Surface Termination Effect on Reflectance Spectra of GaAs

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(Received 15 July 1996)

Dielectric response spectra of GaAs surfaces are determined using surface photoabsorption for surface conversion caused by Ga deposition and H adsorption on As-stabilized (001)-(2×4) surfaces and As desorption from As-rich $(111)B$-(2×2) surfaces. All of these spectra show common peaks at 2.6–3.0 and 4.5–4.7 eV, which coincide with critical points of bulk GaAs dielectric function. Model calculations show that the appearance of these critical points in the surface dielectric response can be explained by assuming that light absorption is quenched in the surface layer because of the terminated electronic wave functions at the surface. [S0031-9007(96)02246-6]

PACS numbers: 78.20.Ci

Surface reflectance (SR) spectroscopies in the visible to near-uv range have successfully been used for monitoring surfaces during epitaxy by molecular beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE). These surface sensitive techniques include spectroscopic elliposometry [1,2], reflectance difference spectroscopy (RDS) [3], normal incidence reflectance spectroscopy [4], and the Brewster-angle-incidence surface reflectance spectroscopy called surface photoabsorption (SPA) [5]. The GaAs (001) surface was extensively investigated using these techniques and a close correlation between surface reflectance spectra and surface reconstructions observed by reflection high energy electron diffraction (RHEED) was established experimentally in the MBE growth environment [6,7].

Chang *et al.* [8,9] calculated the surface band structure of GaAs (001) using tight binding approximation and assigned the observed RDS peaks to electronic transitions localized at As or Ga dimers on the surface. Recent first principles calculations [10,11] provide a more sophisticated picture in which electronic transitions between filled bulklike valence band and empty surface states contribute to optical anisotropy of the GaAs (2×4) and $c(4 \times 4)$ surface. Similar band calculations were also performed for Si (001) surfaces and electronic transitions related to surface dimers were identified [12]. In all of the above calculations, optical transitions that involve electronic states localized at surface dimers were more or less responsible for the optical anisotropy.

In this Letter, we will show experimental evidence that indicates that these surface reflectance spectra for GaAs can originate from modified bulk electronic transitions not related to any specific surface dimers and suggest an explanation for these spectra based on the surface termination of bulk electronic states using simple model calculations. Our calculations show that a peak in the imaginary part of the bulk dielectric function appears in the surface dielectric change, which is consistent with the observation for the Si [1,12–14], Ge [1,14], and GaInAs alloys [15].

Experiments were performed *in situ* using an MBE machine with optical access. Three surface transformations were performed for GaAs surfaces: (i) from (2×4) to (3×1) caused by Ga deposition on the (001) surface, (ii) from (2×2) to ($\sqrt{19} \times \sqrt{19}$) caused by As desorption on the $(111)B$ surface, and (iii) from (2×4) to (1×1) caused by H adsorption on the (001) surface [16,17]. In the hydrogen adsorption experiments, atomic hydrogen was supplied to the GaAs surface by cracking purified H_2.

In contrast to the RD spectra, which are obtained under static conditions, SPA measurements require a surface change. The SPA signal $Q_{pp}(\sigma_0 \rightarrow \sigma_1; \alpha)$ corresponding to surface conversion from σ_0 to σ_1 is defined as a relative change in reflection intensity. This is obtained by $(I^{\sigma_1}_{pp,\alpha} - I^{\sigma_0}_{pp,\alpha})/I^{\sigma_0}_{pp,\alpha}$, where $I^{\sigma}_{pp,\alpha}$ gives the reflected intensities for the p-polarized light with an incidence azimuth α when the surface has reconstruction σ. When the incidence azimuth coincides with one of the principal axes of a biaxial surface, the SPA signal is given by the following formula using the anisotropic three phase model [18],

$$Q_{pp}(\sigma_0 \rightarrow \sigma_1; \alpha) = -\frac{8\pi \varepsilon_a^{1/2}}{\lambda} \cos\phi_0 \, \mathrm{Im}\left[\frac{\varepsilon_b - \varepsilon_a \sin^2\phi_0}{(\varepsilon_b \cos^2\phi_0 - \varepsilon_a \sin^2\phi_0)(\varepsilon_b - \varepsilon_a)} \Delta\varepsilon_s d\right]$$

$$\Delta\varepsilon_s = \Delta\varepsilon_\alpha + \frac{\varepsilon_b^2 \varepsilon_a \sin^2\phi_0}{(\varepsilon_b - \varepsilon_a \sin^2\phi_0)} \Delta\left(\frac{1}{\varepsilon_z}\right),$$

where $\Delta\varepsilon_\alpha$ is the change in the surface dielectric function along the axis α and $\Delta(1/\varepsilon_z)$ is the change in the reciprocal of the dielectric function along the surface normal. The other parameters in the formula λ, ϕ_0, ε_b, ε_a, d are the wavelength

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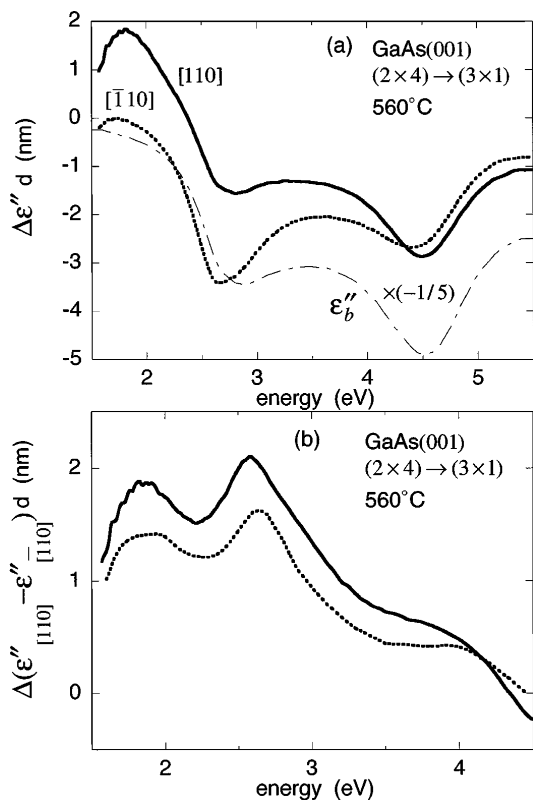

FIG. 1. (a) The imaginary parts of the change in the surface dielectric functions $\Delta\varepsilon_s d$ determined from SPA data for [110] (solid line) and for [$\bar{1}$10] (dotted line) for the surface conversion from (2 × 4) to (3 × 1) caused by Ga deposition. The imaginary part of the bulk dieletric function of GaAs at 550 °C (Ref. [21]) is also shown by the thin dash-dotted line. (b) The imaginary parts of the change in the surface dielectric anisotropy $\Delta(\varepsilon_{[110]} - \varepsilon_{[\bar{1}10]})d$ determined by SPA (solid line) and RDS (dotted line) (Ref. [18]).

in vacuum, the angle of incidence, the dielectric constant of the GaAs substrate and that of the vacuum, and the film thickness, respectively. The effect of the change in the surface dielectric function is represented by $\Delta\varepsilon_s$. Real and imaginary parts of $\Delta\varepsilon_s$ are obtained from Q_{pp} and the accompanying phase shift upon reflection determined by Kramers-Kronig transformation of Q_{pp} [19]. The published dielectric function of GaAs at the appropriate temperature was used for calculating $\Delta\varepsilon_s$ [20,21].

Imaginary parts of the change in surface dielectric function $\Delta\varepsilon_s$ corresponding to these surface conversions are shown in Figs. 1–3. Dielectric changes observed for the surface conversion from As-stabilized (2 × 4) to more Ga-rich (3 × 1) are shown by the solid line ([110] azimuth) and by the dotted line ([$\bar{1}$10] azimuth) in Fig. 1(a); the changes for the surface conversion from (2 × 2) to ($\sqrt{19} \times \sqrt{19}$) due to As desorption on the (111)B surface are shown in Fig. 2 for the [110] azimuth; and those for H adsorption to the (2 × 4) surface are shown by the solid line ([110] azimuth) and the dotted line ([$\bar{1}$10] azimuth) in Fig. 3. For surface conversion on a (111)B surface, the SPA spectrum observed for the [211] azimuth is the same as for the [110] azimuth. No

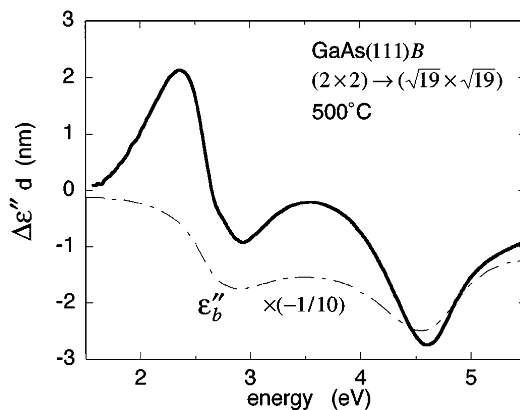

FIG. 2. The imaginary parts of the change in the surface dielectric function $\Delta\varepsilon_s d$ determined from SPA data for [110] (solid line) for the surface conversion from (2 × 2) to ($\sqrt{19} \times \sqrt{19}$) caused by As desorption. The imaginary part of the bulk dieletric function of GaAs at 500 °C (Ref. [21]) is also shown by the thin dash-dotted line.

azimuth dependence was observed, which is consistent with the fact that the (111) surface without reconstruction is optically isotropic.

All of these curves show a peak at 2.6–3.0 eV [an inverted one for Ga deposition and (111)B] and another one at 4.5–4.7 eV [also an inverted one for Ga deposition and (111)B]. The exact peak positions shift to higher energy with decreasing measurement temperature. For comparison, the imaginary part of the dielectric function of bulk GaAs is also shown by the thin dash-dotted lines in Figs. 1–3 [20,21]. The peaks in the surface dielectric change coincide with those that have been assigned to bulk critical points (CP) in the bulk dielectric function.

The solid line in Fig. 1(b) shows the change in the imaginary part of the surface dielectric anisotropy (SDA) $\Delta(\varepsilon_{[110]} - \varepsilon_{[\bar{1}10]})$, which is defined as the difference between the dielectric function along [110] and [$\bar{1}$10] [22] when the surface reconstruction changed from (2 × 4) to

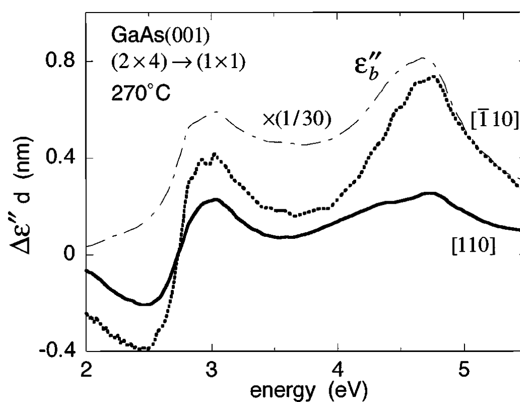

FIG. 3. The imaginary parts of the change in the surface dielectric functions $\Delta\varepsilon_s d$ determined from SPA data for [110] (solid line) and for [$\bar{1}$10] (dotted line) for the surface conversion from (2 × 4) to (1 × 1) caused by H adsorption. The imaginary part of the bulk dieletric function of GaAs at 231 °C (Ref. [20]) is also shown by the thin dash-dotted line.

(3×1) obtained from data shown in Fig. 1(a). The SDA obtained here is consistent with that previously obtained by RDS as shown by the dotted line, which is the SDA calculated from the $\Delta r/r$ and $\Delta\theta$ in Ref. [18]. Both curves agree with each other showing peaks at 1.8 and 2.6 eV and a shoulder at 4.0 eV. As can be seen here, the SPA measurements are not only consistent with the RDS observations of SDA, but also clarify the azimuth with which each peak is associated. It is evident from Fig. 1(a), that a 2.6 eV peak exists for both azimuths.

Common features appearing in the $\Delta\varepsilon_s d$ for the $(111)B$ surface and for the (001) surface calls for an origin of the spectra that is not related to specific surface dimers because it is inconceivable that the $(111)B$ surface has the same surface dimers as those existing on the (001) surface. Furthermore, the same peaks appear for both $[110]$ and $[\bar{1}10]$ azimuths for the surface conversion on the (001) surface, which indicates that the simplified argument of optical transition based on the selection rule of a diatomic molecule does not hold for these surfaces [6]. It was also found theoretically and experimentally that this type of simple selection rule is not valid for a Si (001) surface [12].

The appearance of the bulk CPs in the surface dielectric change suggests that we can explain the spectra on the basis of bulk electronic states modified by the surface. We explored this possibility by choosing a simple model to show that a change in the dielectric function of the surface layer in the three phase model has a peak at the same position as that of the bulk dielectric function because of the surface termination. Del Sole [23] demonstrated that surface termination of electronic wave functions causes the deviation of the normal incidence reflectance from the Fresnel formula. He showed that this effect can be accomodated by replacing the bulk dielectric function of the infinite crystal in the Fresnel formula with the effective dielectric function, which was explicitly obtained for the transition at the Γ point. We extended his calculation [23] to the case of E_1 CP when the light is incident to the (111) surface. Following Del Sole, we assumed that the electronic wave function ψ is terminated at the surface $z = 0$ such that $\psi = 0$ for $z \geq 0$, which indicates that wave function does not permeate the vacuum.

We calculated the effective dielectric function $\langle\varepsilon\rangle = \langle\varepsilon'\rangle + i\langle\varepsilon''\rangle$ for E_1 CP as follows. We assumed E_1 to be a two-dimensional M_0 type, consistent with various modulation spectroscopy results [24,25]. Then we assumed that the model dielectric function of the infinite solid near the E_1 CP is given by [26]

$$\varepsilon_0(\omega) \propto \left(\frac{E_1}{E}\right)^2 \ln\left[1 - \left(\frac{E + i\Gamma}{E_1}\right)^2\right]. \quad (1)$$

Using the same scheme as used by Del Sole [23], we calculated the imaginary part of the effective dielectric function $\langle\varepsilon''\rangle$ for the E_1 CP at $k_{c\nu}$ in the Brillouin zone when the surface is perpendicular to $k_{c\nu}$. We assumed the following E-k relation in terms of local coordinates associated to the CP at $k_{c\nu}$:

$$E(k - k_{c\nu}) = E_1 + \frac{\hbar^2}{2}\left(\frac{1}{m_{e,T}} + \frac{1}{m_{h,T}}\right)k_T^2 + \frac{\hbar^2}{2m_z}(k_{e,L}^2 - k_{h,L}^2),$$

where k_T, $m_{e,T}$, $m_{h,T}$, and k_L, m_z are the components of $k - k_{c\nu}$ perpendicular and parallel to $k_{c\nu}$ and the electron (hole) effective masses along each direction, respectively.

The difference between the model dielectric function and the effective dielectric function $\Delta\varepsilon_{\text{eff}} = \langle\varepsilon\rangle - \varepsilon_0(\omega)$ determined in this way can be converted to the surface dielectric function of the three phase model by equating the complex reflectance change given by the three phase model with that given by the Fresnel formula [27],

$$\Delta\varepsilon_{3\text{-phase}} d = \lambda\Delta\varepsilon_{\text{eff}}/4\pi i \varepsilon_b^{1/2}. \quad (2)$$

The imaginary part of the surface dielectric function $\text{Im}[\Delta\varepsilon_{3\text{-phase}}]$ thus obtained is shown in Fig. 4(b) (solid line) along with the imaginary part of the bulk model dielectric function (dotted line) used for the calculation. As can be seen in Fig. 4, the three phase model dielectric function has its peak at the same position as the bulk, which is consistent with our observation for the $(111)B$ surface shown in Fig. 2.

The physical origin of the appearance of bulk E_1 CP can be understood as follows [23]: the boundary condition at the surface leads to a surface layer in which light is not absorbed because $|\psi|^2$ reduces to zero from the bulk value. Quenched absorption causes a surface dielectric change $\Delta\varepsilon'' = -\varepsilon_b''$ in the layer. The thickness of this layer would be of the order of $1/k_z$, where k_z is the magnitude of wave vector along $[111]$ of the carriers that are responsible for the E_1 transition. Because of the two dimensionality of the E_1 CP, the threshold energy of the valence-to-conduction band transition and the line shape of the transition do not depend on k_z. This results in the dielectric function of the surface layer of the three phase model $\Delta\varepsilon d \sim \sum_{k_z}(-\varepsilon_b)/k_z \propto -\varepsilon_b$.

Next we will discuss the origin of the optical anisotropy on the (001) surface. As shown above, the termination

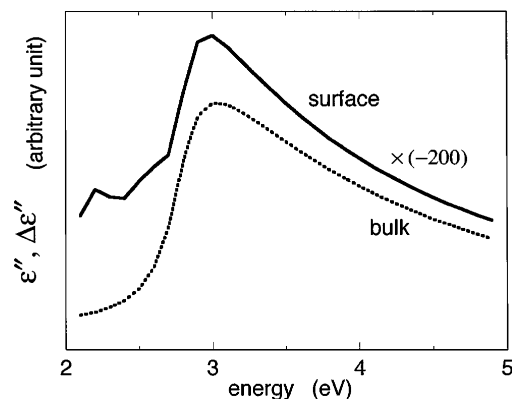

FIG. 4. Solid line: calculated change of the imaginary part of the surface dielectric function determined for the three phase model. Dotted line: the imaginary part of the model dielectric function of the infinite crystal used in the calculation.

of wave functions having k vectors along [111] can lead to the observed surface dielectric change. For the (001) surface with surface reconstruction such as (2×4), eight $\langle 111 \rangle$ valleys are divided into two groups depending on whether the projection of k_{cv} onto the (001) plane is parallel to the [110] ([110] type) or the $[\bar{1}10]$ ($[\bar{1}10]$ type). These two types are not equivalent because of the surface reconstruction and give different effective masses and resultant different joint density of states that are responsible for optical transitions near the surface. For simplicity, we neglect the electric field along surface normal when we consider the interaction between light and electrons in each valley. According to the well established selection rule [25], when the plane of incidence of the monitoring light is parallel to [110], the contribution from $[\bar{1}11]$ and $[1\bar{1}1]$ valleys (the $[\bar{1}10]$ type defined above) is three times larger than that from the [111] and $[\bar{1}\bar{1}1]$ valleys (the [110] type). For the $[\bar{1}10]$ incidence, the contribution is reversed. Thus, when the $[\bar{1}10]$-type valleys and [110]-type valleys are not equivalent because of the surface reconstruction, optical anisotropy between the [110] incidence and the $[\bar{1}10]$ incidence results. This argument leads to a conclusion that the optical anisotropy of the surface is determined by the long-range order on the surface rather than the local bond configuration. If this is the case, the similarity between the RD spectra observed for MBE-grown layers and those for MOVPE-grown layers [28] indicates the existence of similar long-range order on both surfaces.

Several authors have reported the appearance in the SR spectra peaks at the same position of the bulk dielectric function. Kelly *et al.* [1] observed a surface dielectric change caused by H adsorption on Ge (111), Si (001), and Si (111) surfaces. They found that the peaks observed in the surface dielectric functions of various surfaces of Si and Ge invariably showed peaks that coincided with the peaks in the imaginary part of bulk dielectric functions. RDS spectra of Ge (001) [14], Si (001) [13,14], and ordered alloy of InGaAs [15] also show peaks that coincide with those of the imaginary part of the bulk dielectric function. These observations suggest that the surface termination effect discussed here is universally observed irrespective of materials.

However, the present model does not explain all the features observed in the experiments, in particular, those below 2.0 eV. Furthermore, some observations suggest that surface dimers contribute to SR spectra. The abrupt transition of the SPA spectra from a substratelike one to a surface-layer-like one observed when 1–2 monolayers of surface layer were grown for InAs/GaAs and InP/InAs heterostructures seems to support the dimer model [29]. More investigation is necessary to obtain a comprehensive picture of the SR spectra of semiconductors.

In conclusion, we showed that the surface dielectric response of various GaAs surfaces shows peaks that cannot be ascribed to a specific surface dimer and that these peaks correspond to the bulk CPs. We also showed that this is explained by the termination of electronic wave functions at the surfaces using a simple model calculation.

We thank Yoshiji Horikoshi for his valuable comments on this research and Tetsuhiko Ikegami for his support and encouragement.

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