Oxygen-Induced Franz-Keldysh Effect and Surface States on GaAs (110) Surfaces in Ellipsometry

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On (110) GaAs surfaces cleaved in ultrahigh vacuum the changes of the ellipsometric angles $\delta\psi$ and $\delta\Delta$ induced by oxygen adsorption have been measured for photon energies $1.5 < \hbar\omega < 3.5$ eV. The main spectral structure is explained as due to the Franz-Keldysh effect at critical points of the bulk band structure induced by a change of the band bending. From a comparison with electroreflectance data information can be obtained about band-bending changes and about surface states.

Recently ellipsometry[1] has been used, not only to study adsorption processes on crystal surfaces,[2,3] but also as a tool for investigating electronic surface states on semiconductor surfaces.[4-6] For that purpose an ellipsometric spectroscopy is performed in which the changes of the ellipsometric angles $\delta\psi$ and $\delta\Delta$ caused by adsorption of a gas are studied as functions of the photon energy $\hbar\omega$. As a general feature of the ellipsometric spectra measured on semiconducting surfaces,[4-6] a remarkable structure is found not only in the $\delta\Delta(\hbar\omega)$ curves, but also in $\delta\psi(\hbar\omega)$. Since the adsorbed gas layers can be assumed to be optically nonabsorbing[4,5] in most cases, the interpretation of $\delta\psi(\hbar\omega)$ requires the assumption of a surface layer on the clean surface with optical constants different from those of the bulk. Gas adsorption removes this surface layer; i.e., the bulk optical constants after adsorption are valid up to the surface. In previous work this surface layer was interpreted as completely due to surface states which are compensated by the adsorbing gas. The structure found in $\delta\psi(\hbar\omega)$, then, is interpreted as due to the joint density of surface states given on the clean surface. Using this method Meyer and co-workers[4,6] and Morgan[5] derived surface-state transition energies for Si, Ge, and some III-V semiconductor surfaces. In some cases, however, the structure obtained, and also the derived surface-state transitions, is found just at critical points of the bulk electron band structure. Therefore, the question arises if also in these cases surface states cause the structure observed in the ellipsometric spectra. This problem is investigated in detail in the present publication for cleaved (110) GaAs surfaces.

The ellipsometer and the ultrahigh-vacuum (UHV) system used for the present measurements have been described previously.[2] In combination with a series of interference filters, special quarter-wavelength mica plates were used as compensators. The measurements were performed on n-type GaAs (Si-doped with $n = 2.2 \times 10^{17}$ cm^{-3}, $\mu = 3100$ cm^2 V^{-1} sec^{-1}) and p-type GaAs (Cd-doped with $p = 0.9 \times 10^{17}$ cm^{-3}, $\mu = 210$ cm^2 V^{-1} sec^{-1}) crystals. With the use of the double-wedge technique the samples were cleaved in UHV ($< 10^{-10}$ Torr) to expose a (110) surface. Oxygen was used in order to change the surface conditions.[3,7]

The variations $\delta\psi$ and $\delta\Delta$ due to the adsorbed oxygen are plotted versus photon energy in Fig. 1 for n- and p-type samples. As has been shown previously, at these dosages the adsorption pro-

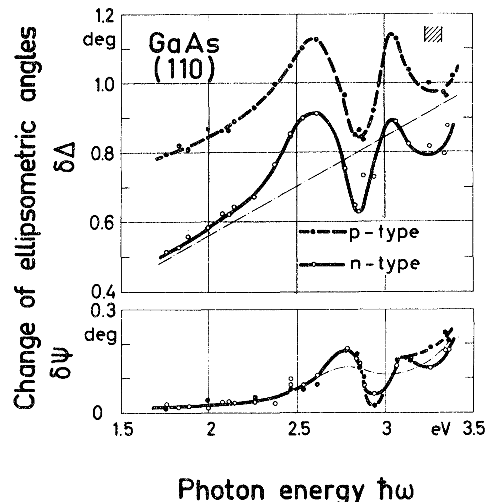

FIG. 1. Changes of the ellipsometric angles $\delta\Delta$ and $\delta\psi$ due to oxygen adsorption at 300 K. The dash-dotted curves describe a calculated contribution which remains after subtraction of the changes induced by the Franz-Keldysh effect.

cess has saturated with a total oxygen coverage of about half a monolayer.[3] $\delta\Delta$ and $\delta\psi$ exhibit a prominent structure between 2.5 and 3.5 eV which is similar for both n- and p-type material concerning sign and absolute amount. The structure of all spectra measured was the same, whereas the absolute height varied over a range which is shown by the two examples plotted.

Two important results must be considered concerning the analysis of the ellipsometric data (Fig. 1). (a) The change $\delta\psi$ is positive all over the spectral range investigated. (b) The main structure of the curves of $\delta\psi$ and $\delta\Delta$ versus photon energy is found just at critical points of the bulk electron band structure.

Result (a) can be explained only by the assumption that the optical absorption within a layer near the surface decreases during the adsorption process.[4] In previous publications this layer was completely attributed to surface states which are removed by the adsorbing gas.

Result (b) bears a great similarity to the well-known electroreflectance spectrum[8] of GaAs [Fig. 2(a)] in which a relative change of the reflectivity $\Delta R/R$ induced by an external electric field is measured as a function of photon energy. A modulated external electric field applied normal to the surface modulates the electric field within the space-charge region (100–1000 Å below the surface) giving rise to a change of the reflectivity mainly near critical points of the bulk band structure[8] (Franz-Keldysh[9,10] effect). Seraphin[11] has already emphasized the importance of electroreflectance measurements for surface studies on semiconductors. The structure in the electroreflectance spectrum on GaAs [Fig. 2(a)] is caused by two critical points at 2.9 and 3.15 eV.[8]

In the present experiments the band bending of the clean surface is expected to be changed as a result of a charge redistribution at the surface during oxygen adsorption. This might cause a change of the optical constants due to the Franz-Keldysh effect. Hoffmann has already observed a change of the reflectivity of ZnO surfaces near band-gap energy during gas adsorption.[12,13]

From $\delta\psi$ and $\delta\Delta$ obtained in the present experiments by oxygen adsorption, reflectivity changes $\Delta R/R$ for normal incidence are calculated. $\Delta R/R$ versus photon energy is compared with the electroreflectance spectrum measured by Cardona, Shaklee, and Pollack[8] in Fig. 2. The main structure found in the electroreflectance spectrum [Fig. 2(a)] is also obtained in the $\Delta R/R$

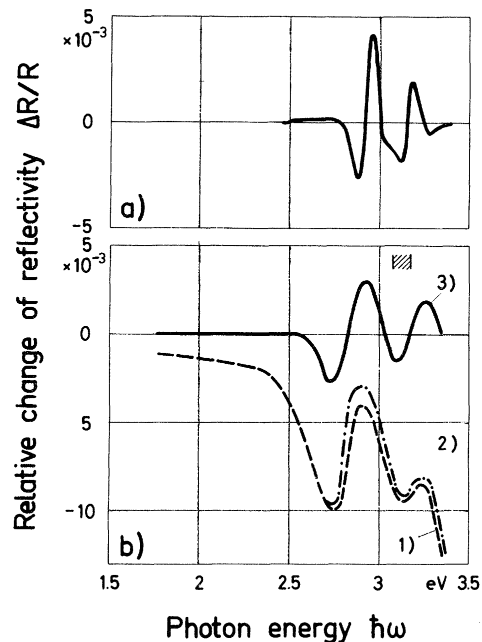

FIG. 2. (a) Electroreflectance spectrum on n-type GaAs after Cardona, Shaklee, and Pollack (Ref. 8). The sign of $\Delta R/R$ is that observed when the negative cycle of the modulating voltage (1 V, rms) is applied to the sample. (b) Relative change of the reflectivity $\Delta R/R$ due to oxygen adsorption as derived from the ellipsometric data: curve 1, calculated from the measured values $\delta\Delta$ and $\delta\psi$; curve 2, corrected by the contribution due to the adsorbed oxygen layer; curve 3, after subtraction of surface-state layer and oxygen contributions.

curves as calculated from the ellipsometric data [Fig. 2(b), curve 1]. Only a monotonic contribution is superimposed.

Good agreement of the ellipsometric with the electroreflectance data is obtained if the whole ellipsometric effect is explained by three contributions: (i) an adsorbed oxygen layer, (ii) a change of the optical constants within the space-charge region due to the Franz-Keldysh effect, and (iii) a change of the optical constants during oxygen adsorption within a very thin surface layer.

Dosages used in the present experiments have been shown previously to produce an oxygen coverage of about half a monolayer.[3] In a macroscopic description this layer [contribution (i)] is assumed to have an effective thickness of 1 Å and a refractive index of $n_{O_2} = 1.5$.[2,3] Contribution (i) does not have much influence on the ellipsometric changes [curves 1 and 2 in Fig. 2(b)].

In order to get best agreement with the electroreflectance data, the difference between the measured and the dash-dotted curves in Fig. 1 is in-

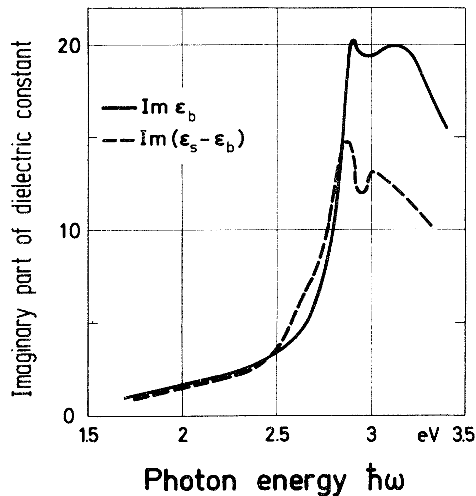

FIG. 3. Imaginary part of the dielectric constant for bulk GaAs, $\text{Im}\epsilon_b$, after Philipp and Ehrenreich (Ref. 15), and additional contribution $\text{Im}(\epsilon_s - \epsilon_b)$ of the surface-state layer (thickness 5 Å).

terpreted as due to the Franz-Keldysh effect. Curve 3 in Fig. 2, then, shows the corresponding reflectivity change induced by the Franz-Keldysh effect [contribution (ii)].

Contribution (iii) might be explained, as in previous work,[2-6] in terms of electronic surface states on the clean surface which are compensated by oxygen adsorption. If the thickness of the surface layer is assumed to be 5 Å[14] (reasonable for the penetration depth of surface states), the optical constants n_s, κ_s and $\text{Re}\epsilon_s, \text{Im}\epsilon_s$, respectively, of this layer can be calculated.[5] Figure 3 shows the imaginary part of the bulk dielectric constant, $\text{Im}\epsilon_b$, as compared with the additional contribution of the surface states $\text{Im}(\epsilon_s - \epsilon_b)$. This comparison indicates that nearly the same transition energies are found between surface-state bands as between bulk electronic bands. Theoretical calculations by Levine[16] also suggest a surface-state band structure for III-V compounds which is similar to that of the bulk. The slight shoulder of $\text{Im}(\epsilon_s - \epsilon_b)$ (Fig. 3) might be explained by an additional critical point of the surface band structure near 2.6 eV.

Another explanation for the similarity between surface-layer and bulk absorption would be that in the spectral range considered the probabilities of bulk electronic transitions very near the surface are decreased because of oxygen adsorption.

The interpretation of contribution (ii) in terms of the Franz-Keldysh effect allows some conclusions concerning the band-bending change induced by oxygen adsorption. In the electroreflectance measurements made by Cardona, Shaklee, and Pollack[8] [Fig. 2(a)], mean electric fields within the space-charge layer of the order of 10^5 V cm^{-1} are applied. Since the absolute height of the present $\Delta R/R$ structure [Fig. 2(b)] is on the order of that of the electroreflectance curves, oxygen is expected to change the space-charge field by a similar amount. As in Gregory *et al.*,[17] the Fermi level at the surface is pinned within ± 0.1 eV for n-type crystals on oxygen adsorption. A band bending of 0.1 eV corresponds to a depth of the space-charge layer of about 400 Å [18]; i.e., the possible maximum band-bending change of 0.2 eV due to oxygen gives a change of the space-charge field between 10^4 and 10^5 V cm^{-1}, in agreement with the estimate derived from the electroreflectance data. This also confirms the interpretation in terms of the Franz-Keldysh effect.

Reflectivity changes induced by the Franz-Keldysh effect depend on the square of the electric field and not on its sign.[9,10] On clean (100) GaAs surfaces of n-type material the space-charge field is directed towards the surface of the crystal (depletion layer).[16] The same field direction is given for the electroreflectance spectrum [Fig. 2(a)] on n-type samples.[8] If in those experiments the space-charge field is decreased, the electroreflectance changes exhibit the same sign as the $\Delta R/R$ curves of the present experiments. Therefore, on clean, cleaved (110) surfaces of n-type samples oxygen must decrease the upward band bending. Because of the uncertainty about the exact amount of the band bending on p-type samples (nearly flat band for $p \approx 10^{17}$ cm^{-3} [18]) the sign of the band-bending change due to oxygen adsorption cannot be derived unequivocally.

The present work shows that electronic surface states can be investigated by ellipsometric spectroscopy but that care must be taken in attributing the spectral structure completely to surface states. This seems justified only if no bulk critical points are found in the considered spectral region.

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[1]In ellipsometry the change of polarization of light upon reflection is measured in terms of the two angles Δ and ψ defined by $r_{\parallel}/r_{\perp}=\tan\psi\,\exp(i\Delta)$, $r_{\parallel}$ and $r_{\perp}$ being the reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively.

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Band Separations and Parity at the L Point in PbTe by Electroreflectance*

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Electroreflectance spectra in PbTe lead to a clear determination of the band separations at L. Our results suggest that the accepted parity labeling of some of these states may be incorrect.

We have made low-temperature electroreflectance (ER) measurements on PbTe which quantitatively establish the band separations at the L point and raise the question of the parity assignments at L. Earlier measurements by Aspnes and Cardona[1,2] and Seraphin[3] indicated the importance of band-population effects in PbTe and other IV-VI materials. We have exploited these effects.

The basis of our study is the knowledge that the fundamental gap is at L and that by changing the band filling at L with the subsequent shift of the Fermi level, the transitions associated with the Fermi level may be spectrally shifted. This has been applied to the study of InSb[4] and PbSe[5] and the basic ideas are discussed in those papers. We now apply this to PbTe.

We have investigated a number of n- and p-type bulk crystals at 10°K over the spectral range 0.3 to 6 eV. The metal-insulator-semiconductor sample preparation and apparatus are essentially the same as that described elsewhere.[4-6]

The results are presented from 0.9 to 2 eV over which we observed the effect of varying the band population. We start with a p sample biasing it so as to move the bands from accumulation toward the flat-band position. The polarity of the nonshifting 1.20-eV $\Delta R/R$ structure is used as the reference for the sign of the surface potential[4,5,7,8] as checked by surface-capacitance measurements. The polarity is negative in our p samples over the available bias range, indicating an accumulation layer. In n material the bands can be moved through the flat-band position as judged again by the polarity of the 1.2-eV structure which now inverts with positive bias. This judgement is complicated by the multiplicity of structure around this energy.

In Fig. 1 we show the ER spectrum for a p sample of carrier concentration $(3-5)\times10^{19}$ cm^{-3}. Note the strong negative peak at 1.20 eV. The negative peaks at 1.5 and 2 eV show a marked red shift with increasing positive bias as indicated by sample p-1, at biases -3 and $+3$ V. There was a shift of 17 meV for the former peak and 27 meV for the latter. Over the bias range -6 to $+6$ V these shifts were 40 and 60 meV, respectively. The bottom spectrum in Fig. 1 is for the same