Energy shift and line broadening of three-dimensional excitons in electric fields

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We measure electric-field-induced energy shifts and line broadening of three-dimensional excitons in thin GaAs layers in reflectance and photoluminescence. We observe a small red shift due to the excitonic Stark effect for small electric fields. Subsequently, we find reversal to a blue shift for higher electric fields, due to mixing with continuum states. The exciton line broadens monotonically with increasing field because of field ionization.

I. INTRODUCTION

The optical properties of excitons in a semiconductor subjected to an electric field have attracted considerable interest[1-12] because of the possible device applications. Two-dimensional (2D) excitons in quantum-well structures exhibit extremely large energy shifts[1-3] due to the strong confining potential (the so-called "quantum-confined Stark effect"[1]), which dominates the Coulomb attraction of the electron-hole pair. Three-dimensional (3D) excitons in a bulk semiconductor, on the other hand, may be weakly bound by the attractive Coulomb potential. The energy shift is thus expected to be only a small fraction of the excitonic binding energy.[4,5]

The field-induced changes of the *excitonic* parameters have not yet been experimentally studied. The inherent lack of knowledge about bulk semiconductors arises from experimental difficulties. (i) Application of an electric field at a Schottky barrier creates *inhomogeneous* electric fields, which decrease linearly into the bulk. This spatial field inhomogeneity complicates the interpretation of the optical spectra.[6,7] (ii) Excitons in bulk semiconductors couple strongly to photons, thus forming excitonic polaritons. These polaritons, however, are strongly affected by local excitonic field effects in a complicated manner, leading to *polariton interferences*, which dominate their reflectance spectra.[7,8]

We have tackled this experimental problem by using ultrathin GaAs layers in which the electric field is homogeneous and polariton effects are unimportant. The optical properties are then purely determined by excitonic features. Application of a homogeneous electric field across the GaAs slab is achieved by a metal-insulator-semiconductor structure. Reflectance as well as photoluminescence experiments then reveal energy shifts and line broadening. We find an initial small red shift of the resonance at low fields (the usual Stark shift), then a blue shift for still higher fields due to the mixing with continuum states. The linewidth equivalent to lifetime broadening increases strongly due to the ionization of the excitons by the electric field.

II. EXPERIMENT

Our experiments were performed on high-quality GaAs-$Al_{0.3}Ga_{0.7}As$ heterostructures, grown by molecular-beam epitaxy (MBE) on n^+ substrates. The thickness of the GaAs layer is about $L_z = 112$ nm. A semitransparent Schottky barrier was formed on the $Al_{0.3}Ga_{0.7}As$ surface by evaporating a guard ring structure with a 10-nm-thick gold film onto the surface of the sample. The backside Ohmic contact is formed by alloying the n^+ substrate with indium. The reflectance experiments were performed using a tungsten iodine lamp with an appropriate broadband interference filter and a single-grating monochromator with an optical multichannel analyzer (nonintensified photodiode array cooled down to -40°C), permitting accurate measurements of reflectance changes in the range of 0.1%. The spectral resolution was about 0.025 nm. The photoluminescence was excited with the 752.5 nm line of a Kr^+-ion laser with a typical excitation intensity of 1 mW/cm^2. The sample was immersed in superfluid helium during our experiments. The electric field strength was determined from the applied voltages and the measured total thickness of the insulating layer of about 347 nm. The uniformity of the insulator is better than 1%, checked by transmission electron microscopy.

III. RESULTS AND DISCUSSION

Figure 1 shows reflectance spectra in the excitonic energy region for a sample with a central GaAs layer of about 112 nm thickness for three typical electric fields. Zero-field condition yields a strong reflectance structure with a dip at 1.5152 eV, which is due to the 1s exciton, and much weaker structures at 1.5166 and 1.5182 eV. These reflectance features are attributed to 1s excitonic transitions, belonging to quantized electronic subbands of index N. We use a heavy-hole mass of $0.45m_0$ and an electron mass of $0.088m_0$ to calculate the excitonic energy levels to be
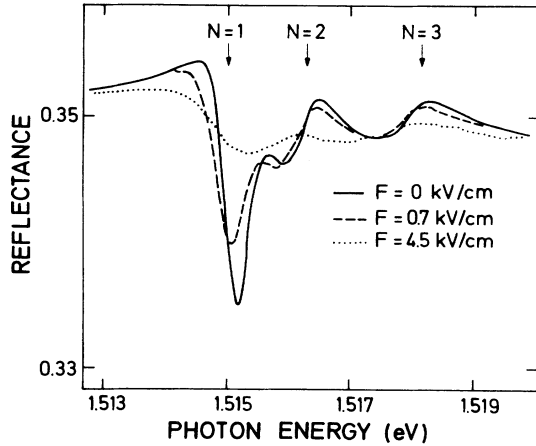
FIG. 1. Reflectance spectra at 2 K for three different electric fields F. The arrows denote the calculated energy levels of the $1s$ exciton transitions belonging to the electronic subbands of index N.

$$E_N = 1.514\,74 \text{ eV} + (0.26 \text{ meV})N^2 , \qquad (1)$$

where a slight increase of the binding energy by 0.26 meV is assumed as compared with the bulk value.

The good agreement with the reflectance features (see Fig. 1) demonstrates that the exciton in our 112-nm-thick GaAs layer (i) is quantized perpendicular to the layer, (ii) the excitonic states are composed of quantized electronic states, and (iii) the binding energy has not changed appreciably, since the exciton has retained its 3D properties.

A field increase to 0.7 kV/cm shifts the reflectance dip to lower energy, and the reflectance amplitude decreases. Electric fields larger than 4.5 kV/cm shift the reflectance dip back to higher energies and broaden it; the reflectance amplitude simultaneously decreases.

A line-shape analysis yields more information on the field dependence of the excitonic parameters. We use first a crude dielectric model, appropriate for optically thin layers. The dielectric properties of our multilayer sample are approximated by one cladding layer (complex dielectric constant ϵ_c and thickness L_c), lumping together the dielectrics of the $Al_{0.3}Ga_{0.7}As$ cladding layers as well as the gold film and a δ-function-type dielectric response of the excitons located at the interface to the substrate of a dielectric constant ϵ_s:

$$\epsilon(\omega,z) = \begin{cases} \epsilon_c & \text{for } 0 \leq z < L_c , \\ L_\delta[\epsilon(\omega)-\epsilon_s]\delta(z-L_c)+\epsilon_s & \text{for } L_c \leq z , \end{cases} \qquad (2)$$

where $\epsilon(\omega)$ is the usual oscillator-type response.[7] L_δ is an effective layer thickness given by $L_\delta = L_z - 4a_0$, where a_0 is the exciton Bohr radius, to account for two exciton-free surface layers. Maxwell's equations then yield the reflectance spectra.

The upper part of Fig. 2 shows the experimental and a theoretical reflectance spectra. The agreement between theoretical and experimental spectra is reasonable. Excitonic parameters, as well as the optical parameters, of the dielectric cladding layer are found by the line-shape
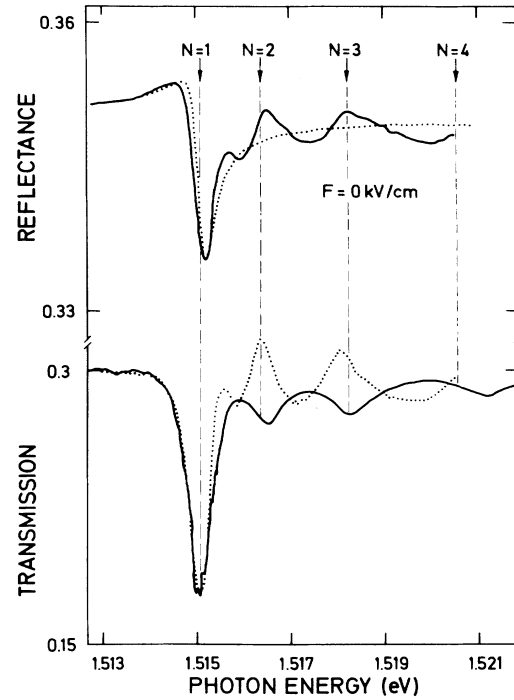

FIG. 2. Experimental (solid line) and theoretical (dotted line) reflectance spectra (upper part), and experimental (solid line) and theoretical (dotted line) transmission spectra calculated by a Kramers-Kronig transformation from the reflectance spectrum (lower part) at zero electric field.

analysis to be $E_T = 1.515$ eV, $E_L = 1.515\,08$ eV, $\Gamma = 0.31$ meV, $\epsilon_s = 11.56$, $\epsilon_c = 11.4 + i6.5$, $L_c = 165$ nm, and $L_\delta = 40$ nm.

The fit also indicates that the line shapes of the $N = 2$ and $N = 3$ excitons differ strongly from that of the $N = 1$ exciton. The energy level of the $N = 1$ exciton roughly corresponds to a reflectance dip, whereas the $N = 2$ and the $N = 3$ exciton levels correspond to a reflectance peak. We attribute this difference to the smaller exciton-free surface layer of the $N = 2, 3$ exciton wave function. The different behavior also indicates that a fit of the complete reflectance structure is impossible within the framework of phenomenological dielectric models.

A second—and far more severe—restriction is that bound exciton states in an electric field become mixed with free-electron–hole pairs. This mixing invalidates all naive oscillator models.

Therefore we now analyze our reflectance data without invoking a specific excitonic response. We transform the reflectance spectra to transmission spectra, from which we determine the eigenenergy from the peak positions and the field-induced line broadening (ionization rate) from the linewidth.

The first step is to complete the reflectance information by means of a Kramers-Kronig transformation. Details of our calculation will be presented elsewhere. The second step involves a simple backtransform of the reflection amplitude from the front side to the transmission amplitude of the substrate interface. The optical parameters are already adjusted by the reflectance fit un-

der flatband condition, therefore such a backtransformation is unambiguous.

The lower part of Fig. 2 shows experimental and theoretical transmission spectra, as calculated with our model. The good agreement for the $N=1$ exciton confirms the validity of our model assumptions and proves consistency of the Kramers-Kronig transformation. Such thin GaAs layers have their transmission minima directly at the excitonic eigenenergy, which simplifies the interpretation of the spectra. The discrepancies for the $N=2,3,4$ exciton transitions are due to the different reflectance line shape as compared with the $N=1$ exciton.

In Fig. 3, we plot the energy shift of the $N=1$ exciton transition versus the electric field. Small electric fields cause a red shift of the excitonic level, which is reversed at intermediate electric fields. At high electric fields, the levels shift back to higher energies.

The initial red shift of the energy corresponds to the usual Stark shift analogous to the hydrogen atom. Perturbation theory gives the Stark shift as

$$\Delta E = -E_B \tfrac{9}{8} f^2 , \tag{3}$$

where E_B is the excitonic binding energy and f is a reduced field in units of the ionization field $E_i = E_B / e a_0$. The field E_i corresponds classically to that energy gain of an electron across the Bohr radius which is necessary to offset its binding energy. From Fig. 3, our results for low electric fields are seen to agree with the perturbational predictions.

The intermediate reversal of the energy shift at fields $f \geq 0.4$ cannot be understood by perturbation theory. A calculation of the exciton problem by Blossey[4,5] revealed a similar field dependence of the excitonic energy level, as also shown in Fig. 3. The peak position agrees, for small electric fields, with perturbation theory. At a field of $f = 0.45$, a maximal red shift of about $0.12 E_B$ is obtained by theory. Much higher fields reverse the trend toward a blue shift.

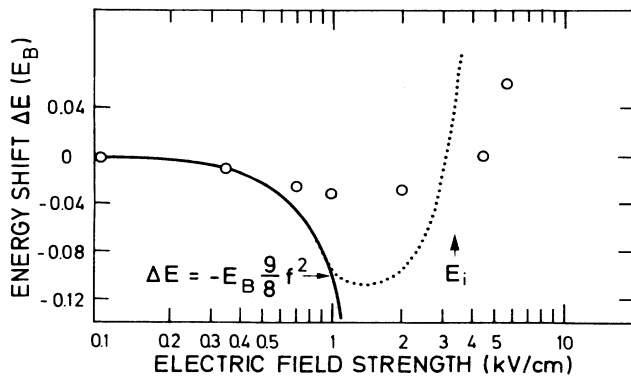These calculations by Blossey[4,5] indicate that the backshift of the energy level is due to mixing with the continuum states. The originally bound exciton states become degenerate with the free continuum states at $f \geq 0.5$. The exciton is then no longer bound, and its energy level corresponds then to a maximum of its density of states. The blue shift now follows an $\sim f^{2/3}$ law, characteristic for the first oscillation peak of a simple band-to-band Franz-Keldysh effect.[9]

Agreement with Blossey's calculations[5] for $f \geq 0.3$ is poor. Conclusive reasons for this discrepancy cannot yet be stated. An initial supposition is that the calculations have been performed for an infinite bulk semiconductor, whereas our GaAs layer is only 112 nm thick. The finite size should lead to a modification of the binding Coulomb potential, albeit small, as well as to a slightly modified energy spectrum of the free carriers in a triangular potential well.[9]

We plot in Fig. 4 the field-induced line broadening $\Delta\Gamma(F) = \Gamma(F) - \Gamma(F=0)$. The linewidth does not change appreciably below electric fields of $f = 0.1$. From a threshold field of $f = 0.2$ the linewidth suddenly increases up to a value of $0.2 E_B$ at $f = 1$. If the linewidth $\Delta\Gamma$ is assumed to be of purely homogeneous origin, the lifetime T_1 of an exciton state is given by $T_1 = 1/\Delta\Gamma$. For a field of $f = 1$ we estimate an exciton lifetime of about $T_1 = 0.75$ ps. However, the mean classical orbit time of an electron-hole pair in GaAs is only about 0.5 ps. Thus the correlation between electron and hole is strongly disturbed by the field ionization, and the absorption peak is mainly due to a Coulomb enhancement.

Also shown in Fig. 4 is the result for the ionization broadening obtained by the semiclassical Wentzel-Kramers-Brillouin (WKB) method[10] which is limited to small electric fields:

$$\Delta\Gamma = \frac{16 E_B}{f} e^{-4/3f} . \tag{4}$$

Below $f = 0.5$, ionization broadening is negligible, in agreement with our observations. For higher fields the theoretical ionization broadening increases much more
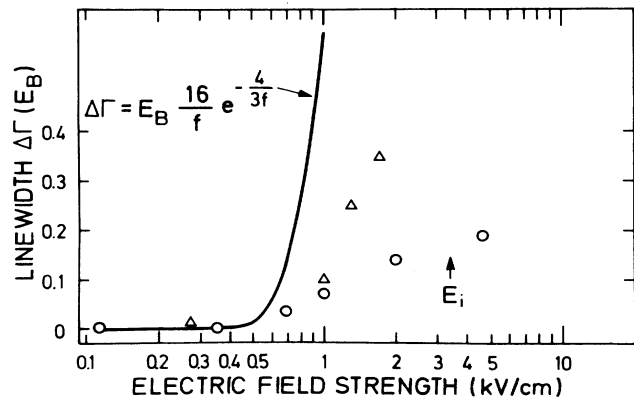

FIG. 3. Experimental ($\bigcirc$) energy shift $\Delta E = E(F=0) - E(F)$ of the $1s$ exciton in GaAs, and theoretical energy shifts according to perturbation theory (thick line) and from Blossey (Ref. 4) (dotted line). f is a reduced field in units of the ionization field E_i.

FIG. 4. Experimental ($\bigcirc$) field-induced linewidths $\Delta\Gamma = \Gamma(F) - \Gamma(F=0)$ and theoretical linewidths calculated by the WKB method (Ref. 10) (thick line) and from Ralph (Ref. 11) (triangles) versus electric field strength F. f is a reduced field in units of the ionization field E_i.

steeply than what is experimentally observed. A better agreement in the intermediate-field regime $0.5 < f \leq 1$ is obtained by comparison with the theoretical results of Ralph.[11] However, discrepancy for higher electric fields still remains.

Figure 5 indicates three characteristic photoluminescence spectra for a low excitation intensity of 1 mW/cm^2. A single excitonic emission line centered at the excitonic eigenenergy is observed for zero electric field. The low-energy side features impurity-related luminescence lines. Increasing the electric field quenches the excitonic luminescence, with a slight red shift for $F = 0.7$ kV/cm. Fields above $F = 4.5$ kV/cm, slightly exceeding the ionization field, quench the excitonic emission completely. An absorption dip at the excitonic energy is observed, owing to the fact that a broad background emission of the n^+ substrate is filtered by the transmission spectrum. The impurity-related luminescence persists to higher electric fields, due to the stronger binding of the excitons at the impurities.

The luminescence results substantiate our simple picture of electric-field-induced line shift and line broadening. The observed strong quenching of the excitonic emission at high electric fields is consistent with field ionization. Rapid spatial separation of the electron-hole pair on a picosecond timescale, as determined from the linewidth, simply acts as an efficient nonradiative process for the excitonic recombination, thus quenching the excitonic luminescence.

IV. CONCLUSIONS

Energy shifts and line broadening of 3D excitons in GaAs are measured by means of reflectance and photoluminescence spectroscopy. A small red shift, in agree-
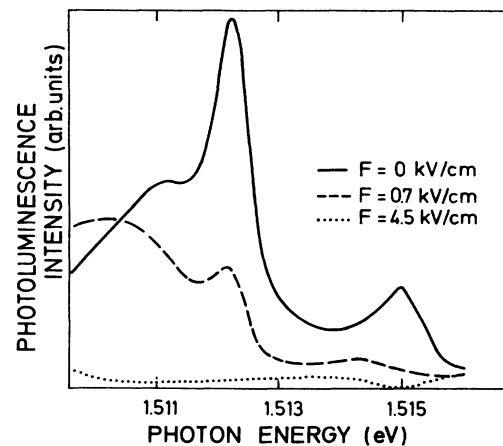
FIG. 5. Photoluminescence spectra for three different electric fields F.

ment with the excitonic Stark effect, and a negligible ionization broadening are observed for small electric fields, confirming the simple hydrogenic picture of an exciton in an electric field. Increasing the electric field reverses the energy shift of the exciton level towards a blue shift and increases the line broadening consistent with theoretical predictions.

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