

## Electronic structure of cleaved clean and oxygen-covered GaAs (110) surfaces

H. Lüth, M. Büchel, R. Dorn, M. Liehr, and R. Matz

2. Physikalisches Institut der Rheinisch-Westfälischen Technischen Hochschule Aachen, 5100 Aachen,  
Federal Republic of Germany

(Received 27 August 1976)

GaAs (110) surfaces of *p*- and *n*-type crystals cleaved in ultrahigh vacuum are investigated by ellipsometry, surface photovoltage (SPV) spectroscopy and low-energy-electron loss spectroscopy (ELS). Changes of the ellipsometric angle  $\delta\Delta$  which are induced by a Franz-Keldysh effect in the space-charge layer due to adsorbed oxygen indicate that oxygen adsorption changes the band bending of the clean surface at dosages ( $\sim 1$  langmuir,  $1 \text{ L} = 10^{-6} \text{ Torrsec}$ ) much lower than those which produce measurable Auger-electron signals. In SPV spectroscopy on a clean, perfectly cleaved (110) surface empty or occupied surface states can not be detected in the forbidden band whereas oxygen adsorption and/or crystallographic defects produce such states. On crystallographic irregularities oxygen also induces a new set of extrinsic surface states close to the valence or the conduction-band edge. The ELS data in combination with SPV results support the interpretation of the Ga(3*d*)-Ga(surface state) transition in terms of a surface exciton. ELS furthermore suggests a contribution of Ga surface atoms to the chemisorption bond of oxygen. The results from ellipsometry and SPV spectroscopy can be understood by means of a model in which two discrete sets of surface states near midgap are induced by adsorbed oxygen.

### I. INTRODUCTION

Although a considerable amount of work has been done on the problem of the electronic structure of clean and oxygen-covered GaAs (110) surfaces the question of band bending, its change due to adsorbed oxygen and of the distribution of surface states does not seem to be answered satisfactorily.

Huijser and Van Laar recently reported work-function measurements on clean GaAs surfaces which imply that on perfect cleaved (110) surfaces no empty surface states exist in the energy region of the band gap ( $\sim 1.4 \text{ eV}$ ).<sup>1</sup> Only on surfaces with measurable step densities Fermi-level pinning near midgap and therefore, surface states in the band gap are observed.<sup>1</sup> These results are in agreement with previous studies of Van Laar and Scheer.<sup>2</sup> From ellipsometric spectroscopy<sup>3</sup> and from high-resolution electron-energy-loss (ELS) studies<sup>4</sup> the conclusions have been drawn that the surface-state distribution on the clean (110) surface is similar to the bulk density of states and that no remarkable surface-state density is found within the forbidden band.

These results are in contradiction to data of Dinan *et al.*<sup>5</sup> which seem to suggest the existence of surface states in the band gap on clean cleaved (110) surfaces. The existence of empty surface states within the forbidden band was further suggested by ELS measurements of Ludeke and Esaki<sup>6</sup> and by photoemission yield spectroscopy performed by Eastman and Freeouf<sup>7</sup> who observed transitions from Ga(3*d*) core levels into states which appeared

to be located in the band gap. Lapeyre and Anderson<sup>8</sup> were the first to point out that these transitions may have excitonic character and that the transition energies not necessarily give the energetic position of single-particle final states. Recent uv photoemission (UPS) and photoemission yield spectroscopic studies of Gudat and Eastman<sup>9</sup> and of Spicer *et al.*<sup>10</sup> now also support the idea that perfect cleaves of (110) surfaces do not exhibit occupied or empty surface states in the band gap, and that defects like steps, etc., and slight contaminations induce surface states and Fermi-level pinning on the cleaved (110) surface.

A further question of controversy is the type of oxygen bonding which has extensively been studied by Dorn *et al.*<sup>11</sup> From As and Ga core-level shifts upon oxidation Spicer *et al.*<sup>10</sup> conclude only bonding to As surface atoms whereas Gudat and Eastman<sup>9</sup> favor a type of chemisorption in which an oxygen atom is bonded simultaneously to an As and a Ga surface atom.

In this controversial situation the present paper is intended to contribute to a better understanding of the GaAs (110) surface. Experimental methods like ellipsometry and surface photovoltage (SPV) spectroscopy<sup>12</sup> which have not generally been applied to this surface up to now have been used to monitor band-bending changes due to oxygen adsorption and to get information about the surface-state distribution within the forbidden band, respectively. Furthermore, ELS studies of the oxygen adsorption on cleaved (110) surfaces of *n*- and *p*-type material support the interpretation of the Ga(3*d*) excitation in terms of a surface

transition and allow the observation of a correlation between this transition and the oxidation process. Similar ELS investigations, but without emphasis on the oxidation process are reported up to now, as far as we know, only on molecular beam prepared GaAs surfaces by Ludeke and Esaki<sup>6,13</sup> and Ludeke and Koma.<sup>14</sup>

## II. METHODS AND EXPERIMENTAL SETUPS

### A. Samples and ultrahigh-vacuum system

All measurements have been performed on ultrahigh-vacuum cleaved GaAs (110) surfaces of *n*-type (Si doped with  $n = 2.2 \times 10^{17} \text{ cm}^{-3}$ ,  $\mu = 3100 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ ) and *p*-type (Cd doped with  $p = 1 \times 10^{17} \text{ cm}^{-3}$ ,  $\mu = 210 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ ) material supplied by HEK (MCP)-GmbH (Lübeck). The crystals had been oriented by x rays and cut into rectangular prisms, usually  $5 \times 5 \text{ mm}^2$  in cross section and 12 mm long. The prisms had grooves on top and bottom for cleavage by means of the double wedge technique. Each cleavage except one (in SPV spectroscopy) resulted in a (110) surface of mirrorlike finish with a very low number of visible tear marks and no crystallographic irregularities. Steps could not be found in low-energy-electron diffraction (LEED) nor with the optical method described previously<sup>15</sup>; i.e., step densities on most of the cleaves must be lower than  $\sim 2\%$ .

The three different types of measurements used in the present investigation were performed in different ultrahigh-vacuum systems (ion pumped stainless-steel chambers,  $p < 1 \times 10^{-10}$  Torr). Like in previous experiments<sup>11</sup> care was taken in avoiding any influence of atomic or ionized oxygen on the measured effects. The ion gauges were hidden in side bent arms and grounded wire grids were used as electrical shields. These procedures, of course, decreased the accuracy of the absolute dosage determination during oxygen exposure.

### B. Ellipsometry

In ellipsometry the change of the state of polarization of light upon reflection is measured in terms of the two ellipsometric angles<sup>16</sup>  $\Delta$  and  $\psi$  (for a review see, e.g., Ref. 17). In the present work only changes  $\delta\Delta = \bar{\Delta} - \Delta$  and  $\delta\psi = \bar{\psi} - \psi$  ( $\bar{\Delta}$ ,  $\bar{\psi}$  values for the clean surface) caused by adsorbed oxygen have been measured. From  $\delta\Delta$  and  $\delta\psi$  changes of the optical constants  $n$  and  $\kappa$  near the surface can be calculated.<sup>3,11</sup> By measuring  $\delta\Delta$  and  $\delta\psi$  in dependence on the incident photon energy  $\hbar\omega$  ellipsometry can be used as a highly sensitive surface spectroscopy to monitor changes in the electronic structure of the surface region (surface states and space-charge layer) (for a review

see, e.g., Ref. 12).

The measurements were performed by means of a "null" ellipsometer in which  $\Delta$  and  $\psi$  are determined by manual compensation. The detailed experimental setup has been described previously.<sup>11</sup>

### C. Surface photovoltage spectroscopy

In SPV spectroscopy the change of the surface potential of a semiconductor due to light irradiation is measured in dependence on the photon energy. Beside electron-hole pair excitation near the band gap energy transitions from bulk impurities and surface states into the bulk conduction band and from the bulk valence band into empty impurity levels and surface states are observed. Knowledge of the Fermi-level position at the surface usually allows to distinguish between these possible types of excitation. A detailed description of SPV spectroscopy and possible experimental equipments has been given elsewhere.<sup>12</sup>

In the present experiments the cleaved GaAs surface is adjusted in front of a fixed opposite electrode (molybdenum grid, mesh width  $250 \mu\text{m}$ ). The monochromatic light incident through the grid onto the cleaved GaAs (110) surface is chopped with 11 Hz, and the resulting ac voltage across crystal and opposite electrode is measured phase sensitively. The whole crystal holder is cooled down to  $\sim 100 \text{ K}$  for cleavage and measurement. Low temperature enhanced the measured signal considerably. A more detailed description of the experimental setup has been given previously.<sup>18</sup>

### D. Electron-energy-loss spectroscopy

In ELS the energy distribution of inelastically scattered electrons is measured. As was shown in a number of publications (see, e.g., Refs. 6, 13, and 19), ELS performed with standard cylindrical mirror analyzers is very useful in studies of the electronic structure of surfaces. Especially, if transitions from sharp well-known core levels into empty bulk and surface states are observed ELS allows the identification of final states with respect to the bulk band structure.<sup>13,14</sup> Measuring the second derivative one can suppress a varying background and gets well-resolved spectra.

The present second-derivative loss spectra have been obtained using a standard cylindrical mirror analyzer (Varian) with integral gun and lock-in differentiation technique. The energy resolution was about 0.7 eV for primary energies below 150 eV. The energetic position of the loss features could be obtained within  $\pm 0.2 \text{ eV}$ .

### III. RESULTS

#### A. Ellipsometry

Spectra of  $\delta\Delta = \bar{\Delta} - \Delta$  obtained by oxygen exposures in the  $10^7$ -langmuir ( $1 \text{ L} = 10^{-6} \text{ Torr sec}$ ) range ( $\frac{1}{2}$  monolayer coverage<sup>11</sup>) are shown in Fig. 1 (inset). The spectra for both  $n$ - and  $p$ -type material are similar except that the absolute values vary from measurement to measurement. The spectral structure between 2 and 3.5 eV has been explained in a previous publication<sup>3</sup> as partially due to a Franz-Keldysh effect within the space-charge layer near bulk critical points at 2.9 and 3.15 eV. Oxygen adsorption changes the band bending of the clean surface, thus also the electric field in the space-charge layer and the optical constants near the surface. Part of the measured effect  $\delta\Delta$  which is shown in dashed-dotted line (Fig. 1, inset) can not be attributed to Franz-Keldysh effect changes of the optical constants but may be due to the removal of intrinsic surface states by the adsorbed oxygen and to the oxygen itself.<sup>3</sup>

Since  $\delta\Delta$  is partially due to an oxygen-induced change of the space-charge field (by Franz-Keldysh effect) it can be used to monitor the corresponding band-bending change. We therefore, have measured  $\delta\Delta$  in the maximum of the spectral structure at 2.54 eV photon energy and in the minimum at 2.85 eV, respectively, in dependence on the oxygen exposure. Figure 1 shows  $\delta\Delta$  (2.54 eV) and  $\delta\Delta$  (2.85 eV) as a function of oxygen dose for  $p$ -type material. First  $\delta\Delta$  changes are observed near 1 L far below those dosages where oxygen starts to

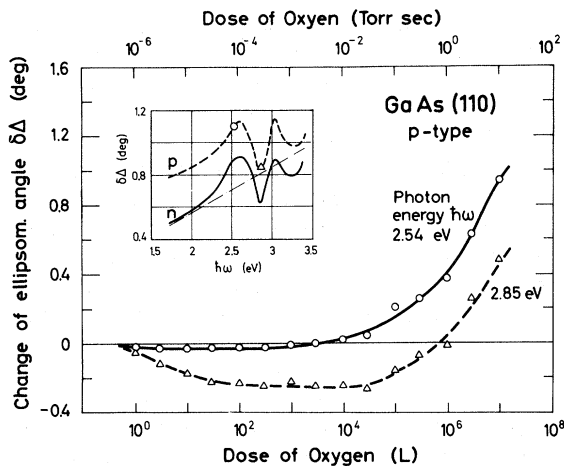


FIG. 1. Change of ellipsometric angle  $\delta\Delta$  vs dose of oxygen measured at the photon energies ( $\hbar\omega$ ) 2.54 and 2.85 eV. Inset: Spectra of ellipsometric changes  $\delta\Delta(\hbar\omega)$  obtained from  $\Delta$  measurements on the clean and oxygen-covered ( $\sim 10^7 \text{ L}$ ) surface [after Dorn and Lüth (Ref. 3)].

show up in Auger electron spectroscopy (AES) [Fig. 5(c)]. In the dosage range  $10^4$ – $10^7 \text{ L}$ , where oxygen appears in the AES spectra a stronger increase of  $\delta\Delta$  (2.54 eV) and  $\delta\Delta$  (2.85 eV) appears which indicates a second effect contributing to the  $\delta\Delta$  changes. Near  $10^7 \text{ L}$  approximately the saturation values shown in Fig. 1 (inset) are reached. The Franz-Keldysh effect part of  $\delta\Delta$  is best described by the difference  $\delta\Delta(2.54 \text{ eV}) - \delta\Delta(2.85 \text{ eV})$  which, therefore, is a measure for the oxygen-induced band-bending change. This quantity in dependence on oxygen exposure is shown in Fig. 5(b) for  $n$ - and  $p$ -type material. Measurable effects are observed near  $10^{-1} \text{ L}$  and  $1 \text{ L}$  for  $n$ - and  $p$ -type surfaces, respectively, i.e., Franz-Keldysh effect starts to show up at dosages far below  $10^2 \text{ L}$ , where on  $n$ -type material  $\frac{1}{100}$  of a monolayer of oxygen is expected to be on the surface according to Fig. 5(c). The difference in the saturation values in Fig. 5(b) near  $10^7 \text{ L}$  should not be taken too serious since absolute values derived from two different experiments can not be compared in detail because of not completely reproducible optical adjustments. The saturation value of  $\delta\Delta(2.54 \text{ eV}) - \delta\Delta(2.85 \text{ eV})$  both for  $n$ - and  $p$ -type material averaged over three different runs is equal and near 0.4 deg.

#### B. Surface photovoltage spectroscopy

Figure 2 shows SPV spectra measured at 100 K on two different cleaved surfaces (cleaves A and B) of the same  $p$ -type material ( $p = 1 \times 10^{17} \text{ cm}^{-3}$ ,  $\mu = 210 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ , Cd doped). Both cleaves

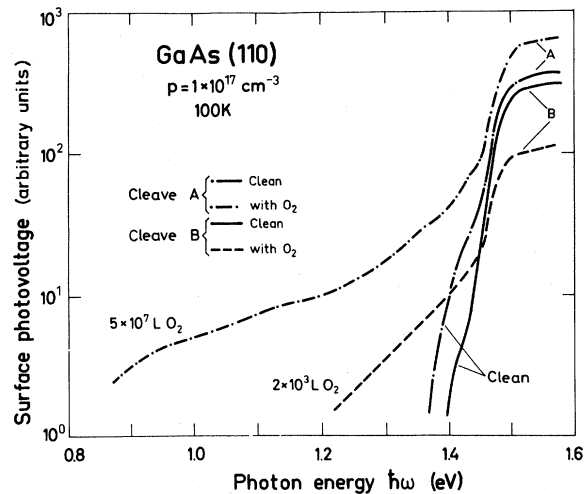


FIG. 2. SPV spectra measured on two cleaves A and B with mirrorlike finish. The curves are normalized to constant photon flux.

were of excellent quality without any detectable crystallographic irregularities (including steps). The spectra on the clean surface exhibit a steep flank near 1.5 eV which is due to electron-hole pair production by irradiation with light of band-gap energy. The detailed shape of this flank varies slightly from cleavage to cleavage (see example A and B in Fig. 2) giving measurable SPV signals down to 1.35 eV in some cases.

Oxygen adsorption changes the absolute height of the SPV signal for energies higher than 1.5 eV, but due to uncontrolled differences in the distance between GaAs surface and opposite electrode for different measurements definite conclusions concerning the absolute height should not be drawn. Furthermore, oxygen produces an additional structure within the band-gap region for energies lower than 1.45 eV (Fig. 2). This structure becomes more prominent with increasing oxygen exposure and for oxygen dosages in the saturation range ( $\geq 10^7$  L) the threshold appears to be between 0.8 and 0.9 eV. More accurate determination of the onset is not possible because of the finite detection limit.

In one experiment with the same crystal material like that used for the spectra in Fig. 2 we happened to produce a cleaved (110) surface of "bad" quality, which can be characterized qualitatively by a number of visible tear marks and irregularities. A photograph of the surface is given as inset in Fig. 3. Since the whole surface area contributes to the measured SPV effect in the experimental setup used, a characterization

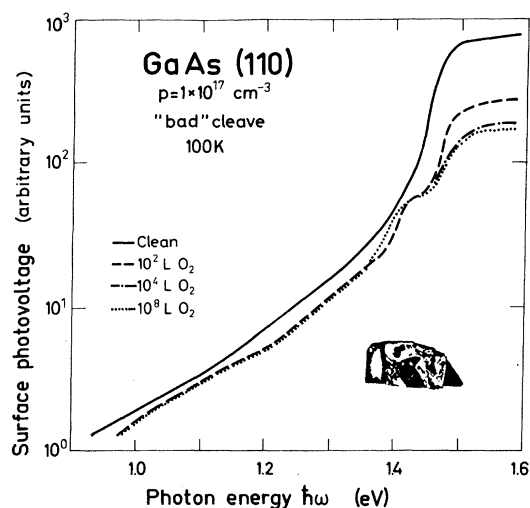


FIG. 3. SPV spectra measured on a "bad" cleave prepared from the same *p*-type material like that used in Fig. 2 (curves normalized to constant photon flux). Inset: Photograph of the cleaved part of the surface with visible crystallographic irregularities.

in terms of step density did not seem reasonable, even though a high step density must be involved in the crystallographic irregularities observed in that cleave. For this surface, SPV signals within the forbidden band are already detected just after cleavage ( $\sim 10$  min, working pressure  $< 10^{-10}$  Torr) before oxygen exposure (Fig. 3). The threshold appears to be below 1.0 eV, i.e., at least 0.5 eV below the band-gap energy. Oxygen exposure at dosages already between 10 and  $10^2$  L decreases the over-all signal and produces a new spectral structure with an onset near 1.36 eV, i.e., about 0.1 eV below the band-gap energy. This shoulder and the threshold below 1.0 eV are not changed significantly with increasing oxygen dosages. In all SPV measurements performed the sign of the light-induced contact potential change was the same for constant dc-illumination and for modulated light chopped with 11 Hz. For *p*-type material the GaAs crystal was positive and the opposite electrode negative upon illumination.

The described effects could only be studied on one sort of *p*-doped (Cd) crystal material supplied by HEK-GmbH. For all other crystals, *n*-type (supplied by HEK-GmbH and Wacker-Chemitronic) and *p*-type (HEK-GmbH) from a different bar bulk impurities not specified by the producer gave rise to remarkable SPV signals within the forbidden band. Therefore, surface effects could not be detected on top of the broad shoulder caused by bulk impurity excitations.

### C. Electron-energy-loss spectroscopy

Figure 4 shows ELS spectra obtained with 80 eV primary energy on a clean cleaved (110) surface of *p*-type material and after different oxygen exposures up to the saturation coverage in the  $5 \times 10^7$ -L range. On the clean surface characteristic loss peaks are observed at 3.7, 6, 8.8, 10.3, 12.3, 16.5, 19.9, 21.4, and 23.6 eV. Except the 12.3-eV loss all loss features have also been found by Ludeke and Esaki<sup>6,13</sup> on molecular beam prepared GaAs surfaces. In some spectra also at lower energies near 2.0 eV a peak has been found which changed upon oxygen exposure. By a mathematical superposition of doubly differentiated structures within the steep negative flank of the primary peak this maximum near 2 eV has been recognized as simulated by the double differentiation process. Corresponding low-energy-loss features near the primary peak simulated by the double differentiation process appear to be found<sup>20</sup> in ELS on Ge(111) and<sup>21</sup> ZnO surfaces. As can be seen from Fig. 4, oxygen exposure causes the loss peak at 10.3 and 19.9 eV to disappear. Furthermore, the shoulders near 8.8 and 12.3 eV may be

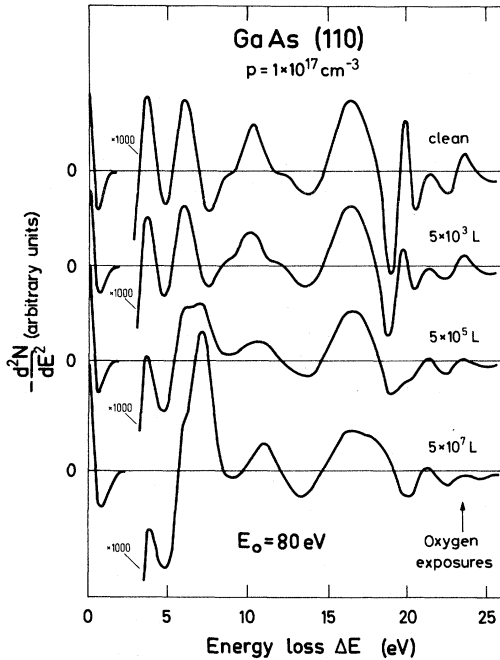


FIG. 4. Doubly differentiated ELS spectra measured with a primary energy of  $E_0 = 80$  eV on the clean surface and after oxygen exposures. The amplification with respect to the primary peak is given with each spectrum.

hidden behind more pronounced oxygen characteristic structures, obtained at 7.2, 11 and probably at 18 eV. These values are somewhat different from those observed previously with a retarding field analyzer.<sup>22</sup> The reason may be seen in the less defined scattering geometry and the more involved scattering mechanism with the retarding field optics.

On cleaved (110) surfaces of  $n$ -type material ( $n = 2.2 \times 10^{17} \text{ cm}^{-3}$ ) exactly the same spectra also after oxygen exposure are obtained like on  $p$ -type crystals except that the oxygen effects start at somewhat lower dosages because of the higher sticking coefficient of oxygen on  $n$ -type material.<sup>11</sup>

The most interesting feature in the present spectra is the loss peak at 19.9 eV which is clearly identified as a surface loss because of its dependence on primary energy  $E_0$  (growing height with decreasing  $E_0$ ) and its sensitiveness to oxygen adsorption (Fig. 4). Figure 5(c) shows the 19.9-eV peak height versus oxygen dosage for  $n$ - and  $p$ -type material. As a measure for the undifferentiated peak intensity the peak-to-peak height of the high-energy flank of the doubly differentiated peak in Fig. 4 was taken. No measurable changes in peak height occur up to dosages of  $10^2$  L. Then, in accordance with the different initial sticking coefficients for  $n$ - and  $p$ -type material [see oxygen

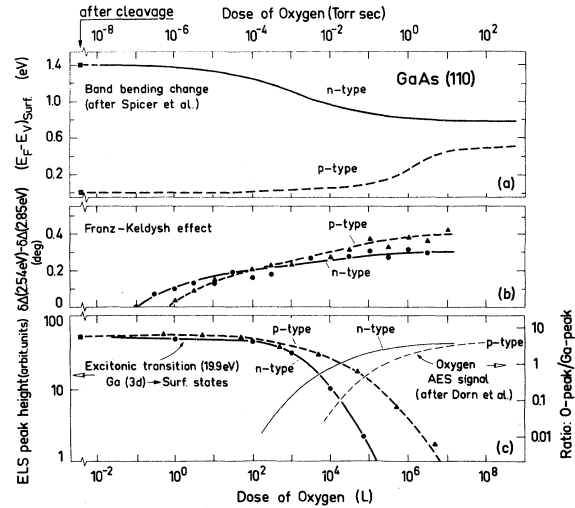


FIG. 5. (a) Energetic position of the Fermi level  $E_F$  with respect to the upper edge of the valence band  $E_v$  at the surface vs oxygen exposure [after Spicer *et al.* (Ref. 10)]. (b) Part of  $\delta\Delta$  change induced by oxygen adsorption which is due to Franz-Keldysh effect in the space charge layer:  $\delta\Delta(2.54 \text{ eV}) - \delta\Delta(2.85 \text{ eV})$  vs oxygen exposure. The photon energies 2.54 and 2.85 eV correspond to the maximum and the minimum, respectively, of the ellipsometric spectra  $\delta\Delta(\hbar\omega)$  in Fig. 1 (inset). (c) Dependence of the peak height of the 19.9-eV loss in Fig. 4 (left-hand scale) and the oxygen AES peak (right-hand scale) on oxygen exposure. The ELS peak height is normalized with respect to the primary peak height and the oxygen AES peak height with respect to the Ga-AES signal. [AES data after Dorn *et al.* (Ref. 11)].

AES signal in Fig. 5(c)] the peak intensity decreases below the detection limit near dosages of  $10^5$  and  $5 \times 10^6$  L for  $n$ - and  $p$ -type material, respectively. In contrast to photoemission yield results<sup>10</sup> no measurable broadening of this loss peak upon oxygen adsorption is observed, only decreasing intensity (Fig. 4), nor does the peak energetically shift with increasing oxygen exposure. A clear inverse relation between the 19.9-eV loss peak height and the oxygen AES signal is evident from Fig. 5(c).

#### IV. INTERPRETATION

##### A. Band bending

The experimental techniques used in the present investigation do not give direct information about the band bending on the clean cleaved surface, but by means of ellipsometry we are able to monitor the band-bending change due to oxygen adsorption. This allows some qualitative conclusions also for the clean surface.

The recently given interpretation<sup>3</sup> of the ellipsometric spectra  $\delta\Delta(\hbar\omega)$  in Fig. 1 (inset) in terms of

a Franz-Keldysh effect in the space-charge layer and an additional change of the optical constants due to adsorbed oxygen and compensation of surface states explains the two different regimes of the  $\delta\Delta$  versus oxygen exposure curves in Fig. 1. Between 1 and  $10^4$  L only the oscillating structure of the  $\delta\Delta(\hbar\omega)$  spectra characterized by  $\delta\Delta(2.54 \text{ eV}) - \delta\Delta(2.85 \text{ eV})$  is built up, i.e., only Franz-Keldysh effect shows up in the low-dosage regime. For dosages higher than  $10^4$  L the additional  $\delta\Delta$  contribution plotted in dashed-dotted line in Fig. 1 (inset) appears. This contribution has been explained by the optical effect of the growing oxygen layer<sup>3</sup> which becomes important for coverages above  $\frac{1}{100}$  of a monolayer.

The difference  $\delta\Delta(2.54 \text{ eV}) - \delta\Delta(2.85 \text{ eV})$  describing the Franz-Keldysh effect cannot be expected to be linearly dependent on the change of the space-charge field or the band bending due to oxygen adsorption. Nevertheless it should vary monotonically with the band bending  $V_s$ .<sup>23,24</sup> Since the change of the optical constants due to Franz-Keldysh effect, i.e., also  $\delta\Delta$ , depends on the absolute amount of the electric field change rather than on its sign<sup>23,24</sup> both for *p*- and *n*-type material the same sign of  $\delta\Delta$  is found even though the band-bending change should have different sign as can be seen from the variation of the Fermi-level position at the surface as determined by Spicer *et al.*<sup>10</sup> from uv photoemission spectroscopy (UPS) [Fig. 5(a)]. Similar results have been obtained by Gudat and Eastman.<sup>9</sup> In agreement with the results of Spicer *et al.* at least for *n*-type material, band bending starts to change near  $10^{-1}$  L. For *p*-type material the present results indicate a band-bending change for lower dosages than those observed by Spicer *et al.*<sup>10</sup> [Fig. 5(a)]. Even though the present ellipsometric measurements do not yield quantitative values for the band-bending change due to oxygen they allow the qualitative conclusion that band-bending changes due to oxygen start at dosages lower by about three orders of magnitude than those where AES signals of oxygen can be detected. Furthermore, the absolute amount of the band-bending change is comparable for *n*- and *p*-type material, in agreement with UPS results<sup>10</sup> [Fig. 5(a)].

#### B. Surface states

The observed band-bending changes due to adsorbed oxygen are correlated with changes in the density of surface states. Neither ellipsometric spectroscopy (Sec. III A) nor ELS (Sec. III C) give any hint for the existence of surface-state transitions in the energy range of the forbidden band gap ( $\sim 1.4 \text{ eV}$ ). High-resolution ELS results

of Froitzheim and Ibach<sup>4</sup> and the ellipsometric spectroscopy data<sup>3</sup> suggest that occupied and empty dangling bond surface states should be located in the energy range of the bulk valence and conduction band, respectively.<sup>9,10</sup>

Further conclusions concerning surface states can be drawn from SPV spectroscopy: Since no information is available at present about the recombination mechanism (probably influenced by traps) an analysis of the absolute height and the sign of the SPV signal is not possible. But spectral changes due to surface treatment as shown in Figs. 2 and 3 can clearly be used as an indication for surface states within the forbidden band gap. The observed effects must be interpreted as follows:

(i) Within the limit of detection, on the clean surfaces of cleaves A and B no measurable SPV signals are detected below 1.35 eV, i.e., there is no indication for empty or occupied surface states near midgap on the clean cleaved GaAs (110) surface which is perfect in the sense that no steps or optical irregularities can be detected. The observed differences between spectra of clean surfaces (e.g., cleaves A and B) might be due to step induced surface states.

(ii) Oxygen adsorption with coverages in the  $\frac{1}{2}$  monolayer range on these "perfect" cleaved (110) surfaces produces surface states which give rise to the SPV signal reaching down to photon energies of about 0.85 eV. The observed shoulder within the band gap should be explained by transitions from the bulk valence band into empty surface states which are at least 0.6 eV below the conduction-band edge. Also transitions from occupied surface states (at least 0.6 eV above the valence-band edge) might explain the effect. Since the Fermi-level position at the surface is near midgap after saturation with adsorbed oxygen [see Fig. 5(a)], and since the threshold of the spectral shoulder in Fig. 2 can not be determined more accurately one cannot distinguish between the two possibilities on an experimental basis.

(iii) Similarly to adsorbed oxygen, surface defects (like steps or other crystallographic irregularities) induce surface states within the forbidden band as can be deduced from the shoulder with an onset below 1.0 eV in Fig. 3. Like for adsorbed oxygen the interpretation must be in terms of empty states at least 0.5 eV below the conduction-band edge or in terms of occupied states at least 0.5 eV above the valence-band edge. The states might be caused by crystallographic irregularities itself or by a reconstruction change<sup>25</sup> which is induced by crystallographic defects like steps, etc.

(iv) As can be seen in Fig. 3 from the shoulder

near 1.4 eV after oxygen adsorption, crystallographic irregularities (maybe steps) produce new adsorption sites for oxygen: The shoulder must be explained by oxygen-induced surface states which are not found upon oxygen adsorption on a "perfect" cleave (see Fig. 2, cleaves *A* and *B*). These states must therefore be related to oxygen adsorbed in a special type of bonding which is only given on surfaces with crystallographic irregularities. The sticking coefficient for oxygen on these new adsorption sites seems to be considerably higher than on a flat surface. The extrinsic surface states are located about 0.1 eV below the conduction-band edge (if empty) or 0.1 eV above the valence-band edge (if occupied).

Concerning surface states and band bending on the clean (110) surface the present results are in good agreement with conclusions from<sup>9,10</sup> UPS: Measurable surface-state densities near midgap and band bending up to about 0.6 eV are only observed as due to contamination and/or crystallographic defects. Maybe this is also the explanation for the upwards band bending (~0.8 eV) Dinan *et al.*<sup>5</sup> have found on cleaved (110) GaAs surfaces of *n*-type material. Viljoen *et al.*<sup>26</sup> have already observed that on freshly cleaved *n*-type GaSb surfaces the work function is not well defined.

### C. Model for band bending and surface states

The question remains, how the band-bending changes are related to extrinsic oxygen-induced surface states or maybe to surface states which arise from a reconstruction change<sup>27</sup> due to slight

contaminations or defects. To get more insight into this problem we have calculated in a simple model<sup>25</sup> the dependence of the band bending  $V_s$  on the density  $N_{ss}$  of the two discrete surface-state levels. For simplicity we assume an acceptorlike level *A* and a donor level *D* as is shown in Fig. 6 (insets). Because of the different charging character (*A*, neutral-negative; *D*, neutral-positive) *A* is responsible for the upwards band bending on *n*-type and *D* for the downwards band bending change on *p*-type material. Total ionization of the shallow bulk donors and acceptors, respectively, has been assumed, and no other bulk impurities have been taken into account. The results in Fig. 6 show that the observed band-bending changes [Fig. 5(a)] can be explained by surface-state densities  $N_{ss}$  between  $10^{14}$  and  $10^{15}$  cm<sup>-2</sup> for the saturation regime and that half of the maximum band-bending change is already reached for surface-state densities of about  $\frac{1}{1000}$  of the surface atom density. Fermi statistics controls the occupation of these levels such that in the regime of maximum band bending not more than about  $10^{13}$  acceptors are occupied or donors are empty. The Fermi level is pinned just below the level *A* for *n*-type and just above *D* for *p*-type material when the maximum band bending is reached.

If we assume that every adsorbing oxygen atom produces one surface-state conclusions from the Franz-Keldysh effect curves [Fig. 5(b)] can be compared with the present model calculations: For *n*-type material  $\delta\Delta(2.54 \text{ eV}) - \delta\Delta(2.85 \text{ eV})$  has reached about half of its maximum value at  $10^1$  L ( $\frac{1}{1000}$  monolayer). In our model this coverage pro-

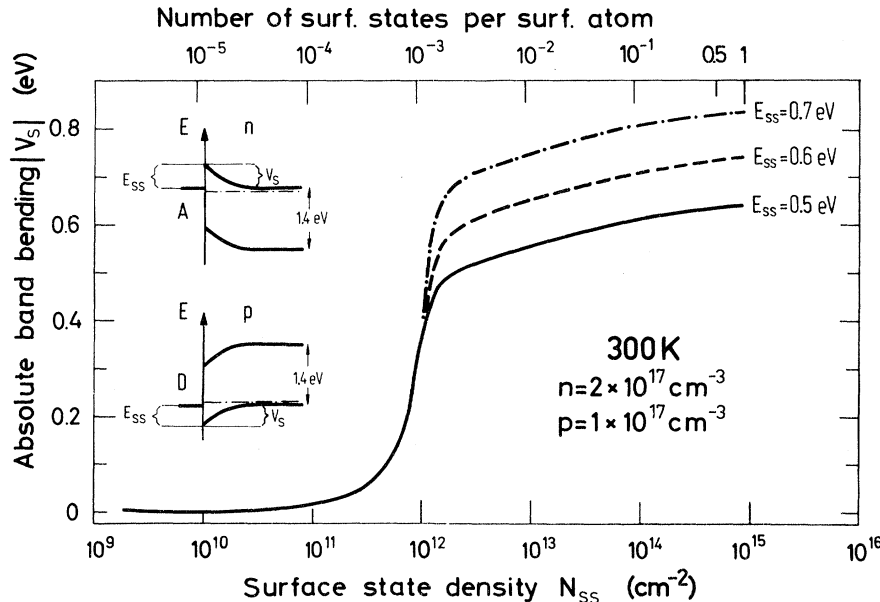


FIG. 6. Calculated absolute band bending  $|V_s|$  due to an acceptor surface-state level *A* and a donor level *D* for *n*- and *p*-type material in dependence on surface-state density  $N_{ss}$ . With the different definition of the energetic position  $E_{ss}$  for *n*- and *p*-type crystals (insets) the calculated curves  $|V_s|$  for *n* and *p* type are not distinguishable on the scale used.

duces a band-bending change of about 0.3 eV. The maximum-band bending change in the saturation regime ( $\sim 0.5$  monolayers), therefore, is expected to be between 0.5 and 0.6 eV in agreement with the UPS results in Fig. 5(a).<sup>10</sup> Our simple model, therefore, allows a quantitative understanding of the band-bending changes due to oxygen on *p*- and *n*-type material as observed by Spicer *et al.*<sup>10</sup> [see Fig. 5(a)]: One has to attribute the two different surface-state levels to extrinsic oxygen characteristic surface states or to states which are related to a reconstruction change which is induced by oxygen adsorption. A gradual formation of these states with increasing oxygen exposure near fixed energetic positions  $E_{ss}$  is expected rather than a gradual shift of states from the conduction- or valence-band region into the forbidden band because the 19.9-eV ELS peak (see Sec. IV D) directly related to the empty Ga dangling bond states is not energetically shifted upon oxygen adsorption.

With regard to our calculation (Fig. 6) the observed band-bending changes can be explained with the assumption that the surface-state density is approximately proportional to the oxygen coverage even down to  $10^{-4}$  monolayers. The origin of these surface states might be the adsorbed oxygen itself or a reconstruction change<sup>27</sup> which gradually appears upon oxygen adsorption. A sudden reconstruction change of the clean surface due to very low contamination coverages seems less probable.

The best fit between the calculated maximum band-bending changes and the experimental results [Fig. 5(a)] is given with  $E_{ss} = 0.5$  eV, i.e., acceptor and donor states should be about 0.5 eV below the conduction-band and 0.5 eV above the valence-band edge, respectively. This is in good agreement with the energetic positions as obtained from SPV spectroscopy (Chap. IV B).

In the above discussion *A* is necessary to explain the band-bending change on *n*-type and *D* the band bending on *p*-type material. For  $E_{ss}$  being about 0.5 eV (*A* and *D* are separated from each other by 0.4 eV and do not interact), the same curve like in Fig. 6 is calculated in a two-level model in which *A* and *D* are simultaneously present on both *n*- and *p*-type material. From the present calculation, therefore, we cannot decide if oxygen produces only an *A* level on *n*-type and a *D* level on *p*-type material (less probably) or if both levels symmetrically spaced around midgap are produced simultaneously on both types of crystals. In the two-level model *A* and *D* are not necessarily acceptors and donors, respectively, but they must have different charging characteristics. In contrast to the results in Fig. 6 the two-level model with  $E_{ss} > 0.6$  eV, i.e., with two inter-

acting levels, yields Fermi-level pinning for both *p*- and *n*-type material at midgap near surface state densities  $N_{ss}$  of  $10^{13}$  cm<sup>-2</sup>. This is not observed in Fig. 5(a). In the two-level model, therefore, *A* and *D* (not specified as acceptors and donors) should be separated from each other by at least 0.4 eV.

#### D. ELS spectra and oxygen adsorption

Since there is no significant difference between the present ELS data for the clean cleaved (110) surface and the clean molecular beam prepared surfaces of Ludeke and Esaki<sup>6,13</sup> the interpretation of the ELS spectra can be done according to previous work.<sup>6,13</sup> The loss peaks at 3.7, 6, 21.4, and 23.6 eV are clearly bulk transition losses<sup>6,13</sup> which are of minor interest in the present context. At 16.5 and 10.3 eV the bulk plasmon and the surface plasmon excitation, respectively, are observed.<sup>6,13</sup> The structures near 8.6 and 12 eV cannot be further specified at present.

In the present ELS studies the main emphasis lies on the surface excitation at 19.9 eV, particularly on its dependence on oxygen adsorption. From the well-known bulk density of occupied states in GaAs only the Ga(3*d*) core level can be the initial state for this excitation, the empty final states then being located  $\sim 1.0$  eV above the valence-band edge within the forbidden band gap.

In agreement with results of other authors<sup>1,2,9,10</sup> the present investigation, however, suggests that on a "perfect" cleaved GaAs (110) surface no empty surface states exist within the forbidden band. The interpretation of the 19.9-eV peak in terms of a "Frenkel"-type surface exciton,<sup>8</sup> therefore, is strongly supported. The idea of a strongly excitonic transition in this case has first been presented by Lapeyre and Anderson<sup>8</sup> based on angular resolved photoemission yield results. Their data are best understood in terms of an excitation localized at the Ga surface atoms. The final states for the 19.9-eV loss therefore, are most probably Ga dangling bond surface states within the energy range of the bulk conduction band. An excitonic binding energy of at least 0.5 eV then decreases the transition energy down to the observed value of 19.9 eV. Similar large excitonic shifts have been observed for localized electronic transitions in molecular crystals.<sup>28</sup>

Even though the energetic position of the 19.9-eV loss does not give the direct location of the single-particle Ga dangling bond surface states this excitonic transition can be used to monitor the Ga surface-state behavior upon oxygen adsorption.

The evident inverse relation between the peak



height of the 19.9-eV loss and the oxygen AES signal both for *n*- and *p*-type material [Fig. 5(c)] shows that adsorbed oxygen strongly effects the excitonic Ga(3d)-Ga(surface state) transition. This might be (i) due to chemical bonding of the adsorbed oxygen to Ga surface atoms or (ii) due to a change of the excitonic interaction by the adsorbed oxygen (without any chemical bonding to the Ga atom itself). The latter explanation is less probable since no measurable broadening of the 19.9-eV loss with increasing oxygen exposure is observed, only decreasing intensity. Furthermore, the energetic position of the loss is not changed upon oxygen adsorption. We, therefore, believe that additionally to the As also the Ga surface atoms are involved in the chemical bonding of oxygen to the GaAs (110) surface. This seems to be in contradiction to the core-level shifts of only the As surface atoms which have been observed by Spicer *et al.* upon oxygen adsorption.<sup>10</sup> But Gudat and Eastman<sup>9</sup> point out that a large As and a not observable Ga core-level shift upon oxide formation is not a necessary indication of a predominant anion bonding, since much larger chemical shifts always occur for As oxides than for clean In and Ga oxides even though strong In- and Ga-oxide bonding occurs.

## V. SUMMARY AND CONCLUSIONS

The most interesting results derived from the present work can be summarized as follows:

(a) Detectable band-bending changes due to adsorbed oxygen are observed for both *n*- and *p*-type material at dosages which are at least two orders of magnitude lower than those for producing approximately  $\frac{1}{100}$  of a monolayer coverage. The absolute amount of the band-bending change in the saturation regime ( $\geq 10^7$  L) is similar for both *n*- and *p*-type material. The results are in agreement with the idea that on a clean perfectly cleaved (110) surface flat band situation is given and that oxygen bends the bands upwards on *n*-type and downwards on *p*-type material.<sup>10</sup>

(b) From SPV spectroscopy there is no indication for empty or occupied surface states near midgap on the clean cleaved GaAs (110) surface which is perfect in the sense that no steps or optical irregularities can be detected. This result strongly supports the interpretation of the 19.9-eV ELS transition in terms of a surface exciton.<sup>8</sup>

(c) On *p*-type material optical excitation from the bulk valence band into empty surface states or from occupied surface states into the conduc-

tion band is observed after oxygen adsorption or on clean surfaces with crystallographic defects ("bad cleaves"). The surface states should be located at least 0.5 eV above the valence-band edge, if occupied or at least 0.5 eV below the conduction-band minimum, if they are empty.

(d) A new type of extrinsic surface states due to oxygen adsorption on defect sites (maybe steps) is observed near  $\sim 0.1$  eV below the conduction-band edge (empty states) or  $\sim 0.1$  eV above the valence-band edge (occupied states). The sticking coefficient for oxygen on these sites seems to be considerably higher than on a flat surface.

(e) The strong correlation between the intensity of the "excitonic" 19.9-eV transition [from Ga(3d) to Ga dangling bond surface states<sup>8</sup>] and the oxygen coverage suggests an adsorption bonding of oxygen atoms not only to the As but also to the Ga surface atoms.

(f) The observed results concerning surface states and band-bending changes due to oxygen adsorption are consistent with the assumption of the formation of two discrete sets of surface states. These levels, about 0.5 eV below the conduction band and 0.5 eV above the valence band, are caused by adsorbed oxygen or crystallographic defects. If these states are due to adsorbed oxygen atoms itself or due to a reconstruction change induced by oxygen or defects can not be decided at present. Concerning surface state distribution the situation on the oxygen covered GaAs (110) surface resembles that on the clean (111) Si and Ge surfaces.<sup>29</sup>

Owing to the recent application of a variety of different experimental techniques the picture of the electronic structure of the cleaved GaAs (110) surface seems to become more and more consistent even though some interesting questions like that of a possible reconstruction change and the exact type of the oxygen bonding are waiting for further studies.

## ACKNOWLEDGMENTS

We are grateful to Professor G. Heiland for stimulating discussions and critical reading of the manuscript. We want to thank Dr. D. E. Eastman and Professor W. E. Spicer for conveying to us results prior to publication. Furthermore, we appreciate the help of Dr. H. Venghaus (MPI Stuttgart) who performed some photoluminescence measurements on the crystal material used. The work was financially supported by the Deutsche Forschungsgemeinschaft (SFB 56-Aachen).

- <sup>1</sup>A. Huijser and J. van Laar, *Surf. Sci.* **52**, 202 (1975).
- <sup>2</sup>J. van Laar and J. J. Scheer, *Surf. Sci.* **8**, 342 (1967).
- <sup>3</sup>R. Dorn and H. Lüth, *Phys. Rev. Lett.* **33**, 1024 (1974).
- <sup>4</sup>H. Froitzheim and H. Ibach, *Surf. Sci.* **47**, 713 (1975).
- <sup>5</sup>J. H. Dinan, L. K. Galbraith, and T. E. Fischer, *Surf. Sci.* **26**, 587 (1971).
- <sup>6</sup>R. Ludeke and L. Esaki, *Surf. Sci.* **47**, 132 (1975).
- <sup>7</sup>D. E. Eastman and J. L. Freeouf, *Phys. Rev. Lett.* **34**, 1624 (1975).
- <sup>8</sup>G. J. Lapeyre and J. Anderson, *Phys. Rev. Lett.* **35**, 117 (1975).
- <sup>9</sup>W. Gudat and D. E. Eastman, *J. Vac. Sci. Technol.* **13**, 831 (1976).
- <sup>10</sup>W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, *J. Vac. Sci. Technol.* **13**, 780 (1976).
- <sup>11</sup>R. Dorn, H. Lüth, and G. J. Russell, *Phys. Rev. B* **10**, 5049 (1974).
- <sup>12</sup>H. Lüth, *Appl. Phys.* **8**, 1 (1975).
- <sup>13</sup>R. Ludeke and L. Esaki, *Phys. Rev. Lett.* **33**, 653 (1974).
- <sup>14</sup>R. Ludeke and A. Koma, *Phys. Rev. Lett.* **34**, 817 (1975).
- <sup>15</sup>H. Ibach, K. Horn, R. Dorn, and H. Lüth, *Surf. Sci.* **38**, 433 (1973).
- <sup>16</sup>The ellipsometric angles  $\Delta$  and  $\psi$  are defined by  $r_p/r_s = (\tan\psi)\exp(i\Delta)$ ,  $r_p$  and  $r_s$  being the complex reflection coefficients of the light field components parallel ( $p$ ) and normal ( $s$ ) to the plane of incidence.
- <sup>17</sup>Proceedings of the Symposium on Recent Developments in Ellipsometry, Nebraska, 1968, *Surf. Sci.* **16**, (1969).
- <sup>18</sup>M. Büchel and H. Lüth, *Surf. Sci.* **50**, 451 (1975).
- <sup>19</sup>H. Ibach and J. E. Rowe, *Phys. Rev.* **9**, 1951 (1974).
- <sup>20</sup>J. von Wienskowski and H. Lüth (unpublished).
- <sup>21</sup>R. Dorn and H. Lüth (unpublished).
- <sup>22</sup>H. Lüth and G. J. Russell, *Surf. Sci.* **45**, 329 (1974).
- <sup>23</sup>W. Franz, *Z. Naturforsch. A* **13**, 484 (1958).
- <sup>24</sup>L. V. Keldysh, *Zh. Eksp. Teor. Fiz.* **34**, 1138 (1958) [*Sov. Phys.-JETP* **7**, 788 (1958)].
- <sup>25</sup>A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland, Amsterdam, 1965), p. 136.
- <sup>26</sup>P. E. Viljoen, M. S. Jazzar, and T. E. Fischer, *Surf. Sci.* **32**, 506 (1972).
- <sup>27</sup>A. R. Lubinsky and C. B. Duke, and B. W. Lee, and P. Mark (unpublished).
- <sup>28</sup>D. Fox and O. Schnepp, *J. Chem. Phys.* **23**, 767 (1955).
- <sup>29</sup>F. G. Allen and G. W. Gobeli, *Phys. Rev.* **127**, 150 (1962).