Impact ionization of excitons and shallow donors in InP

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Quenching of neutral-donor- and exciton-related photoluminescence in high-purity liquid-phase-epitaxial and vapor-phase-epitaxial InP samples is studied as a function of applied weak electric fields at liquid-He temperatures. Field-dependent suppression of neutral-donor-to-acceptor and free- and bound-exciton recombination peaks in the spectrum is attributed to impact ionization of the shallow donors and excitons by hot electrons which were accelerated by the applied field. More rapid quenching of the neutral-donor-bound and neutral-acceptor-bound exciton peaks with increasing field strength as compared to neutral-donor and free-exciton peaks is attributed to the dissociation of free excitons from the neutral centers by impact ionization.

I. INTRODUCTION

The application of weak electric fields to *n*-type semiconductor samples at temperatures such that the uncompensated shallow donors are neutral may result in impact ionization of the neutral donors by energetic electrons heated by the field.[1] In the case of an optically excited sample, impact ionization of both free and bound excitons may also occur. The impact-ionization phenomenon produces a sharp breakdown in the current-voltage characteristic, and in high-purity samples is frequently accompanied by a pronounced negative differential conductivity at the onset of breakdown. Simultaneous monitoring of the quenching of the various features in the photoluminescence (PL) spectrum associated with neutral donors and excitons as the field is increased permits a detailed study of the various impact-ionization mechanisms which are involved.

Impact ionization of shallow donors in GaAs was first studied systematically by Reynolds[2] using current-voltage measurements. Quenching of donor-acceptor (D^0-A^0) pair luminescence in favor of conduction-band—to—acceptor (e-A^0) luminescence was first observed as a function of applied bias by Schairer and Stath.[3] Bludau, Wagner, and Queisser fitted a drifted Maxwellian energy distribution to the line shape of the e-A^0 peak under applied bias to infer the carrier mobility in GaAs under photoexcited conditions,[4] and Bludau and Wagner subsequently used impact ionization of the shallow donors to separately measure the lifetime of conduction-band electrons due to e-A^0 recombination and to capture into ionized-donor levels.[5] Both luminescence[6,7] and reflectance[8,9] measurements have been used to study free-exciton—polariton behavior in GaAs under applied bias, while the quenching of free- and bound-exciton luminescence in GaAs was investigated by Bludau and Wagner.[10] In InP, the polariton reflectance under applied bias has been described,[11] but to our knowledge no systematic study of the quenching of exciton and neutral-donor-related luminescence has previously been performed. The present paper reports the results of such an investigation on high-purity epitaxial InP samples grown by liquid-phase epitaxy (LPE) and PH_3-VPE (where VPE denotes vapor-phase epitaxy) techniques. The results are compared to previously reported data for GaAs.

II. EXPERIMENTAL

The electrical properties of the samples which were measured are listed in Table I. Luminescence measurements were made with the samples freely suspended in superfluid He pumped to a temperature of 1.7 K, using an unfocused beam of 5145-Å light from an Ar^+ laser at power levels at 1 mW—1.0 W as the excitation. The luminescence was dispersed by a 1-m spectrometer and detected by a cooled S-1 photomultiplier tube. The spectral resolution was typically about 0.2 Å.

The electric field bias was applied parallel to the surface of the layers through contacts formed by alloying 0.020-in.-diam Sn spheres. The bias was typically pulsed at a frequency of 100 Hz using a 10% duty cycle to minimize possible sample heating effects. The luminescence was detected synchronously with the bias pulses using a boxcar

TABLE I. Electrical properties of the epitaxial layers.

Sample	T (K)	n (cm^{-3})	μ (cm^2/V s)
VPE-1	300	6.2×10^{14}	92
	77	a	a
VPE-2	300	6.9×10^{14}	2680
	77	3.4×10^{14}	86 500
VPE-3	300	1.2×10^{15}	2240
	77	5.0×10^{14}	46 000
LPE-1	300	3.7×10^{14}	5100
	77	6.3×10^{14}	74 900
LPE-2	300	3.5×10^{14}	4480
	77	3.9×10^{14}	112 000

[a]Unmeasurable (highly resistive).

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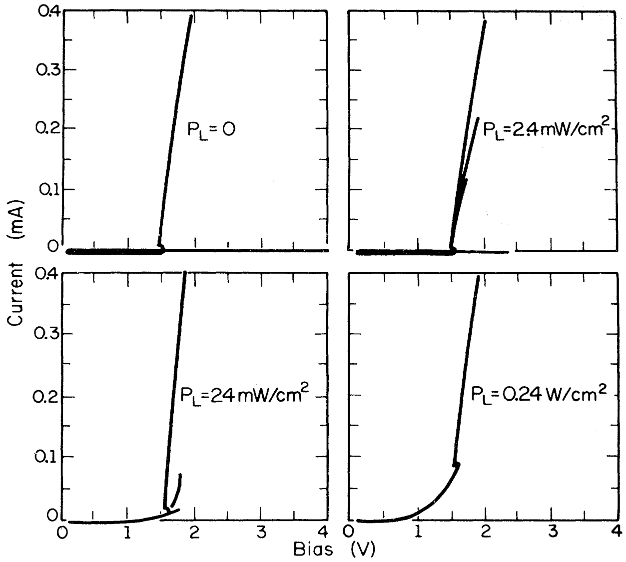

FIG. 1. *I-V* characteristics for sample LPE-1 at 1.7 K for four different laser excitation levels. Contact spacing was about 0.52 cm; laser spot diameter about 0.65 cm.

integrator whose aperture was slightly shorter than the pulse duration. To prevent heating, the average power dissipated in the sample was limited to a few mW or less. Values quoted here for the electric field represent the applied voltage divided by the contact spacing, which yields only a very approximate value of field under nonuniform photoexcitation conditions.

III. RESULTS

Measurements of the *I-V* characteristics of sample LPE-1 using a curve tracer yielded the results shown in Fig. 1 for various illumination levels. Under dark or low illumination conditions the sample resistance is nearly infinite until the breakdown voltage is reached (which is >4 V in the dark); after breakdown is initiated the sustaining voltage is much lower, as reported previously for GaAs.[2] The linear high-current portion of the characteristic is typically observed to jitter between several straight-line segments, which is most likely due to the unstable filamentary nature of the current at the onset of breakdown.[12] At higher photoexcitation intensities the presence of photocreated free carriers results in a nonzero current prior to breakdown, although a kink in the characteristic at the breakdown voltage is still apparent.

A plot of the PL emission intensity of the D^0-A^0 and e-A^0 peaks in the same sample is given in Fig. 2 for several values of applied field. The acceptor responsible for these two peaks is the sole residual acceptor level in our LPE samples and was first reported by Hess *et al.*, who denoted it "A_1."[13] This acceptor has been generally assumed to be C, but we have recently performed experiments which show that it must actually be Be or Mg.[14] It is apparent from a comparison of Figs. 1 and 2 that the neutral donors must be undergoing impact ionization to produce

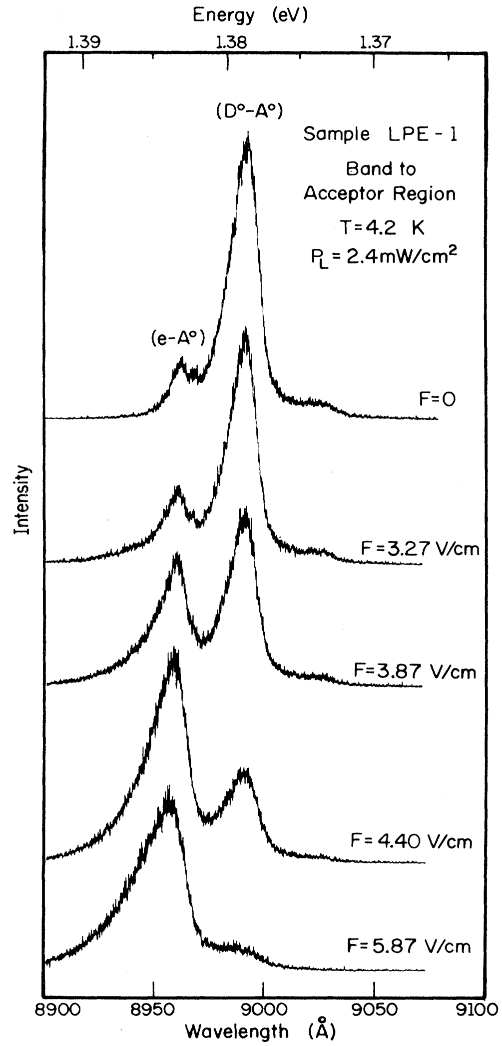

FIG. 2. Portion of the PL spectrum of sample LPE-1 for several values of applied field strength. Curves are shifted vertically for clarity but the intensity scale for each curve is the same.

free electrons at the same field strengths which cause breakdown, in agreement with previously reported results in GaAs.[3–5] The shift from D^0-A^0 to e-A^0 recombination and the broadening of the e-A^0 peaks for high electron temperatures, corresponding to large values of applied field, are virtually identical to the effects observed by increasing the lattice temperatures with no applied bias. An increase in the lattice temperature due to field-induced heating can be ruled out in the present case by the absence of detectable shifts in the positions of the exciton lines, which depend on the band gap and hence on the lattice temperature.

Impact ionization of shallow donors can also be useful in studying the behavior of peaks whose origin is uncertain. One such peak is labeled "unknown" at 1.3964 eV in

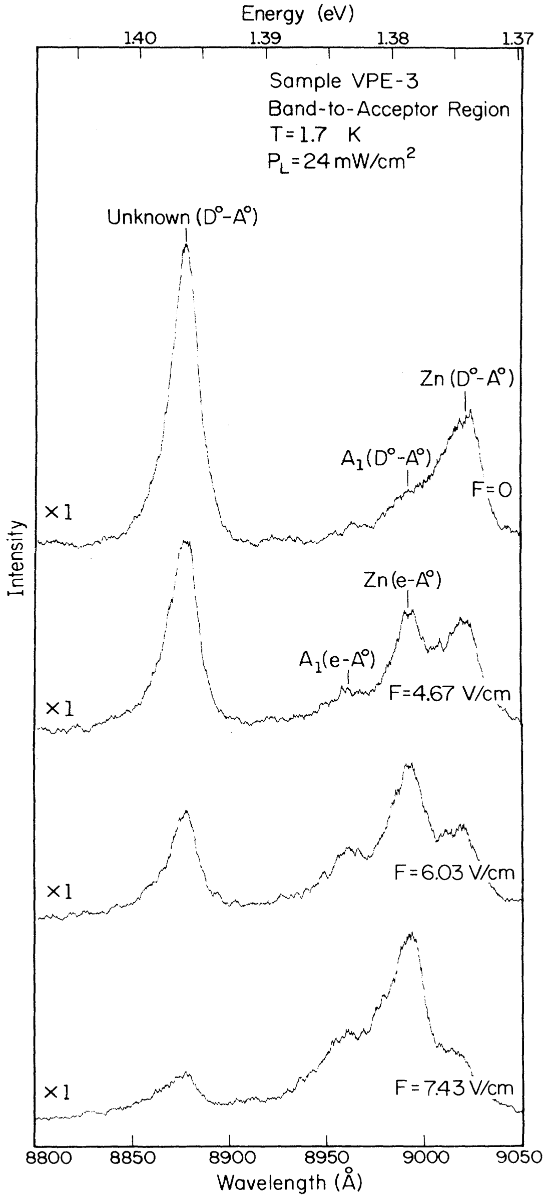

FIG. 3. Electric field dependence of the D^0-A^0 emission peak associated with an acceptor level of unknown origin in sample VPE-3. Intensity scale is the same for all four curves.

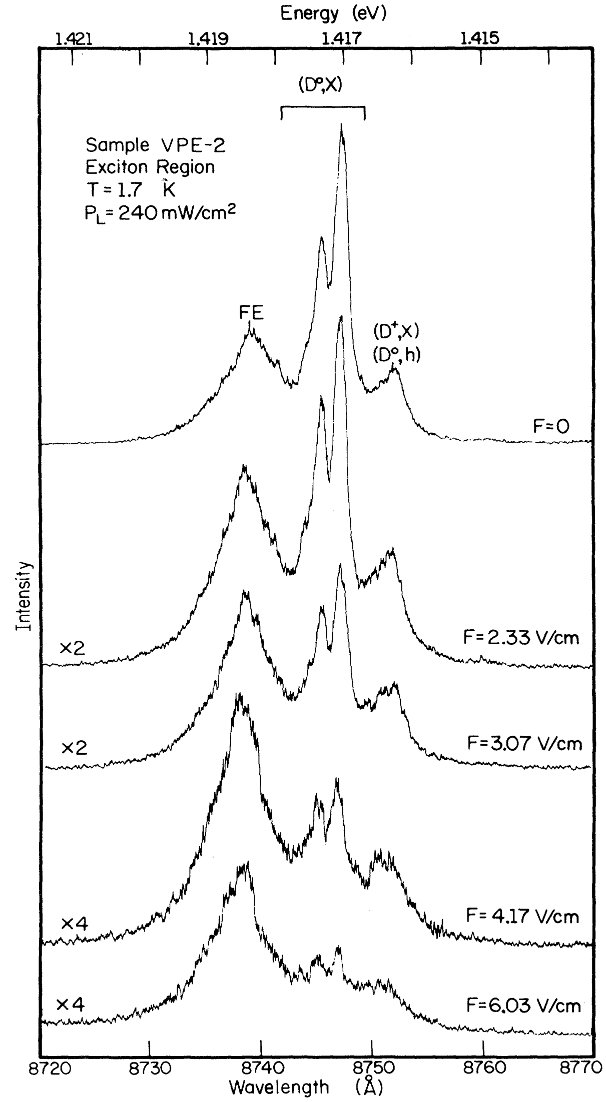

FIG. 4. PL spectra of the near-band-edge exciton recombination for an n-type sample as a function of applied field. Lower four traces are expanded in intensity by the indicated factors.

the spectrum in Fig. 3. This peak has been observed in undoped PCl_3-VPE (Ref. 15) and PH_3-VPE (Ref. 16) samples, including the present one, and has been ascribed to D^0-A^0 recombination involving an unidentified shallow ($E_A \simeq 21$ meV) acceptor level on the basis of its temperature and excitation intensity dependence. The field dependence of this peak in Fig. 3 is seen to be the same as that of the "normal" D^0-A^0 peaks associated with the Zn and A_1 acceptors also present in this sample. However, no corresponding e-A^0 peak is observed at the higher fields for the unidentified level. While the absence of any e-A^0 peak associated with the unidentified level is consistent with the observed lattice temperature dependence,[16] the reason for this absence is not understood.

We previously reported another emission band in undoped PH_3-VPE InP samples, consisting of a sharp no-phonon line at 1.2885 eV and a vibronic sideband structure extending to lower energies.[16] This emission band was subsequently identified by Skolnick *et al.* as being due to an isoelectronic center involving Cu.[17] The electric field dependence of this band was measured in samples VPE-1 and VPE-2. A monotonic decrease in the intensity of both the no-phonon line and the vibronic structure was observed with increasing field strength. Presumably, this behavior is due to the impact ionization of the excitons bound to the isoelectronic center.

Spectra of the exciton-related emission lines in a high-purity n-type sample (VPE-2) as a function of bias are shown in Fig. 4. The various peaks in the spectrum corre-

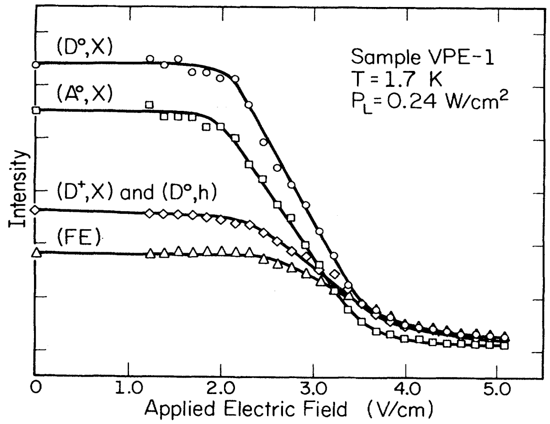

FIG. 5. Field-dependent quenching rates of the various exciton recombination peaks in a highly compensated n-type sample. Zero of intensity and the absolute intensity scale for all four curves is the same.

spond to the recombination of free excitons (FE), neutral-donor-bound excitons (D^0,X), ionized-donor-bound excitons (D^+,X), and free-hole—to—neutral-donor transitions (D^0,h).[18] For the latter two mechanisms, the expected photon energies are virtually indistinguishable and separate peaks due to the two processes have not yet been reported in InP, as they recently were in GaAs.[19] No peaks due to acceptor-bound exciton recombination (A^0,X) can be discerned in this spectrum, which is typical of our high-purity n-type PH_3-VPE samples. Quenching of the D^0,X peaks is seen to start sooner and proceed more rapidly than the quenching of the FE and $D^+,X/D^0,h$ peaks as the field is increased. This trend, together with the dominance of the FE peak at high-field strengths, was common to all of the samples studied.

Sample VPE-1 was highly compensated and as a result it exhibited relatively strong A^0,X peaks, in addition to the peaks present in VPE-2; it is therefore used to illustrate the relative dependence on field of the quenching of all four types of emission peaks in Fig. 5. The onset of quenching occurs earlier and the relative rate of quenching with field is much more rapid for the D^0,X and A^0,X peaks than for the FE and $D^+,X/D^0,h$ emissions.

IV. DISCUSSION

In the absence of detectable shifts in the position of the exciton lines in Fig. 4 with increasing field, it must be concluded that the behavior of the spectra in Figs. 2 and 3 is due to heating of the electron distribution by the field rather than heating of the lattice. Since the field strengths employed are orders of magnitude smaller than those required for direct field ionization of the donors, it can safely be concluded, as was done for GaAs in Refs. 2—5 and 10, that the observed luminescence quenching effects are indeed due to impact ionization of the donors and excitons by hot majority carriers (electrons).

It has recently been argued that the peak which we have labeled as e-A^0 recombination is actually a result of excited-state donor-to-acceptor pair transitions, denoted D^1-A^0.[20] The present results by themselves do not allow one to distinguish between the e-A^0 and D^1-A^0 mechanisms, since both types of peaks would be expected to be enhanced by a field-induced heating of the electron distribution. However, the broadening of the higher-energy peak for both high electron and lattice temperatures, together with observation of a third distinct peak ascribable to the D^1-A^0 mechanism, strongly support the e-A^0 interpretation. The third peak is in fact barely discernible in Fig. 2 as a small bump on the low-energy side of the e-A^0 peak at low fields; details of this observation will be described in a separate paper.[21]

TABLE II. Some possible dissociation mechanisms for free and bound excitons and the associated threshold energies. The notations e and h symbolize free electrons and holes, respectively; A^0, D^0, and D^+ denote neutral acceptors, neutral donors, and ionized donors. Donor and free-exciton (X) binding energies are denoted E_D and E_X; E_{BX} is the binding energy of an exciton to the indicated center. A^+,X complexes are not considered due to their predicted instability in InP. Partial Auger processes were not included. Values are taken from Ref. 18: $E_D=7.65$ meV, $E_X=4.8$ meV, $E_{BX}^{D^0}=1.7$ meV, $D_{BX}^{A^0}=3.8$ meV, $E_{BX}^{D^+}=3.0$ meV, and $\alpha=m_e/m_h=0.13$. The dissociation energy formula for FE is from Ref. 10.

Dissociation process		Minimum dissociation energy
$FE_{n=1}\rightarrow$	$e+h$	$E_X\left[\frac{1+2\alpha}{1+\alpha}\right]=5.4$ meV
$D^0,X\rightarrow$	D^0+X	$E_{BX}^{D^0}=1.7$
	D^0+e+h	$E_X+E_{BX}^{D^0}=6.5$
	$(D^+,X)+e$	$E_D+E_{BX}^{D^0}-E_{BX}^{D^+}=6.4$
	D^++e+X	$E_D+E_{BX}^{D^0}=9.4$
$A^0,X\rightarrow$	A^0+X	$E_{BX}^{A^0}=3.8$
	A^0+e+h	$E_X+E_{BX}^{A^0}=8.6$
$D^+,X\rightarrow$	D^0+h	$E_X-E_D+E_{BX}^{D^+}=0.2$
	D^++h	$E_{BX}^{D^+}=3.0$

Various possible mechanisms of exciton dissociation by impact ionization in GaAs and their associated energy thresholds were given by Bludau and Wagner.[10] Corresponding dissociation paths and the relevant threshold energies for InP are given in Table II. Given the deviation from the relationship $E_d\propto F^2$ (where E_d is the drift energy and F is the field strength) that was observed in GaAs,[4] we have not attempted to extract numerical values for the threshold drift energies from Fig. 5. Qualitatively, however, the earlier and stronger quenching which was consistently observed for the A^0,X and D^0,X peaks relative to the quenching of the D^0,h luminescence, whose threshold energy is just the donor energy (7.65 meV), strongly suggests that the excitons are being dissociated intact from the neutral donors and acceptors by collisions. The energies for dissociation of excitons from neutral centers are seen from Table II to be substantially less than for the processes in which single or multiple free carriers are split off from the complex.

Our conclusions regarding the mechanism of D^0,X and A^0,X quenching in InP are in accord with the conclusions reached for GaAs in Ref. 7 but not with the conclusions in Ref. 10, where it was inferred that the splitting off of singly charged carriers was the predominant mechanism. However, the experimental data in Ref. 10 showed the quenching rate of the A^0,X peak in GaAs to be the least rapid, while it has one of the more rapid rates in the data of Fig. 5 for InP. Another apparent discrepancy between the two materials is the observation that the FE emission dominates the spectrum of the InP samples at high field strengths, while this did not appear to be the case for GaAs.[10] This phenomenon could just be a result of the differences in polariton structure in the two materials[18]; a study of the field dependence of the FE(LO) emission in the two materials might be instructive in this regard, but the present samples did not exhibit sufficiently strong FE(LO) emission to permit such a comparison.

If the dissociation mechanism described above for the A^0,X and D^0,X complexes, whereby free excitons are dissociated intact from the neutral centers, is correct, the resulting increase in free-exciton concentration might account in part for the relatively slow suppression of the FE peak. An actual increase in the FE emission intensity at the onset of breakdown was reported for one InP sample in Ref. 10, but such an effect was never observed in the present investigation. Given the complexity of the overall process, it is difficult to draw definite conclusions regarding the exciton dissociation mechanisms.

The relatively slow suppression of the $D^+,X/D^0,h$ peak would tend to support the latter interpretation of its origin, given the very low threshold energy for the splitting off of a free hole from the D^+,X complex as given in Table II. It might still be conceivable that a sharp line due to D^+,X recombination is superimposed on the more slowly quenched and broader D^0,h peak, such as was observed in GaAs,[19] but the purity of the present samples is not sufficient to resolve any such structure.

Finally, a rather interesting observation relative to sample VPE-3 may be noted. For a constant applied dc voltage, larger than the breakdown voltage (or smaller if the breakdown had already been initiated), we observed that the current at first decreased somewhat with increasing laser illumination, up to a few mW, and then began to increase normally. The reason for this negative differential photoconductivity is not understood at present, but further investigation is underway.

V. SUMMARY

Impact ionization of shallow donors and both free and bound excitons was found to take place in InP at low temperature for very low applied electric field strengths (on the order of a few V/cm). Behavior of D^0-A^0 and e-A^0 peaks as a function of electron temperature, when the electrons are heated by the applied field, was found to closely replicate the dependence of these peaks on lattice temperature in the absence of external fields. Qualitative consideration of the data indicates that the most likely dissociation path involved in impact ionization of excitons bound to neutral centers is the dissociation of free excitons from these centers. This process has also been reported as characteristic of the low-temperature thermal dissociation process for this type of complex.[22] Several discrepancies between our results regarding exciton dissociation in InP and previous data for GaAs (Ref. 10) have been discussed and some possible explanations considered.

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