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Electro-optic effects in the optical anisotropies of (001) GaAs

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We report on both optical reflectance anisotropy and electroreflectance measurements carried out in order to determine the physical origin of the impurity-dependent anisotropy observed in the reflectance spectrum of (001) GaAs. We found that such anisotropy is actually a bulk-related, linear electro-optic effect produced by the electric field present at the semiconductor surface. This electric field is due to the pinning of the Fermi level at this surface because of the presence of surface states. Our results are important for the application of optical reflectance anisotropy measurements to the study of surface processes in zinc-blende semiconductors.

The measurements of above-band-gap anisotropies in the reflectance spectrum of cubic semiconductors is emerging as a tool for the study of surface processes in such materials.[1,2] This is due to the fact that the bulk of cubic semiconductors is nominally isotropic, so that any observed reflectance anisotropy should be related to the lower symmetry of the semiconductor surface. However, bulk-related reflectance anisotropies could be produced by spatial dispersion effects,[3] or, as shown in this paper, by the breakdown of the cubic symmetry of the semiconductor by a directional perturbation. An unambiguous identification of the origin of the observed anisotropies is then essential in order for the measurement of reflectance anisotropies to be useful in the study of surface processes in cubic semiconductors.

Above-band-gap optical anisotropies were first observed by Cardona, Pollack, and Shaklee in the reflectance spectrum of (110) Si.[4] A systematic study of such anisotropies by a reflectance-difference (RD) technique was reported by Aspnes and Studna for (110) Si and Ge.[1] Optical anisotropies were predicted for the (110) surface of diamond-type semiconductors by Mochan and Barrera on the basis of a surface local-field model.[5] Surface (many-body screening) as well as bulk (spatial dispersion) related mechanisms have been identified as responsible for the anisotropic effects in Si and Ge.[1,5,6] Above-band-gap optical anisotropies have also been reported for the (110) surface of GaAs and have been attributed to spatial dispersion.[3] Berkovits *et al.*[7] investigated reflectance anisotropies in (110) surfaces of InSb and GaAs and concluded that they are partially due to the electric field induced by the pinning of the Fermi level at the oxidized surface of the semiconductor. In a previous paper,[8] we reported on a systematic experimental study of optical anisotropies (2.3–5.5 eV energy range) in the (001) surface of GaAs by a RD technique. We concluded that (001) GaAs anisotropy spectra have two components with a different physical origin: one component which is highly dependent on both GaAs impurity concentration and conductivity type and another component which does not depend on these two parameters. The first component was suggested to have an electro-optic origin.[8]

The purpose of this paper is to report on both RD and electroreflectance (ER) experiments carried out in order to determine the physical origin of the impurity-dependent component of the anisotropy in the reflectance spectrum of (001) GaAs. By comparison of RD and ER experimental line shapes we show that such component is due to a linear electro-optic, bulk-related effect induced by the sample surface electric field. The origin of this electric field is the well-known electric charge exchange between the bulk and the surface states of the semiconductor, in order for the material to attain thermodynamic equilibrium.[9] As a result of this process, the Fermi level becomes pinned at the semiconductor surface at an energy somewhere in the forbidden gap. The presence of the surface electric field results in the breakdown of the cubic symmetry of GaAs near the surface and, consequently, in the loss of the optical isotropy in this region. We stress the importance of our result for the application of the RD technique as an optical probe for the study of surface processes in zinc-blende semiconductors.

For the RD experiments, we use both a (001)-oriented n-type GaAs commercial wafer with a doping concentration of 10^{16} cm^{-3}, and a vapor-phase-epitaxy (VPE) n-type epitaxial layer with a doping level of 3×10^{15} cm^{-3} grown on (001) GaAs. Prior to the measurements, the GaAs wafer was chemomechanically polished with bromine-methanol as described elsewhere.[8] The epitaxial layer was used without any surface treatment. For the ER experiments, we used the same commercial wafers used in the RD measurements. In this case, samples were prepared in the form of Schottky barriers by evaporating a semitransparent (~150-Å) Au film on one of the surfaces of the GaAs wafer. Previously, a Au-Ge Ohmic contact had been alloyed to the opposite surface of the wafer. Prior to the evaporation of the semitransparent film the sample was chemically etched with 1:3:1 H_2O:H_2SO_4:H_2O_2. The Schottky diodes had an area of about 4 mm^2 and were mounted on transistor headers with the Schottky barrier face up.

In the RD experiments, we subtracted the near-normal GaAs reflectance for light polarized along the $[1\bar{1}0]$ and $[\bar{1}\bar{1}0]$ directions on the GaAs reflecting surface. RD spectra are defined as such reflectance difference normalized to the reflectance average. The spectrometer employed to

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carry out the RD experiments as well as the experimental procedure are described elsewhere.[8] In the ER experiments, monochromatic, linearly polarized light incided near normally on the sample surface with the polarization vector along either the [1$\bar{1}$0] or the [$\bar{1}\bar{1}$0] crystal direction. The relative change in the reflectance of the sample due to an ac voltage applied to the Schottky barrier was measured as a function of energy in the region around the E_1 and $E_1+\Delta_1$ transitions. As explained below, the ER spectrum to be compared to the RD spectrum is obtained by taking the difference between the [1$\bar{1}$0] and [$\bar{1}\bar{1}$0] ER spectra. We employed the longitudinal ER configuration in which the applied electric field is perpendicular to both sample surface and light polarization vector.[10]

We will first discuss the RD results. In Figs. 1(a) and 1(b), we show the RD spectra for samples with doping levels of 10^{16} cm^{-3} and 3×10^{15} cm^{-3}, respectively. We can see that, in agreement with the trend observed in the spectra reported in Ref. 8, the amplitude of the oscillation observed around the E_1 and $E_1+\Delta_1$ transitions is lower for the sample with the lower doping level. As a matter of fact, this oscillation is barely seen in the spectrum of Fig. 1(b). This is consistent with the assumption that such an oscillation is associated with the electric field due to the pinning of the Fermi level at the sample surface, as mentioned above. Recalling the results of Ref. 8, we can isolate the field-dependent component of the RD spectrum of Fig. 1(a) by subtracting from it the spectrum of Fig. 1(b). The dashed line of Fig. 2 shows the subtracted RD spectrum obtained in this way. It should be noted that this spectrum was vertically offset for 0.43 units (in the $\Delta R/R$ scale of this figure) in order to make it coincide with the linear ER spectrum. As reported elsewhere,[8] RD line-shape offsets with no intrinsic origin appear because of the lack of perfect alignment of the surface of the sample perpendicular to the rotation axis of the sample holder. Although in our experimental setup such offsets are in general wavelength dependent, in the spectral region shown in Figs. 1 and 2 this dependence is weak enough that no appreciable line-shape distortion occurs.

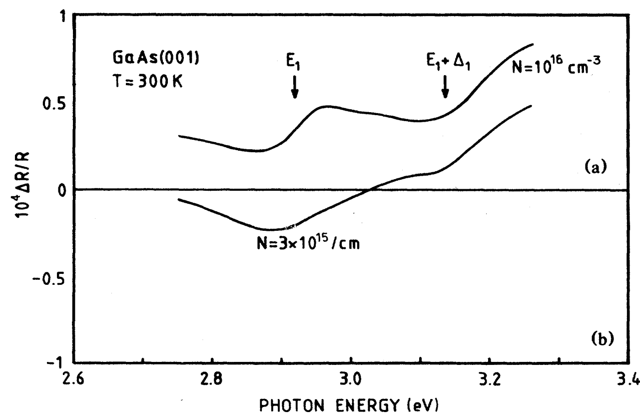

FIG. 1. (a) RD spectra for n-type (001) GaAs with $N=10^{16}$ cm^{-3} and (b) $N=3\times10^{15}$ cm^{-3} doping levels, in the energy region around E_1 and $E_1+\Delta_1$. $\Delta R/R$ is given in terms of rms values; peak-to-peak values are $2\sqrt{2}$ times higher.

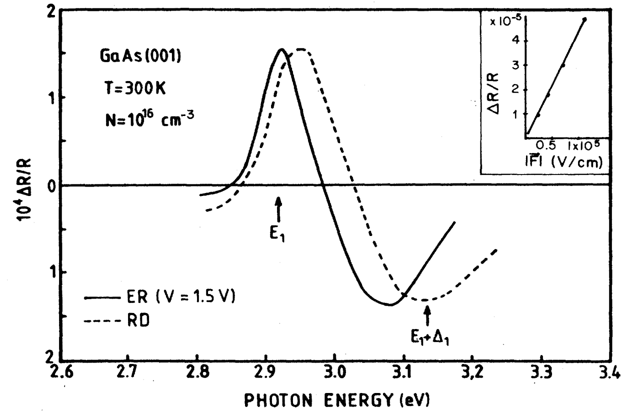

FIG. 2. Impurity-dependent component of the RD spectrum of (001) GaAs (dashed line) along with the linear electro-optic component of the ER spectrum of the same sample (continuous line). The GaAs sample was unintentionally doped (n-type) at a level of 10^{16} cm^{-3}. $\Delta R/R$ is given in terms of rms values; peak-to-peak values are $2\sqrt{2}$ times higher.

The subtracted RD spectrum of Fig. 2 has to be compared with the linear ER spectrum of the same sample (continuous line of Fig. 2) obtained as explained in the following. Neglecting terms higher than second order in the electric field, the effect that such a field has on the dielectric function of a semiconductor is given by

$$\Delta\epsilon_{ij}=Z_{ijk}F_k+\Gamma_{ijkl}F_kF_l\ , \tag{1}$$

where Z_{ijk} and Γ_{ijkl} are the components of the tensor giving the change in the semiconductor dielectric function due to an electric field with components $F_{k,l}$. Z_{ijk} and Γ_{ijkl} are tensor components describing, respectively, the linear and quadratic electro-optic effects.[11] Because of the tensorial character of Eq. (1), the corresponding normalized change of semiconductor reflectivity $\Delta R/R$, in general, gives anisotropic results.[11] It is found that, for normal incidence on a (001) zinc-blende surface, only the linear term in Eq. (1) contributes to the $\Delta R/R$ anisotropy for **F** perpendicular to (001) (Ref. 10) (longitudinal geometry). Taking into account only the linear term in Eq. (1), the anisotropy of $\Delta R/R$ is described by[10]

$$\Delta R/R=2(akl+bhl+chk)g(E)\,|\mathbf{F}|\ , \tag{2}$$

where $|\mathbf{F}|$ is the magnitude of the electric field, $g(E)$ is a function that depends on the energy and on the crystal structure, (a,b,c) are the directional cosines of the electric field, and (h,k,l) are the directional cosines of the optical polarization. For a longitudinal geometry with incidence on a (001) surface, Eq. (2) reduces to

$$\Delta R/R=g(E)\sin(2\theta)\,|\mathbf{F}|\ , \tag{3}$$

where θ is the light polarization vector measured counterclockwise from the [100] direction. From Eq. (3), the principal axes of the (001) reflectance anisotropy are the [1$\bar{1}$0] and [$\bar{1}\bar{1}$0] directions. The longitudinal electroreflectance spectrum of a (001) zinc-blende surface shows both linear and quadratic electro-optic components.

However, by taking into account the isotropic nature of the quadratic electro-optic effect in this face, the linear component of the electroreflectance spectrum can be obtained by subtracting two ER spectra taken with polarization vectors along [1$\bar{1}$0] and [$\bar{1}\bar{1}$0].

In Fig. 3 we show the obtained (001) GaAs electroreflectance spectra for [$\bar{1}\bar{1}$0] (solid line) and [1$\bar{1}$0] (dashed line) polarization directions. The spectra were obtained in the energy range around the E_1 and $E_1+\Delta_1$ transitions. In Fig. 2 we plot (continuous line) the difference of the two curves of Fig. 3, along with, as pointed out before, the impurity-dependent component of the anisotropy spectrum of the same sample (dashed line). The difference electroreflectance (DER) spectrum of Fig. 2 corresponds to an ac peak-to-peak modulation voltage of 1.5 V with a 0.75-V dc reverse-bias offset voltage. The dc voltage was applied in order to prevent the Schottky from becoming polarized in the high-conductivity forward-bias direction. The DER spectrum of Fig. 2 is in reasonable agreement with that reported by Kyser and Rhen[10] using a transverse ER configuration. It should be noted that $\Delta R/R$ in Figs. 1–3 is given in terms of rms values; peak-to-peak values are $2\sqrt{2}$ times higher.

To prove that the DER spectrum of Fig. 2 is indeed linear in the electric field, we obtained a series of DER spectra for several applied ac voltages. In all the measurements we applied a reverse-bias voltage of half the peak-to-peak ac value in order to avoid the high-conductivity regime of the Schottky diode. In the inset of Fig. 2 we show a plot of the peak-to-peak DER spectra amplitude as a function of $F-F_0$, where F is the maximum electric field at the surface of the diode and F_0 is the field with no applied voltage (F and F_0 are obtained, respectively, at the minimum and maximum of the ac applied voltage cycle). From this plot we can see that the DER spectrum amplitude does depend linearly on the applied electric field, thus demonstrating its linear electro-optic origin.

Assuming that the impurity-dependent RD spectrum of Fig. 2 is associated with the GaAs surface electric field, the relationship of such a spectrum to the linear electro-optic ER spectrum shown in the same figure can be established as follows. First, we note that both spectra would be due to a longitudinal surface electric field. Second, from Eq. (3) we note that increasing angle θ by 90°, i.e., rotating the sample by 90°, is equivalent to inverting the sense of the electric field **F**. Thus, the impurity-dependent spectrum of Fig. 2 would be the same as that obtained from a (001) longitudinal ER experiment with an incident light polarization vector along [1$\bar{1}$0] (or [$\bar{1}\bar{1}$0]) and in which the surface electric field is symmetrically modulated around zero. On the other hand, it is noted that such modulation cancels out the ER quadratic electro-optic component so that only the linear term is retained. In this way, although in the ER experiments reported here it is not possible to symmetrically modulate the electric field around zero, the DER spectrum of Fig. 2 would be the same as that obtained from a symmetrically modulated experiment. Thus, we can conclude that, by assuming an electro-optic origin for the impurity-dependent component of the (001) RD spectrum, the line shapes of the spectra of Fig. 2 should be the same.

It is noted that the above conclusion is based on the assumption that electro-optic terms of order higher than second are absent in both (001) ER and field-dependent (001) RD spectra. As a matter of fact, higher than second-order electro-optic terms would make the line shape of this last spectrum not necessarily the same as that of the DER spectrum of Fig. 2, as they correspond to different values of surface electric field.

From Fig. 2 we can see that although the two spectra shown there are slightly displaced in energy, one with respect to the other, the coincidence between them is remarkable. Both spectra show a single oscillation and, in both cases, the maxima and minima of the oscillation occur at energies around the E_1 and $E_1+\Delta_1$ transitions, respectively. Such coincidence establishes the linear electro-optic origin of the impurity-dependent component of the (001) GaAs anisotropy spectrum. Henceforth, this component turns out to be a bulk-related effect and it is expected to be present in the anisotropy spectrum of the (001) surface of any cubic semiconductor with a zinc-blende lattice. As it was mentioned above, the ER spectrum of Fig. 2 corresponds to a peak-to-peak modulation voltage of 1.5 V with a 0.75-V reverse-bias offset voltage. The peak-to-peak amplitude of the modulation voltage was chosen so that the amplitude of the subtracted ER spectrum of Fig. 2 resulted equal to that of the RD spectrum of the same figure. From this result, a value of ~0.4 V is deduced for the GaAs surface potential and a maximum electric field in the Schottky barrier of 3.5×10^4 V/cm.

The question arises on whether an electric-field–dependent component is also present in the anisotropy spectra of the (110) surfaces of zinc-blende semiconductors. For these surfaces, according to Eq. (2), the linear electro-optic effect is absent. The quadratic effect, on the other hand, does exist and presents an anisotropy with the [001] and [1$\bar{1}$0] directions as principal axis.[11] Thus, any impurity-dependent anisotropy should be related to the quadratic electro-optic effect. In the low-field

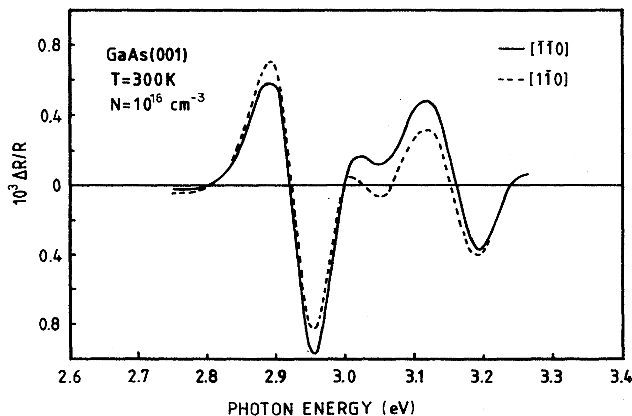

FIG. 3. Schottky barrier ER for n-type (001) GaAs with a doping level of 10^{16} cm^{-3}. Continuous and dashed lines correspond to orientations of the incident light along [$\bar{1}\bar{1}$0] and [1$\bar{1}$0], respectively.

electroreflectance theory of Aspnes,[12] the ER line shape for (110) surfaces is independent of the orientation of the light polarization vector. Thus, within the limits of the low-field regime, the field-dependent RD line shape should be the same as that of low-field electroreflectance. In this way, the contributions of E_1 and $E_1+\Delta_1$ to the (110) RD line shape should have the same sign, as it occurs for ER line shapes. From the RD spectrum reported in Ref. 8, we can see that, although such a spectrum does indeed show the same sign for the E_1 and $E_1+\Delta_1$ contributions, it does not show the sharpness characteristic of low-field ER spectra. This, however, could be due simply to spectrum broadening associated to high doping levels. On the other hand, it should be noted that Aspnes and Studna have described the RD spectrum of (110) GaAs and InP on the basis of a spatial dispersion model.[3]

In conclusion, we have determined the linear electro-optic origin of the impurity-dependent component of the (001) GaAs reflectance anisotropy spectrum in the region around the E_1 and $E_1+\Delta_1$ transitions. The electric field giving rise to the electro-optic effect is due to the electric charge exchange between the bulk and surface states of the semiconductor. This exchange is produced in order to attain thermodynamic equilibrium and results in the pinning of the Fermi level at a given energy at the surface of the material. The obtained results are important for the application of the RD technique to the study of surface processes in zinc-blende semiconductors.

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