasonable.

All three of these difficulties are eliminated by the use of the GFF. First, upon fitting the EER spectra in the vicinity of both E_1 and $E_1+\Delta_1$, the GFF yields an accurate fit over the entire experimental energy range. Second, because for fixed Γ_j the new terms L_1 and L_2 are much broader than is the third-derivative term, L_3, the GFF gives a value

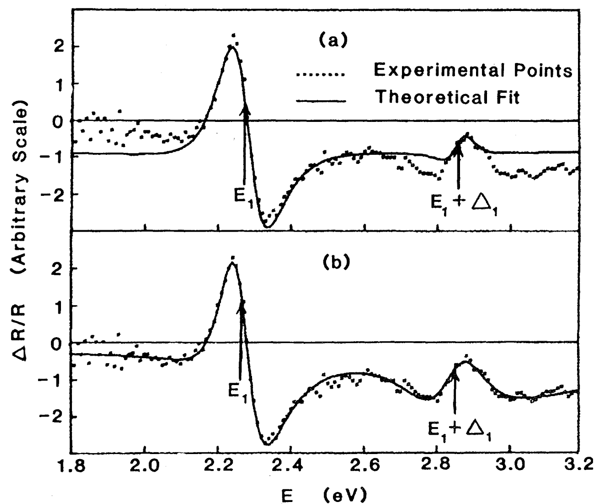

FIG. 2. Comparison of the results obtained by fitting the same experimental data using (a) the TDFF and (b) the GFF. The values obtained for the energies E_1 and $E_1+\Delta_1$ by the two methods are in very good agreement. The TDFF yields 2.275 and 2.861 eV while the GFF yields 2.265 and 2.856 eV. The values for Γ_j yielded by the TDFF are 100 and 60 meV, while the values yielded by the GFF are 90 and 139 meV.

of Γ_j in agreement with that found from ASE data. Finally, upon zeroing of the average value of the EER spectra over the entire experimental range, the use of the GFF, unlike that of the TDFF, does not require the introduction of an additional background term.

Two questions remain: (1) Does the GFF yield correct or physically reasonable values for the remaining parameters, namely θ_j, ΔE_j, and $\Delta\sigma^2$? (2) Can one rule out all causes for the difficulties encountered in using the TDFF in the study of defectuous materials other than the neglect of the interaction of the electric field with the defects?

Both questions can be answered affirmatively. We consider first the values of the remaining parameters. Upon assuming a value of 10 to 20 meV for $\hbar\Omega_j$, we find quite plausible ranges of values for ΔE_j and $\Delta\sigma^2$, namely $\Delta E_j \leq 1$ meV and $\Delta\sigma^2 \approx 2\sigma\Delta\sigma \leq 100$ meV^2.[14] Moreover, the variations in the values of ΔE_j and $\Delta\sigma^2$ make physical sense. In areas of high strain, such as epilayer/substrate interfaces, or in areas with many extended defects (as measured by etch-pit densities), ΔE_j tends to be comparatively large. On the other hand, for the one sample we measured in which etch-pit density was low and in which piezoelectric effects were symmetry forbidden,[11] ΔE_j was found to vanish. For samples with high impurity concentrations (as measured by low-temperature mobilities), it is $\Delta\sigma^2$ which tends to be large. In especially defectuous samples both are very large. Finally, the value of θ_j can also be accurately determined if the Seraphin coefficients[13] are introduced in the GFF.

With respect to the second question, there are only two other approximations to consider—the low-field approximation and the parabolic-band approximation. The first of these allows us to expand the second complex exponential in Eq. (1) in a Taylor series, retaining only the first-order terms. To establish its validity, we have performed calculations using an expression for the line shape in which higher-order terms in the expansion are retained. Those terms were found to be very small, the quality of the fit to our data was not improved significantly, and the values of the parameters E_j, Γ_j, ΔE_j, and $\Delta\sigma^2$ were essentially unchanged. Thus, the low-field approximation is valid even for the case of highly defectuous materials. The validity of the parabolic-band approximation is easily established by the use of the GFF to fit a TDL. We find that in such a fit both ΔE_j and $\Delta\sigma$ become vanishingly small, which they must, and that the TDFF fits the TDL perfectly. Thus, because the parabolic-band approximation is not involved in the

TDL, this approximation cannot be responsible for the failure of the TDL to fit EER data. Finally, because ΔE_j and $\Delta\sigma^2$ are found to become a factor of 10 smaller in relatively defect-free samples than in defectuous samples, it is clear that in defectuous samples the dominant contributions to these quantities arise from defects. Polarization analysis will shed further light on this question.

We conclude that for all noncentrosymmetric semiconductors and for defectuous narrow-gap semiconductors the line shape of Eq. (2) is the appropriate generalization of the conventional TDFF. It not only is phenomenologically far superior to the TDFF, but also is more physically meaningful for at least two reasons. First, it takes into account the electrostriction and the polarization of the bulk and near-surface defects by the modulating electric field. Second, it takes into account the linear piezoelectric effect, which is important in all noncentrosymmetric semiconductors, both in compounds such as the blendes and in all alloyed or severely defectuous semiconductors. For example, the theory presented here allows one for the first time to fit the line shape of the linear piezoelectric spectrum of GaAs, which was isolated and observed by Rehn.[11] The GFF yields an excellent fit to that line shape with no third-derivative term and with the ratio $\Delta E_1/\Delta\sigma^2$ much larger than in $Hg_{1-x}Cd_xTe$, as one would expect. We conclude that the parameter ΔE_j contains a part linear in $\vec{E}$ which measures the linear piezoelectric effect and a part primarily quadratic in $\vec{E}$ which measures at least qualitatively plasticity and long-range strains, and that the parameter $\Delta\sigma^2$ is proportional to the density of polarizable defects and contains parts linear and quadratic in $\vec{E}$.

This generalization enables the EER to provide significant new information not available from ASE measurements. Moreover, the simplicity of the technique and of the fitting procedure makes EER particularly valuable for the exploration of the effects of surface treatments in semiconductors.

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