Surface-field effect in piezoreflectance spectra

C. Alibert, A. M. Joullie, and G. Bordure

Groupe d'Electronique des Matériaux et Composants, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex, France

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Using a heterojunction Ge-Cu₂S sample, we show that the surface electric field modifies considerably the piezoreflectance spectra of germanium near the fundamental direct threshold. We show experimentally that piezomodulation is first derivative, which allows us to apply the theory of Seraphin and Aspnes.

Currently it is recognized that a surface electric field in a semiconductor could affect the reflectance and the first-derivative modulation spectra.¹ For optical transitions above the fundamental absorption edges, a theoretical analysis predicts very few consequences.¹ The first experimental investigations involving wavelength modulation have not revealed significant variations with electric field.²⁻⁴ Very recently Aspnes and Sell⁵ using a high-precision reflectometer have shown that for these transitions, the surface electric field modifies the first-derivative modulation spectra as predicted by theory.¹ Near the fundamental absorption edge the small value of the broadening parameter Γ leads to a more important effect. Precise reflection measurements on the n = 1 exciton of GaAs made by Sell and co-workers could be explained by the surface electric field.⁶ Electroreflectance measurements in the region of the fundamental energy gap of GaAs made by Evangelisti and co-workers confirm this effect. 7 In this paper we report a direct investigation of the effect of the surface electric field on piezoreflectance (PR) spectra. Because of the piezoelectrical properties of noncentrosymmetric III-V compounds,⁸ we have chosen to study germanium.

The experimental conditions are as follows. The material was Sb doped with $n = 2 \times 10^{14}$ cm⁻³. An Ohmic contact is obtained by diffusion of an Au-Sb alloy on the rear face of the sample: This face is glued on a piezoelectric transducer (Quartz et Silice P 60). The sample has to be thin enough to be driven by the transducer but sufficiently thick to prevent back-reflection effects.^{9,10} Optical and mechanical properties of germanium give 200 μ m as a convenient thickness. A small back-reflection effect appears in the lower energies of the spectrum. A heterojunction Ge-Cu₂S is made on the front of the sample as previously described.¹¹ This heterojunction allows us to control the surface electric field.¹² The sample is illuminated near normal incidence and the spectra are measured by standard optical- and phase-sensitive-detection techniques.¹¹

A preliminary low-field electroreflectance (ER) study (2-mV modulation) determines the dc bias value corresponding to the flat-band (FB) position with an accuracy of 5 mV and gives 800.5 meV for the energy gap. A set of PR spectra is reported on Fig. 1, with different dc bias conditions. We can observe that the surface-electric-field effect on the PR spectrum is very important and cannot be neglected. The peak that appears near the FB is generated by the exciton level. Far from the FB the spectra have similar line shape for both polarizations. A PR spectrum corresponding to a part of the sample without Cu₂S was similar to spectra (a) and (e). It is important to remark that the energy of the peaks is very sensitive to the surface electric field while the zero crossing (near 798 meV) is relatively unaffected which suggests that this spectral feature is preferred for spectral analysis.

The field which gives rise to the ionization of the n = 1 exciton level is defined by

$E_i = R/ea$,

R is the effective Rydberg energy and *a* the effective Bohr radius. For germanium this field¹³ is $E_i = 550 \text{ V cm}^{-1}$. In the case of the Ge-Cu₂S heterojunction, a previous study has shown that for small negative bias the barrier is quite well described by a Sckottky model¹⁴: This feature enables us to evaluate the electric surface field. We can note that the field value 2.1 kV cm⁻¹, which corresponds to Fig. 1(d), is large compared with E_i although the exciton effect is still present in this spectrum. This can be explained by the fact that the reflected beam does not come only from the sample surface but also from planes parallel to the surface of the space-charge region where the electric field is not large enough to ionize the exciton.⁷

By comparison of derivation of reflectance, wavelength modulation and PR spectra, Aggarwal and co-workers have shown that the effect of PR is first derivative.¹⁵ We have verified this result by deriving ER spectra by piezomodulation. The experimental conditions are as follows: The piezo-

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9



FIG. 1. Effect of band bending on piezoreflectance of germanium near the E_0 transition. Voltage values are measured from the flat-band position. The arrow shows the energy of the E_0 transition measured from low-field electroreflectance spectra.

electric transducer is low-frequency (f_1) driven while the applied electric field is high-frequency (f_h) modulated with $f_h \gg f_1$ and $f_h \neq n f_1$ (n is an integer). The double-modulated optical signal is detected by a first lock-in amplifier tuned at f_h with an integration time τ_h such as $f_1 \tau_h \ll 1$. The output of this lock-in is observed by means of a second phase-sensitive detector tuned at f_1 .¹⁶ We can note that with low-frequency electric field and high-frequency piezomodulation this technique provides directly the effect of the electric field on the PR spectrum. In Fig. 2(b) the dashed line is obtained deriving directly the low-field ER spectrum represented in Fig. 2(a); the full line is given by the method given above. The spectra are scaled to give the same high-energy-peak amplitude. We can note the good agreement between the two curves in spite of a small discrepancy in their lower-energy part: This is probably due to the sample-thickness modulation.¹⁰

As piezomodulation is first derivative like, we can compare our data with the Seraphin-Aspnes theory.¹ Let ΔS be the strain induced by the piezo-electric transducer. We can write

$$\frac{1}{R}\frac{\Delta R}{\Delta S} = k\frac{1}{R}\frac{\Delta R}{\Delta E}$$

By neglecting the valence-band spliting produced by the stress, k is given by¹⁷

$$k = -(2-\lambda)a$$
.

For our (100) surface¹⁸ sample

$$\lambda = 2C_{12}/C_{11}$$

 C_{ij} are elastic constants and a is the deformation potential for isotropic dilation.

Using the value a = -10.2 eV obtained from recent piezoelectroreflectance measurements^{12,14} we have k = 12.7 eV. From Seraphin and Aspnes, the line shape obtained in a wavelength-modulation measurement is

$$\frac{1}{R(\mathscr{E})}\frac{dR(\mathscr{E})}{dE} = \frac{1}{R(0)}\frac{dR(0)}{dE} + \frac{1}{R(0)}\frac{d}{dE}\Delta R(\mathscr{E}) \quad .$$

R(0) is the intrinsic reflectivity and $R(\mathcal{E})$ is the electric field \mathcal{E} -modified reflectivity.

For piezoreflectance, this equation becomes

$$\frac{1}{R}\frac{dR}{dS} = \frac{1}{R_0}\frac{dR_0}{dS} + \frac{k}{R_0}\frac{d(\Delta R)}{dE}$$



FIG. 2. (a) Low-field electroreflectance spectra of germanium near the E_0 transition. (b) solid line piezo-modulation derivative of (a); dashed line direct derivative of (a).

9

High-electric-field ER measurements made on this sample gives -0.55 eV^{-1} for the error term $(1/R_0) d(\Delta R)/dE$.¹⁹ This leads to $(k/R_0) d(\Delta R)/dE$ = -7. This value is in good agreement with the experimental one, -8.7 (Fig. 1).

In conclusion we have reported the first direct observation of electric field effect on piezoreflectance spectra. Our results are in good agreement

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with the Seraphin-Aspnes theory and show that surface electric field can be taken into account in piezoreflectance spectra fitting. These experiments have been made on germanium. Recent studies on very pure gallium antimonide have given a more important electric field effect which can be due to the noncentrosymmetrical structure of this compound.

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