Observation of Transitions between Electronic States at the (111) *A* Face of CdTe by Electrolyte Electroreflectance

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The observation of a large piezoelectric contribution to the electroreflectance signal from the (111) *A* face of CdTe is reported. This contribution, which is absent from the *B*-face signal, is associated with two-dimensional interfacial strains between the *A* face and a thin native oxide film. Line-shape analysis is used to verify the nature of this contribution and to obtain values for the transition energy and other quantities which characterize the electronic band structure at the interface.

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We report here the results of a comparative study of the *A* and *B* polar (111) faces of CdTe by electrolyte electroreflectance (EER). Even though the use of an ambient technique such as EER to study CdTe makes inescapable the presence of a native oxide layer which inhibits[1] surface reconstruction, a giant local piezoelectric contribution to the *A*-face signal was observed, whereas the *B*-face signal contained no such contribution. A large signal of the type which we have observed from the *A* face of CdTe can arise only from unusually large electric-field–driven local distortions on or near that surface, i.e., only from a large local piezoelectrical effect. Therefore, we must conclude that there exists a region of greatly lowered stability associated with the oxidized *A* face but not with the oxidized *B* face, which exhibits no such signal. We interpret this lowered stability as arising from bond bending at the *A* interface between the CdTe and its native oxidized surface film. As is shown in detail in this communication, a careful analysis of the data imposes the conclusion that the observed giant piezoelectric signal arises primarily from a two-dimensional interfacial region having a thickness of no more than two or three atomic layers.

We believe these striking results to be related to differences between the reconstruction of the clean *A* face of CdTe and that of the clean *B* face. It is well known both experimentally[2] and theoretically[3] that the reconstruction of the clean *A* face of zinc-blende materials differs substantially from that of the clean *B* face. In particular, the *A*-face reconstruction involves a much greater lowering of the energy; thus it is more difficult for an oxide film to inhibit totally the reconstruction of the *A* face. Also, the *A*-face reconstruction involves the formation of a large number of cation vacancies[1-4] which would remain after oxidation, whereas the *B*-face reconstruction does not.[1-3]

Recently, we have generalized[5] the electroreflectance (ER) theory of Aspnes[6] to account quantitatively for the effects of piezoelectricity, strain, polarizable defects, and alloy disorder (where applicable). Our results show that piezoelectric shifts as small as 10^{-4} eV in either local or bulk interband transition energies give rise to ER signals not previously understood. These signals, which were observed[7,8] as early as 1966, have a line shape substantially different from that of the usual ER line shape[6] and in the absence of inversion symmetry also have a different dependence on the modulating electric field $\mathbf{E}_M$. This effect is greatly enhanced by the existence of lowered structural stability, such as that expected at the *A* face of CdTe. In the absence of this effect, because the light penetration in the energy range of interest is at least of order 100 Å one would expect the ER line shape to contain only a very small contribution from the interface region. However, our theory suggests that a marked lowering of the structural stability at the *A*-face interface could lead to an electrostrictive polarizability large enough to allow one to sample the two-dimensional interface region independently of the bulk, even though it occupies only a small fraction of the total volume probed.

Our experimental results have confirmed this suggestion in a spectacular manner. For the same crystals we found very similar bulk EER signals from the *A* and *B* faces but found the *A* faces to exhibit a large additional linear piezoelectric signal at a somewhat higher critical energy. We have confirmed the nature of this additional signal by line-shape analysis and by a study of its dependence on E_M. The EER system, which is described elsewhere,[9] was use to obtain spectra in the vicinity of the E_1 critical point from (111)-oriented CdTe samples.

Typical EER spectra obtained from *A* and *B* faces of the same sample are shown in Fig. 1; the difference between the two line shapes is obvious. This difference is independent of the electrolyte used (organic[9] or $\frac{1}{10}N$ KOH or $\frac{1}{5}N$ lactic acid) and was observed for all our single-crystal samples. These samples were of varied origin and were grown by different methods. The quantitative results discussed here were obtained from a sample carefully selected to be of exceptional structural quality which was given a careful chemomechanical bromine/methanol polish to produce relatively damage-free surfaces. This treatment is standard for CdTe wafers prior to epitaxial HgCdTe growth. Both A and B faces are easily polished and epitaxial layers can be grown on both types of surfaces.

EER spectra were obtained at six different modulation voltages from 5 to 30 V in order to analyze the dependence on E_M of the amplitudes of the various contributions to the total line shape. In addition, automatic spectroscopic ellipsometry (ASE) was used to determine the optical properties of both the Cd and the Te faces, and the third-derivative spectra were numerically computed and compared to the EER results.

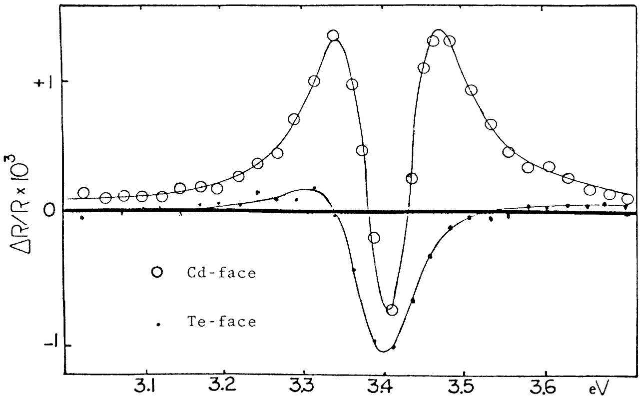

FIG. 1. Best fits of Eq. (2) to the ER signals from the Cd and Te faces (or A and B faces) of a CdTe crystal. The Te-face signal was obtained with a modulation voltage $V_M = 4$ V, whereas the Cd-face signal was obtained with $V_M = 30$ V. Thus, the Te-face signal is a factor of 7.5 smaller than the third-derivative component of the Cd-face signal which digs a sharp hole in the positive first-derivative piezoelectric component.

For any derivative spectroscopy, such as ER, the line shape arises primarily from interband transitions in the immediate vicinity of critical points in the Brillouin zone. In general, the contribution of a given interband transition and given critical point to the low-field ER line shape is given by the expression

$$L_j(E) = A\{-\Delta E_j D_j^{(1)}(E) + [\Delta\sigma^2 + \tfrac{1}{2}(\Delta E_j)^2] D_j^{(2)}(E) + \tfrac{1}{3}(\hbar\Omega_j)^3 D_j^{(3)}(E)\}. \tag{1}$$

Here, A is a constant independent of the modulating field $\mathbf{E}_M$, ΔE_j and $\Delta\sigma^2$ are the shifts due to $\mathbf{E}_M$ in the critical-point interband transition energy E_j and in the mean squared scattering potential σ^2 from defects and/or alloy disorder, respectively, and $\hbar\Omega_j$ is the energy gained from the field $\mathbf{E}_M$ by the optically excited carriers. The term quadratic in ΔE_j, which is negligible in most cases, is included because ΔE_j is expected to be unusually large for the A face, whereas $\Delta\sigma^2$ is expected to be relatively small. The functions $D_j^{(m)}(E)$ are given by the equations

$$D_j^{(m)}(E) = E^{-2}[\alpha\, \partial^m E^2 \epsilon_{1j}/\partial E^m + \beta\, \partial^m E^2 \epsilon_{2j}/\partial E^m],$$

where α and β are the Seraphin coefficients[10] and ϵ_{1j} and ϵ_{2j} are the real and imaginary parts of that part of the dielectric function which arises from the given interband transition in the vicinity of the given critical point. Note that ΔE_j and $\Delta\sigma^2$ contain parts linear in $\mathbf{E}_M$ for any crystal not having inversion symmetry and for surface effects, whereas $(\hbar\Omega_j)^3$ is strictly quadratic in $\mathbf{E}_M$.

For the E_1 critical point, which for CdTe has dimensionality $d = 2$, when we make the usual approximations,[6] Eq. (1) reduces to the closed form

$$L_1(E) = C\{-\tfrac{3}{2}[\Delta E_1 L_1^{(1)}(E) + (2\Delta\sigma^2 + (\Delta E_1)^2) L_1^{(2)}(E)] + (\hbar\Omega_1)^3 L_1^{(3)}(E)\}. \tag{2}$$

Here C is another constant independent of $\mathbf{E}_M$, and

$$L_1^{(m)}(E) = \frac{\cos(\theta_1 - m\Phi_1)}{[(E-E_1)^2 + \Gamma_1^2]^{m/2}}, \tag{3}$$

where θ_1 is a phase angle which is treated as a parameter, Γ_1 is a phenomenological broadening parameter, and Φ_1 is given by the expression

$$\Phi_1 = \tan^{-1}[\Gamma_1/(E - E_1)].$$

Both Eqs. (1) and (2) reduce to the corresponding Franz-Keldysh results of Aspnes[6] for the case in which $\Delta E_j = \Delta\sigma^2 = 0$.

The final expression used to fit our EER data was obtained by substitution of Eq. (3) into Eq. (2) and allowing an adjustable constant background, which is assumed to arise from any surface film present and/or from the tails of signals from critical points distant in energy. The quantities $C\Delta E_1$, $C\Delta\sigma^2$, $C(\hbar\Omega_1)^3$, θ_1, E_1, and Γ_1 usually are treated as free parameters, although E_1 and Γ_1 could have been determined from ASE and held fixed.

The B-face line shape contained only a negligible first-derivative term and a small second-derivative term and could be well fitted in terms of a single transition between bulk states in the vicinity of a single critical point. On the other hand, the A-face spectra contained a large first-derivative contribution associated with a giant electrostrictive polarizability on that face and a substantial second-derivative term in addition to the usual third-derivative Franz-Keldysh term.

In considering the physical interpretation of these results we must examine the implications of the fact that our measurement was not made in vacuum and therefore that both surfaces of the crystal were covered by a native oxide. Our ASE measurements and others[11] show that such oxide layers grow only two or three atomic layers (~ 7 Å) in the period of time after etching during which we carry out our measurements. Their spectra are featureless in the spectral region of interest and make no observable contribution to the EER signal; moreover, the difference between the A- and B-face signals is unaffected by the thickness of the native oxide (at most 30 Å). Therefore, *the semiconductor/oxide interface of the A face must differ markedly from that on the B face, and the large magnitude of the additional first-derivative A-face signal must arise from a large linear electrostrictive polarizability associated with the A interface.*

In order to test whether the large first-derivative contribution to the A-face line shape arises from the interface region or from the bulk, we attempted first to fit the A-face line shape in terms of a single transition between bulk states. Somewhat to our surprise, we found a reasonable fit, although the data displayed a small asymmetry not reproduced well by the fit. In this fit we found $\Delta\sigma^2$ to be comparable for the two faces but found ΔE_1 to be large for the A face. However, we found E_1 to be 25 meV higher and Γ_1 to be 25 meV smaller for the A face than for the B face, showing the fit and hence the assumption of a single bulk transition to be incorrect for the A face. This conclusion was confirmed by comparison with ASE, which showed the E_1 value to be correct for the B face but not for the A face. Also, the B-face line shape could be fitted after being numerically differentiated, but the A-face line shape could not be. Thus, the first-derivative piezoelectric signal must arise from different transitions from those which give rise to the bulk third-derivative signal. Those transitions must be confined to a region near the A face with depth considerably less than the depth of light penetration.

Having established that the first-derivative signal arises from an interfacial region which includes no more than one layer of oxide and does not reach far into the bulk, we then addressed the question. "Does that region include only one or two atomic layers or does it extend several atomic layers into the bulk?" In order to answer this question we fitted the A-face data as the sum of two line shapes—one from the bulk having no first-derivative (piezoelectric) term and one from the interfacial region having no third-derivative term. Second-derivative terms, which result from polarizabile defects, were allowed in both line shapes. Because the two line shapes had been shown to arise from different regions of the crystal, we allowed all parameters to vary independently for each of them. Best fits to the data for both faces are shown in Fig. 1, and values of the significant field-independent parameters obtained from those fits are shown in Table I. The bulk values found for E_1 were essentially the same for the A and B faces, but the first-derivative signal from the interfacial region gave a transition energy larger by ~ 44 meV and a broadening parameter of only ~ 60 meV, smaller than the A-face bulk value by ~ 33%. If the interfacial region extended several atomic layers into the bulk, the transition energy would vary smoothly as a function of depth, leading to an inhomogeneous broadening of the first-derivative signal, contrary to what is seen. *Thus, the first-derivative piezoelectric signal must arise from an interfacial region having a thickness of no more than one or two atomic layers.* The origin of the observed narrowing of the line shape in the interfacial region is not clear; it could arise from a different atomic structure at the interface. The best fits also give a value of $\Delta\sigma^2$ for the A-face bulk line shape approximately 3 times as large as that for the B-face line shape. We attribute this result at least in part to the effect of vacancies associated with the original A-face reconstructions which remained after oxidation.

In order further to check the validity of our model for the observed A-face line shape, we determined the dependence of the parameters $(\hbar\Omega_b)^3$, ΔE_s, $(\Delta\sigma^2)_b$, and $2(\Delta\sigma^2)_s+(\Delta E_s)^2$ on the modulation voltage V_M, which according to the Schottky barrier theory is proportional to E_M^2. (Here, the subscripts s and b denote surface and bulk values, respectively.) We found the following results in agreement with theory, which

TABLE I. Values of the interband transition energy E and broadening parameter Γ for bulk states (b) and surface states (s) as measured by EER on the A and B faces of CdTe.

	E_b (eV)	Γ_b (eV)	E_s (eV)	Γ_s (eV)
A face	3.388 ± 0.006	0.092 ± 0.006	3.432 ± 0.006	0.062 ± 0.006
B face	3.379 ± 0.005	0.075 ± 0.005	· · ·	· · ·

predicts that $(\hbar\Omega_b)^3$ is proportional to V_M and that ΔE and $\Delta\sigma^2$ both must be of the form $aV_M^{0.5}+bV_M$:

$$C_b(\hbar\Omega_b)^3=0.0574\,V_M, \tag{4}$$

$$C_s\Delta E_s=-17.29\,V_M^{0.5}+0.38\,V_M, \tag{5}$$

$$C_b(\Delta\sigma^2)_b\approx 0.71\,V_M^{0.5}-0.043\,V_M, \tag{6}$$

$$C_s(\Delta\sigma^2)_s\approx 0, \tag{7}$$

and

$$C_s(\Delta E_s)^2=(C_s\Delta E_s)^2/C_s\approx 0.1724\,V_M. \tag{8}$$

Here, $\hbar\Omega$, E_s, and σ are measured in units of electronvolts, and V_M is measured in volts. From Eqs. (5) and (8) we find $C_s\approx 1.7\times 10^3$ and thus find

$$\Delta E_s\approx -0.01(V_M^{0.5}-0.02\,V_M).$$

The fits of $C_b(\hbar\Omega_b)^3$ and $C_s\Delta E_s$ by Eqs. (4) and (5) are shown in Fig. 2. The relative scatter in the fits by Eqs. (6) and (8) are larger by a factor of about 2 because the quantities being fitted are much smaller. If we assume $(\hbar\Omega_b)^3\approx 3\times 10^{-6}V_M$, which is consistent with estimates of Aspnes,[12] we find $C_b\approx 2\times 10^4$ or $|C_s/C_b|\approx 0.08$. This result is reasonable because the ratio C_s/C_b should be of the same order as the ratio of the thickness of the interfacial region to the depth of light penetration.

Although our results say nothing quantitative about the structure of the *A*-face CdTe/oxide interface, the following possible model for the interface suggests itself. On the *A* face the interface is between a Cd face and the oxide matrix, whereas on the *B* face, it is between a Te face and the oxide matrix. There is no reason to expect the oxide to destabilize the Te face, the reconstruction of which does not involve vacancy formation. However, it is conceivable that oxygen atoms in the first monolayer bond with the Cd face, more or less as Te atoms would, giving a sort of epitaxy between the CdTe and the oxide and inhibiting the reconstruction observed on clean Cd faces. This would explain the observed disappearance of the Cd-face reconstruction upon oxidation. However, because of the Cd-vacancy formation which accompanies the original reconstruction, it would allow large strains and a high polarizability at the interface. The additional *A*-face signal would then come from a highly polarizable two-dimensional Cd(Te,O) crystal residing at the interface between the CdTe *A* face and the native oxide. We summarize our results as follows.

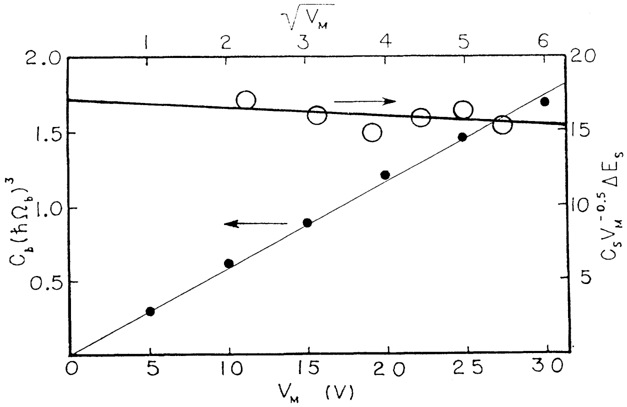

FIG. 2. Straight-line fits of the parameters $C_b(\hbar\Omega_b)^3$ and $C_sV_M^{-0.5}\Delta E_s$ as functions of V_M and $V_M^{0.5}$, respectively, yielded by Eqs. (4) and (5).

We have found that the electroreflectance spectrum of the (111) *A* face of CdTe contains a large anomalous contribution from the linear piezoelectric effect, which is absent on the *B* face. We interpret this contribution as arising from electronic transitions occurring in the two-dimensional *A*-face CdTe/oxide interfacial region, verifying this interpretation by using our generalized theory[5] of electroreflectance to perform a detailed analysis of our EER spectra, including their field dependence. We also offer a model for the structure of this interfacial region. The critical energy and other quantities related to the band structure in the interfacial region were found from an analysis of the EER data.

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