Excitonic reflectance of GaAs crystals cleaved in liquid helium

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We report optical reflectance spectra near the $n = 1$ excitonic resonance of GaAs. The experimental results from crystals cleaved in liquid helium and exposed to air exhibit noticeable changes of the line shape. Comparison with a model based on the adiabatic approximation indicates that line-shape distortions by surface electric fields are unavoidable for air-exposed GaAs surfaces.

INTRODUCTION

Optical reflectance measurements at energies near excitonic resonances in direct-gap semiconductors have contributed considerably to the understanding of excitons near surfaces.[1-5] The reported spectra depend on surface treatment[2,3] and illumination intensity[6,7] because band bending influences the excitonic behavior. This effect is so pronounced in GaAs that the achievement of flat bands is highly questionable for conventionally prepared surfaces. In the absence of surface electric fields the electron-hole motion is influenced only by cut-off forces at the crystal surface and by image-charge forces.[4,5] The resulting quenching of the resonant polarization can be described by phenomenological parameters such as the dead-layer thickness[1,3] or by refined theories without adjustable parameters.[5,8]

In the present paper we report reflectance and luminescence spectra of GaAs surfaces obtained by cleaving in liquid helium in order to prevent contamination of air. The reflectance spectra recorded immediately after cleavage and subsequently after exposure to air exhibit noticeable differences. We compare these reflectance spectra with results from calculations in which an electric field is included in an adiabatic treatment of the electron-hole motion. The luminescence spectra are compared with previously reported results on the influence of air exposure on the luminescence of GaAs cleaved in ultrahigh vacuum.[9] In view of these comparisons, it is reasonable to assume that a GaAs surface cleaved in liquid helium has essentially flat bands, and that surface electric fields of at least 0.2 times the excitonic ionization field account for the reflectance line shape of the air-exposed surfaces.

EXPERIMENTAL

We have performed our experiments with high-purity n-type GaAs crystals grown by liquid-phase epitaxy on a (001) surface. The carrier concentration is about $\sim 10^{14}$ cm^{-3} with mobilities at 77 K of more than 90 000 cm^2/V s. The thickness of the epilayers is typically about 40 μm. The samples are cleaved along a (110) surface during immersion in liquid helium, pumped well below the λ point. For reflection measurements we use a tungsten-iodine lamp as a light source. Photoluminescence is excited by the 488-nm line of an Ar$^+$ laser with an intensity of about 1 mW/mm^2. The reflected or emitted light passes a double grating monochromator with a spectral resolution of 0.01 nm and is detected with a cooled photomultiplier (GaAs cathode), photon counting electronics, and digital data acquisition.

For conversion from vacuum wavelength to energy, a factor of 1239.852 nm eV is used.[10] In addition, the refractive index of air is included.[11]

EXPERIMENTAL RESULTS

We have measured photoluminescence and reflectance immediately after cleavage in superfluid helium and after an exposure to air. In Fig. 1 we show the luminescence spectra of GaAs near the $n = 1$ excitonic resonance. The emission is dominated by the recombination peak due to excitons bound to neutral donors (D^0, X) at 1.5141 eV followed by the broad polariton emission band on the high-energy side.[12] The luminescence intensity of the freshly cleaved surface (A) is by a factor of 5 higher than the air-contaminated one (B). This result agrees quite well with previous observations by Fischer and Stolz[9] on UHV- and air-cleaved GaAs surfaces and indicates the proper surface conditions obtained by cleavage in liquid helium.

Photoemission measurements have indicated that flat bands can be obtained at n-type GaAs (110) surfaces by cleavage in UHV.[13] Contamination with air, especially oxygen, causes surface states via adsorption near the middle of the gap.[13,14] The high density of surface states pins the Fermi level and bends bands, creating an electric field which decreases into the crystal bulk. The electron-hole pairs
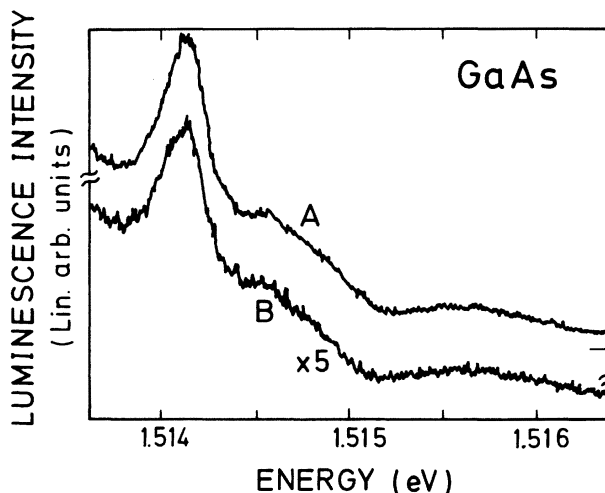

FIG. 1. Luminescence spectra of GaAs (at 1.8 K) cleaved in liquid helium (curve A) and after exposure to air (curve B).
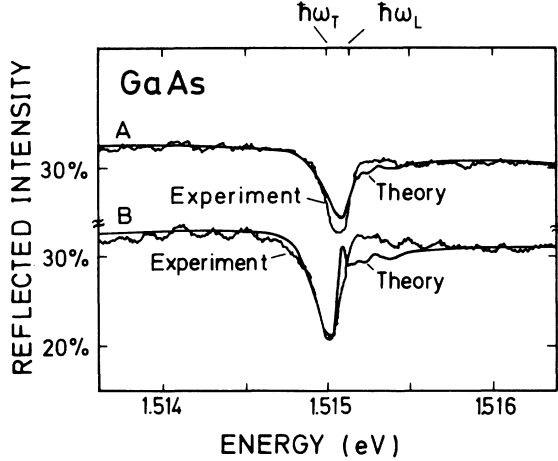
FIG. 2. Reflectance spectra of GaAs. The full curves are experimental results obtained for a freshly cleaved surface (curve A) and the same surface after exposure to air (curve B, displaced 10%). The theoretical curves are calculated with the parameters $\hbar\omega_T = 1.5150$ eV, $\hbar\omega_{LT} = 0.13$ meV, $m_h/m_e = 5$, $E_x = 4$ meV, $\epsilon_b = 12.6$, and $a_B = 11$ nm. The curve fitted to A has $F_0 = 0$ while the curve fitted to B has $F_0 = -0.20E_x/ea_B$ and $d = 440$ nm. A small damping of 0.02 meV is included.

created by illumination are separated by this electric field, thereby discharging the surface states and the ionized donors. This effect flattens the electron bands. Field cancellation may occur if the steady-state excess carrier concentration is high enough for discharging. However, a residual electric field suppresses radiative excitonic recombination by spatial separation of electrons and holes, and thus decreases luminescence intensity. Furthermore, surface states enable fast nonradiative recombination,[14] which also drastically reduces the emission intensity. Which of the two mechan-

isms dominates cannot be decided by photoluminescence alone. Reflection experiments are more suitable than luminescence for extracting detailed information on excitonic surface effects. We have measured the reflectance of the same surfaces as studied by luminescence. Figure 2 shows the reflection spectra of GaAs in the vicinity of the $1s$ excitonic resonance of a freshly cleaved surface (A) and of a surface after exposure to air (B). Comparing the two spectra, one can see that exposure to air causes a red shift of the reflection minimum and alters the line shape.

CALCULATED RESULTS

The present treatment is based on the effective-mass approximation applied to a simple direct gap characterized by the energy E_g and the effective masses m_e and m_h of electrons and holes, respectively. The masses and the static dielectric constant ϵ_s define the Bohr radius a_B and the Rydberg energy E_x of bulk excitons. The bulk polaritons derived from $n = 1$ excitons are characterized by a resonance frequency $\omega_0 = (E_g - E_x)/\hbar$, a longitudinal-transverse splitting ω_{LT}, and a spatial dispersion given by the mass $M = m_e + m_h$.

Turning to the half-space geometry, we consider a crystal filling the region $z > 0$. In the present calculations, we assume an electric field $\vec{F}(\vec{r})$ perpendicular to the surface,

$$\vec{F}(\vec{r}) = (0, 0, F_0 e^{-z/d}) \ , \tag{1}$$

where F_0 is the field at the surface and d is an appropriate screening length. This field leads to a two-particle potential,

$$\phi_F = eF_0 d(e^{-z_h/d} - e^{-z_e/d}) \ , \tag{2}$$

where $\vec{r}_e = (x_e, y_e, z_e)$ and $\vec{r}_h = (x_h, y_h, z_h)$ are coordinates of electrons and holes, respectively.

In addition to the extrinsic potential of Eq. (2), we consider the image charge potential[4]

$$\phi_I = \frac{\epsilon_s - \epsilon_0}{\epsilon_s + \epsilon_0} \frac{e^2}{4\pi\epsilon_s} \left[\frac{1}{4z_e} + \frac{1}{4z_h} - \frac{1}{[(x_e - x_h)^2 + (y_e - y_h)^2 + (z_e + z_h)^2]^{1/2}} \right] \tag{3}$$

and cut-off forces at $z = 0$ included by the boundary conditions

$$\begin{aligned} \psi = 0, \quad \text{for } z_e \leq 0 \ , \\ \psi = 0, \quad \text{for } z_h \leq 0 \ , \end{aligned} \tag{4}$$

where ψ is the electron-hole envelope wave function. In Eq. (3) ϵ_0 is the permittivity of free space.

In the adiabatic approximation[4,5] the center of mass is kept fixed when solving for the relative motion. Consequently, we first study the single-particle problem in relative space given by the total potential

$$\phi_{\text{tot}} = \phi_F + \phi_0 - \frac{e^2}{4\pi\epsilon_s |\vec{r}_e - \vec{r}_h|} \tag{5}$$

evaluated for fixed center of mass. The ground state of this single-particle problem has the energy $E_r(z)$, where z is the depth below the surface of the center of mass. Thus $E_r(\infty) = -E_x$. We estimate $E_r(z)$ by using a trial wave

function

$$\psi_{\text{trial}} = (1 - e^{-z_e/a_B})(1 - e^{-z_h/a_B})(\psi_{1s} + \alpha\psi_{2p} + \beta\psi_{2s}) \ , \tag{6}$$

where ψ_{1s}, ψ_{2p}, and ψ_{2s} are bulk hydrogenic wave functions, and α and β are variational parameters determined by minimizing the expectation value of the energy. The prefactors in Eq. (6) assure that the boundary conditions (4) are fulfilled.

Examples of the dependence $E_r(z)$ are shown in Fig. 3. Also shown is the quadratic Stark shift[15] given by

$$\Delta E_r/E_x = 9[F(z)ea_B/E_x]^2/8 \ .$$

The combined effects of the surface and the electric field are complicated. For example, the $E_r(z)$ depends on the polarity of the field (unless $m_e = m_h$).

As in Ref. 5, we derive the optical properties by consideration of the polariton equations with a depth-dependent resonance frequency $\omega_T(z)$ given by
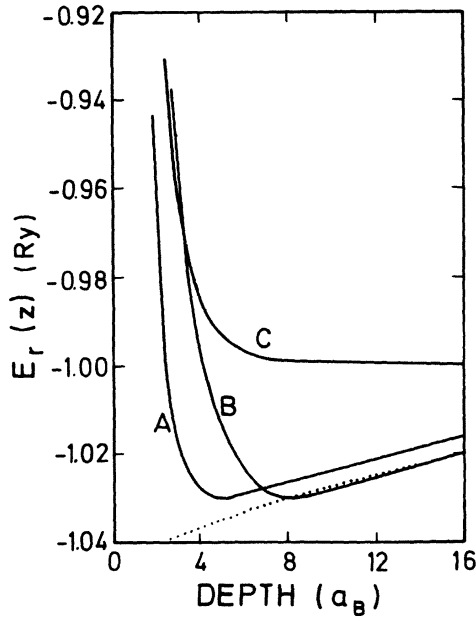
$$\hbar\omega_T(z) = E_g + E_r(z) \ . \tag{7}$$

FIG. 3. The dependence $E_r(z)$ for different surface electric fields calculated for $m_h/m_3 = 5$, $d = 40a_B$, $\epsilon_s/\epsilon_0 = 12$, and $F_0 = -0.2$ E_x/ea_B (curve A), $F_0 - 0.2$ E_x/ea_B (curve B), and $F_0 = 0$ (curve C). The dotted curve shows the quadratic Stark shift.
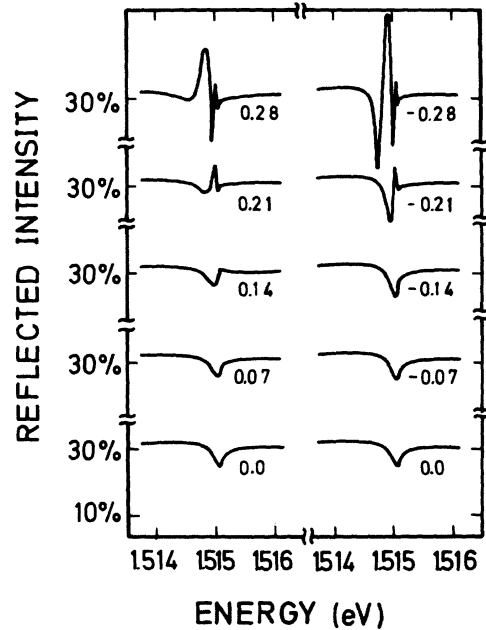

FIG. 4. Reflectance of GaAs calculated for the same parameters as in Fig. 2, but with different fields F_0. (The values are in units of E_x/ea_B.) The curves are displaced vertically for clarity.

Neglecting the spatial dependence of the oscillator strength we obtain, for normal incidence,

$$-\frac{h}{2M}\frac{d^2}{dz^2}P - [\omega - \omega_T(z)]P = \omega_{LT}\epsilon_0\epsilon_b E \ , \qquad (8a)$$

$$\frac{d^2}{dz^2}E + \frac{\omega^2\epsilon_b}{c^2}E = \frac{\omega^2}{\epsilon_0 c^2}P \ , \qquad (8b)$$

where ϵ_b is the relative background dielectric constant, E and P are electric and resonant polarization fields of polaritons, ω is the polariton frequency, and c is the vacuum velocity of light. Equation (8) is integrated numerically under the assumption that $P = 0$ at the crystal surface and with boundary conditions at $z \to \infty$ relevant for a reflectance experiment (no left-running polariton waves for $z \to \infty$). Applying, in addition, Maxwell's boundary conditions at $z = 0$, one can calculate the optical reflectance.

Reflectance spectra calculated for parameters typical for GaAs are shown in Fig. 4 for different fields F_0. The line shape becomes quite complicated for $F_0 \gtrsim 0.2$ E_x/ea_B, but a common trend is the red shift of the primary minimum for increasing fields F_0. The parameters F_0, d, $\omega_T(\infty)$, and ω_{LT} are fitted to the experiments assuming $F_0 = 0$ for the freshly cleaved surface. The result of the calculation is shown in Fig. 2. The agreement with the experiments is reasonably good except near the longitudinal frequency, where the adiabatic approximation is known to underestimate the reflectance for the mass ratio used.[16]

CONCLUSIONS

We conclude that GaAs surfaces cleaved in liquid helium have flat electron bands. Exposure to air leads to a red shift

of the reflectance dip and an enhanced reflectivity near the longitudinal frequency. This enhancement appears as a spike in most previously reported spectra[2,6] and is due to rather small surface electric fields. For example, a pronounced spike is developed for a band bending of only 40 meV ($F_0 \approx 0.21E_x/ea_B$) (see Fig. 4).

Previous authors assumed[7,17] that flat bands can be obtained by strong illumination of a crystal surface. However, the presence of a spike in such spectra indicates that illumination is insufficient to produce completely flat bands.

It is interesting to note that our result $\hbar\omega_{LT} = 0.13$ meV is somewhat lower than those usually obtained from reflectance spectra.[2] The surface electric fields are responsible for a wider reflectance minimum and, as a consequence, a larger apparent value of $\hbar\omega_{LT}$. Our value, however, is still significantly higher than 0.08 meV obtained from resonance Brillouin scattering.[18,19]

The good agreement between the observed spectra and our treatment based on the adiabatic approximation encourages further calculations on the influence of surface electric fields. As suggested by Lagois[20] it may be possible in this way to deduce sign, magnitude, and penetration depth of the surface electric fields from optical measurements.

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