Electric field effects on excitons in gallium nitride

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Electric-field effects on Wannier exciton are observed in GaN thin films. Using both absorption and photo-current measurements, we have studied the excitonic Franz-Keldysh effect in thin epitaxial GaN films at temperatures between 80 and 300 K. We have measured the Stark shift, quenching, and broadening of the exciton peak with applied field. These results are compared with theoretical calculations from the literature. The physics of exciton ionization at varying temperatures is discussed, which explains the interplay between absorption and photocurrent. [S0163-1829(96)03735-6]

I. INTRODUCTION

Since the early work of Franz[1] and Keldysh[2] on photon-assisted tunneling between bands, the theory of electroabsorption has progressed a long way. These early theories[1-4] predicted a field-induced shift to lower energy of the absorption edge in direct-band-gap materials. Excitonic effects were not taken into account. However, the exponential absorption edge assumed by Franz anticipated the excitonic absorption tail. These results were experimentally verified[5-8] with a F^n dependence of the absorption edge shift on the applied electric field F. The value of n was between 1 and 2 depending on materials. The importance of excitonic effects on the field dependence of the absorption spectrum appeared clearer in the following years.[9] As pointed out by Handler (see P. Handler and the discussion with M. Cardona in Ref. 10), excitonic features have to be taken into account in almost all materials. Field effects on excitons were observed in direct-band-gap materials (see for instance Gumlich *et al.*, Nikitine *et al.*, and Gross *et al.* in Ref. 9) and also in indirect-band-gap materials such as Ge (Refs. 10 and 11). Photoluminescence studies under electric field in Cu_2O, CuBr, or PbI_2 have shown that the exciton intensity and energy decrease as the field increases.[9] However, the exciton Bohr radius in these halide compounds is of the same order of magnitude as the unit cell, so that these are Frenkel excitons. As far as Wannier excitons are concerned, quantitative measurements of electric-field-induced modification of the excitonic absorption were very limited mainly because of experimental difficulties: Epitaxial thin films were not available for all materials, the field in p-n junctions was not uniform,[12,13] and electrolytes could not be used at low temperatures. Theoretical treatments of field effects on absorption, including excitons, were not carried out until 1966. Then approximate solutions were given,[14,15] indicating that the optical-absorption coefficient below the gap should vary as $\exp(-C_0|h\nu-E_0|^{1.5}/F)$, where $h\nu$ is the photon and C_0 and E_0 are constants. As the same dependence was found in calculations without excitonic effects, it could be thought that electron-hole interaction does not alter the asymptotic form of the field-induced absorption. Finally, Dow and

Redfield[16] and Blossey[17,18] were the first to perform exact numerical calculations of the optical-absorption coefficient for direct, excitonic transitions in a uniform applied field. Dow and Redfield showed that the optical-absorption coefficient should vary as $\exp(-C_0'|h\nu-E_0'|/F)$, where C_0' and E_0' are constants, and they pointed out the importance of excitonic effects even far above or below the gap. In the meantime, experimental studies have been mostly directed towards electroreflectance (see, for instance, Seraphin in Ref. 9) and UV spectroscopy of solids.[19] As a result, to our knowledge there has not been any quantitative study and comparison with theory of electric-field effects on the excitonic absorption.

In this paper, we present experimental data of field effects on excitonic absorption in GaN, and we compare our results with the full quantum mechanical treatment of excitonic absorption under electric field performed by Dow and Redfield.[16] Gallium nitride exhibits a wide direct band gap[20,21] (3.4 eV), with an unusual ionic bond as in halide compounds. However, excitons belong to Wannier's type, since the Bohr radius of those excitons (30 Å) is considerably larger than the lattice constant (3.4 Å), so that the aforementioned theoretical results can be used. GaN is particularly well adapted for this study for the following reasons: (i) Thin films of high-quality GaN can be obtained by molecular-beam epitaxy (MBE) or metal-organic chemical-vapor deposition (MOCVD) on a transparent substrate (Al_2O_3), so that transmission measurements can be performed. (ii) The exciton binding energy R (28 meV) being larger than kT even at room temperature, excitons may be easily observed in GaN. (iii) Ohmic contacts can be fabricated on GaN, thus allowing the application of an electric field. (iv) Finally, the extremely large breakdown field (>1 MV/cm) makes GaN the ideal candidate for studying electric-field effects on excitons.

Here we present results obtained in absorption and photo-current on GaN(001) at varying temperatures. We show the broadening, quenching, and energy shift of the exciton as the electric field increases. We also show the field-induced absorption below the gap, and its photon energy and field dependence, and compare our results with Dow's theory.

II. EXPERIMENT

The GaN sample used in this work was grown by low-pressure metalorganic vapor phase epitaxy on (0001) sapphire.[22] After nitridation of the substrate, a thin GaN nucleation layer was grown at 500 °C prior to the growth of the 1-μm-thick nominally undoped GaN main layer at 1000 °C. It had a mirrorlike surface and a fairly narrow peak in x-ray diffraction (400 arcsec). The low-temperature photoluminescence spectrum was dominated by 5-meV-wide bound exciton peak. The GaN layer had a wurtzite symmetry with its c axis normal to the surface.

The structure consists of a square (100×100 μm^2) metal contact on GaN separated from the surrounding metal (used as the ground) by a 15-μm-wide open GaN region. We actually made an array of these concentric square devices with a spatial period of 200 μm. The metal is thick enough so as to be opaque to UV light. The sample was set on an open ceramic, allowing for transmission measurements. The squares and the ground were wire bonded so that an electric field could be applied across the 15-μm GaN region. Transmission line measurement structures (for contact resistance determination) were fabricated at the same time on the GaN layer. Electrical measurements on these structures gave us the ohmic contact resistance (10^4 Ω mm) and the square resistance of the GaN layer (1.75 MΩ). Given the square structure geometry, this indicates that about one half of the total voltage is actually applied along the 15-μm-wide GaN region, the remaining voltage being applied to the contacts. A higher doping of the GaN layer would have reduced the contact resistances, but also increased the current in the GaN layer, thus heating the device. Moreover, excitons would have been broadened or even smeared out by a larger doping. For practical reasons, we have applied a continuous field instead of an alternative one. So it is important to give an estimation of the structure heating under operation. At the maximum total voltage (100 V), the current was less than 1 mA. Given the geometry and thermal conductivities of GaN, Al$_2$O$_3$, and the metal, we estimated the temperature elevation under operation at the maximum voltage to be of the order of a few degrees. This estimation was confirmed by measuring the currents on square devices close to the device under test. These currents were found to be slightly larger than those without the bias on the device under test, corresponding to a temperature elevation ΔT that increases as we measured closer and closer to the device under test. A maximum ΔT for the device under test smaller than 10 K could be deduced.

A 70-W Xe lamp filtered by a monochromator with a 1200-lines/mm grating was used as the probe beam. A pinhole of 50-μm diameter and an imaging lens system created a spot of a few μm dimension, so that there was no light but in the free GaN region. The 40 Hz modulated, transmitted light was synchronously detected by a photomultiplier. The photocurrent was also synchronously measured, so that the experiment provided at the same time the photocurrent and the transmission (or the absorption). The results were recorded as a function of photon energy for a given applied field or as a function of the field for a given photon energy. Optical measurements presented here were carried out with a field ranging from 0 to 40 kV/cm. The field is expressed in reduced units $f = e \times F \times a / R$ by comparing the potential
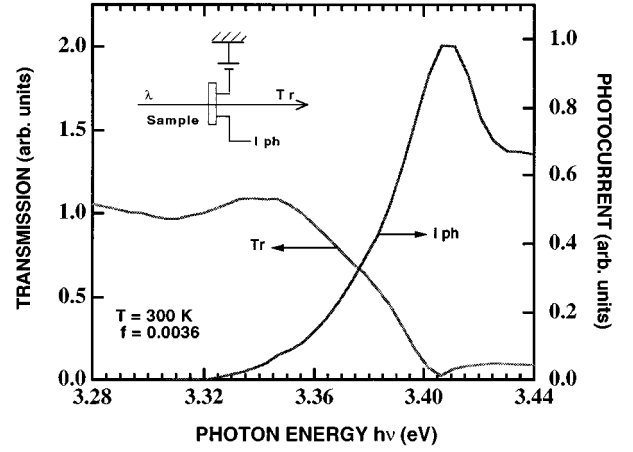

FIG. 1. Transmission and photoresponse spectra of a metal/GaN/metal device showing an excitonic behavior. The experimental setup is sketched in the inset. The transmission is measured through GaN in between two metal contacts acting as ohmic contacts. $T = 300$ K, and the applied electric field in GaN tends to zero ($f = 0.0036$).

drop $e \times F \times a$ along the exciton radius a and the exciton Rydberg R. We note that e is the electron charge. The photon energy $h\nu$ is also expressed in dimensionless units $E = (h\nu - E_{\text{gap}})/R$ by comparison with the exciton and gap energies.

III. ELECTRIC-FIELD EFFECTS ON EXCITONS AT 300 K

The transmission and photocurrent spectra at a vanishingly small field ($f = 0.007$) are presented in Fig. 1. Photocurrent and transmission spectra are normalized by the incident flux. The exciton appears in transmission as a dip at 3.406 eV, in good agreement with reflection measurements on the sample before metallization. As expected, A, B, and C excitons are not resolved at 300 K as their energy separation[20,21] ($E_A - E_B = 6$ meV and $E_B - E_C = 18$ meV) is less than kT. The photoconductive response also shows a very clear excitonic behavior at 3.408 eV, in excellent agreement with transmission measurements. In order to understand the relations between absorption and photocurrent, it is important to discuss the physics of photoconduction. The calculation of the transition probability for excitonic absorption[16] leads to the dipole matrix between Bloch functions, and to the calculation of the pair-correlation function U that satisfies[16]

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{\varepsilon r} + \frac{fRz}{a} \right) U = E_{\text{el}} U, \qquad (1)$$

where E_{el} is the electron energy measured relative to the zero-field energy gap. This equation describes the relative motion of the electron in the hydrogenic potential of the hole (with reduced masses) responsible for the excitonic effect, and in an electric field applied along the z direction. The transition probability is then found to be proportional to $|U(0)|^2$. Solving this equation for $f = 0$ gives bound states for negative energies (exciton levels) and free states (positive energies). The electron energy in bound levels will thereafter be expressed in reduced units as $E_{\text{binding}} = E_{\text{el}}/R$. On the other hand, for $f \neq 0$, there is no pure bound state as the potential is
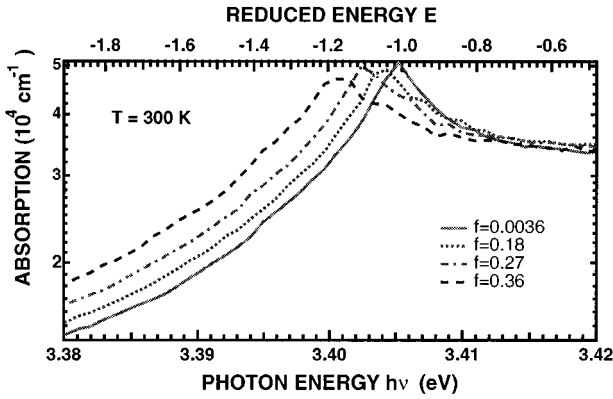
FIG. 2. Absorption spectra at 300 K of GaN under increasing electric field.

FIG. 3. Theoretical absorption at 300 K (in arbitrary units) as a function of reduced energy $(h\nu - E_{gap})/R$. The curves were obtained by a convolution of the theoretical absorption curve calculated by Dow and Redfield (Ref. 16) at 0 K by a Lorentzian curve with a full width at half maximum equal to kT.

unbounded below for infinite z values. Resonant states appearing for negative energies in the well (bound) are connected through a finite potential barrier with free states outside the well. Thus an electron photocreated in the well may become delocalized and contribute to the current, thus breaking the exciton. This exciton-reduced lifetime is associated with its broadening and quenching. On the other hand, the excitonic photocurrent (more precisely, we consider here the exciton amplitude relative to the band-to-band transition in order to separate the additional field dependence of the carrier velocity), equal to zero at $f=0$, should increase with the field (increasing ionization probability p_i), then saturate ($p_i \sim 1$), and finally decrease as the excitonic absorption decreases. Up to now, thermal effects have been neglected, and the above quantum-mechanical considerations apply at 0 K only. At higher temperatures, we have to consider the phonon interactions. Thermal creation of an exciton is obviously negligible at room temperature ($kT \ll E_{gap}$). The only effect to be considered here is the phonon interaction with the electron (in the relative motion, interactions with the electron or the hole are equivalent). Given the optical-phonon energy of 90 meV (3.2 in Ry units), the Fröhlich single phonon interaction is the relevant mechanism as multiphonon interaction are unlikely at $kT/R < 1$ and a single-phonon absorption is very efficient for breaking the exciton [$E_{binding}(f \neq 0) \ll 3.2$]. Now, at high temperature, one can consider that the exciton is rapidly dissociated ($\tau_{phonon} < \tau_{recombination}$, where τ_{phonon} and $\tau_{recombination}$ are the phonon interaction and exciton recombination times, respectively) and even at low field an important photocurrent should be measured. This is exactly what is observed in Fig. 1. Note that this dissociation is not in contradiction with the observation of the exciton as pointed out by Dow and Redfield.[16] As the field increases, the photocurrent should, like the absorption, exhibit a quenching of the excitonic peak. This will be discussed later in the paper.

We would like to mention an additional observation on the field orientation and light polarization. Different measurements were done on focusing the light on either side of the square (thus rotating the electric field by 90° relative to the crystallographic axes) and for two perpendicular light polarizations. The same results were obtained within experimental accuracy, showing that excitons and fields effects do not reveal here the crystallographic C_{3v} symmetry of the material.

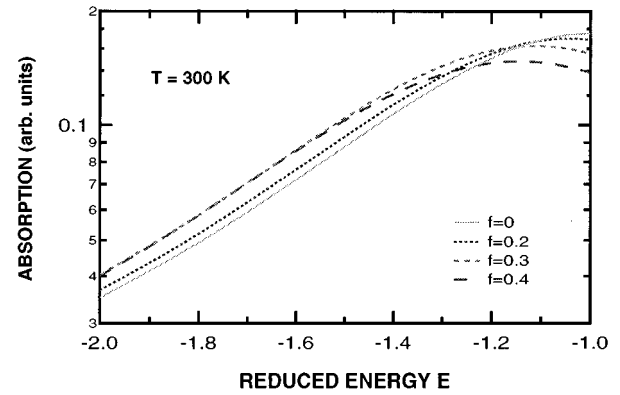Figure 2 shows absorption spectra for different electric fields. The features predicted by Dow and Redfield are experimentally verified here. As the field increases, one sees the shift, broadening, and quenching of the exciton. The energy shift is about 4.5 meV for $f=0.36$, in good agreement with the theory[16] which predicts a shift of $0.15 \times R = 4.2$ meV for $f=0.36$ at 0 K. The exciton broadening and quenching measured at room temperature were also theoretically expected.[16–18] In order to make quantitative comparisons, we added a thermal broadening to $|U(0)|^2$ curves[16] obtained at 0 K by a convolution by a Lorentzian function with a full width at half maximum equal to the thermal energy kT. The resulting curves which are proportional to the absorption coefficient are presented in Fig. 3 for fields up to $f=0.4$. The theoretical peaks appear to be smoother than the experimental ones, and the theoretical induced absorption well below the edge tends to saturate for fields larger than 0.3. This seems to indicate that a more detailed analysis of thermal effects is needed in order to improve the theoretical calculation. However, the general agreement between theory and experiment is good. At 0 K, the theory[16] predicts that the energy dependence of the absorption well below the edge ($E \ll -1$) follows an asymptotic behavior $\ln\alpha \sim (c+E)/f$, where c is a constant. At 300 K, this asymptotic behavior is visible neither theoretically (Fig. 3 and calculated curves for $E < -2$, not shown in Fig. 3) nor experimentally (Fig. 2). Actually, even at temperatures as low as 4 K, the theoretical spectra (the curves, calculated by convolution, are not presented here) do not exhibit a clear asymptotic behavior.

In order to show the exciton shift with the field more clearly, we set the monochromator at a given energy and measured the transmission as a function of the field. The transmission curves normalized to unity are shown in Fig. 4. First, the photon energy is set to 3.388 eV ($E=-1.6$). As the field increases, the transmission decreases due to the field-induced absorption below the gap. For $f > 0.05$, the effect is linear with the field as the excitonic peak shifts almost linearly with eF. Note that heating due to the current would lead to a perfectly quadratic effect as the electrical power varies as F^2. Second, we set the energy to 3.406 eV ($E=-1.1$). At low fields, we observed the same behavior as for $E=-1.6$. Then, for higher fields, the transmission increases again as the photon energy is now on the high-energy side of
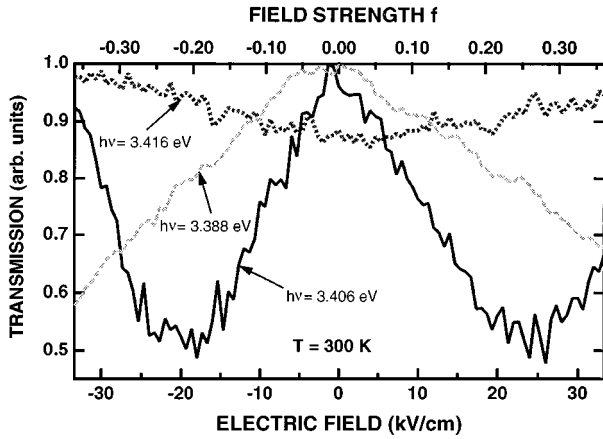
FIG. 4. Transmission of GaN as a function of applied field (positive or negative) for three different photon energies: $h\nu = 3.416$ eV or $E = -0.4$ is on the high-energy side of the exciton. $h\nu = 3.406$ eV, or $E = -1.1$ is close to the exciton peak. $h\nu = 3.388$ eV or $E = -1.6$ is on the low-energy side of the exciton.

the excitonic peak. Finally, we set the photon energy to 3.416 eV ($E = -0.4$), i.e., on the high-energy side of the exciton for $f = 0$. As f increases, the absorption decreases and the transmission increases. These measurements definitely prove that the exciton peak not only broadens but also shifts with the field.

In order to compare the field dependence of the absorption with Dow and Redfield's[16] linear dependence with $1/f$, in Fig. 5 we have plotted the absorption below the edge ($E = -2$) in a logarithmic scale versus $1/f$. The variation is not linear but roughly follows a f^{-s}, dependence with s around 0.65. This, again, comes as no surprise as thermal broadening dominates at 300 K. Even at lower temperature, residual broadening is likely to prevent the observation of the $1/f$ slope, as already discussed in Sec. II.

Observing the shift, broadening, and quenching of the excitonic peak with applied field in transmission (Fig. 2) was difficult, as the transmitted power is very small at the exciton energy. On the other hand, the photoconductive response is huge at the exciton peak, and can be used to measure the field effect on the exciton. As already explained, at high temperature the photocurrent and the absorption should exhibit a similar exciton quenching with the applied field as
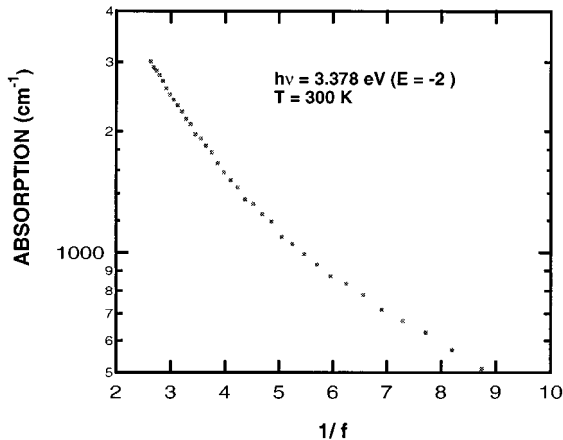

FIG. 5. GaN absorption coefficient at 300 K and $h\nu = 3.378$ eV (or $E = -2$) as a function of the inverse of the applied field.
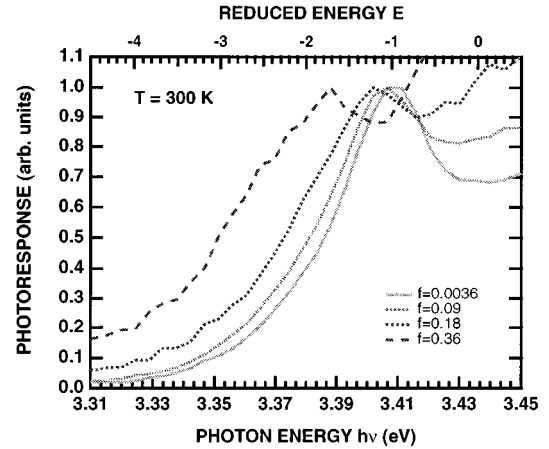

FIG. 6. Photocurrent spectra at 300 K for varying applied fields. The currents are normalized to unity at the exciton peak.

thermal dissociation is important. In Fig. 6, we present the photoresponse spectra at 300 K with the excitonic peak normalized to unity for different applied fields. As the field increases, the excitonic peak is clearly reduced (in comparison to the band-to-band transition measured on the high-energy side of the peak). Heating can be ruled out, as the temperature change has been shown to be much less than 10 K which cannot appreciably quench the exciton at 300 K. The exciton quenching increases continuously between $f = 0$ and 0.36. This is in general agreement with absorption measurements (Fig. 2), as expected. Quantitatively, the quenching measured from the photocurrent is slightly larger than that measured in Fig. 2, which can be explained by a better resolution in the photocurrent measurement. The exciton shift in photocurrent is larger than the shift measured in absorption (Fig. 2). For $f = 0.36$, the shift reaches 20 meV with some uncertainties due to the noise and the large exciton quenching. This large shift may be explained by the field dependence of the ionization probability, as will be discussed further below.

IV. PHOTOIONIZATION AND ABSORPTION UNDER ELECTRIC FIELD AT LOW TEMPERATURE

As we pointed out in Sec. I, from quantum-mechanics considerations, the excitonic photocurrent at low temperature should first increase with field, then saturate, and finally decrease (omitting the field dependence of carrier velocities, as already explained). This would occur for thermal energies $kT/R < 1$. In Fig. 7 we present the field dependence of excitons at 80 K, i.e., $kT/R = 0.23$. Again, the exciton peaks are normalized to unity. We clearly observe the increase (compared to band-to-band transition) of the excitonic peak with applied field, and also its saturation for the largest fields. We could not, for practical reasons, go to higher fields and observe the exciton quenching in photocurrent at 80 K. We also observe the exciton energy shift with applied field. The shift reaches 18 meV, i.e., 13 meV more than the one obtained in absorption. This can be explained by the dependence of the ionization probability with the field as pointed out by Dow and Redfield[16] and Blossey.[17,18] In an applied field the exciton ground level moves slightly deeper in the hydrogenlike potential well due to the quadratic Stark effect, at least up to $f \sim 0.5$.[18] At the same time, the classical ionization level
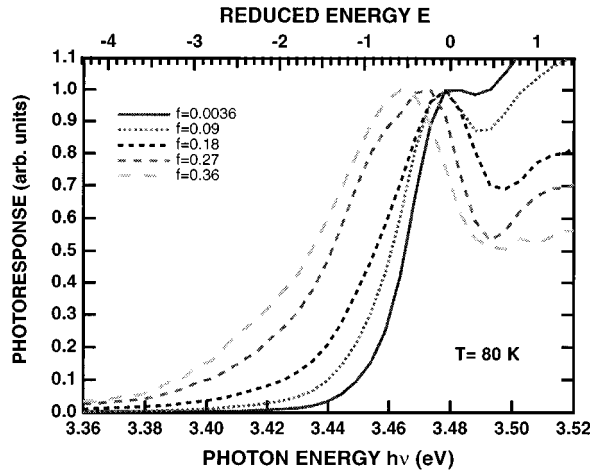
FIG. 7. Photocurrent spectra at 80 K for varying applied fields. The currents are normalized to unity at the exciton peak.

(top of the well) moves to lower energies as $V_{ion} = -2e\sqrt{(eF/\varepsilon)}$ or in reduced units $-\sqrt{(8f)}$. Thus the field effect on the ionization probability (photocurrent) is stronger than that on the ground-level energy (absorption).

Comparing Figs. 6 and 7, one obviously would like to study the field effects on the photocurrent at intermediate temperatures. The result of these measurements is shown in Fig. 8 where we plot the exciton amplitude (response ratio between the exciton and the band-to-band transition measured on the high-energy side of the peak) measured in the photocurrent. The continuous increase at 80 K and decrease at 300 K of the exciton peak are indicated. At intermediate temperatures, the exciton peak is first reinforced when the field increases, and then quenched when the field is larger than a given value that we called the transition field. This transition field decreases with increasing temperature. This figure clearly illustrates the interplay between the three energies involved here; the exciton binding energy, the field potential energy, and the thermal energy.

The last observation is related to the photocurrent tail at low energy. A comparison of Figs. 6 and 7 shows that this tail is more field sensitive at 80 K than at 300 K. This is to be related to the change of slope of the absorption tail predicted by Dow and Redfield[16] at 0 K, not visible at 300 K either in
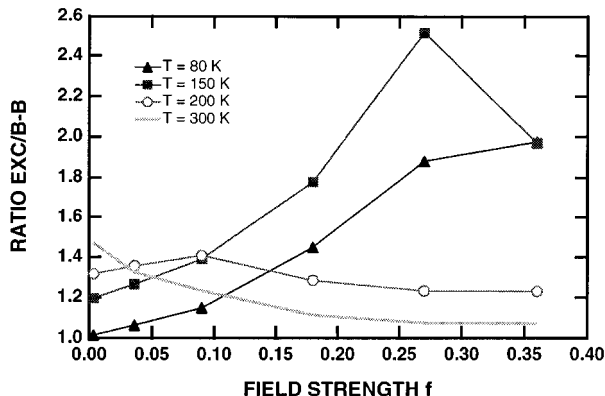

FIG. 8. Exciton peak amplitude (defined as the ratio between the exciton and band-to-band transitions) as a function of field for varying temperatures.
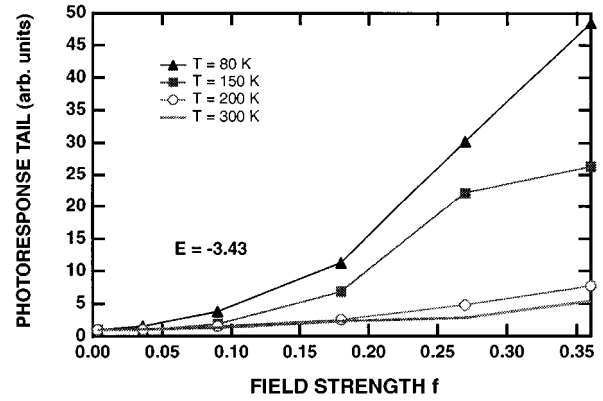

FIG. 9. Photocurrent tail as a function of field for varying temperatures. The tail is defined as the ratio between responses at field f and field $f=0.0036$. The energy is constant in reduced units ($E = -3.43$). It is a measure of the field dependence of the response well below the edge.

transmission or in photocurrent measurements because of the thermal broadening. This evolution can be studied as a function of temperature. Figure 9 presents the field dependence of the tail. For this, we calculated the ratio between the response at field f and the response at vanishingly small field $f=0.0036$. Both responses are measured for a given temperature T at the same energy ($E = -3.43$ in reduced units) below the edge at T. As the temperature increases, the tail becomes less and less field sensitive due to thermal broadening. We should not forget, on the other hand, the spectral dependence of the ionization probability that varies with field, which introduces an additional modification of the excitonic tail measured by the photocurrent.

V. CONCLUSION

We have presented a study of field effects on excitons in GaN layers. Thanks to some properties of these layers (quality, thickness, exciton binding energy), theoretical predictions[16–18] about field effects on Wannier excitons could be tested. Correlated measurements of both the absorption and the photocurrent show that some of the predictions are quantitatively verified (exciton Stark shift) while others are only qualitatively verified: At 300 K, the energy exponential dependence of the absorption under a field well below the gap cannot be observed due to thermal broadening. For the same reasons, the $1/f$ field dependence expected at 0 K is not verified either. These theoretical predictions are better verified when the temperature is reduced from 300 K to 80 K (steeper tail on the low-energy side of the exciton, larger field dependence). The study of the photocurrent excitonic peak as a function of temperature and field have allowed us to give some physical insight into the relation between absorption and photocurrent.

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