

Hydrogen adsorption on GaAs(110): A study of the surface optical properties

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The linear optical response of the GaAs(110) surface has been investigated by studying the adsorption of hydrogen on semi-insulating and variously doped GaAs(110) using both ellipsometry and reflectance difference spectroscopy. The surface optical properties were influenced by the hydrogen-induced change in surface geometry and, hence, the microscopic surface electronic structure, and by macroscopic band bending effects. We detected surface electronic transitions of the clean surface at 2.75 eV that disappear with hydrogen adsorption, as well as significant hydrogen-induced changes of the surface optical properties near the bulk critical points. Furthermore, it was observed that hydrogen adsorption leads to a significantly lower surface anisotropy, as compared to the clean surface, in the case of semi-insulating GaAs(110), where the band bending effects are negligible; the energy dependence of the surface anisotropy is similar to that reported in the literature for oxidized GaAs(110), but with a much smaller amplitude. The influence of doping is discussed in light of the band bending effects—the electric-field effect and the unscreening of impurities in the depletion layer. We estimate the strength of these two contributions and conclude that the unscreening of impurities predominates over the electric-field effect.

I. INTRODUCTION

In the past two decades clean semiconductor surfaces and the influence of adsorbates on their properties have been studied extensively. Adsorbates influence the surface optical properties by the change in surface geometry (relaxation, reconstruction) and, hence, the microscopic surface electronic structure, and by macroscopic band bending effects. The GaAs(110) surface is an appropriate candidate to study both contributions separately. No band bending is apparent for the clean GaAs(110) surface since surface states within the gap are absent.¹ The outermost atomic layers are relaxed while still retaining a (1×1) configuration.^{2–4} Adsorption of gases such as oxygen or hydrogen yields surface states within the gap giving rise to band bending effects.⁵ Different surface Fermi level positions were reported for *n*- and *p*-type GaAs: midgap for *n* type and 0.4 eV above the valence band maximum for *p*-type GaAs, similar for both hydrogen and oxygen adsorption.^{6,7} The surface relaxation of the clean surface is reduced by hydrogen or oxygen adsorption.^{8,9,43} Hydrogen adsorption has been studied less extensively than oxygen, still leaving some open questions, e.g., the structure of the hydrogenated surface.¹⁰

Undoped GaAs allows the study of microscopic surface effects, i.e., effects related to the atomic geometry at the surface and, therefore, to the surface electronic structure. Surface transitions of the clean GaAs(110) surface were detected in reflection anisotropy measurements around 2.6 eV and 2.8 eV, disappearing with oxygen exposure,¹¹ whereas the investigation of the oxygen-induced change in reflectivity from low to high dosages identified only one transition around 2.9 eV.¹² A distinct feature around 3.6 eV was found in the hydrogen- and

oxygen-induced change in reflectivity using unpolarized light.¹³ Surface-induced changes in the optical properties due to microscopic surface effects can in general also have other sources besides transitions between surface states, i.e., surface-induced changes of bulk states.^{10,14,15}

Doped GaAs(110) is additionally influenced by the effects of band bending: the electric-field effect¹⁶ and the unscreening of impurities in the concomitant depletion layer.¹⁷ The anisotropy of oxygen exposed GaAs(110) surfaces was found to be influenced by doping due to the surface electric field.^{18,19} The unscreening of impurities escaped attention in past studies of the influence of doping on the reflectivity or dielectric function.

In this paper, we present a detailed ellipsometric and reflectance difference study (2–6 eV) of the adsorption of hydrogen on semi-insulating and variously doped *n*- and *p*-type cleaved GaAs(110) surfaces. Surface transitions and band bending effects, i.e., the electric-field effect and the unscreening of impurities, are discussed. It is concluded that the doping influence on the surface optical properties is dominated by the unscreening of impurities, whereas the electric-field effect does not play as exclusive a role as attributed in the literature.^{12,16,18,19}

II. EXPERIMENT

A. Experimental setup and samples

The optical properties of cleaved *n*- and *p*-type GaAs(110) were determined before and after hydrogen adsorption using rotating analyzer ellipsometry and reflectance difference spectroscopy. Several doping levels were considered: semi-insulating, $p = 2 \times 10^{18} \text{ cm}^{-3}$,

$p = 7 \times 10^{19} \text{ cm}^{-3}$, and $n = 4.7 \times 10^{18} \text{ cm}^{-3}$. For each doping level the ellipsometric measurements were performed both with the [001] and [110] axis in the plane of incidence, in order to determine the $\langle \epsilon \rangle_{[001]}$ and $\langle \epsilon \rangle_{[110]}$ components of the dielectric tensor.²⁰ Reflectance difference spectroscopy was used to measure the surface reflectance anisotropy $(r_{[001]} - r_{[110]})/\bar{r}$ with high sensitivity ($<0.1\%$). Details about these techniques can be found elsewhere in the literature.^{21,22} All measurements were performed in an ultrahigh-vacuum system at a pressure of 10^{-10} Torr at room temperature. The incident and reflected light beam were fed into the chamber via two nearly-strain-free windows so as to minimize their effect on the polarization state of the light.²³ Hydrogen adsorption was performed *in situ* by exposure to atomic hydrogen. Molecular hydrogen introduced into the chamber, which does not adsorb on GaAs(110),²⁴ was dissociated at a hot tungsten filament. The cleaved GaAs(110) surfaces were subsequently exposed to different amounts of atomic hydrogen. We express the exposure in Langmuir ($1 \text{ L} = 10^{-6} \text{ Torr molecular hydrogen} \times 1 \text{ s}$).

B. Data evaluation

The adsorption of hydrogen changes the optical properties of GaAs(110) in a thin surface layer whose optical properties can be determined from the measured ellipsometric angles using a three-phase model (vacuum, surface layer, bulk). We chose the surface normal along the z axis with the x axis in the plane of incidence. If the surface layer thickness is small compared to the light wavelength, the difference in the dielectric function of the surface layer $\Delta\epsilon_{x,y,z}$ (with respect to the bulk dielectric function) is connected to the surface excess function δd by (the x - z plane corresponds to the plane of incidence):¹⁵

$$\begin{aligned} \delta d &= \left[\left(\Delta\epsilon_x + \epsilon_b \Delta \frac{1}{\epsilon_z} \right) \right. \\ &\quad \left. + \left(\frac{1}{\epsilon_b} - \frac{\cos^2 \Theta}{\sin^2 \Theta} \right) (\Delta\epsilon_y - \Delta\epsilon_x) \right] d \\ &= \frac{ic(\epsilon_b - 1)}{2\omega\epsilon_b\sqrt{\epsilon_b - \sin^2 \Theta}} [\langle \epsilon \rangle - \epsilon_b], \end{aligned} \quad (1)$$

where ϵ_b represents the bulk dielectric function, $\langle \epsilon \rangle$ the pseudodielectric function calculated from the measured ellipsometric angles as if the bulk+surface system represents a homogeneous medium and Θ the angle of incidence. The surface excess function δd corresponds directly to the difference in the surface dielectric function $\Delta\epsilon_x d$ (with respect to the bulk dielectric function) if the difference in surface anisotropy is small ($\Delta\epsilon_y - \Delta\epsilon_x \approx 0$; we assume $\epsilon_b \Delta \frac{1}{\epsilon_z}$ to be negligible). A large anisotropy destroys this simple relationship, and the optical response must be treated using Eq. (1). To determine $\Delta\epsilon_{x,y,z}$ as hydrogen surface-induced properties minus those of the clean surface we substituted in ϵ_b of Eq. (1) the GaAs(110) optical properties in the presence of the clean surface $\langle \epsilon \rangle_{\text{clean}}$, i.e., prior to hydrogen exposure. $\langle \epsilon \rangle$

represents the GaAs(110) optical properties after hydrogen exposure. Note: $\langle \epsilon \rangle_H - \langle \epsilon \rangle_{\text{clean}}$ can be written as $(\langle \epsilon \rangle_H - \epsilon_b) - (\langle \epsilon \rangle_{\text{clean}} - \epsilon_b)$.

The hydrogen-induced change of the surface anisotropy $(\Delta\epsilon_{[001]} - \Delta\epsilon_{[110]})d$ was determined from the complex reflectivity $\Delta r/r$ as measured by reflectance difference spectroscopy:²⁵

$$\begin{aligned} (\Delta\epsilon_{[001]} - \Delta\epsilon_{[110]})d &\simeq \frac{ic(\epsilon_b - 1)}{2\omega} \left[\left(\frac{\Delta r}{r} \right)_H \right. \\ &\quad \left. - \left(\frac{\Delta r}{r} \right)_{\text{clean}} \right]. \end{aligned} \quad (2)$$

III. RESULTS

Hydrogen adsorption changes the optical properties of the GaAs(110) surface predominantly in the vicinity of the critical points (the main critical points are E_1 at 2.91 eV, $E_1 + \Delta_1$ at 3.14 eV, E'_0 at 4.44 eV and E_2 at 4.96 eV) (Ref. 26) as evidenced from Fig. 1, comparing the pseudodielectric function $\langle \epsilon \rangle$ of $p = 2 \times 10^{18}\text{-cm}^{-3}$ -doped GaAs(110) before and after 100-L hydrogen exposure. The [001] axis was oriented along the plane of incidence (further denoted as [001] polarization). The measurement yields in first approximation the $\langle \epsilon \rangle_{[001]}$ component of the dielectric tensor.^{15,20}

We describe the hydrogen-induced change in the surface optical properties using the surface excess function δd [Eq. (1)]. Figure 2 shows for a series of hydrogen exposures on (a) and (b) semi-insulating, (c) and (d) $p=2 \times 10^{18}\text{-cm}^{-3}$, and (e) and (f) $p=7 \times 10^{19}\text{-cm}^{-3}$ -doped GaAs(110) the imaginary part of the surface excess function in the [001] (left panel) and [110] polarization (right panel). The surface excess function δd corresponds, to a first approximation, to the hydrogen-induced change in the dielectric function of the surface layer: $\Delta\epsilon_{[001]}d$ and $\Delta\epsilon_{[110]}d$, respectively. The spectra are dominated

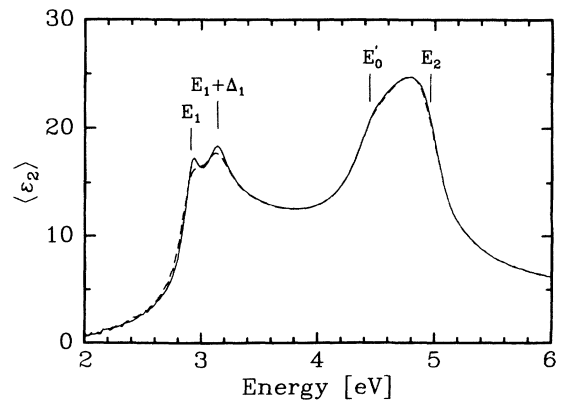


FIG. 1. Imaginary part of the pseudodielectric function of $p = 2 \times 10^{18}\text{-cm}^{-3}$ -doped cleaved GaAs(110) before (full line) and after 100-L hydrogen exposure (dashed line) (in the [001] polarization).

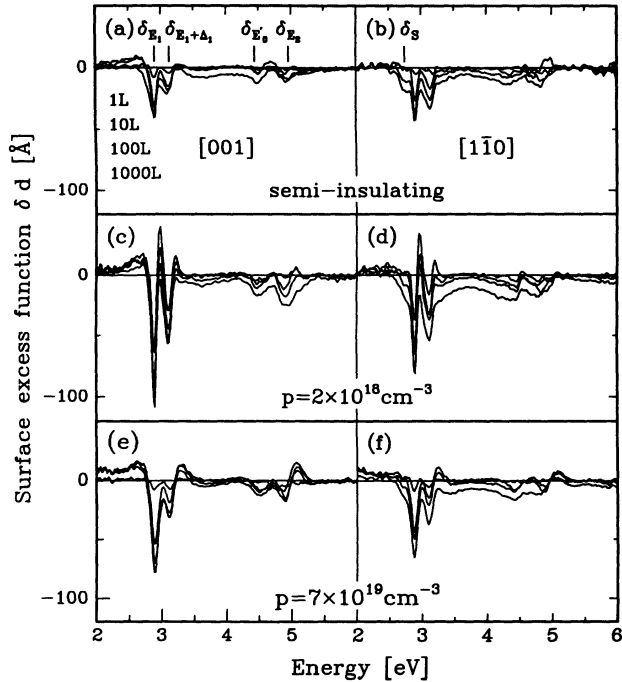


FIG. 2. Imaginary part of the surface excess function of (a) and (b) semi-insulating, (c) and (d) $p = 2 \times 10^{18}\text{-cm}^{-3}$, and (e) and (f) $p = 7 \times 10^{19}\text{-cm}^{-3}$ -doped GaAs(110) in the [001] (left panel) and $[1\bar{1}0]$ polarization (right panel) for several hydrogen exposures.

by two minima around the E_1 and $E_1 + \Delta_1$ bulk critical points, which will be denoted as δ_{E_1} and $\delta_{E_1+\Delta_1}$, while weaker structures are also visible around E'_0 and E_2 . δ_{E_1} and $\delta_{E_1+\Delta_1}$ increase with hydrogen exposure. This is illustrated in more detail in Fig. 3 where for the $p = 2 \times 10^{18}\text{-cm}^{-3}$ -doped sample the magnitude of the δ_{E_1} minimum is plotted as a function of hydrogen exposure. Hydrogen adsorption starts to change the optical properties for exposures as low as 1 L. In the 10–100-L regime δ_{E_1} exhibits a plateau (observed for all doping levels and polarizations), whereas for higher hydrogen exposures further increase in δ_{E_1} is visible. The latter increase is related to the appearance of a (structured) background in δd (Fig. 2). As will be discussed later this background is most likely due to surface etching. Figure 3 illustrates as well the fact that the hydrogen-induced changes around E_1 are stronger in the [001] polarization.

The hydrogen-induced changes were found to decrease with time (in one case about 30% within several hours), which is probably due to the desorption of arsenic hydride or hydrogen.²⁴ Further investigations are in progress. We measured the hydrogen-induced changes directly after hydrogen exposure so that, due to its large time constant, this effect can be neglected.

Hydrogen adsorption should influence the optical properties of semi-insulating GaAs(110) only through microscopic surface effects, since surface band bending is negligible. The minima, $\delta_{E_1} = (2.91 \pm 0.01)$ eV and $\delta_{E_1+\Delta_1} = (3.13 \pm 0.01)$ eV, correspond within the limits of error to the bulk E_1 (2.91 eV) and $E_1 + \Delta_1$ (3.14 eV) critical points.²⁶ They are stronger in the [001] polarization.

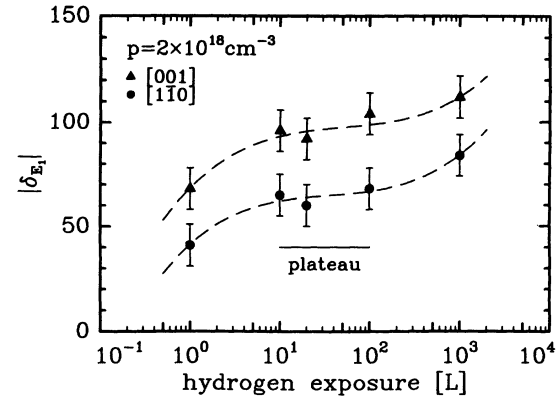


FIG. 3. Dependence of the δ_{E_1} magnitude on hydrogen exposure for $p = 2 \times 10^{18}\text{-cm}^{-3}$ -doped GaAs(110) in the [001] and $[1\bar{1}0]$ polarization. δ_{E_1} exhibits a plateau in the 10–100-L regime. The dashed lines represent a guide to the eye.

In the $[1\bar{1}0]$ polarization, a shoulder at (2.75 ± 0.02) eV appears in the imaginary part of the surface excess function [δ_S in Fig. 2(b)] which is absent in the other polarization. The hydrogen-induced change in the surface anisotropy is seen in Figs. 4 and 5(a). Figure 4 displays the reflection anisotropy $\Delta R/R = 2\Delta r/r$ (Ref. 22) for a semi-insulating GaAs(110) sample before (full line) and after 1000-L hydrogen exposure (dashed line) as determined from the reflectance difference spectroscopy. Hydrogen adsorption leads to a significantly lower surface anisotropy as compared to the clean surface. The anisotropy was found to be approximately independent of hydrogen exposure beyond 10 L. We calculated using Eq. (2) the hydrogen-induced change in the anisotropy of the surface dielectric function: $(\Delta\epsilon_{[001]} - \Delta\epsilon_{[1\bar{1}0]})d$. Its imaginary part is shown in Fig. 5(a) and shows, in agreement with the ellipsometric results, a positive contribution to $(\Delta\epsilon_{[001]} - \Delta\epsilon_{[1\bar{1}0]})d$ for δ_S , whereas δ_{E_1} and $\delta_{E_1+\Delta_1}$ produce a negative one. A change in anisotropy due to hydrogen adsorption was also observed near the E'_0 and E_2 bulk critical points again with larger changes in the [001] polarization.

Doping enhances the hydrogen-induced change in the

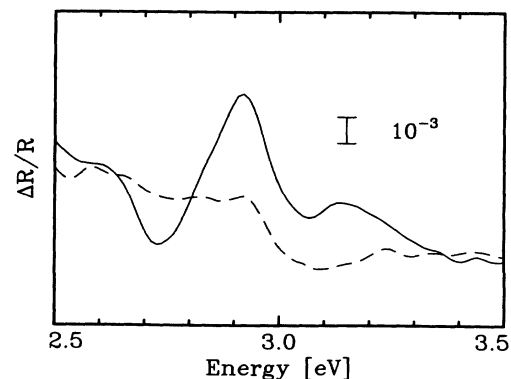


FIG. 4. Reflection anisotropy $(R_{[001]} - R_{[1\bar{1}0]})/\bar{R}$ of semi-insulating cleaved GaAs(110) before (full line) and after 1000-L hydrogen exposure (dashed line).

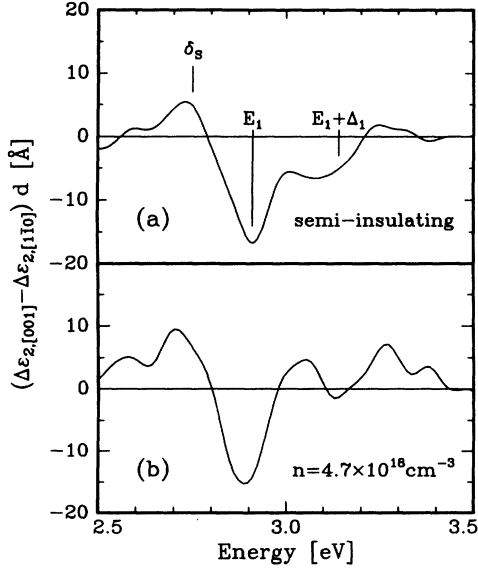


FIG. 5. Imaginary part of the hydrogen-induced change in the anisotropy of the surface dielectric function of (a) semi-insulating and (b) $n = 4.7 \times 10^{18} \text{ cm}^{-3}$ -doped GaAs(110) for 1000-L hydrogen exposure (determined from reflectance difference spectroscopy).

surface optical response of GaAs(110) due to the additional appearance of surface band bending. This is clearly seen in Figs. 2(c) and (d) where the imaginary part of the surface excess function for $p = 2 \times 10^{18} \text{ cm}^{-3}$ -doped GaAs is shown. The δ_{E_1} and $\delta_{E_1 + \Delta_1}$ minima are significantly enhanced in comparison to semi-insulating GaAs [Figs. 2(a) and (b)] and, in addition, the maximum separating both minima becomes much more pronounced. The hydrogen-induced changes are again stronger in the [001] polarization. N doping of comparable concentration was found to give similar results. The δ_S structure, however, appears to be unaffected by doping and thus it proves to be a microscopic surface effect. A further increase in doping to $p = 7 \times 10^{19} \text{ cm}^{-3}$ results in a weakening of the structures in δd [Figs. 2(e) and (f)]. Since the depletion layer thickness decreases as $p^{-1/2}$,²⁷ $\delta \approx \Delta \epsilon_x$ increases slower than $p^{1/2}$ with doping in the high doping regime. This is an obviously weaker increase as compared to the low doping regime (stronger than $p^{1/2}$) indicating a weakening of the band bending effects at high doping levels.

Despite the significant doping enhancement of the total hydrogen-induced changes, the changes in the surface anisotropy $(\Delta \epsilon_{[001]} - \Delta \epsilon_{[110]})d$ show no strong dependence on doping. The anisotropy spectra of a $n = 4.7 \times 10^{18} \text{ cm}^{-3}$ -doped sample exposed to 1000 L hydrogen [Fig. 5(b)] has similar line shape and magnitude as compared to semi-insulating GaAs(110) [Fig. 5(a)]: the δ_S structure is still present, the amplitude of the δ_{E_1} minimum anisotropy is at most only 1/3 larger than for the semi-insulating one. Only the maximum separating δ_{E_1} and $\delta_{E_1 + \Delta_1}$ appears to change strongly with doping. We note that the hump around 3.25 eV (above $\delta_{E_1 + \Delta_1}$) is, at least in part, a consequence of the approximations of

Eq. (1) in the case of the large surface depletion layer thickness as will be discussed later.¹⁵

IV. DISCUSSION

The hydrogen-induced changes in the surface optical properties are fully established around 10–100-L hydrogen exposure as evidenced by the plateau of the δ_{E_1} minimum in the surface excess function (Fig. 3). Etching of the surface changes the optical properties above 100 L: probably through the evolution of AsH_3 leaving a Ga-rich surface.²⁴ A negative (structured) background appears in the surface excess function (Fig. 2). To study the GaAs(110) surface properties we will concentrate on the region of hydrogen exposure where etching does not appear, namely on the plateau regime.

Two different mechanisms are responsible for the change in surface optical properties produced by hydrogen adsorption. The change in surface structure and, hence, the surface electronic response will directly influence the surface optical properties. It is established that hydrogen adsorption reduces strongly the original surface relaxation.^{8,43} This mechanism affects only the first few monolayers. The second mechanism is associated with the appearance of band bending due to the emergence of surface states within the gap.⁵ It is only expected in doped material and influences the optical properties in the much thicker depletion layer with its thickness proportional to $p^{-1/2}$ ($n^{-1/2}$), where p (n) represents the dopant concentration.^{16,17,27}

A. Surface contribution

The microscopic surface contribution can be studied on semi-insulating GaAs(110) since band bending effects due to background doping are negligible.²⁸ The surface excess function shown in Figs. 2(a) and (b) corresponds to a first approximation to the hydrogen-induced change in the surface dielectric function $\Delta \epsilon_{[001]}d$ and $\Delta \epsilon_{[1\bar{1}0]}d$, respectively. However, $\Delta \epsilon_{[001]}d$ and $\Delta \epsilon_{[1\bar{1}0]}d$ can be determined with higher accuracy if the surface anisotropy is taken into account [using Eq. (1)]. Note: Since we could not obtain the ellipsometric measurements for both orientations on the same sample, we have used the reflectance difference measurements to obtain $(\epsilon_{\text{clean}} - \epsilon_H)d$. The so-determined imaginary part of $(\epsilon_{\text{clean}} - \epsilon_H)d$ is shown in Fig. 6(a) for both polarizations. We assume $\epsilon_b \Delta \frac{1}{\epsilon_x}$ to be negligible in this spectral region. In order to compare our results to other measurements, as well as to theoretical calculations,¹⁰ we also evaluated the differential reflectivity $(R_{\text{clean}} - R_H)/R_H$ [Fig. 6(b)] assuming a 5 Å thick surface layer.²⁹

The two pronounced maxima in the imaginary part of $(\epsilon_{\text{clean}} - \epsilon_H)d$ at 2.91 and 3.12 eV [Fig. 6(a)] agree rather well with the energies of the E_1 and $E_1 + \Delta_1$ bulk critical points. These originate from transitions in the Λ direction, i.e., \vec{k} along $\langle 111 \rangle$ of the Brillouin zone.³⁰ The change in surface structure due to hydro-

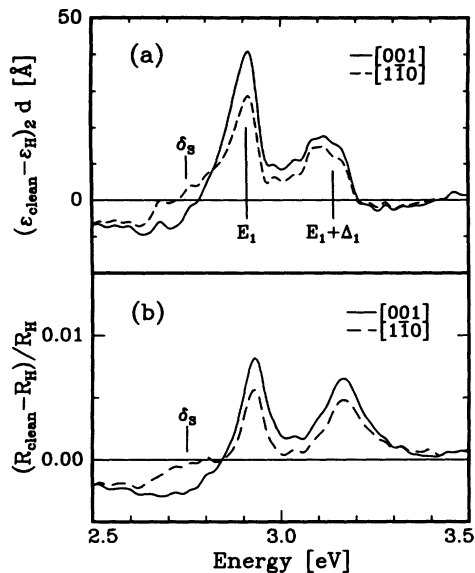


FIG. 6. (a) Imaginary part of the change in the surface dielectric function $(\epsilon_{\text{clean}} - \epsilon_H)d$ for semi-insulating GaAs(110) exposed to 100-L hydrogen (in the [001] and [110] polarization, as evaluated from the surface excess function using Eq. (1) taking the surface anisotropy into account) and (b) the resulting differential reflectivity $(R_{\text{clean}} - R_H)/R_H$ (assuming a 5 Å thick surface layer).

gen adsorption will change the wave functions and transition matrix elements in the surface region,³¹ resulting in the observed features and anisotropy (around E_1 : $\Delta\epsilon_{[001]}/\Delta\epsilon_{[110]} = 1.39 \pm 0.03$, i.e., larger changes in the [001] polarization). Note that for the optical response of an infinite crystal with zinc-blende-structure such as GaAs no polarization dependence should be detectable, i.e., $\epsilon_{[001]} = \epsilon_{[110]}$. The features of the surface excess function around E'_0 and E_2 [Figs. 2(a) and (b)] seem to have similar origin. Studies of hydrogen adsorption on Ge(111) and Si(111) also found structures in the bulk critical point region.¹⁵

It is worthwhile to consider the anisotropy of the clean and hydrogenated surface in more detail (Fig. 4). Hydrogen adsorption reduces significantly the anisotropy of the clean surface (full line), which is consistent with the reduction in surface relaxation as reported in the literature.^{8,43} The residual anisotropy is similar in line shape to that found on oxidized GaAs(110),¹¹ but with a much smaller amplitude. Thus the hydrogenated GaAs(110) surface relaxation,⁸ as well as the local-field corrections to the optical response,³² both influencing the surface anisotropy, prove to be different from that on oxidized GaAs(110).

Two surface transitions of the clean GaAs(110) surface, S_1 around 2.6 eV and S_2 around 2.8 eV, were identified in room temperature reflection anisotropy measurements.¹¹ Similar surface transitions were found in high-resolution electron-energy-loss spectroscopy studies.³³ The disappearance of the S_2 surface transition due to hydrogen adsorption appears to be the origin for the δ_s feature at (2.75 ± 0.02) eV present in the [110] polarization in the

surface excess function [Fig. 2(b)], in the surface dielectric function [Fig. 6(a)], as well as in the differential reflectivity [Fig. 6(b)]. This feature is, therefore, related to the clean surface and should give a direct measure of the removal of the surface relaxation. It is fully established within the 10–100-L regime [Fig. 2(b)] which is consistent with the plateau of the δ_{E_1} feature (Fig. 3). Self-consistent local-density calculations have attributed it to transitions between bulk states of the truncated crystal.¹⁰ Note that these surface specific features are still retained in doped material where additional band bending effects enhance the hydrogen-induced changes [Figs. 2(c) and (d)]. No hydrogen-specific surface state transitions could be detected in this study. The distinct feature around 3.6 eV reported in Ref. 13 was not detected here [Figs. 2(a) and (b)].

Theoretical calculations of the optical properties of the hydrogenated GaAs(110) surface are hindered by the poor knowledge of its structure. Different models were used:¹⁰ H sitting on top of the atoms of the first overlayer and H sitting in the direction of the bonds. We could not find quantitative agreement between the calculations and our results.

B. Band bending effects

Band bending effects can be studied in doped material. They contribute to the hydrogen-induced changes in the surface optical response and can be extracted from the surface excess function after subtracting the contributions from microscopic surface effects, such as the δ_s feature. Subtraction yields a line shape that is similar to that of the surface excess function in the [001] polarization [Fig. 2(c)] with two pronounced minima around E_1 and $E_1 + \Delta_1$ and a strong maximum separating both. Note that the critical points are shifted to lower energies with doping due to the impurity potential influence on the band structure,^{34,35} which makes this subtraction more complicated in practice.

Despite the large depletion layer thickness (e.g., about 170 Å for $p = 2 \times 10^{18}\text{-cm}^{-3}$ -doped GaAs)²⁷ we use the approximation of the surface excess function (first-order approximation in the surface layer thickness) due to its simplicity and direct connection to measured quantities.¹⁵ To justify this procedure, we also calculated the surface layer properties using the exact three-phase model (vacuum-surface layer bulk), which, however, still only approximates the inhomogeneous electric field as an average. We found that the line shape and amplitude of the surface dielectric function from the surface excess treatment agree rather well with the result of the exact three-phase model. However, the energy position of the minima is somewhat shifted, and there is a hump around 3.2 eV (above $E_1 + \Delta_1$) which seems to be at least in part due to the approximations of Eq. (1). We focus on the analysis of the band bending effects for the $p = 2 \times 10^{18}\text{-cm}^{-3}$ -doped sample around the E_1 and $E_1 + \Delta_1$ critical points.

Two different effects of band bending must be considered: the electric-field effect and the unscreening of im-

purities in the resulting depletion layer. Anisotropy due to band bending originates solely from the electric-field effect as will be shown below, a fact which allows separating both contributions. Anisotropy reflection measurements on oxidized doped GaAs(110) reported recently¹⁸ considered, therefore, only the electric-field effect. The importance of the unscreening of impurities has been pointed out recently:¹⁷ the doping-induced redshift of the E_1 and $E_1 + \Delta_1$ critical points in GaAs was found to be significantly enhanced due to the unscreening of impurities in the depletion layer. Both contributions will be discussed below in more detail.

In the low-field limit, i.e., at low doping levels, the electric field induces a change in the dielectric function $\Delta\epsilon$ proportional to the third derivative of the dielectric function and the square of the electric-field strength \mathcal{E} :³⁶

$$\Delta\epsilon_{\text{field}} \propto \mathcal{E}^2 \frac{1}{E^2} \frac{\partial^3}{\partial E^3} (E^2 \epsilon). \quad (3)$$

The influence of the linear electro-optic effect in GaAs has been shown to be much weaker and, therefore, will not be discussed here in detail.^{37,38} Note that the electric field is not homogenous in the depletion region so that an average field strength has to be used in Eq. (3): it decreases linearly from a maximum value proportional to $p^{1/2}$ ($n^{1/2}$) at the surface to a negligible value at the depletion layer depth [$d \propto p^{-1/2}$ ($n^{-1/2}$)].²⁷ For most of the doping levels considered here the low-field limit of Eq. (3) is no longer valid and the expression for the electric-field-induced changes becomes much more complicated.³⁹ However, the main features are approximately retained, but with an amplitude saturating at high electric fields due to the two-dimensional character of the E_1 and $E_1 + \Delta_1$ critical points.^{39,40}

The Coulomb potential of the impurities, i.e., dopants, screened by the free carriers results in the bulk in a redshift and broadening of the E_1 and $E_1 + \Delta_1$ critical points.^{34,35} The removal of free carriers in the surface depletion layer, i.e., the unscreening of impurities, increases the impurity potential influence on the optical response;¹⁷ an enhanced redshift and broadening of the critical points with doping occurs. The hydrogen-induced change in the dielectric function $\Delta\epsilon$ can then be approximated by

$$\Delta\epsilon \simeq (C_1 + iC_2)\delta\epsilon/\partial E \quad (4)$$

where C_1 accounts for the enhanced energy shift and C_2 for the enhanced broadening. The unscreening of impurities results obviously in isotropic changes.

The electric-field mechanism represents the only anisotropic band bending effect as will be shown below. Therefore, anisotropy can be used to separate both band bending effects. The principal axes of the dielectric tensor in the presence of an electric field along [110] are oriented along [001], $[1\bar{1}0]$, and $[110]$ and the changes in the dielectric function are given by⁴¹

$$\begin{aligned} \Delta\epsilon_{[001]} &= 2\pi\mathcal{E}^2 [2\chi_{12}], \\ \Delta\epsilon_{[1\bar{1}0]} &= 2\pi\mathcal{E}^2 [\chi_{11} + \chi_{12} - \chi_{44}], \\ \Delta\epsilon_{[110]} &= 2\pi\mathcal{E}^2 [\chi_{11} + \chi_{12} + \chi_{44}], \end{aligned} \quad (5)$$

where χ_{11} , χ_{12} , χ_{44} represents the three independent nonzero elements of the fourth-rank susceptibility tensor. We find for the E_1 region $\chi_{11} = \chi_{12}$ and $\chi_{44} = \frac{1}{2}\chi_{11}$ using the low-field-limit equation,³⁶ assuming (i) cylindrical symmetry for transitions along $\langle 111 \rangle$ with parallel bands along $\langle 111 \rangle$ and (ii) transitions for polarization perpendicular to $\langle 111 \rangle$. This results in an anisotropy of

$$\frac{\Delta\epsilon_{[001]}}{\Delta\epsilon_{[1\bar{1}0]}} \simeq \frac{4}{3}, \quad (6)$$

i.e., the electric-field effect results in larger changes in the [001] polarization. The dominant feature of the surface excess function is the δ_{E_1} minimum. We find that for a n or p doping in the mid- 10^{18} - cm^{-3} range, most of the hydrogen-induced change in the surface anisotropy near δ_{E_1} [Fig. 5(b)] originates from microscopic surface effects, which is evident when comparing to semi-insulating GaAs(110) [Fig. 5(a)]; at most 1/3 originates from the electric-field effect. The total electric field contribution to the δ_{E_1} minimum of the surface excess function, e.g., in the [001] polarization [Fig. 2(c)], can be evaluated using Eq. (6). We find that less than 1/3 originates from the electric-field effect, whereas more than 1/3 is left to the unscreening of impurities. The remaining 1/3 represents the microscopic surface effects which are the sole contribution in the case of semi-insulating GaAs. Thus for a mid- 10^{18} - cm^{-3} doping the most pronounced feature in the hydrogen-induced changes, the δ_{E_1} minimum, is not determined by the electric-field effect as previously assumed. This conclusion should also be valid for other doping levels, since both, the electric-field effect and the unscreening of impurities are expected to scale similarly with doping.¹⁷ The electric-field effect, however, is responsible for the pronounced maximum separating δ_{E_1} and $\delta_{E_1 + \Delta_1}$ [Figs. 2(c), (d), and 5(b)], evident from its strong doping-enhanced anisotropy.

The reduction of doping influence on the surface excess function δd found for the $p = 7 \times 10^{19}$ - cm^{-3} -doped sample [Figs. 2(e) and (f)] indicates that $\delta \approx \Delta\epsilon_x$ must increase slower than $p^{1/2}$ with doping in the high doping regime—an obviously weaker increase as compared to low doping levels (note that the depletion layer thickness d is proportional to $p^{-1/2}$).²⁷ A weakening of the doping dependence of the band bending effects at high doping levels is responsible for this effect: the doping dependence of the enhanced redshift and broadening due to the unscreening of impurities weakens¹⁷ and the electric-field effect saturates due to the two-dimensional character of the E_1 and $E_1 + \Delta_1$ critical points.^{26,39} The similar doping dependence of the surface response function found for n - and p -type GaAs is due to the comparable barrier heights at the surface.^{6,42}

V. CONCLUSION

The surface optical response of GaAs(110) was investigated by studying the change in optical properties induced by hydrogen adsorption. We have shown that op-

tical methods can be used to characterize surface properties. Microscopic surface effects, i.e., effects related to the surface geometry and, therefore, to the microscopic surface electronic structure, were studied on semi-insulating GaAs. Surface electronic transitions of the clean surface were detected at 2.75 eV which disappear with hydrogen exposure, whereas hydrogen specific ones could not be identified. Significant hydrogen-induced changes of the surface optical properties were observed near the bulk critical points. We found that hydrogen adsorption leads to a significantly lower surface anisotropy, as compared to the clean surface; the energy dependence of the surface anisotropy is similar to that reported in the literature for oxidized GaAs(110), but with a much smaller amplitude. The results have been compared to theoretical calculations. Band bending effects—the electric-field effect and

the unscreening of impurities in the depletion layer—were studied in doped material. Their relative strength was estimated. It is concluded that the electric field does not produce the dominant contribution to the effect of band bending on the optical response.

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- ¹ A. Huijser and J. van Laar, *Surf. Sci.* **52**, 202 (1975).
- ² C. B. Duke, *Appl. Surf. Sci.* **11/12**, 1 (1982), and references therein.
- ³ C. Mailhot, C. B. Duke, and Y. C. Chang, *Phys. Rev. B* **30**, 1109 (1984).
- ⁴ J. R. Chelikowsky and M. L. Cohen, *Phys. Rev. B* **20**, 4150 (1979).
- ⁵ W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, *J. Vac. Sci. Technol.* **13**, 780 (1976).
- ⁶ J. P. Landesman, R. Mabon, G. Allan, M. Lannoo, C. Priester, and J. E. Bonnet, *J. Vac. Sci. Technol.* **7**, 882 (1989).
- ⁷ T. U. Kampen, L. Koenders, K. Smit, M. Rückschloss, and W. Mönch, *Surf. Sci.* **242**, 314 (1991).
- ⁸ C. Astaldi, L. Sorba, C. Rinaldi, R. Mercuri, S. Nannarone, and C. Calandra, *Surf. Sci.* **162**, 39 (1985).
- ⁹ C. M. Bertoni, M. Buongiorno Nardelli, F. Bernardini, F. Finocchi, and E. Molinari, *Europhys. Lett.* **13**, 653 (1990).
- ¹⁰ F. Manghi, R. Del Sole, A. Selloni, and E. Molinari, *Phys. Rev. B* **41**, 9935 (1990).
- ¹¹ V. L. Berkovits, I. V. Minashvili, and V. I. Safarov, *Solid State Commun.* **56**, 449 (1985).
- ¹² F. Ciccacci, S. Selci, G. Chiarotti, P. Chiaradia, and A. Cricenti, *Surf. Sci.* **168**, 28 (1986).
- ¹³ P. Chiaradia, G. Chiarotti, F. Ciccacci, and R. Memeo, *J. Phys. Soc. Jpn.* **49A**, 1109 (1980).
- ¹⁴ A. Selloni, P. Marsella, and R. Del Sole, *Phys. Rev. B* **33**, 8885 (1986).
- ¹⁵ M. K. Kelly, S. Zollner, and M. Cardona, *Surf. Sci.* **285**, 282 (1993).
- ¹⁶ H. Lüth, M. Büchel, R. Dorn, M. Liehr, and R. Matz, *Phys. Rev. B* **15**, 865 (1977).
- ¹⁷ M. Kuball, M. K. Kelly, M. Cardona, K. Köhler, and J. Wagner, *Phys. Rev. B* **49**, 16 569 (1994).
- ¹⁸ V. L. Berkovits, Y. A. Gol'dberg, T. V. L'vova, E. A. Posse, and R. V. Khasieva, *Fiz. Tekh. Poluprovodn.* **24**, 353 (1990) [*Sov. Phys. Semicond.* **24**, 217 (1990)].
- ¹⁹ V. L. Berkovits, A. O. Gusev, and T. V. L'vova, *Fiz. Tekh. Poluprovodn.* **26**, 1264 (1992) [*Sov. Phys. Semicond.* **26**, 705 (1992)].
- ²⁰ D. E. Aspnes, *J. Opt. Soc. Am.* **70**, 1275 (1980).
- ²¹ See, e.g., R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977).
- ²² D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Flores, *J. Vac. Sci. Technol. A* **6**, 1327 (1988).
- ²³ A. A. Studna, D. E. Aspnes, L. T. Florez, B. J. Wilkens, J. P. Harbison, and R. E. Ryan, *J. Vac. Sci. Technol. A* **7**, 3291 (1989).
- ²⁴ W. Mokwa, D. Kohl, and G. Heiland, *Phys. Rev. B* **29**, 6709 (1984).
- ²⁵ D. E. Aspnes, Y. C. Chang, A. A. Studna, L. T. Florez, H. H. Farrell, and J. P. Harbison, *Phys. Rev. Lett.* **64**, 192 (1990).
- ²⁶ P. Lautenschlager, M. Garriga, S. Logothetidis, and M. Cardona, *Phys. Rev. B* **36**, 4813 (1987).
- ²⁷ H. Lüth, *Surfaces and Interfaces of Solids*, edited by M. Cardona (Springer, Berlin, 1992).
- ²⁸ S. F. Pond and P. Handler, *Phys. Rev. B* **6**, 2248 (1972).
- ²⁹ J. D. E. McIntyre and D. E. Aspnes, *Surf. Sci.* **24**, 417 (1971).
- ³⁰ J. R. Chelikowsky and M. L. Cohen, *Phys. Rev. B* **14**, 556 (1976).
- ³¹ F. Manghi, E. Molinari, R. Del Sole, and A. Selloni, *Phys. Rev. B* **39**, 13 005 (1989).
- ³² W. L. Mochán and R. G. Barrera, *Phys. Rev. Lett.* **55**, 1192 (1985).
- ³³ S. Nannarone, S. D'Addato, J. A. Schaefer, Y. Chen, J. Anderson, and G. J. Lapeyre, *Surf. Sci.* **211/212**, 524 (1989).
- ³⁴ L. Viña, S. Logothetidis, and M. Cardona, *Phys. Rev. B* **30**, 1979 (1984).
- ³⁵ F. Lukès, S. Gopalan, and M. Cardona, *Phys. Rev. B* **47**, 7071 (1993).
- ³⁶ D. E. Aspnes, *Surf. Sci.* **37**, 418 (1973).
- ³⁷ S. E. Acosta-Ortiz and A. Lastra-Martinez, *Phys. Rev. B* **40**, 1426 (1989).
- ³⁸ S. Tachi, A. Moritani, and J. Nakai, *J. Appl. Phys.* **50**, 5461 (1979).
- ³⁹ M. Cardona, *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, New York, 1969), Suppl. 11.
- ⁴⁰ D. E. Aspnes and A. A. Studna, *Phys. Rev. B* **7**, 4605 (1973).
- ⁴¹ J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, Oxford, 1976).
- ⁴² F. Bartels, L. Surkamp, H. J. Clemens, and W. Mönch, *J. Vac. Sci. Technol. B* **1**, 756 (1983).
- ⁴³ A. Ruocco, S. Nannarone, M. Sauvage-Simkin, N. Fedrecy, R. Pinchaux, and A. Waldhauer, *Surf. Sci.* **307-309**, 662 (1994).