Nonthermal microwave modulation of photoluminescence in III-V semiconductors

M. C. DeLong, W. D. Ohlsen, I. Viohl, X. Yin, and P. C. Taylor
Physics Department, University of Utah, Salt Lake City, Utah 84112

D. Sengupta and G. E. Stillman
Center for Compound Semiconductor Microelectronics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

J. M. Olson
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

W. A. Harrison
Department of Applied Physics, Stanford University, Palo Alto, California 94305
(Received 7 January 1993)

The effects of microwave electric fields on the photoluminescence (PL) from binary III-V semiconductors are compared to those of fields applied directly via Ohmic contacts. Significant differences are seen between the electric-field dependences of luminescence intensity changes for microwave and directly applied fields, particularly in cases where the directly applied fields lead unequivocally to impact ionization. Hence, in contrast to previously published reports, it appears that mechanisms other than impact ionization are significant in the microwave-PL coupling. We have also performed Monte Carlo simulations. These calculations indicate that the energy dependence of the cross sections for capture of photoexcited carriers into competing radiative and nonradiative processes plays an important role.

INTRODUCTION

In a previous paper we reported that in a set of III-V semiconductors which exhibits a propensity to form an ordered structure the coupling between an applied microwave electric field and an ongoing photoluminescence (PL) process is predominantly the result of simple lattice heating.[1] In the majority of samples we have investigated, however, including binary and ternary III-V's, II-VI's, and quantum wells, the coupling mechanism is not thermal, i.e. it is not the result of the fact that different competing luminescence processes have different dependences of PL intensity on temperature in a spectroscopy where the sample temperature is being modulated by the application of a microwave electromagnetic field.[1] Over the years there have been numerous reports of changes in PL spectra induced by microwaves.[2–10] In many cases the effects of microwaves on PL intensity have been ascribed to impact ionization,[2–8] although the energy dependence of the cross section for capture of free carriers into bound states,[9,10] heating,[5] and effects involving applied static magnetic fields[5,8] have also been mentioned as explanations. We have previously discussed heating effects in considerable detail.[1] Because many experimental configurations, including the one to be discussed below, contain no applied static magnetic field, the following discussion will focus primarily on mechanisms involving impact ionization and the energy dependence of capture cross sections.

The attribution to impact ionization of changes in luminescence intensity in materials subjected to microwave electric fields was originally based on the fact that in Si a plot of luminescence intensity changes as a function of applied microwave powder did not extrapolate to the origin but rather to a relatively large microwave power,[2,3] suggesting that a minimum electric field is required for an observable effect, as is the case in a conventional impact ionization mechanism.[11] Also in one sample of GaAs the PL intensity decreased superlinearly as a function of applied microwave power.[4] In this paper we investigate the plausibility of impact ionization as the dominant cause of changes in PL intensity by presenting a detailed comparison of PL changes in samples subjected to microwave electric fields with changes resulting from electric fields generated by applying a potential along the epilayer via Ohmic contacts.

In this work impact ionization refers to inelastic scattering of an energetic free carrier by a shallow bound center wherein sufficient energy is transferred to the bound center to ionize it. Such phenomena are well known.[11] Their presence is recognizable by the existence of a strongly superlinear dependence of sample current on applied voltage. The current avalanches as a function of applied electric field as a result of carriers being impact ionized from excitons (under photoexcitation) and shallow donors. It is important to note that a precondition for the *observation* of this avalanche process is the freezeout of carriers. It is equally important to note that the inverse of the previous statement is *not* true; i.e., failure to observe an avalanche in the current-voltage (I-V) characteristics of a material does not preclude a reduction in the concentrations of neutral donors and excitons via impact ionization when an electric field is applied. Impact ionization of shallow excitons and neutral donors

0163-1829/93/48(8)/5157(10)/$06.00

by electrons accelerated in an applied electric field may occur in cases where only a relatively small fraction of donors are neutral, even at low temperatures. However, in these cases, a causal assignment cannot be definitively made from the associated *I-V* curve, which does not show the characteristic avalanche.

In contrast to the results just discussed in which the effect of microwave fields on PL are attributed to impact ionization, Booth and Schwerdtfeger[9,10] rejected the impact ionization explanation on the grounds that the amount of energy an electron could gain from the microwave electric field in the scattering time appropriate for dephasing a cyclotron resonance signal is an order of magnitude too small (0.5 meV) to impact ionize shallow donors and excitons (typically 3–5 meV in III-V semiconductors). Unfortunately this argument is flawed for two reasons. The dephasing time associated with cyclotron resonance is typically an *elastic* scattering time; hence electrons would continue to gain energy even after being scattered. Furthermore, even if the scattering were inelastic, it is an average time. Some members of the ensemble could still gain enough energy to impact ionize despite the fact that on average they cannot. Booth and Schwerdtfeger[9,10] argue instead that the influence of the microwaves on the PL process is via the energy dependence of capture cross sections for free carriers into the bound states involved in radiative recombination. This conclusion is based on their observation of a linear decrease in PL intensity with microwave power, as predicted by a reciprocal dependence of capture cross section on free-carrier energy. Clearly there is no general agreement in the literature concerning the mechanism whereby a microwave electric field influences ongoing photoluminescence processes.

Investigations of the effects of electric fields on photoluminescence date back at least to the work of Schairer and Stath,[12] who observed a shift from donor-acceptor pair to band-acceptor recombination in GaAs as increasing current was passed through an epilayer in which PL was being monitored. Coincidence of an avalanche in the current-voltage characteristics with a sharp decrease in luminescence intensity from processes associated with bound states as well as transfer of luminescence to free carrier processes supports their explanation of the coupling in terms of impact ionization. Decreases in the intensity of optical emission associated with excitonic and donor-acceptor recombination resulting from an electric field being applied via contacts to the sample have been reported in GaAs by Bludau and Wagner,[13] in InP by Skromme and Stillman,[14] and in Si by Weman, Zhao, and Monemar.[15–17] Because changes in PL intensity can be directly correlated to the avalanche behavior in the *I-V* curves, the assignment of the rapid decrease in PL intensity with increasing electric field to impact ionization can be made, *in these cases,* with a relatively high degree of certainty.

In addition to the experimental work described above, Smith, Pan, and McGill[18] have calculated the effect of an applied electric field on the concentration of excitons at low temperatures. They found the critical field for impact ionization to be about 2 V/cm in Ge and 20 V/cm in Si. It is noteworthy that if one calculates the energy gained by a free electron within the scattering time associated with the mobility appropriate for the extremely pure Ge and Si assumed by Smith, Pan, and McGill the resulting values correspond to the exciton binding energies in these materials, to within no worse than a factor of 3.

Changes in PL intensity may also be effected through the application of microwave electromagnetic fields. Well-understood examples include magnetic resonance spectroscopies such as optically detected magnetic resonance[19] (ODMR) and optically detected cyclotron resonance.[20] Unfortunately, despite the clear understanding of changes in PL intensity in terms of resonant effects in the presence of a strong magnetic field, a nonresonant effect exists that remains even in the absence of an applied dc magnetic field. In some cases this nonresonant effect can be definitively identified as simple heating of the lattice by the microwaves.[1] In cases where thermal effects appear not to be relevant, Wang, Monemar, and Ahlström[4] attributed the change in PL intensity to impact ionization of bound centers by free carriers accelerated in the microwave electric field. Their evidence for impact ionization was a superlinear dependence of PL intensity reduction on applied microwave power.[4] Omling has recently applied the technique as a modulation spectroscopy to investigate exciton trapping at monolayer steps in GaInAs/InP quantum wells,[6] based on the interpretation of the coupling between the PL and microwaves as via impact ionization. In a similar study Lin *et al.*[21] arrived at similar conclusions despite the fact that they interpreted the PL changes in terms of a thermal coupling. Although in these cases the outcome was independent of coupling mechanisms, we have seen other examples[22] where the microwave modulated PL (MMPL) spectra are very different for the thermal and non-thermal coupling mechanisms. If the spectra depend on the coupling mechanism, then using those spectra to obtain insight into the underlying physical processes certainly requires a knowledge of which coupling mechanism is operating.

A number of explanations for the effect of electric fields on PL in addition to impact ionization and heating have been put forth. In the case where direct contacts were used, Bludau and Wagner[13] also considered Stark effect ionization, changes in radiative lifetime, and field-induced enhancement of nonradiative processes. Field ionization of excitons can easily be excluded by simple calculations which show that the required electric fields are three orders of magnitude larger than experimentally used. Changes in the matrix elements determining recombination rates (and hence lifetimes) will be of the same order as those for field ionization and hence will also be too small to explain the observed effects. Redistribution of carriers among the various competing radiative and nonradiative processes will be discussed at length below.

In earlier work on microwave induced effects, Wang and Monemar,[5] working in an ODMR geometry (i.e., where the sample is placed in the microwave magnetic-field maximum and electric-field minimum), cited four different mechanisms as dominating under different experimental conditions. These include cyclotron resonance and magnetically enhanced surface recombination at high magnetic fields, in addition to lattice heating and enhanced impact ionization. In many cases microwave effects on PL take place under conditions of essentially zero static magnetic field.

In this work we report on changes in PL intensity induced by microwave electromagnetic fields as well as from the application of low-frequency pulsed dc electric fields generated via direct electrical contact. Although impact ionization is certainly a factor in modifying PL spectra in the presence of a microwave field, our results, including numerical modeling, suggest that the energy dependence of capture cross sections for trapping carriers plays an important role.

EXPERIMENTAL PROCEDURE

Two pairs of samples were used in this work. One was very high-purity InP grown by organometallic vapor phase epitaxy (OMVPE) at American Cyanamid using tertiary butyl phosphine. The epitaxial layer, having a thickness of about 5 μm, was grown on a semi-insulating substrate. Analysis of variable temperature Hall effect measurements gave total electrically active donor and acceptor concentrations of $N_D = 9.9\times10^{14}/\text{cm}^3$ and $N_A = 5.1\times10^{14}/\text{cm}^3$, respectively. Photothermal ionization spectroscopy measurements indicated that the dominant residual donor species were S and Si. The maximum electron mobility occurred at 62.5 K and was 78 000 $\text{cm}^2/\text{V s}$. Impact ionization measurements on the sample at 4.2 K with no illumination gave a breakdown voltage of 2.2 V. The *I-V* characteristic showed a negative resistance, with the sustaining voltage switching back to 1.5 V and remaining at this value for currents from low values up to as high as 80 μa. The sample to which an electric field was directly applied via Ohmic contacts, to be described in detail below and referred to as DCMPL, had a cloverleaf geometry appropriate for Hall measurements. In its application here, the two alloyed In contacts on adjacent corners of one side were tied in parallel and a voltage applied between opposite sides. Because of the indentations cut to generate the cloverleaf geometry, the actual electric field is difficult to calculate. The values plotted below were determined by dividing the applied voltage by the diagonal dimension of the wafer surface. The error introduced by this simplification will be a constant shift in all field values and is inconsequential to the functional dependences which are of most interest to us here. This sample evidences carrier freezeout below approximately 20 K as well as an avalanche in *I-V* characteristics at low temperature. The avalanche in the *I-V* characteristics is unequivocal evidence of impact ionization of neutral donors in the absence of photoexcitation.

The second pair of samples investigated was nominally undoped 6-μm-thick *n*-type GaAs epilayers grown on a *p*-type substrate by the National Renewable Energy Laboratory using atmospheric pressure OMVPE. The *p-n* junction restricted current flow to the epilayer. Gold contacts with a separation of 1 mm were electroplated onto one member of the pair and leads attached with silver paint. The room-temperature carrier concentration was estimated to be $5\times10^{15}/\text{cm}^3$, assuming a mobility of 8500 $\text{cm}^2/\text{V s}$. (The sample width was also 1 mm.) In this case the carriers did not freeze out at low temperature. In fact the conventionally measured resistance between the contacts changed by less than a factor of 2 between room temperature and 1.8 K.

Conventional photoluminescence was performed using a mechanically chopped 514-nm Ar^+ laser. The illumination intensity for the measurements reported below was 1.0-mW unfocused light apertured to 2 mm diameter, equivalent to approximately 30 mW/cm^2. This level of illumination was chosen to be high enough to give adequate signal so that modulation spectroscopy could be performed over many orders of magnitude in applied electric field yet the illumination was weak enough to permit significant carrier freezeout in the InP samples at low temperature. PL was dispersed with a Spex 0.75-m spectrometer and detected with an *S*-1 photomultiplier. Spectra are not corrected for system response. This fact is particularly relevant in the case of MMPL, where astigmatism induces small apparent shifts in energy resulting solely from the fact that the microwave cavity is located off the optical axis of the system. These small energy shifts are not important to the objective of this research.

For the DCMPL measurements optical excitation was continuous while a unipolar dc voltage was applied parallel to the epilayer via Ohmic contacts. The applied voltage was gated at 500–1000 Hz. Phase sensitive detection was referenced to the gating signal. The gated dc measurements were designed to cause electric field-induced PL changes similar to those reported and associated with unequivocal impact ionization phenomena.[13–17] *I-V* characteristics were measured quantitatively with a pair of Keitley 177 digital multimeters while attached to a constant current supply and observed semiquantitatively with a Tektronix 575 transistor curve tracer.

For MMPL the sample was mounted on a Teflon holder in the electric field maximum of a rectangular TE_{011} mode 16-GHz microwave cavity. Photoluminescence was excited continuously using a small prism mirror and collected at 180° through a slot along one of the four cavity edges where the microwave fields and currents are all zero. The microwave electric field was parallel to the surface of the sample films. The microwaves were gated with a solid state switch driven by a function generator, which was also used for the lock-in reference signal. The maximum microwave power delivered to the cavity was projected to be 400 mW (measured to be 4 mW at 20 db attenuation).

EXPERIMENTAL RESULTS AND DISCUSSION

In the previous paper[1] criteria were formulated which unequivocally establish the presence of a thermal coupling between microwaves and PL, i.e., a situation in which changes in PL intensity result primarily from changes in the lattice temperature. The presence of a thermal microwave-PL coupling is established by the fact that the time dependence (frequency response) of the MMPL amplitude is determined by the heat transfer properties of the system: if the interaction is thermal one observes that (a) in He gas at 5 K the roll-off frequency for the MMPL amplitude is on the order of 20 Hz and (b) when the sample is immersed in superfluid He the MMPL amplitude decreases 1–2 orders of magnitude but is frequency independent over the range 10 Hz–100 kHz. Neither of the samples investigated in this work showed such properties. Although work is ongoing to determine the circumstances under which the microwave-PL interaction is thermal or nonthermal as well as the underlying physical cause of the distinction, there is no current model for our observations.

The current-voltage characteristics of the two samples at 1.8 K are shown in Fig. 1, referenced to the right axis (solid symbols). Multiple data points at the same voltage refer to repeated measurements and give some idea of reproducibility and uncertainty. Because of the sharp avalanche in current over a narrow range of voltage, it is reasonable to conclude that impact ionization is occurring in the case of the InP. That the avalanche behavior disappears at temperatures greater than about 20 K, coincident with the *I-V* characteristics becoming Ohmic, is also supportive of the impact ionization interpretation. The behavior of the GaAs is nearly Ohmic.

Changes in the amplitude of the PL peak associated with excitonic recombination are also plotted as a function of applied voltage and referenced to the left axis. The quantity being plotted on the left vertical axis (open symbols) is the magnitude of the ratio of the DCMPL to PL signals, both being measured at the energy of the exciton peak. In all cases the excitonic recombination is quenched. Hence the MMPL amplitude is negative and the quantity being plotted is the negative of the MMPL to PL amplitude ratio. (The actual spectra are shown in Figs. 7 and 8 and will be discussed in a later section.) Because the relative change in PL intensity for the InP sample is also a sharp function with the same turn-on voltage it is also reasonable to conclude that the decrease in exciton concentration is due to impact ionization of excitons by free carriers accelerated in the electric field. The slope of a straight line approximating the linear portion of the GaAs curve describing the relative change in luminescence intensity is approximately 1.7. Because carrier freezeout is not observed in the GaAs sample, no definitive conclusions may be drawn about the mechanism whereby the exciton concentration is reduced. Certainly impact ionization cannot be excluded.

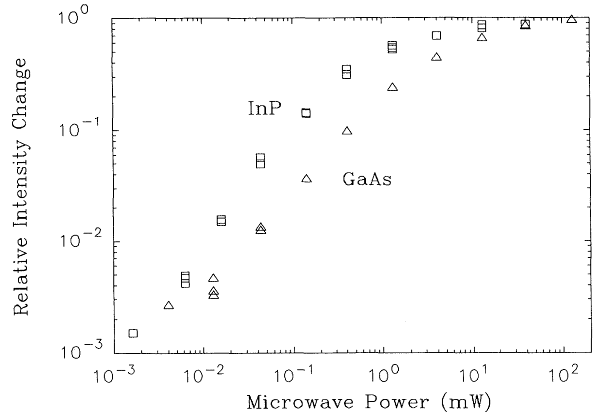

FIG. 2. Relative change in excitonic luminescence intensity as a function of applied microwave power for the samples referred to in Fig. 1.

Figure 2 shows the corresponding dependence of MMPL amplitude on the *microwave power* applied to the cavity when samples nominally identical to the previous pair are used. (Note that power is the quantity controlled in MMPL experiments, voltage in DCMPL. Hence as long as sufficient power is available in the DCMPL case, it is not surprising that the current can avalanche. Although the effect of limiting power in the MMPL case is not obvious, it is certainly reasonable that one may not observe an avalanche even if impact ionization is taking place.) It is immediately obvious that, below saturation, the InP sample has a linear dependence of MMPL intensity change on applied microwave power. The GaAs

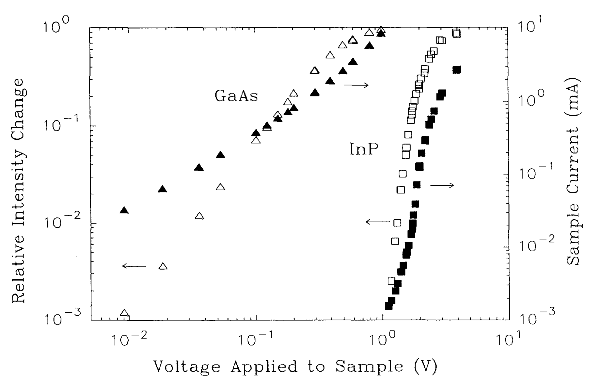

FIG. 1. Current (right axis, solid symbols) and relative PL intensity change $\Delta I/I$ (left axis, open symbols) resulting from application of a potential difference across epilayers of GaAs with impurity concentration of approximately 10^{16} donors/cm^3 (triangles) and InP with approximately 10^{14} donors/cm^3 (squares). In all cases the intensity decreases.

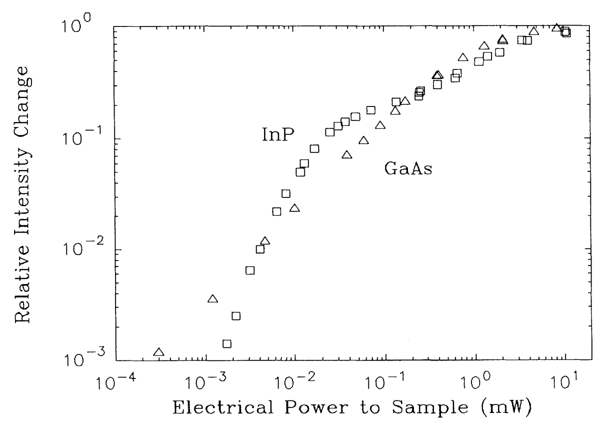

FIG. 3. Relative change in excitonic luminescence intensity as a function of applied pulsed dc power for the samples referred to in Figs. 1 and 2. Data are those of Fig. 1 plotted as a function of applied power.

sample is slightly sublinear.

For a better comparison between the MMPL and DCMPL, the $|\Delta I/I|$ (Ref. 23) data from Fig. 1 are replotted as a function of applied pulsed dc power (Fig. 3). Below saturation the GaAs curve may be reasonably well fitted with a straight line whose slope is approximately 0.87; the slope of the corresponding portion of the curve in Fig. 2 is indistinguishable from this value. Note that both the MMPL and DCMPL curves achieve saturation at powers on the order of 10 mW, with slightly higher power required for MMPL. That higher power is required to achieve saturation via MMPL is expected. The measured power is that delivered to the microwave cavity, not that actually dissipated in the sample. Some fraction of the microwave power will definitely be dissipated in the cavity walls. This fraction will be somewhat dependent on the applied microwave power since the sample properties will change with power.

Below the knee at $\Delta I/I \approx 0.1$, the InP curve in Fig. 3 has a superlinear slope; above that value it is sublinear. Clearly the two curves in Fig. 2 depicting $\Delta I/I$ as a function of applied microwave power resemble each other much more strongly than either resembles the unambiguous impact ionization case depicted in Fig. 3 for InP. For the case of InP, which shows carrier freezeout, the luminescence intensity still has a strongly superlinear dependence on applied power in the low frequency case for $\Delta I/I < 0.1$. The same is definitely not true for the MMPL in the same sample. The strong difference in functional dependences of the changes in PL intensity on applied power in the cases of microwave and low-frequency directly applied electric fields may be due to frequency dependent details of the impact ionization mechanism. They may also be due to an entirely different mechanism, either acting alone or in concert with impact ionization. At the very least the impact ionization model must be modified to explain these results. Consequently, previously published reports attributing changes in PL intensity in the presence of microwaves solely to impact ionization[3-6] should be reevaluated.

The nearly linear dependence of $\Delta I/I$ on microwave power is neither restricted to the two samples on which we have performed DCMPL nor to excitonic recombination nor to MMPL in the E-field maximum of the cavity. In fact a nearly linear dependence of $\Delta I/I$ on microwave power is observed in all samples we have investigated. This set of samples includes a high-purity GaAs epilayer containing approximately 10^{14} donors/cm^3 and definitely expected to show carrier freezeout and hence conventional impact ionization. In the case of this high-purity sample we were able to measure a linear dependence of $\Delta I/I$ on microwave power down to a level of 0.2 μW.[24] A similar linear dependence on applied power is also observed in CdS, where the binding energy of hydrogenic donors is 32 meV. A linear dependence of $\Delta I/I$ on applied microwave power has also been reported for InP:Zn where the same sample was investigated in both our E-field maximum cavity and a conventional ODMR cavity where the sample is located in the B-field maximum.[25] The only significant difference observed between the two cavities was that approximately 1.5 orders of magnitude more power was required to achieve the same value of $\Delta I/I$ in the case where the sample was located in the B-field maximum. This result supports the expectation that it is the microwave electric field which is ultimately responsible for the effects observed.

NUMERICAL MODELING AND DISCUSSION

In addition to our experimental investigations of the correlation between excitonic PL intensity changes and applied microwave or pulsed dc power, a numerical study of the effect of an electric field on the dynamics of conduction-band electrons, patterned on the method described by Jacoboni and Reggiani,[26] was performed.[25] In particular, the impact ionization rate of neutral donors (for which material parameters are better known than for excitons) was studied as a function of the applied power (electric field squared), the frequency of the electric field, the donor concentration (neutral and ionized), and the energy dependence of the capture rate. Where possible, values of modeling parameters were chosen to be appropriate for the samples used in our experiments. Because the decrease of luminescence by bound carriers is expected to be monotonically related to the rate of impact ionization of neutral donors, the latter was monitored in the numerical modeling. In our experiments the dependence of $\Delta I/I$ for donor-acceptor pair (DAP) recombination generally followed that for excitonic recombination, but in some cases the DAP peak was strongly influenced by the associated band-acceptor peak of opposite sign, leading to problems in quantifying the intensity change. Hence, although the decrease in exciton intensity was the quantity monitored experimentally, the comparison of experimental results and the Monte Carlo simulation is still quite valid. Because the impact formation rate for excitons has a weak dependence of applied field,[18] similar to that found at low energies for donors in our calculations, and because the binding energies of excitons and shallow donors are quite comparable in III-V's, the Monte Carlo simulation can be expected to describe either of the qualitatively similar excitonic and donor-related processes.

The Monte Carlo simulation assumed free carriers (conduction-band electrons with effective-mass ratio $m_e/m_0 = 0.067$) were subjected to a sinusoidal 16 GHz or 1 kHz electric field. The initial magnitude and direction of a seed electron's velocity were chosen stochastically from the velocity distribution of a free-electron gas in thermal equilibrium at 2 K. There are obvious departures from equilibrium in a system undergoing photoexcitation by 2.54-eV photons in which photoelectrons initially have energies of about 0.5 eV above the band edge. However, for carrier energies above the LO-phonon emission energy, kinetic energy is dissipated on the picosecond time scale through LO-phonon emission. Indeed, one of the results of the Monte Carlo simulation is to show that the hot photocarriers thermalize to within an LO-phonon energy of the band edge within a few picoseconds. The exact energy distribution below the LO-phonon emission threshold then depends on the exact nature of the inelastic-scattering mechanisms present.[27]

Hence a thermal equilibrium distribution serves only as an approximation.

The simulation allowed for scattering of electrons by acoustic and optical phonons[26] (inelastic) as well as scattering by ionized and neutral impurities[28–32] (elastic). Of critical importance is the fact that both the energy dependences of the scattering rates and the rate of capture by ionized donors[33,34] were included in the Monte Carlo simulation. Not included in the calculation were the energy dependences of any recombination channels that compete with the ionized donors, although this competition is likely to be important in many details of the spectra. Neutral donor scattering was considered inelastic when a scattering event took place in which the electron energy exceeded the neutral donor binding energy (5 meV). In this event the neutral donor was impact ionized and an additional free carrier was created. The new electron was included in subsequent calculations, allowing for the possibility of avalanche. When the electron was captured by an ionized donor the electron history, including lifetime, initial, and final energies, etc., was recorded. Lifetime is defined here as the time interval between launch or creation by an impact ionization process and capture by an ionized donor, the only final outcome allowed in the simulation. The loop was repeated for remaining free electrons until all were captured. A new seed electron was then launched. The life histories of 5000 seed electrons and their progeny were simulated for each condition. The impact ionization rate was then calculated to be the number of impact ionization events divided by the product of the average lifetime and the total number of seed electrons and their progeny. If, during the simulation, the population of free carriers was found to increase by more than a factor of 20, avalanche was deemed to have occurred. (No significant difference was found in avalanche electric field if the cutoff criterion was set at a 200-fold increase.) For simplicity scattering was assumed to be isotropic and the neutral and ionized donor concentrations under photoexcitation were considered constant throughout the simulation. Donor concentrations of 10^{14} and 10^{16} cm^{-3} were chosen to model our InP and GaAs samples, respectively. To simulate cases where carrier freezeout was and was not observed it was assumed that 10% of the donors were ionized and neutral, respectively. It is important to note that since the ionized and neutral donor concentrations are assumed constant, the simulation cannot be valid for impact ionization rates approaching the radiative recombination rate ($1/\tau_R$ where τ_R is the radiative lifetime, ≈ 1 ns for excitons and 1–3 orders of magnitude longer for impurity-related processes). The material parameters used in the simulation were taken from the properties of GaAs since it is the best characterized binary semiconductor. However, since GaAs and InP have similar optoelectronic properties, errors resulting from modeling one by the other are expected to be small compared to those resulting from other assumptions (e.g., constant neutral and ionized impurity concentrations).

The impact ionization rate R_I was calculated as a function of electric field for the various combinations of parameters described above. Figure 4(a) shows the results at high and low frequency for a sample with an ionized donor concentration of $10^{16}/cm^3$ and no carrier freezeout, similar to our GaAs sample. The computer simulation showed no avalanche for electric fields below 100 V/cm. Extension to higher fields is meaningless for the calculations because the impact ionization rate would exceed the radiative recombination rate and is meaningless experimentally because the luminescence process would already have been completely quenched at 10 V/cm, as shown in Fig. 1. Lack of avalanche behavior is attributed to enhanced ionized impurity scattering of free carriers. The greater the *rate* of isotropic elastic scattering, the lower the probability that a carrier will randomly walk down the electric field far enough to acquire sufficient kinetic energy to impact ionize a neutral donor within one *inelastic*-scattering time. Hence, for example, in our GaAs sample, an avalanching current and corresponding reduction in PL intensity due to impact ionization is not a viable process and is not observed either experimentally or in the Monte Carlo simulation.

A second system was modeled to have 10^{13} neutral donors/cm^3 and 10^{12} ionized donors/cm^3, similar to our

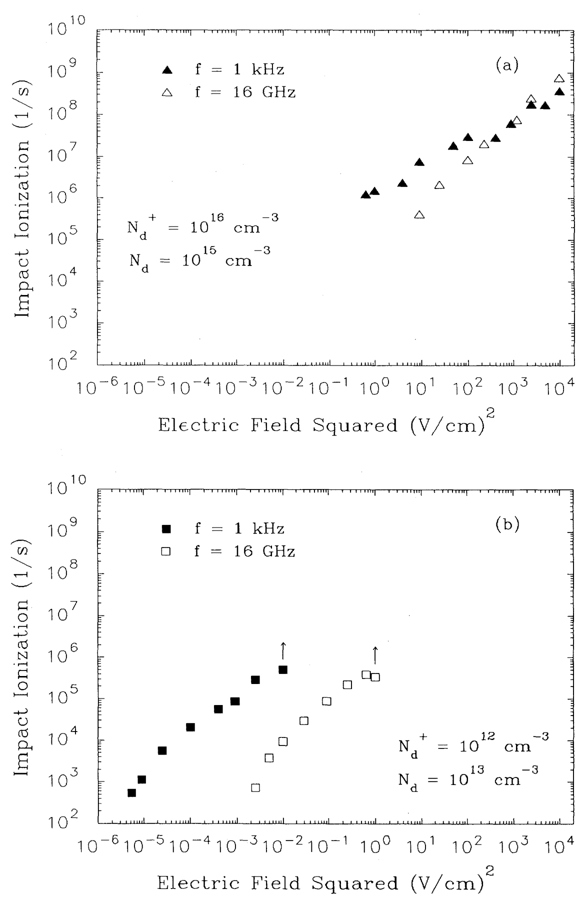

FIG. 4. Computer simulation of impact ionization rate as a function of applied electric field squared (power). Fields are modulated at 1 kHz (solid symbols) and 16 GHz (open symbols). Donors are assumed to be in (a) primarily ionized at $10^{16}/cm^3$ and in (b) primarily neutral at $10^{13}/cm^3$. Arrows signify avalanche behavior at the associated electric fields.

InP. Figure 4(b) shows the results. The onset of avalanche in the impact ionization rate, occurring at electric fields of 0.1 V/cm at low frequency and 1 V/cm at high frequency, is indicated by arrows in Fig. 4(b). In our experiments the onset of avalanche at low frequency was determined to be at a field of about 2 V/cm. In previous dc work the onset of avalanche was found experimentally to occur at electric fields of about 2.5 V/cm in InP (Ref. 14) and 1.5 V/cm in GaAs.[13] Hence our Monte Carlo calculations predict the correct avalanche electric field within an order of magnitude. This underestimation of the field required for avalanche in the impact ionization rate is probably the result of having assumed a fixed concentration of neutral donors. A more realistic model would include the dynamics of neutral and ionized impurity concentrations and hence allow for a decrease in the neutral donor concentration, thereby providing a negative feedback mechanism in the impact ionization rate.

As mentioned earlier, no avalanche was experimentally observed in the microwave case. This may be reconciled with the prediction of avalanche by the Monte Carlo simulation if one accepts, based on the calculations, that the required microwave electric field is an order of magnitude larger than in the case where the field is applied via leads. Such a field, approximately 20 V/cm, is comparable to the microwave electric field we estimate to be associated with a power of approximately 10 mW. Experimentally, at 10 mW the neutral centers are nearly fully ionized and the luminescence almost completely quenched, and hence no avalanche can occur.

An important feature of our model is the inclusion of the carrier energy dependence of the capture cross section. The capture of electrons by ionized donors can be described in a cascade model, e.g., a chain of successive one-phonon transitions along a ladder of excited levels with the continuous reduction of the electron energy.[34,35] In this model, the process of carrier capture by a center consists of two stages. First, the moving carrier, while crossing the center, emits a phonon as a result of a single collision and ends up in a highly excited bound state of the donor. Second, by absorbing or emitting phonons, the carrier changes its energy and either escapes or thermalizes to the ground state, thereby neutralizing the center. The trapping rate for free carriers by ionized donors $R_t(\varepsilon)$ can be written as[33–35]

$$R_t(\varepsilon)=N_D^+\sigma(\varepsilon)v(\varepsilon) \tag{1}$$

where ε is the free-carrier kinetic energy, N_D^+ is the ionized donor concentration, $\sigma(\varepsilon)$ is the capture cross section, and $v(\varepsilon)$ is the free-carrier velocity. In GaAs at a temperature of 2 K and subject to the assumption of a fixed ionized donor concentration the capture rate R_t was found[25] to obey a power-law dependence on free-carrier energy:

$$R_t(\varepsilon)=R_{t0}\epsilon^x . \tag{2}$$

The exponent was found to be $x \approx -1/4$ for $\varepsilon < 0.1k_BT$ and to be $x \approx -3$ for $\varepsilon > 0.2k_BT$, where k_B is the Boltzmann constant and T is the absolute temperature. The results of this calculation are shown in Fig. 5. If the carrier energy increases linearly with applied electric field and the trapping rate decreases with the third power of the carrier energy, then the trapping rate is expected to decrease with the third power of the applied field or the $\frac{3}{2}$ power of the applied electrical power.

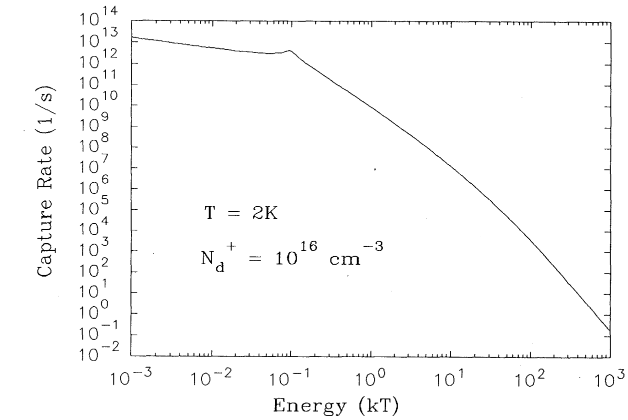

FIG. 5. Capture rate by ionized donors at 2 K as a function of free-carrier energy for a material with 10^{16} ionized donors/cm^3 as determined using methods outlined in Refs. 30–32.

This analysis has several important implications for free carriers in an electric field. The trapping rate decreases rapidly and smoothly with increasing electron energy, emphasizing the importance of low-energy carriers in the luminescence process. Hence, as the free carriers are heated by the microwaves, a process widely agreed to be the immediate consequence of applying a microwave electric field, the probability of capture into ionized donors (or binding into excitons) is reduced. Radiative recombination processes depending on this capture rate are consequently also reduced.

In order to estimate the effects of the energy dependence of the capture rate on the impact ionization rate, we also performed Monte Carlo simulations with a constant capture rate (chosen to be the capture rate at an energy of $1.5k_BT$, with $T=2$ K) at 16 GHz, both for cases where the carriers were assumed to freeze out and where they did not. Shown in Fig. 6 are the results of calculations including and excluding the corresponding energy-dependent capture rate (EDCR). As seen in Fig. 6(a), inclusion of EDCR enhances the impact ionization rate at low electric fields (or microwave powers) for the case of a relatively high concentration of carriers which do not freeze out. This is due to the increase in free-carrier lifetime and hence the probability that a carrier can acquire sufficient energy to participate in an impact ionization process. At higher electric fields, particularly in the case of a relatively low concentration of carriers which freeze out, Fig. 6(b), the onset of avalanche, marked by arrows, is shifted to a higher field (or power) when the effects of EDCR are included. In this case, where the material has a high mobility (long scattering time) impact ionization will be a major source of low-energy free carriers, since the process will typically occur as soon as the carrier acquires the minimum required energy. The enhanced probability of these low-energy carriers to be captured into donors and excitons has a generally retarding effect on the avalanche behavior associated with impact ionization.

In a more realistic model where several radiative and nonradiative processes compete with each other for free carriers, the branching ratios for these various processes would also be affected by the change in free-carrier energy distribution. Specifically, the increase in free carrier lifetime prior to trapping will enhance the probability that those carriers can migrate to nonradiative recombination centers. Experimental evidence for the importance of such an effect is provided by the observation, as seen in Figs. 7 and 8, that PL quenching is significantly more common than enhancing, i.e., the negative peaks are more prominent than the positive ones. Alternatively, the enhanced free-carrier lifetime also increases the probability that a carrier will remain free long enough to acquire sufficient energy to participate in an impact ionization process. This mechanism is particularly important at fields (or microwave powers) significantly lower than those required for avalanche.

The general conclusion of our numerical modeling is

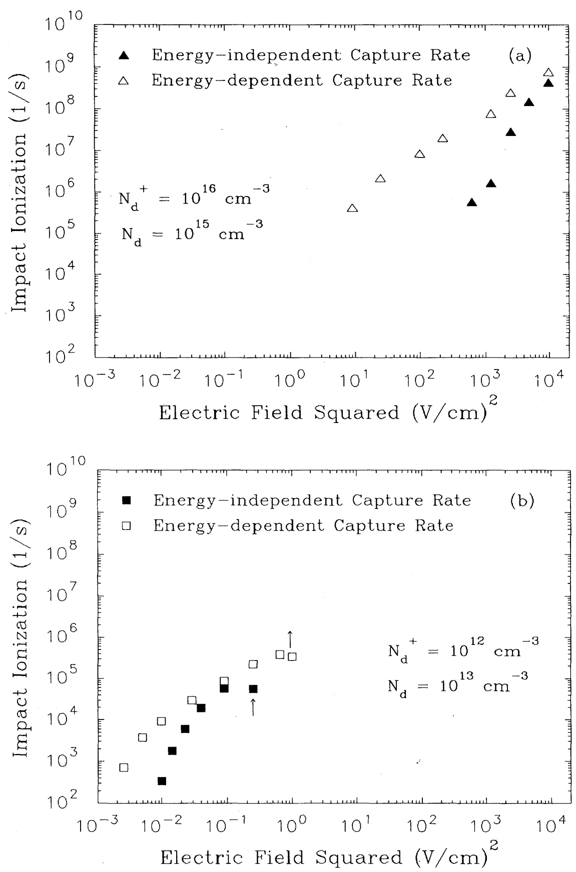

FIG. 6. Computer simulation of impact ionization rate as a function of applied electric field squared (power). Capture rate into ionized donors is assumed to be energy dependent (open symbols) or independent (solid symbols). The value chosen for the energy-independent rate was that of the energy dependent rate at 2 K. Donors are assumed in (a) primarily ionized at $10^{16}/cm^3$ and in (b) primarily neutral at $10^{13}/cm^3$. Open symbols in this figure are identical to corresponding symbols in Figs. 4(a) and 4(b).

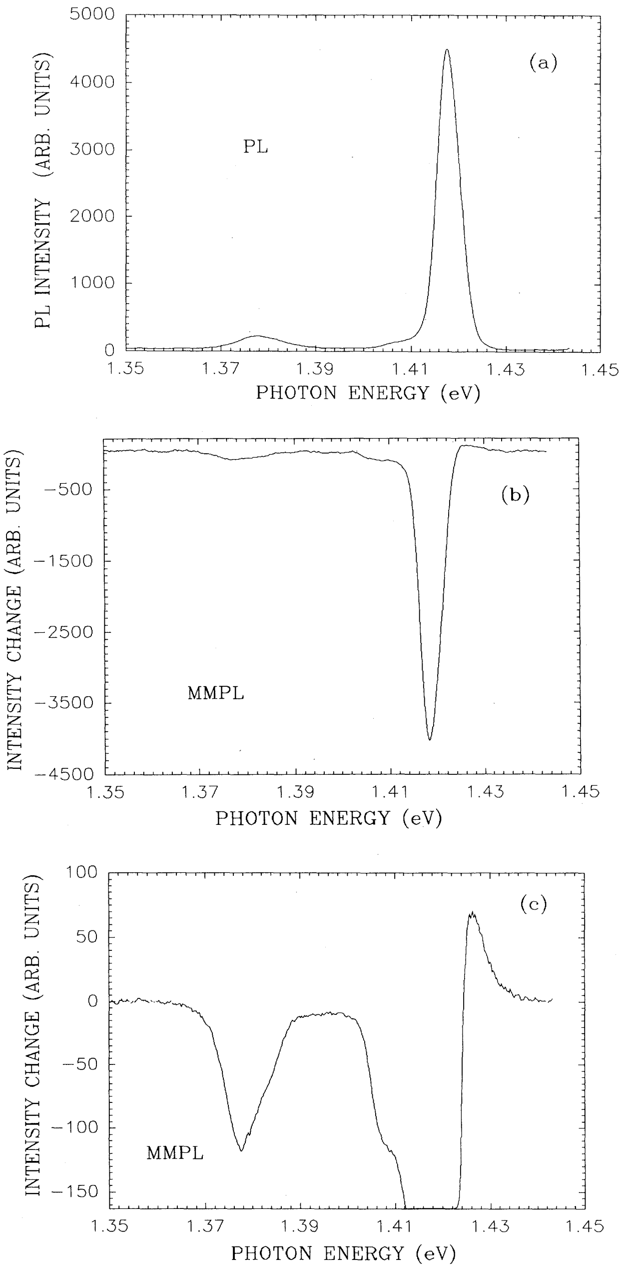

FIG. 7. (a) PL and (b) and (c) MMPL spectra from high-purity InP sample used previously to study the effects of applied dc and microwave electric fields. Spectrum in (c) is expanded by a factor of 50 compared to (b) to show detail of processes not seen in conventional PL. Negative peaks at 1.418 and 1.377 eV correspond to decreased emission from excitonic and donor-acceptor pair recombination, respectively. Positive peak at 1.426 eV probably results from enhanced free excitonic recombination.

that the observed changes in PL intensity in a microwave electric field are strongly affected by the energy dependence of the capture cross sections for the various competing radiative and nonradiative processes. The energy dependences of capture cross sections are doubtless present but display no identifying signature in the case where the electric field is applied via leads. This situation is analogous to that of impact ionization in the GaAs sample with 10^{16} donors/cm^3, which is also present but not easily observed experimentally.

APPLICATIONS

Despite the complexity of the mechanism of MMPL, it still constitutes a potentially useful spectroscopy and promises to be even more important when the mechanisms are fully understood. As an illustrative example, Fig. 7 presents spectra for cases where the optical processes are well understood: high-purity InP. The 2-K PL spectrum with 300-mW/cm^2 laser excitation intensity is shown in Fig. 7(a). All spectra presented in Figs. 7 and 8 were taken in conjunction with the directly applied electric field (via Ohmic contacts) and microwave power dependences of PL intensity shown in Figs. 1–3. Impurity concentration, lifetime, and illumination intensity parameters appropriate to these samples were also used in the numerical modeling calculations.

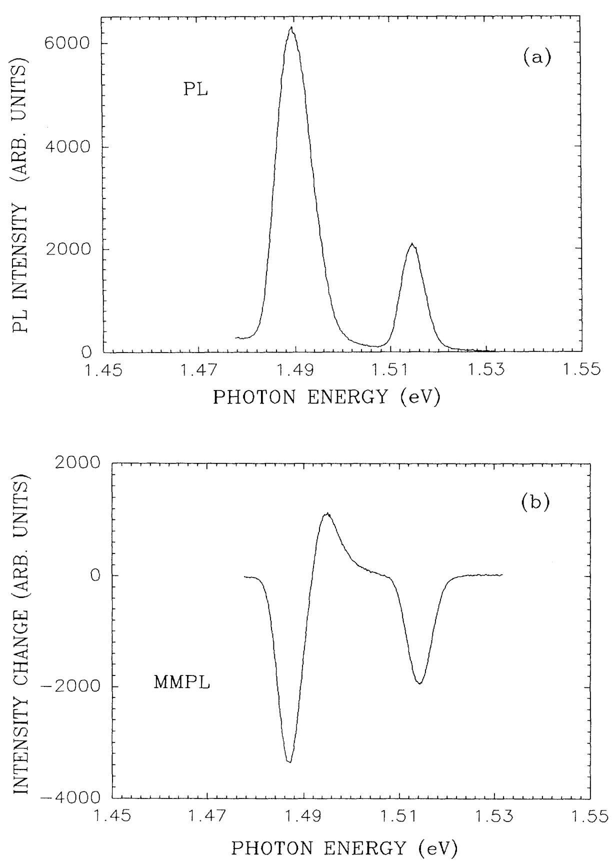

FIG. 8. (a) PL and (b) MMPL spectra from undoped GaAs containing approximately 10^{16} donors/cm^3. Negative peaks at 1.514 and 1.486 eV correspond to reduction in excitonic and donor-acceptor pair emission intensities, respectively; positive peak at 1.494 eV corresponds to enhancement of band-acceptor recombination under application of microwaves.

The very high quality of the InP sample is attested to by the fact that the PL spectrum, Fig. 7(a), is dominated by excitonic recombination (1.417 eV), with only a small donor-acceptor pair peak (1.378 eV). Figure 7(b) shows that the dominant effect of the microwaves is to decrease the rate of excitonic recombination. The same spectrum is shown in Fig. 7(c), expanded by a factor of 50. The most prominent new features are small negative shoulders on the high-energy side of the DAP peak and the low-energy side of the exciton peak (also visible in the PL) and the surprising positive peak on the high-energy side of the main exciton band. The positive sign corresponds to an increase in PL amplitude, suggesting that the peak, completely unresolved in the normal PL, is associated with free exciton or band-to-band recombination. Hence it is most likely that the high-energy PL emission in this InP sample consists of both bound and free excitonic recombination.

Another example of the utility of the technique is shown in Fig. 8, which shows the PL spectrum of the GaAs sample referred to above. The high-energy peak (1.514 eV) is due to excitonic recombination, the low-energy one (1.490 eV) is impurity related. The associated MMPL spectrum is shown in Fig. 8(b). This spectrum is typical of many nominally undoped, relatively high-purity semiconductors. The high-energy peak is negative, again signifying a decrease in the intensity of excitonic recombination under the influence of the applied electric field. In this case the impurity peak splits into a pair of peaks, the one at higher energy positive, the one at lower energy negative. The negative peak corresponds to a decrease in the neutral donor concentration in a donor-acceptor pair process. The positive peak corresponds to an increase in free-electron concentration in the associated band-acceptor process. After the processes have been identified, further insight may be gained by curve fitting the spectrum. Once experience is gained by applying the technique to materials where the optical processes are well understood, it may be used with considerable benefit in new materials to help identify the optical processes.

CONCLUSIONS

Presented here are the results of a comprehensive comparison of the applied electric-field dependence of pulsed dc and microwave modulated PL. It is most likely that the direct effect of MMPL is to raise the temperature of the free-carrier gas (electron and hole). This can occur both as a result of accelerating carriers and inhibiting photocarrier thermalization to the band edge. The precise mechanism whereby this new, more energetic collection of carriers impact ionizes neutral donors and excitons and is itself distributed among various recombination processes is still not thoroughly understood. Numerical modeling shows that impact ionization and the carrier energy dependence of the capture cross sections of shallow donors and excitons play significant roles in changing the relative intensities of competing luminescence processes in the presence of applied electric fields, specifically the electric fields in a microwave cavity.

ACKNOWLEDGMENTS

We wish to thank W. M. Duncan and Q. Montague of Texas Instruments for providing high-purity GaAs samples and for assisting with very low microwave power MMPL measurements. This work was supported by the Office of Naval Research under Contract No. N0001491C0104 and National Renewable Energy Laboratory under Contract No. XR-2-12121-1.

---

[1]M. C. DeLong, I. Viohl, W. D. Ohlsen, P. C. Taylor, and J. M. Olson, Phys. Rev. B **43**, 1510 (1991).

[2]M. Godlewski, H. Weman, F. P. Wang, B. Monemar, W. M. Chen, and Q. X. Zhao, in *Spectroscopy of Impurities and Complex Defects in Silicon in Electric and Microwave Fields,* edited by M. Stavola, S. J. Pearton, and G. Davies, MRS Symposia Proceedings No. 104 (Materials Research Society, Pittsburgh, 1988), p. 117.

[3]H. Weman, M. Godlewski, and B. Monemar, Phys. Rev. B **38**, 12 525 (1988).

[4]F. P. Wang, B. Monemar, and M. Ahlström, Phys. Rev. B **39**, 11 195 (1989).

[5]F. P. Wang and B. Monemar, Phys. Rev. B **41**, 10 780 (1990).

[6]P. Omling, Appl. Phys. Lett. **59**, 2022 (1991).

[7]M. Godlewski, K. Fronc, M. Gajewska, W. M. Chen, and B. Monemar, Phys. Rev. B **44**, 8357 (1991).

[8]A. Moll, C. Wetzel, B. K. Meyer, P. Omling, and F. Scholz, Phys. Rev. B **45**, 1504 (1992).

[9]I. J. Booth and C. F. Schwerdtfeger, Solid State Commun. **55**, 817 (1985).

[10]I. J. Booth and C. F. Schwerdtfeger, Phys. Status Solidi B **130**, 749 (1985).

[11]R. A. Smith, *Semiconductors,* 2nd ed. (Cambridge University Press, Cambridge, England, 1978), p. 384.

[12]W. Schairer and N. Stath, J. Appl. Phys. **43**, 447 (1972).

[13]W. Bludau and E. Wagner, Phys. Rev. B **13**, 5410 (1976).

[14]B. J. Skromme and G. E. Stillman, Phys. Rev. B **28**, 4602 (1983).

[15]H. Weman, Q. X. Zhao, and B. Monemar, Phys. Rev. B **36**, 5054 (1987).

[16]H. Weman, Q. X. Zhao, and B. Monemar, Solid State Electron. **31**, 791 (1988).

[17]H. Weman, Q. X. Zhao, and B. Monemar, Phys. Rev. B **38**, 6185 (1988).

[18]D. L. Smith, D. S. Pan, and T. C. McGill, Phys. Rev. B **12**, 4360 (1975).

[19]S. Geschwind, R. J. Collins, and A. L. Schlawlow, Phys. Rev. Lett. **3**, 545 (1959).

[20]R. Romestain and C. Weisbuch, Phys. Rev. Lett. **45**, 2067 (1980).

[21]Z. H. Lin, T. Y. Wang, G. B. Stringfellow, and P. C. Taylor, Appl. Phys. Lett. **52**, 1590 (1988).

[22]M. C. DeLong, I. Viohl, W. D. Ohlsen, P. C. Taylor, F. P. Dabkowski, K. Meehan, J. E. Williams, and M. Hopkinson, Spectroscopic Characterization Techniques for Semiconductor Technology IV, edited by Orest J. Glembocki [Proc. SPIE **1678**, 221 (1992)].

[23]It is conventional to use the symbol I for both current and intensity. To avoid confusion we use only the compound symbols I-V for current-voltage and $\Delta I/I$ for relative intensity change.

[24]M. C. DeLong, W. M. Duncan, and Q. Montague (unpublished).

[25]I. Viohl, Ph.D. thesis, University of Utah, 1991.

[26]C. Jacoboni and L. Reggiani, Rev. Mod. Phys. **55**, 645 (1983).

[27]V. N. Abakumov, V. I. Perel, and I. N. Yassievich, Zh. Eksp. Teor. Fiz. **72**, 674 (1977) [Sov. Phys.—JETP **45**, 354 (1977)].

[28]C. Erginsoy, Phys. Rev. **79**, 1013 (1950).

[29]A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).

[30]H. S. W. Massey, E. H. S. Burhop, and H. B. Gilbody, *Electronic and Ionic Impact Phenomena,* 2nd ed. (Clarendon, Oxford, 1969), Vol. 1.

[31]R. K. Nesbet, *Variational Methods in Electron-Atom Scattering Theory* (Plenum, New York, 1980).

[32]T. C. McGill and R. Baron, Phys. Rev. B **11**, 5208 (1975).

[33]M. Lax, Phys. Rev. **119**, 1502 (1960).

[34]L. Reggiani and V. Mitin, Nuovo Cimento **12**, 1 (1989).

[35]V. N. Abakumov and I. N. Yassievich, Zh. Eksp. Teor. Fiz. **71**, 657 (1976) [Sov. Phys.—JETP **44**, 345 (1976)].