Microwave thermal modulation of photoluminescence in III-V semiconductors

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The effects of an applied microwave field on low-temperature photoluminescence (PL) have been investigated in epitaxial $Ga_{0.52}In_{0.48}P$ and GaAs. The modulation-frequency dependence of the microwave-modulated PL was compared with the frequency response in nominally identical samples directly heated by an alternating current passing through the sample substrate. We give strong evidence that (1) the mechanism, whereby the microwaves interact with the PL in $Ga_{0.48}In_{0.52}P$, is via simple heating of the lattice and (2) in superfluid helium the time constant for thermal equilibration of the epilayer to its environment is less than 2 μsec, in agreement with theoretical estimates. This thermal-coupling mechanism has been observed in $Ga_{0.52}In_{0.48}P$, $GaAs_xP_{1-x}$, and $GaAs_{1-x}Sb_x$, all of which exhibit a propensity to form ordered structures. The coupling in GaAs, InP, CdS, InP/$Ga_{0.47}In_{0.53}As$/InP, and GaAs/$Al_xGa_{1-x}As$/GaAs is not thermal but may involve impact ionization.

INTRODUCTION

Although the effect of microwave electromagnetic fields on radiative recombination processes in semiconductors has been widely reported, there is considerable disagreement on the nature of the interaction. Monemar and co-workers[1,2] attribute decreases in photoluminescence (PL) intensities in the presence of microwaves to impact ionization of excitons and shallow donors by free photocarriers accelerated in the microwave electric field. In contrast to this view, Lin and co-workers[3–5] have interpreted the coupling between applied microwave fields and PL to be thermal, based on good agreement between the resulting modulated spectra and similar spectra achieved with externally applied temperature variations.

Others have investigated the effects on PL of pulsed electric fields applied parallel to the sample surface and through the region where PL was monitored. Skromme and Stillman[6] observed a sharp increase in the free-to-acceptor transition in InP at the expense of the donor-acceptor intensity as the electric-field strength was increased. The field strength at which this change in the PL took place coincided with the field at which the current-voltage curve increased precipitously. The correspondence of the change in optical properties to the field at which the current avalanches strongly suggests impact ionization as the mechanism affecting the PL. Similar effects were observed in high-mobility GaAs by Bludau and Wagner.[7] In both cases the authors worked at 1.8 K and argued that thermal effects could be neglected because they used a short duty cycle. In the following we shall demonstrate that thermal processes can influence PL on time scales at least as short as 10 μsec at 1.8 K and that at least in some cases a thermal mechanism can explain the changes observed in PL caused by applied microwave electric fields.

THEORETICAL MODEL

The temperature distribution in a one-dimensional isotropic solid with conduction as the dominant heat-transfer mechanism is governed by the heat-conduction equation[8–10]

$$\frac{\partial T(x,t)}{\partial t}=\alpha\frac{\partial^2 T(x,t)}{\partial x^2}+\frac{\alpha}{k}\frac{\partial k}{\partial x}\frac{\partial T(x,t)}{\partial x}+\frac{\alpha}{k}Q(x,t) \quad \text{for } 0\le x\le L \qquad (1)$$

where T is the temperature, k is the thermal conductivity, ρ is the mass density, c is the specific heat, $\alpha=k/(\rho c)$ is the thermal diffusivity, and L is the sample thickness. The source term $Q(x,t)$ indicates the energy generated per unit time and unit volume by some internal or external mechanism. For temperature-independent thermal properties Eq. (1) simplifies to

$$\frac{\partial T(x,t)}{\partial t}=\alpha\frac{\partial^2 T(x,t)}{\partial x^2}+\frac{\alpha}{k}Q(x,t)\ . \qquad (2)$$

In order to study the amplitude of the temperature modulation as a function of the modulation frequency, heat-transfer coefficients, and other parameters, the source term in Eqs. (1) and (2) was assumed to be of the form

$$Q(x,t)=q_0[1+\sin(\omega t)]H(x-\xi)\ , \qquad (3)$$

where $H(x-\xi)$ is the Heaviside unit-step function and $0<\xi\le L$. This implies uniform heating of the sample for $\xi=0$.

If one assumes Newton's law of cooling,[8–10] the following boundary conditions are obtained:

$$-k\frac{\partial T}{\partial x}=h_0(T_A-T) \quad \text{at } x=0, \quad t>0 ;$$
$$-k\frac{\partial T}{\partial x}=h_L(T-T_A) \quad \text{at } x=L, \quad t>0 ; \tag{4}$$

where h_0 and h_L are the heat transfer coefficients at the respective boundaries and T_A is the ambient bath temperature (either helium gas or superfluid). With these assumptions an infinite series solution can be found using an eigenfunction expansion technique[9–12] and the temperature distribution is given by

$$[T(x,t)]_{t\to\infty}=T_{\text{mean}}+A(\lambda,\xi,\omega,x)\sin(\omega t+\phi) , \tag{5}$$

where

$$T_{\text{mean}}=T_A+q_0\frac{\alpha}{k}\sum_{\lambda_1\le\lambda\le\lambda_\infty}\frac{F(\lambda,\xi)\Psi(\lambda,x)}{\tau}, \quad \tau=\alpha\lambda^2$$

$$A(\lambda,\xi,\omega,x)=q_0\frac{\alpha}{k}\left[\left[\sum_\lambda\frac{\tau F(\lambda,\xi)\Psi(\lambda,x)}{\tau^2+\omega^2}\right]^2+\left[\sum_\lambda\frac{\omega F(\lambda,\xi)\Psi(\lambda,x)}{\tau^2+\omega^2}\right]^2\right]^{1/2},$$

$$\tan\phi=-\frac{\sum_\lambda\left[\frac{\omega F(\lambda,\xi)\Psi(\lambda,x)}{\tau^2+\omega^2}\right]}{\sum_\lambda\left[\frac{\tau F(\lambda,\xi)\Psi(\lambda,x)}{\tau^2+\omega^2}\right]},$$

$$F(\lambda,\xi)=\frac{2h_0\{h_0[\cos(\lambda\xi)-\cos(\lambda L)]+\lambda k[\sin(\lambda L)-\sin(\lambda\xi)]\}}{[\lambda^3k^2L+(\lambda^2k^2-h_0^2)\cos(\lambda L)\sin(\lambda L)+2\lambda kh_0\sin^2(\lambda L)+\lambda Lh_0^2]},$$

$$\Psi(\lambda,x)=\sin(\lambda x)+\frac{k\lambda}{h_0}\cos(\lambda x) ,$$

and λ satisfies the equation

$$(h_0h_L-k^2\lambda^2)\sin(\lambda L)+k\lambda(h_0+h_L)\cos(\lambda L)=0 . \tag{6}$$

The thermal properties, i.e., the specific heat and thermal conductivity, needed in the above equations were calculated from the following empirical-phenomenological equations[13–21] for molar heat capacity and thermal conductivity

$$C_v=\sum_n a_nT^n, \quad n=1,3,5,\ldots \tag{7}$$

and

$$k=\frac{k_B}{2\pi^2v_s}\left[\frac{k_BT}{\hbar}\right]^3\int_0^{\Theta/T}\frac{x^4e^x}{\tau_c^{-1}(e^x-1)^2}dx+k_2 , \tag{8}$$

where k_B is the Boltzmann constant, Θ the Debye temperature, and v_s the average phonon velocity. The overall relaxation time τ_c in Eq. (8) is defined as

$$\tau_c^{-1}=A\left[\frac{k_BT}{\hbar}\right]^4x^4+(B_1+B_2)\left[\frac{k_BT}{\hbar}\right]^2T^3x^2+\frac{v_s}{L_s} , \tag{9}$$

where A represents impurity and isotope scattering, B_1 includes umklapp processes, B_2 involves normal processes (N processes), and v_s/L_s represents the boundary scattering involving some characteristic length L_s. The additional term k_2 is considered to be a small correction and is usually neglected.[15] Since no thermal conductivity data were available for the specific samples studied, a set of parameters within the range published for n-type GaAs was used. These parameters are listed together with others in Table I.

The heat transfer coefficients h_0 and h_L in Eq. (4) determine the heat flux from the solid sample into the surrounding helium bath and play an essential role in the thermal modeling. Even though some efforts have been made to calculate heat-transfer coefficients in superfluid helium (Kapitza resistance) from classical phonon scattering (elastic) theory,[22,23] no satisfactory theory exists. Hence in these calculations the heat-transfer coefficients between semiconductor and superfluid were considered to be adjustable parameters having values within the range published by Van Sciver (4–9 kW/m^2 K).[22] However, no such data could be found for heat transfer into gaseous helium. In addition, several of the other parameters, including the boundary scattering length L_s and microwave power actually absorbed into the sample, are not explicitly known. These parameters, including the heat-transfer coefficients into the helium gas, were chosen according to the following criteria.

(a) In order to match the experimental data to be discussed below, the rolloff frequency (e^{-1} point) at 5 K was assumed to be less than or equal to 150 Hz. This assumption yielded heat-transfer coefficients which are both reasonable for heat transfer between semiconductor and gaseous helium at 5 K and considerably smaller than those published for transfer between semiconductor and superfluid, as expected. In contrast to this case, it was not possible to obtain the very large rolloff frequencies (>100 kHz) and simultaneous large changes in PL intensity observed in some samples with microwave modula-

TABLE I. Parameters used for the thermal calculations.

Temperature T_A	5 K	2 K
Sample length L	300×10^{-4} cm	
Characteristic scattering length L_s	6×10^{-4} cm	
Average phonon velocity v_s	3.3×10^{5} cm/sec	
Debye temperature Θ	345 K	
Impurity scattering A	1×10^{-42} sec^3	
U and N processes (B_1+B_2)	1×10^{-21} sec/K^3	
Molar heat capacity parameters a_1,a_3,a_5	2.48, 46.73, 0.143 [μJ/(g-atom K^{n+1})]	
Fraction of the sample heated ξ	uniform heating $\xi=0$	
Power input	0.25 W/cm^3	
Heat transfer coefficients $h_0=h_L$	0.025 kW/m^{2}K	5 kW/m^{2}K

tion at 5 K using reasonable values for the heat-transfer coefficient.

(b) The temperature modulation amplitude was assumed to be less than or equal to 1.5 K at 5 K. This assumption was also motivated by experimentally determined values to be discussed below.

(c) The thermal conductivity (and hence the characteristic scattering length) was assumed to be such that the temperature gradient within the sample is less than 0.05 K over 150 μm. This is necessary to assure the validity of the infinite series solution, which neglects any thermal gradients and has no critical bearing on the results. When finite difference calculations, which are not limited to small temperature gradients, were performed the results were close to those calculated using the series solution when similar parameters were used. Therefore, because of the calculational convenience of the series technique, small gradients were assumed.

Criteria (a) and (b) set an upper limit on the power delivered to the sample (0.25 W/cm^3 $\Longrightarrow$ 1.1 mW) and an upper limit to the heat-transfer coefficients ($h_0,h_L<2.5\times10^{-2}$ kW/m^{2}K). These parameters cannot be chosen independently since, at least over some range, the temperature modulation amplitude is directly proportional to the power input q_0 and inversely proportional to the heat-transfer coefficients.

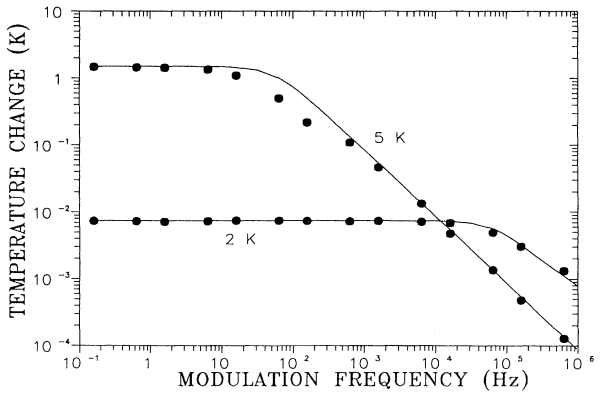

FIG. 1. Calculated temperature modulation amplitude as a function of frequency of applied heating for n-type GaAs under conditions typical of those used in this work. Solid circles refer to the finite-difference calculation, solid curves to the infinite-series calculation.

If the thermal conductivity is chosen according to criterion (c), the minimum allowed boundary scattering length is $L_s=6$ μm. In this case the rolloff frequency at 5 K is solely determined by the heat-transfer coefficients, i.e., increasing the thermal conductivity will not change the rolloff frequency. Based on this set of parameters the temperature modulation amplitude was calculated as a function of the applied-power modulation frequency using the infinite series solution given in Eq. (5). The results for 5 and 2 K ambient bath temperatures are shown in Fig. 1 as the upper and lower solid curves, respectively. In addition, the solutions obtained from a finite-difference technique[12,24] are shown as solid circles. As one would expect, the two calculations yield essentially the same results since the temperature gradients within the sample are small. The parameter sets for the 2 and 5 K calculations were identical except for the heat-transfer coefficients[22] (see Table I). The results of these calculations, as shown in Fig. 1, allow drawing two conclusions. Even though thermal processes are slow in helium gas ($\tau=1.1$ msec), fast nonballistic[25,26] processes ($\tau=0.8$ μsec) are possible in superfluid liquid helium. Also the temperature modulation amplitude, monotonically related to the intensity of the temperature-modulated photoluminescence signal, should show a significant decrease accompanying the change from helium gas to superfluid helium.

EXPERIMENTAL DETAILS

Samples of $Ga_{0.52}In_{0.48}P$ and GaAs were grown using organometallic vapor phase epitaxy at a total pressure of 1 atm. In both cases lightly zinc-doped epitaxial layers approximately 1 μm thick were grown lattice matched to heavily n-type silicon-doped GaAs substrates. Both were grown at 700 °C on substrates misoriented 2° toward (110) from (100). The $Ga_{0.52}In_{0.48}P$ epilayer was actually a het-

erostructure with selenium-doped $Al_{0.50}In_{0.50}P$ barriers. Both structures were designed such that the passage of current through the substrate could affect the PL in the epilayer only via the joule heating of the substrate and subsequent conduction of heat to the epilayer. No electroluminescence was detected from either sample. Electrical contacts were applied to the substrates by first electro-depositing gold films, then attaching small indium dots which were subsequently annealed in hydrogen at approximately 250 °C for 15 min. Copper wires 0.125 mm in diameter were attached with indium. The Ohmic nature of the contacts was verified with a standard curve tracer. Sample dimensions were approximately 0.3 mm × 1.5 mm × 6 mm (GaAs) or 10 mm ($Ga_{0.52}In_{0.48}P$). Total resistances between contacts were approximately 1 Ω at both room temperature and 2 K.

Conventional luminescence was excited with the unfocused 514-nm line of an Ar^+-ion laser, dispersed with a SPEX Industries 0.75-m-focal-length spectrometer and detected with an *S*-20 photomultiplier using standard lock-in techniques. In the PL and Joule-heated, thermally modulated photoluminescence (JTMPL) experiments the temperature in the Janis Vari-temp cryostat was measured and controlled with a Lake Shore Cryotronics controller using a GaAs diode and the epitaxial faces of the samples were attached with rubber cement to a copper block. Optical access to the samples was via a hole in the block. Hence at modest laser power (typically 1 mW) and substrate heating power, the measured temperature is a reasonable indicator of the actual temperature of the epilayer, especially at 1.8 K. In the microwave-modulated PL (MMPL) experiments, however, the substrate side of the sample was attached with rubber cement to a Teflon holder in the microwave cavity. In superfluid helium the sample temperature is expected to be very nearly 2 K. Experiments in He gas, however, were performed with the sample approximately 1 cm above the surface of the liquid helium (LHe). Although the LHe level was kept constant to within approximately 2 mm throughout the experiments, it must be understood that the sample temperature designation of "5 K," used in analogy with the substrate-heated case, is neither accurate nor constant throughout the experiments. The 5-K MMPL spectrum of the $Ga_{0.52}In_{0.48}P$ sample has a shape more similar to the JTMPL spectrum with the sample holder at 8 K than to spectra taken at 10 or 5 K. Hence it is reasonable to estimate that the application of 50 mW of microwave power with a 50% duty cycle to a sample with dimensions and a thermal environment similar to ours leads to a sample temperature of approximately 8 K.

JTMPL was accomplished by applying a square pulsed voltage. Care was taken to assure that no voltage was applied during one half cycle, i.e., that the power applied to the sample was in the form of square pulses at the voltage modulation frequency. (Note that a symmetric square wave will deliver no time-dependent power to the sample; a symmetric sine wave delivers power at twice the voltage modulation frequency.) The applied voltage was also used as the reference signal for a lock-in amplifier and the laser excitation was unchopped. The important innovation of this work is that heat pulses are applied directly to the sample rather than via an external heater with significant impedance mismatch between itself and the sample.[27,28] Conversely, the conventional impact ionization geometry[6,7] is also avoided. In that configuration, where current is passed through the epilayer, it is virtually impossible to separate the electrodynamic effects of the applied field from the joule heating which results from the induced current.

For MMPL the sample was located in the electric-field maximum of a rectangular TE_{011}-mode, 16-GHz microwave cavity. Photoluminescence was excited and collected 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 chopped with a solid-state switch driven by a function generator, which was also used for the lock-in reference signal. Microwave powers of 5–50 mW were typically used.

RESULTS AND DISCUSSION

Typical PL, substrate-heated, temperature-modulated PL (JTMPL) and MMPL spectra from the $Ga_{0.52}In_{0.48}P$ sample are shown in Figs. 2(a), 2(b), and 2(c), respectively. All were taken in superfluid helium at 1.8 K. Spectra 2(a) and 2(b) were taken contemporaneously on the same sample. It will be noted that the peaks in spectrum 2(c) occur about 10 meV higher in energy than the corresponding ones in 2(b). This shift was also seen in the associated PL spectrum. Part of this shift in the PL is known to be caused by an astigmatism in the collection optics. Other sources may be compositional inhomogeneity in the sample and/or calibration errors in the spectrometer. In any case, this small shift is not relevant to the effects being studied here. (A smaller shift in the opposite direction was observed for the GaAs sample.) These spectra are similar to the analogous set taken at 5 K, although, as mentioned above, the 5-K MMPL spectrum bears the strongest resemblance to a JTMPL spectrum taken at a base temperature of 8 K. To the best of our knowledge none of the features seen in the PL spectra of $Ga_{0.52}In_{0.48}P$ grown under various conditions has yet been unambiguously identified.

The dominant feature in the PL spectrum, which shifts to lower energy at a rate as large as 3.5 meV/decade with decreasing excitation intensity, actually consists of several peaks. Under some conditions of temperature, excitation intensity, modulation power, and modulation frequency, the negative higher-energy peak in the modulation spectra, Figs. 2(b) and 2(c), can also be resolved into two peaks. This additional structure is indicative of the utility of applying modulation spectroscopy to complex materials such as $Ga_{0.52}In_{0.48}P$. Also in ideal cases, such as very pure or intentionally doped semiconductors where the recombination paths are known unambiguously, one can quantify small energy differences from the positions and line shapes of the positive and negative peaks of the modulated PL spectrum. This allows the determination of quantities such as exciton or impurity binding energies, which are ordinarily not resolvable using conventional PL.

In the case of $Ga_{0.52}In_{0.48}P$ the situation is much more complicated, but speculation concerning a plausible interpretation of the modulated PL spectra will serve to illustrate the potential power of this technique. For example, it is well known that an excitation intensity-dependent emission energy can be associated with donor-acceptor pair recombination.[29] That explanation can probably be eliminated here because of the signs of the correlated parts of the modulated PL spectrum. The negative and positive peaks shift together with excitation intensity and hence are coupled. However, if they were associated with free-to-bound (high-energy) and donor-acceptor pair (low-energy) recombination, increasing the sample temperature would lead to an increase in the number of free carriers at the expense of those bound to impurities. Hence the JTMPL spectrum should contain a positive peak at higher energy and a negative peak at lower energy. Precisely the opposite is seen here. This explanation assumes, of course, that competing recombination processes have no influence, an assumption which is probably unjustified in a material as complex as $Ga_{0.52}In_{0.48}P$. If the moving emission in $Ga_{0.52}In_{0.48}P$ cannot be explained in terms of donor-acceptor pair recombination, one must search for an alternative explanation. We shall show elsewhere[30] that the spectra are consistent with the band-edge fluctuations and spatially separated recombination centers that can occur in partially ordered materials like $Ga_{0.52}In_{0.48}P$. It should also be noted that derivativelike spectra, such as those reported here, can result from rigid translations of the unmodulated spectra as a function of the modulation parameter. Although we have no evidence that such an interpretation is consistent with our results, one should bear in mind that a combination of spectral translation and broadening as a function of the modulation parameter may explain results obtained under other circumstances.

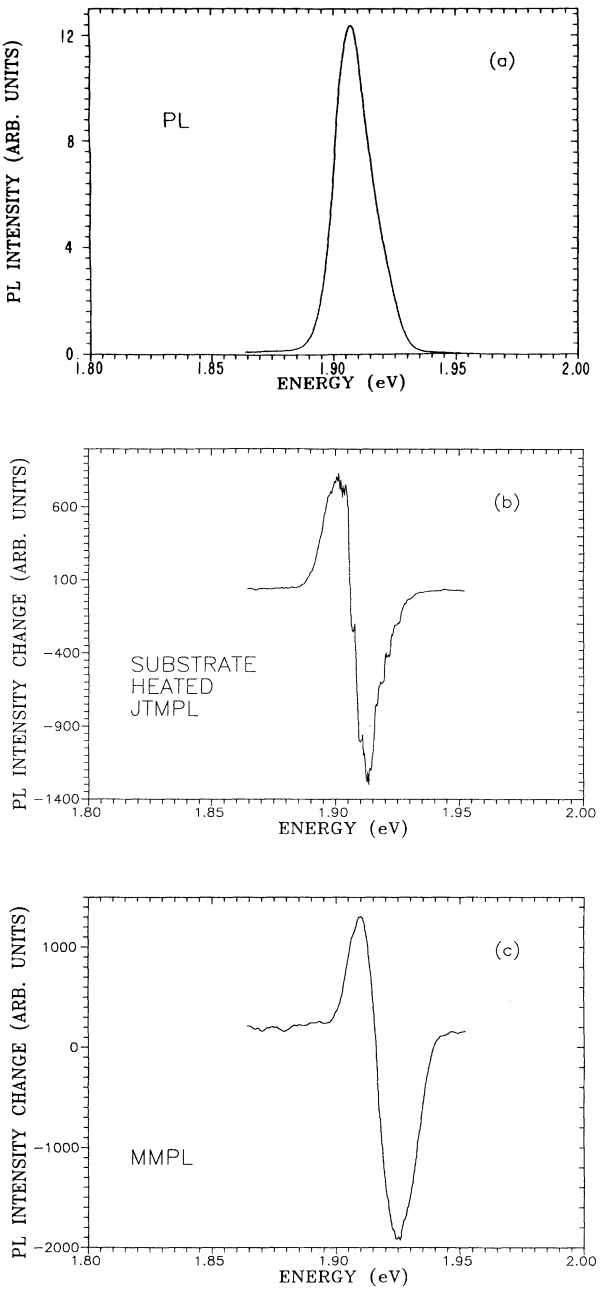

FIG. 2. 1.8-K (a) photoluminescence (PL), (b) substrate-heated thermally modulated PL (JTMPL) with 47-mW heater power, and (c) microwave-modulated PL (MMPL) with 50-mW microwave power, all from a $Ga_{0.52}In_{0.48}P$ double heterostructure grown at 675 °C excited with 1-mW unfocused excitation intensity.

The strongest evidence for the thermal nature of the interaction between microwaves and the PL process comes from Fig. 3. This figure shows the dependence of the amplitude of the JTMPL signal on modulation frequency over the range 2 Hz to 100 kHz. It is important to remember that in the experimental configuration used here heat pulses are delivered directly to the substrate. It will also be argued below that the thermal impedance mismatch between a substrate and lattice matched epilayer is negligible. Data were taken for both the positive (low-energy) and negative (high-energy) peaks in superfluid and in helium gas at approximately 5 K. Data were not taken in superfluid at frequencies below 100 Hz because the combination of small signal and large noise made impossible the detection of changes in the nearly frequency-independent response. Figure 3(b) shows data taken under similar conditions except that a different piece of the sample is subjected to chopped microwaves rather than heat pulses applied to the substrate. In both cases the maximum available power, 20–50 mW, was used in order that the modulation process could be followed to the highest possible frequency. Dashed lines having unit slope have been drawn on both figures and indicate that the rolloff has essentially a single time constant. The characteristic times (rolloff frequencies) for the thermal processes at 5 K are 1.6 msec (100 Hz) for substrate heating and 5 msec (31 Hz) for microwave modulation. Additional evidence for the thermal nature of the microwave-modulation process comes from the decrease in relative PL intensity change of 1–2 orders of magnitude on going from a helium-gas ambient to

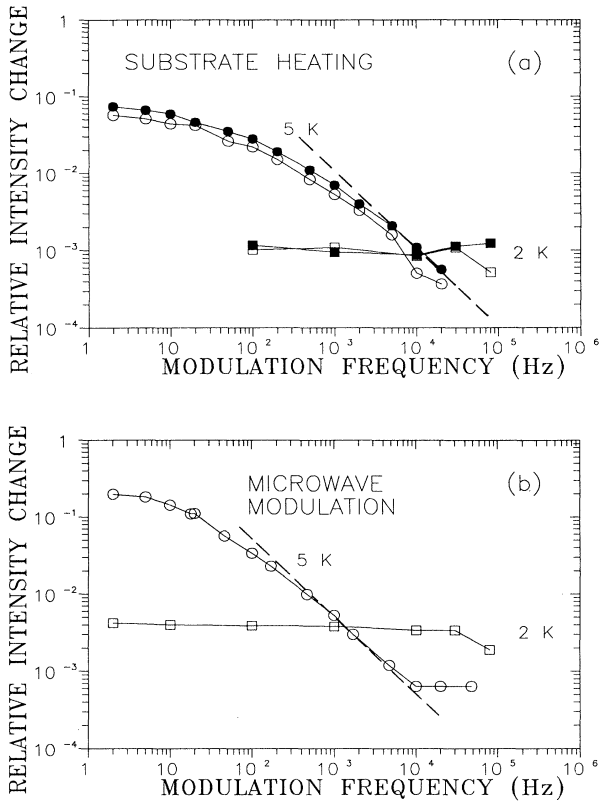

FIG. 3. Relative change in luminescence intensity ($\Delta I/I_{PL}$) as a function of (a) substrate heating and (b) microwave-modulation frequency for a $Ga_{0.52}In_{0.48}P$ double heterostructure grown at 675 °C. Open symbols refer to high-energy (negative) peak, solid symbols to low-energy (positive) peak.

superfluid. Such a decrease is seen in Figs. 3(a), 3(b), and 5(a) and is consistent with the calculated results shown in Fig. 1. By linear interpolation of the difference between PL spectra taken at 1.8 and 4 K as well as among 4, 5, and 6 K, we estimate the temperature rises associated with the changes in PL intensity reported here to be approximately 20 mK at 1.8 K and 1.5 K at 4 K. The 1.8-K value is in good agreement with the calculated value shown in Fig. 1. The 4-K amplitude was used to estimate the heat-transfer coefficient into helium gas. The result is consistent with expectations.

The frequency response of the modulated PL of a sample of GaAs was also investigated under both substrate heating and microwave modulation. By growing a lightly zinc-doped *p*-type epilayer onto a heavily *n*-type substrate, we were able to ensure that the electrons injected into the substrate to effect thermal modulation did not directly affect the PL process. The epilayer doping level was low enough that excitonic recombination is clearly visible in the spectrum, having an amplitude of 26% of that of the impurity peak at 1.8 K. As shown in Fig. 4(a), the near-gap PL spectrum of this sample consists of two peaks. The high-energy peak occurs at approximately 1.509 eV, the low-energy one at 1.488 eV. Ashen *et al.*[31] report emission from excitons bound to zinc acceptors at 1.5122 eV and a band-to-zinc-acceptor emission at 1.4888 eV. From the substrate-heated JTMPL spectrum, Fig. 4(b), one sees that the low-energy peak is actually a doublet. If one assumes that the high-energy component of the doublet is associated with the band-to-zinc-acceptor component, it occurs at an energy of 1.491 eV. Hence it is reasonable to ascribe the high-energy peak in the PL to

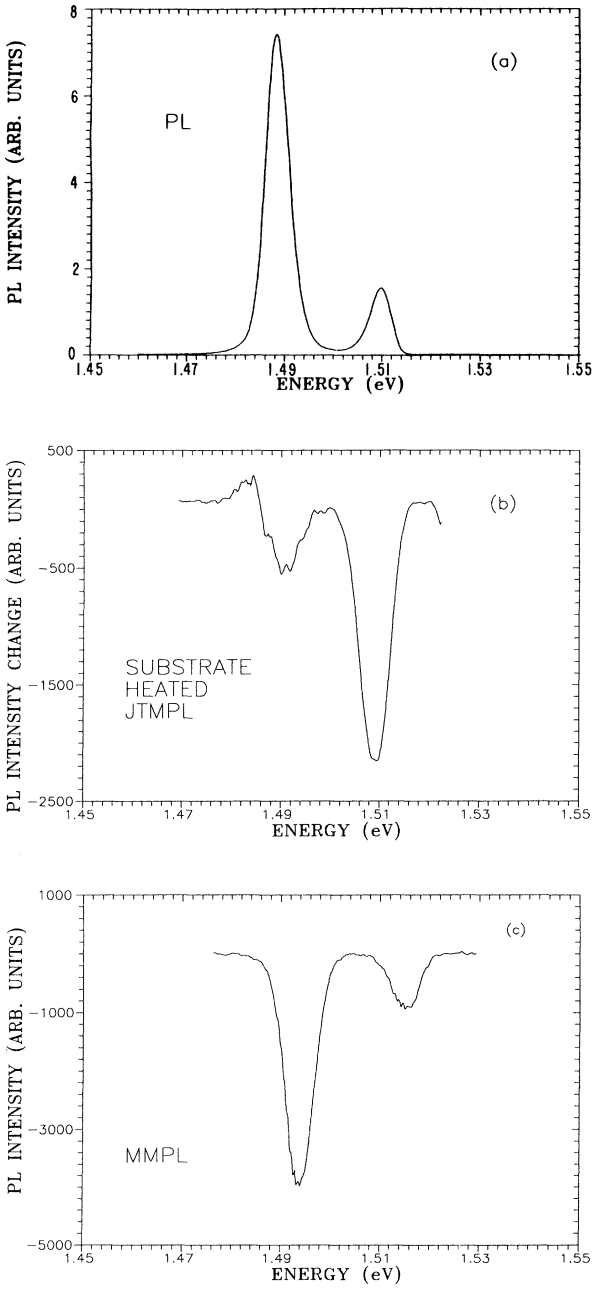

FIG. 4. 1.8-K (a) PL, (b) substrate-heated JTMPL with 17-mW heater power, and (c) MMPL with 50-mW microwave power, all from zinc-doped GaAs epilayer excited with 1-mW unfocused excitation.

the recombination of an exciton bound to a zinc acceptor. The low-energy peak is most likely related to the zinc impurity, but, as in the case of the $Ga_{0.52}In_{0.48}P$, the signs of the JTMPL peaks appear to be inconsistent with assigning them to only a band-acceptor and the associated donor-acceptor pair transitions. The associated MMPL spectrum is shown in Fig. 4(c). In this case there is no strong resemblance between the MMPL and JTMPL spectra.

The most striking difference between the JTMPL and MMPL effects in GaAs is seen by comparing Figs. 5(a) and 5(b). Figure 5(a) is qualitatively similar to Fig. 3(a) where JTMPL of $Ga_{0.52}In_{0.48}P$ was depicted. In both cases the frequency response is essentially flat to 100 kHz at 1.8 K, but rolls off at very low frequency in helium gas at approximately 5 K. For the substrate-heated GaAs the characteristic time for equilibration is 5 msec (33 Hz). In strong contrast to the 5-K frequency dependences listed above is that of the GaAs sample with microwave modulation, as depicted in Fig. 5(b). One immediately sees that the frequency response is essentially flat to 100 kHz, except for a small component which is seen at frequencies below 100 Hz and which may have a thermal origin. In strong contrast to the 1–2 order of magnitude decrease in signal amplitude predicted in Fig. 1 and seen in Fig. 3 for $Ga_{0.52}In_{0.48}P$ when the operating ambient is changed from helium gas to superfluid, here one sees a negligible change in signal amplitude when the thermal environment (mainly heat-transfer coefficient) is changed. In fact, in some of the samples discussed below the signal amplitude increases to very large values in superfluid. Hence it appears that one hallmark of a thermal process in III-V semiconductors at low temperatures, at least for geometries and sample sizes comparable to the ones we used here, is a time constant for equilibration with a gaseous-helium ambient in the neighborhood of 1–10 μsec or longer, but limited to approximately 1 μsec in superfluid. A second characteristic feature is the magnitude of the low-frequency modulated response, which may be tens of percent of the luminescence signal itself in a gaseous-helium environment, but is at least an order of magnitude smaller in superfluid.

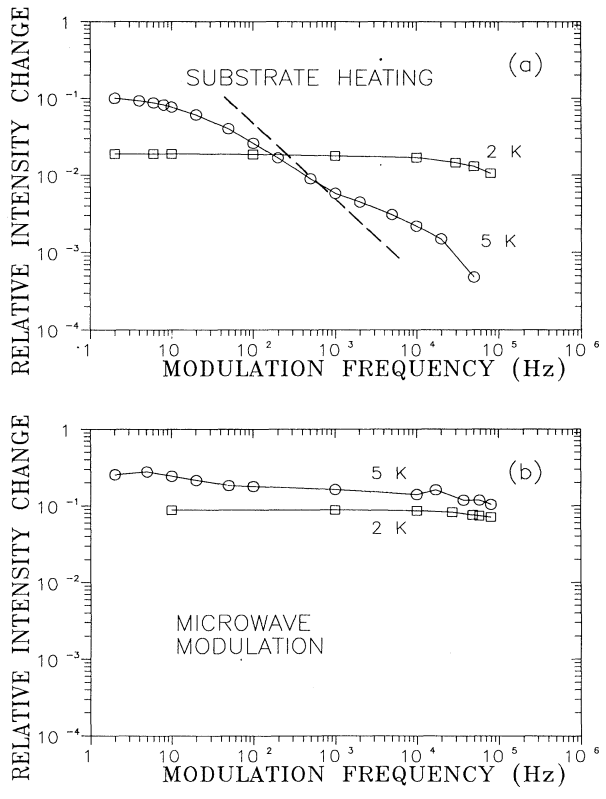

FIG. 5. Relative change in luminescence intensity ($\Delta I/I_{PL}$) as a function of (a) substrate heating and (b) microwave-modulation frequency for zinc-doped GaAs epilayer.

The time constant for response to an applied microwave field at 5 K has been measured for a diverse collection of samples and is tabulated in Table II. In all cases the quantity measured is the frequency at which the microwave modulated PL signal, always detected at the microwave chopping frequency, has decreased by a factor of e^{-1} from its low-frequency value. The samples investigated fall naturally into two groups, having response times separated by more than four orders of magnitude. The first group includes a number of $Ga_{0.52}In_{0.48}P$ samples grown under a wide variety of conditions. Five of those samples were grown simultaneously on different substrates under conditions chosen to give a small band gap and excitation intensity-dependent low-energy emission.[32] The degree of coupling of these samples to the microwaves, as evidenced by the cavity Q, varied markedly among them. The frequency responses of these samples were quite similar to each other. One of the five merits specific attention. The substrate is relatively high-purity undoped GaAs, having a room-temperature carrier concentration of approximately 10^{15} cm^{-3}. On one side was grown a molecular-beam-epitaxy (MBE) epilayer of high-purity GaAs, with a room-temperature carrier concentration of approximately 10^{14} cm^{-3}. Nominally undoped $Ga_{0.52}In_{0.48}P$ was grown onto the other side simultaneously with the other four substrates. The time constant of the MMPL for the $Ga_{0.52}In_{0.48}P$ side is greater than 16 msec; on the GaAs side it is 0.8 μsec. Hence the microwaves interact predominantly thermally with the $Ga_{0.52}In_{0.48}P$ epilayer but not with the GaAs.

Other $Ga_{0.52}In_{0.48}P$ samples were specifically chosen to have large band gaps and not evidence a strong dependence of emission energy on excitation intensity. It is expected that the degree of ordering will vary considerably among these samples because of differences in the growth conditions.[33,34] Despite the variation in degree of ordering, no significant difference in response time is seen. Ordering has also been reported in materials chosen for two other samples which have long characteristic MMPL response times: $GaAs_xP_{1-x}$ (Ref. 35) and $GaAs_{1-x}Sb_x$,[36] although the specific composition of $GaAs_{1-x}Sb_x$ investigated here, with $x_{Sb}=0.6$, is not expected to order extensively.[37] Hence it appears that the thermal nature of the effect of microwaves on PL is unique to materials which show a propensity to order, but is not directly related to the extent of ordering within

TABLE II. Characteristic times for rolloff of MMPL spectra at "5 K." A variety of excitation intensities (typically 10 mW unfocused) and microwave power levels (typically 5–50 mW) were used. Materials listed in group I all show significant rolloff in the range 2 Hz $\leq f \leq$ 5 Hz. Those in group II designated as having $\tau \ll 0.8$ μsec show negligible attenuation at 200 kHz.

Sample	Characteristics	τ
I. $Ga_{0.52}In_{0.48}P$	on GaAs:Si; $T_G=675$ °C; 2° to (110)	≈ 15 msec
	on GaAs:Cr; $T_G=675$ °C; 2° to (110)	>16 msec
	on GaAs:*EL*2; $T_G=675$ °C; 2° to (110)	>14 msec
	on $10^{15}/cm^3$ pure GaAs; $T_G=675$ °C; 2° to (110)	>16 msec
	on *p*-type GaAs; $T_G=675$ °C; 2° to (110)	>8 msec
	$T_G=750$ °C; 2° to (111)	>12 msec
	$T_G=600$ °C; 2° to $(1\bar{1}1)$	>15 msec
$GaAs_{1-x}P_x$	strained-layer superlattice	>15 msec
$GaAs_{1-x}Sb_x$	$x_{Sb}=0.6$	>20 msec
II. GaAs	high purity	0.8 μsec
Al_xGa_{1-x} As	$x_{Al}=0.27$	0.8 μsec
InP	shows deep bound excitation	$\ll 0.8$ μsec
$InP/Ga_{0.47}In_{0.53}As/InP$	13-Å quantum well	<0.8 μsec
$Ga_{0.47}In_{0.53}As$	bulk, matched to InP	<0.8 μsec
$GaP_{1-x}Sb_x$	$x_{Sb}=0.29$	<0.8 μsec
InP:Zn	bulk; $p(300\text{ K})\approx 10^{16}/cm^3$	
InP:Zn	"thermal component"	>12 msec
InP:Zn	"nonthermal component"	$\ll 0.8$ μsec
CdS	μ (12 K) = 7800 cm^2/V sec	1 μsec

those materials. In order to establish that the long-time constant of the MMPL is not inherent to the luminescence process itself, we also measured the time dependence of the decay of the PL in $Ga_{0.52}In_{0.48}P$.[38] PL decay times were typically microseconds or less, depending on the recombination process. The longest decay time measured was 35 μsec. Hence the PL lifetime itself cannot account for the slow response to imposed microwaves seen in $Ga_{0.52}In_{0.48}P$.

The second group of materials listed in Table II has characteristic time constants less than 1 μsec. It includes all binaries which have been investigated as well as quantum wells and the III-V ternaries $Al_{0.73}Ga_{0.27}As$ and $Ga_{0.47}In_{0.53}As$ lattice matched to InP. Those samples having time constants labeled "$\ll 0.8$ μsec" have frequency responses which remain flat to 200 kHz and show minimal evidence of phase shift in response at 200 kHz. Also noteworthy is the fact that in two of these samples, the high-purity GaAs and InP:Zn, although the frequency response is flat over the frequency range 100 Hz to 200 kHz, the amplitude increases with decreasing frequency below 100 Hz, suggesting the admixture of a slow (thermal) process with the rapid one seen in the other members of this set. The magnitude of the thermal contribution is equal to that from the nonthermal one for the GaAs and about four times as large in the InP:Zn case. Note also that there is no obvious difference between the heterointerfaces forming boundaries between $Al_{1-x}Ga_xAs$ and GaAs, GaP_xSb_{1-x} and GaAs, or $Ga_{1-x}In_xAs$ and InP, all of which have MMPL time constants of microseconds or less and heterointerfaces between $Ga_{1-x}In_xP$, $Al_{1-x}Ga_xAs$ or $GaAs_xSb_{1-x}$, and GaAs, all of which have MMPL time constants of tens of milliseconds. Hence we conclude that the binary-ternary interface probably does not have a significant effect on determining the influence of microwave electric fields on radiative recombination.

As mentioned above, those ternary samples which show little or no propensity to order and all binary samples investigated to date exhibit MMPL spectra at temperatures above 4 K which have high rolloff frequencies (>100 kHz) and often have large amplitudes at 1.8 K (relative intensity changes of 0.1 to essentially unity). The present model calculations clearly indicate that in these samples the mechanism is not primarily thermal. We show elsewhere[39] that this mechanism is probably impact ionization even though the mobilities, and hence the elastic scattering times, may be very small.

CONCLUSIONS

Heat transfer within a solid piece of GaAs as well as to an ambient of gaseous or superfluid helium at low temperatures has been modeled using both infinite-series and finite-difference methods. Both methods predict thermal equilibration times in superfluid He of 1–10 μsec for millimeter-size samples. For equilibration to a gaseous environment at low temperatures, knowledge of the interfacial heat-transfer coefficient is of critical importance. These coefficients are not well known. Calculations have

been performed using the heat-transfer coefficient as an adjustable parameter. The numerical values of the heat-transfer coefficient required to simulate the rolloff frequencies characteristic of the semiconductor samples investigated here are at least reasonable.

In $Ga_{0.52}In_{0.48}P$ both the spectral and frequency dependences of microwave and thermally modulated PL are very similar, strongly suggesting that the mechanism coupling the applied microwaves to the PL is thermal. Thermal equilibration of the sample to its environment takes place on a time scale of less than 2 μsec in superfluid helium and greater than 10 msec in helium gas in the neighborhood of 5 K. Similar thermal behavior is observed in GaAs, but in that case the time scale for microwave modulation is also less than 2 μsec. Hence (i) thermal equilibrium is established between these semiconductors and their superfluid environment on a microsecond time scale and (ii) there is strong evidence to suggest that the coupling mechanism between an imposed microwave field and photoluminescence in $Ga_{0.52}In_{0.48}P$, $GaAs_{1-x}P_x$, and $GaAs_{1-x}Sb_x$ is thermal. In other binary and ternary semiconductors which have been investigated the coupling mechanism between microwaves and PL is not predominantly thermal but may be related to impact ionization.[39] This analysis of thermal and nonthermal interaction between microwaves and PL applies equally well to the zero-field base line offset which has been observed in optically detected magnetic resonance.[1,12]

We have also demonstrated the importance of microwave-modulation spectroscopy, whether the mechanism is thermal or not, in giving information in addition to that obtainable from standard photoluminescence investigations. Here spectra that had single peaks in PL were resolved into multiple processes in the modulation spectra. Furthermore, in cases where the modulation mechanism was known to be thermal, conclusions could be drawn concerning the types of physical processes which could and could not be involved. As understanding of the mechanism of nonthermal microwave modulation increases, similar information, revealing structure in PL spectra without the need for the special sample configurations required for JTMPL, will be forthcoming from microwave-modulation studies.

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