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Metastable state of EL2 in the $GaAs_{1-x}P_x$ alloy system

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The photocapacitance quenching effect of EL2 previously observed in GaAs has been studied in the $GaAs_{1-x}P_x$ alloy system, and optical and thermal properties of the metastable state have been determined. It is shown that the spectral distribution of the optical transition rate for the population of the metastable state ($EL2^0 \rightarrow EL2^*$) is nearly independent of the alloy composition. A previously unknown temperature dependence of the spectral distribution of the transition $EL2^0 \rightarrow EL2^*$ in GaAs is reported and a possible explanation is discussed.

I. INTRODUCTION

Owing to its technical importance and interesting physical properties the EL2 center in GaAs has been the subject of many detailed studies during the last decade.[1] Since both the origin and properties of the center are poorly understood a new approach towards a better understanding of this center is taken in this paper by studying the properties of the EL2 level as a function of the composition in the alloy system $GaAs_{1-x}P_x$.[2,3] One of the most intriguing properties of GaAs:EL2 is the existence of a metastable state.[1,4–6] In samples with low carrier concentrations this state can be populated, at sufficiently low temperatures ($T \lesssim 140$ K), by illuminating the sample with photons in the energy range $1.0 \lesssim h\nu \lesssim 1.3$ eV. Once populated the metastable state is inaccessible to extrinsic light, and can be depopulated thermally by, for example, heating the sample to temperatures above about 110 K. Another way of depopulating the state is to let free carriers interact with the metastable state. This process is already active for temperatures below 110 K.

So far there have been no reports on metastable properties of EL2-related defects in materials other than GaAs. The purpose of this paper is therefore to present a study of the metastable state of EL2 in an alloy system, namely in $GaAs_{1-x}P_x$. Photocapacitance data are presented on the optical and thermal properties of the metastable state of EL2 for different compositions. It will also be shown that the depopulation process of the metastable state can be expressed in one formula, valid for the part of the alloy system investigated. Furthermore, data are presented which reveal for the first time an unexpected temperature dependence of the spectral distribution of the optical cross section for the population of the metastable EL2 state in GaAs.

II. EXPERIMENTAL

All measurements were performed on undoped n-type $GaAs_{1-x}P_x$ epitaxial layers grown on GaAs substrates by metal-organic vapor-phase epitaxy. Details about the epitaxial growth and the electrical and optical properties of the layers have been published previously.[2,7]

The electrical characterization of the samples includes capacitance-voltage (C^{-2}-V) measurements for the determination of carrier concentrations ($|N_d - N_a|$) and deep-level transient spectroscopy[8,9] (DLTS) measurements to evaluate deep level concentrations (N_T). Photocapacitance measurements were performed in a temperature-controlled cryostate (10–300 K) using a Boonton 72BD capacitance meter and a Zeiss MM3 prism monochromator. A Bausch and Lomb grating monochromator was employed for broadband illumination. Some important parameters of the samples investigated are collected in Table I.

III. EXPERIMENTAL RESULTS

A. Background

Even though the photocapacitance kinetics of the EL2 center have been described previously[1,5,10] it may be useful for the understanding of this paper to give a brief summary of the results found in GaAs. In an n-type Schottky diode at temperatures higher than $T \simeq 150$ K but lower than $\simeq 250$ K (in order to avoid thermal emission processes) the EL2 centers respond to optical excitation as a single deep midgap level at an energy position $E_c - E_T \simeq 0.75$ eV. Choosing the initial condition in a reverse biased diode such that the EL2 levels are occupied by electrons, and illuminating the diode with photons of energy $h\nu$ (where $E_c - E_T \leq h\nu < E_c - E_v$), the observed change in capacitance is given by[11] (notations according to Ref. 11)

$$\Delta C(t) = \frac{e_n^0}{e_n^0 + e_p^0} N_{TT} \frac{1}{2} \left[\frac{\epsilon\epsilon_0 A^2 q}{2(V_D - V_R) N_d} \right]^{1/2} \times \{1 - \exp[-(e_n^0 + e_p^0)t]\} . \quad (1)$$

TABLE I. Characteristics of the n-type Schottky samples used in this work.

x in $GaAs_{1-x}P_x$	$\lvert N_d - N_a \rvert$ (10^{16} cm^{-3})	EL2 conc. (10^{14} cm^{-3})	$\vec{E}$ (10^4 V/cm)
0	0.66	2.0	4.5
0.04	0.54	1.9	4.1
0.08	0.62	1.4	4.4
0.20	1.3	0.6	6.5
0.26	1.3	0.7	6.5

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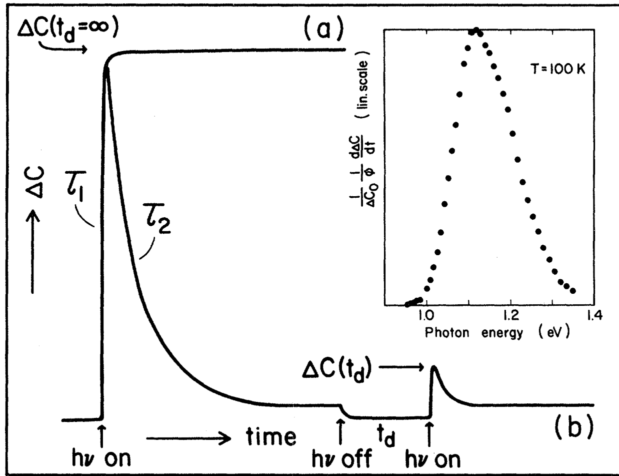

FIG. 1. Photocapacitance signal due to EL2 in GaAs for two different temperatures. Curve (a) corresponds to Eq. (1) ($T=200$ K) and curve (b) shows the photocapacitance quenching effect ($T=77$ K). The spectral distribution for the $EL2^0 \rightarrow EL2^*$ transition at $T=100$ K is inserted. Also illustrated by curve (b) is the measurement of the thermal regeneration as discussed in Sec. III D. $\Delta C(t_d=\infty)$ is proportional to N_t and $\Delta C(t_d)$ is proportional to the concentration of $EL2^0$ ($[EL2^0]$).

It is readily seen that the time dependence of the capacitance signal is exponential with the time constant $\tau_1=(e_n^0+e_p^0)^{-1}$. This behavior corresponds to curve a in Fig. 1. Performing the same experiment at temperatures lower than 100 K, the time dependence of the photocapacitance signal becomes more complicated [curve (b) in Fig. 1]. Before reaching the steady-state occupancy $(n_T(\infty)=[e_p^0/(e_n^0+e_p^0)]N_T)$ observed at $T \geq 150$ K the capacitance signal decreases towards the initial capacitance value with a time constant τ_2. This is the photocapacitance quenching effect of EL2 in GaAs. From several arguments[10] it has been concluded that the effect is caused by the transformation of the "normal" EL2 center ($EL2^0$) into a metastable state ($EL2^*$) of the same charge state. Once populated, the state is no longer affected by extrinsic light. The spectral distribution of the optical transition rate for the population of the metastable state is shown in the inset of Fig. 1. The regeneration (from the metastable state, $EL2^*$, to the normal state, $EL2^0$) is often described by an empirical regeneration rate r, which in turn can be divided into the thermal regeneration rate,

$$r^{\rm th}=r_0^{\rm th}\exp(-\Delta E^{\rm th}/kT) \quad (2)$$

and the electron-induced regeneration rate

$$r^{\rm el}=\sigma^{\rm el}n\langle v_{\rm th}\rangle=\sigma_0^{\rm el}n\langle v_{\rm th}\rangle\exp(-\Delta E^{\rm el}/kT)\ . \quad (3)$$

$\langle v_{th}\rangle$ is the thermal velocity of free electrons and $\sigma^{\rm el}$ is the capture cross section.[5,10] Both rates are temperature activated ($\Delta E^{\rm th}\approx 0.34$ eV and $\Delta E^{\rm el}\approx 0.11$ eV), and in addition, $r^{\rm el}$ is proportional to the free-electron concentration n.

B. Identification of EL2 in $GaAs_{1-x}P_x$

The identification of the deep donor observed in $GaAs_{1-x}P_x$ as being the EL2 center observed in GaAs is based on three arguments. First, thermal emission rates studied as a function of temperature show continuous trends with alloy composition, both for activation energies and thermal emission rates.[3] Second, we observe continuous variations of details in the photoionization cross sections when the alloy composition is varied. Third, broadband illumination ($h\nu \approx 1.15$ eV) at low temperatures causes the same characteristic photocapacitance quenching effect of the studied center for $x \leq 0.26$ as for EL2 in GaAs (Fig. 2). The quenching effect was not observed for $x \geq 0.38$, although the EL2 center seems still to be present according to the first two arguments.

C. Spectral distribution

Figure 3 shows the spectral efficiency $(\phi\tau_2)^{-1}$ vs $h\nu$ (ϕ is the photon flux) of the photocapacitance quenching ef-

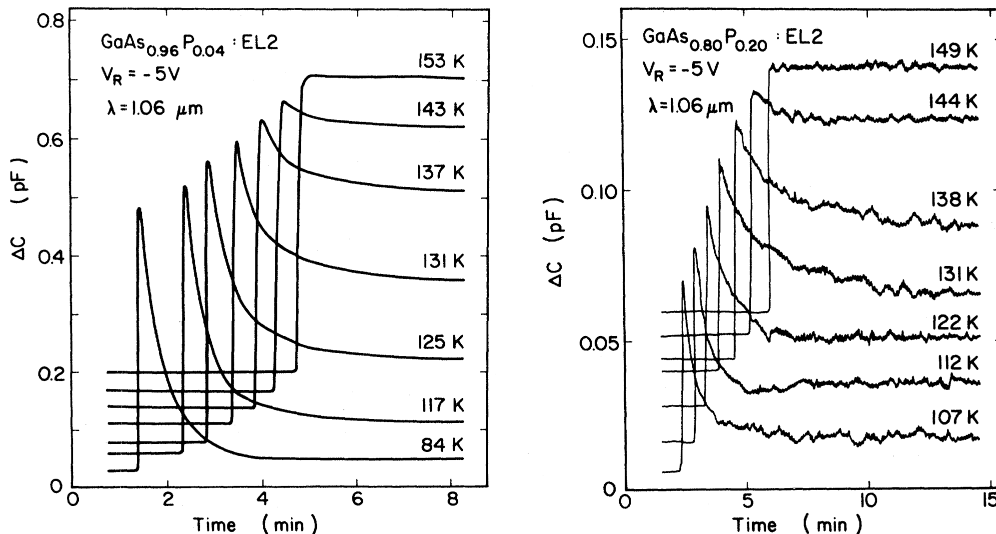

FIG. 2. Photocapacitance quenching effect, typical for EL2 in GaAs as observed for the corresponding defect for two $GaAs_{1-x}P_x$ alloy compositions.

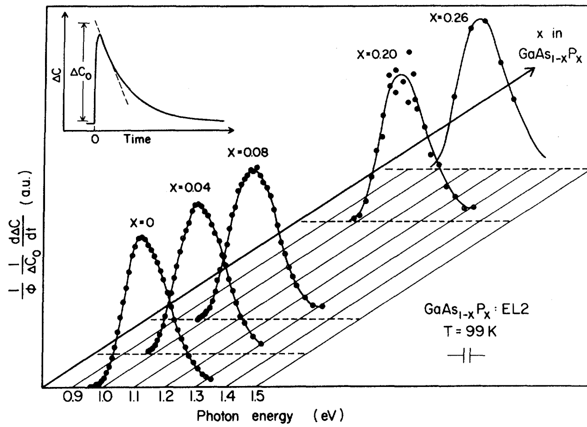

FIG. 3. Spectral distribution of the $EL2^0 \rightarrow EL2^*$ optical cross section for different alloy compositions.

fect for different alloy compositions. Low effective capture cross sections for the $EL2^0 \rightarrow EL2^*$ transition made it impossible to obtain reasonable resolution and to simultaneously monitor the full transient. τ_2 was therefore deduced (as in Refs. 10 and 12) from the initial slope of the quenching transient, i.e.,

$$\tau_2^{-1} = \frac{1}{\Delta C_0} \frac{d\Delta C}{dt}\bigg|_{t=0} . \quad (4)$$

For notation see the inset of Fig. 3. Each spectrum has been normalized at its peak position.

D. Thermal regeneration

As mentioned earlier the thermal regeneration rate of the metastable state of GaAs:EL2 ($EL2^* \rightarrow EL2^0$) is temperature dependent[5,10] and can be expressed as shown in Eq. (2). r^{th} was measured using the isothermal method[10] illustrated in Fig. 1. After having transformed all $EL2^0$ states into $EL2^*$ states r^{th} was obtained for GaAs by measuring the difference $\Delta C(t_d=\infty)-\Delta C(t_d)$ (which is proportional to [EL2*], see Fig. 1) as a function of t_d, the time after the light source has been removed (see Fig. 4). E^{th} can then be calculated from an Arrhenius plot of rth. In contrast to GaAs a nonexponential time dependence is observed in $GaAs_{1-x}P_x$ (see Fig. 4). An apparent regeneration rate $r^{th'} = r_0^{th'} \exp(-\Delta E^{th'}/kT)$ (which becomes the true regeneration rate r^{th} for $x=0$) has therefore been used in alloys by taking the time t_d' at which the capacitance signal decreased to $\Delta C(t_d=\infty)-\Delta C(t_d') = \Delta C(t_d=\infty)/e$ and defining $r^{th'} = 1/t_d'$ (see Fig. 4). It is interesting to note that the Arrhenius plots of $r^{th'}$ for all compositions investigated gave straight lines (Fig. 5) from which the thermal activation energy $\Delta E^{th'}$ could easily be deduced. The activation energy $\Delta E^{th'}$ was found to be independent of the definition of $r^{th'}$, i.e., $\Delta E^{th'} = \Delta E^{th}$ is a well-defined activation energy. The values obtained for $r_0^{th'}$ and ΔE^{th} in samples of different compositions are summarized in Table II.

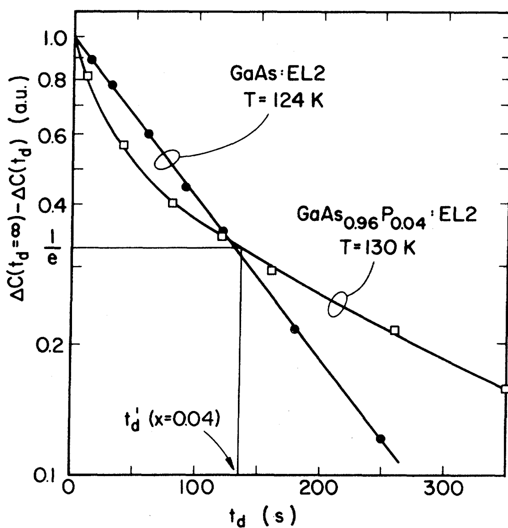

FIG. 4. Plot of the concentration of EL2 centers remaining in the metastable state as a function of the elapsed time in darkness, t_d. The concentration $[EL2^*] \propto \Delta C(t_d=\infty)-\Delta C(t_d)$ where ΔC is the peak height in the capacitance transient in Fig. 1. A nonexponential behavior is observed in the alloy. Also indicated is the evaluation of $r^{th'}$ in the alloys (see Sec. III D).

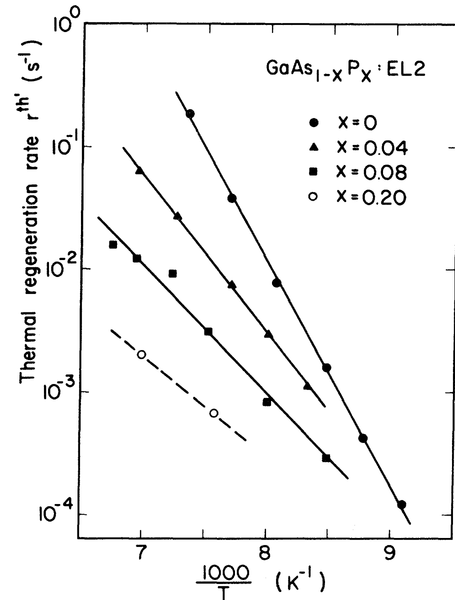

FIG. 5. Logarithm of the thermal regeneration rates, $r^{th'}$, plotted vs $1/T$ for different alloy compositions.

E. Electron-induced regeneration

In GaAs the regeneration of $EL2^*$ is accelerated by the presence of free electrons. Similar effects have been observed in our alloys for $x \leq 0.08$. For larger values of x the measurements were disturbed by the presence of another deep center which was thermally active in the temperature range in which the measurements were performed. In principle, the electron-induced regeneration rate [Eq. (5)] can be measured by a similar method as the one described in Sec. III D. However, due to experimental difficulties a simpler measuring technique was used. Keeping the electrical filling pulse length (0 V) t_e con-

TABLE II. Collected parameters for thermal and electron-induced regeneration ($EL2^* \rightarrow EL2^0$).

$GaAs_{1-x}P_x$:EL2	$r_0^{th'}$ (s^{-1})	ΔE^{th} (eV)	σ^{el} (cm^2)	ΔE^{el} (eV)
$x=0$				
Ref. 9	2×10^{11}	0.30	1.4×10^{-13}	0.108
Ref. 5	8.6×10^{11}	0.34	1.9×10^{-14}	0.107
This work	3.6×10^{12}	0.36	2.8×10^{-14}	0.106
$x=0.04$	5.1×10^{7}	0.25	2.5×10^{-17}	0.060
$x=0.08$	2.3×10^{5}	0.21	3.3×10^{-18}	0.043
$x=0.20$	8×10^{2}	0.16		

stant, $\Delta C(t_e=\infty)-\Delta C(t_e)$ was measured as a function of temperature. Since it is not unreasonable to assume that

$$[EL2^*](t_e)=[EL2^*](t_e=0)\exp(-n\langle v_{th}\rangle\sigma^{el}t_e)$$

and $\sigma^{el}=\sigma_0^{el}\exp(-\Delta E^{el}/kT)$, it is readily seen that a plot of $\log(\log\{[EL2^*](t_e=0)/[EL2^*]\ (t_e)\})$ vs $1/kT$ yields the activation energy ΔE^{el}. The results obtained are summarized in Table II.

IV. DISCUSSION

The spectral distribution of the optical transition from the normal to the metastable EL2 state has been measured in previous studies using three different methods. The first method employed photocapacitance measurements (80 K) in epitaxial layers[10] (as in this work), the second method used the fatigue effect of the 0.63-eV photoluminescence (4 K) in semi-insulating bulk GaAs,[12] and in the third method the difference between absorption and photocurrent spectra (80 K) in n-type bulk GaAs was studied.[13] The different methods gave similar results, but small differences were observed. Our peak position at 100 K was about 30 meV lower in energy than the photocapacitance data at 80 K,[10] which in turn were about 30 meV lower than the 4-K photoluminescence data.[12] To investigate whether these discrepancies reflect a temperature dependence or whether they are caused by differences in experimental conditions, the spectra of the $EL2^0 \rightarrow EL2^*$ optical cross section were measured at different temperatures [Fig. 6(a)]. For comparison the 4-K photoluminescence data are also plotted, however, with an adjusted peak height. The data clearly reveal a shift in peak position and a change in the position of the onset on the low-energy side. This is seen more clearly in Fig. 6(b) where the 4-K photoluminescence data have been substracted from the photocapacitance measurements at higher temperatures. This temperature behavior suggests a possible splitting of either the initial state or the final state, i.e., either a variation in absorption strength with temperature or a difference in branching efficiency from an intermediate excited state to the metastable state. In fact, the existence of an intermediate excited state has previously been proposed.[13]

If the temperature dependence in Fig. 6 is caused by a splitting of the initial state (i.e., the $EL2^0$ ground state) the same temperature dependence should be observed in absorption experiments. However, neither a shift to lower energies nor an overall increase in the absorption coefficient with increasing temperature has been reported.[13] Judging from this comparison with absorption data the temperature dependence in Fig. 6 may indicate the presence of a more complex intermediate state, or states, with a temperature dependent transfer to the metastable state.

The shift in the optical cross-section spectrum with temperature agrees well with the data in Refs. 10 and 12,

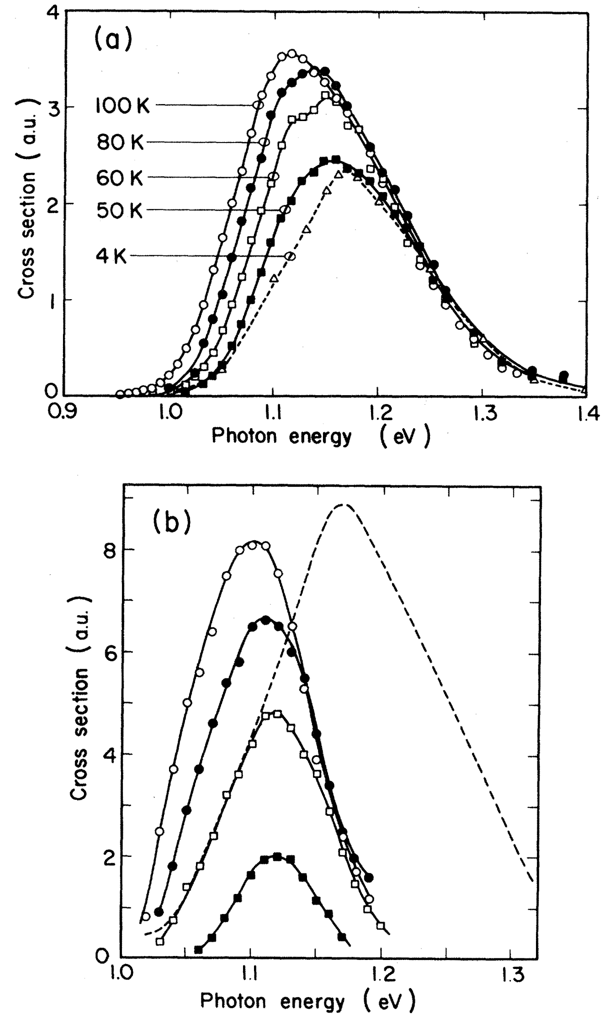

FIG. 6. (a) Optical cross section for population of the metastable state plotted vs photon energy for different temperatures (solid lines). The dashed line is a low-temperature spectrum (4 K) obtained from photoluminescence quenching (Ref. 12). (b) Same data as in (a) but with the 4-K spectrum subtracted from each spectrum.

but not with those in Ref. 13 where the peak position is slightly higher in energy ($h\nu=1.18$ eV, $T=80$ K). Furthermore, it is claimed in Ref. 13 that the peak position shifts to higher energies with increasing temperatures. These discrepancies may be due to uncertainties in subtracting results from two different measuring techniques.

Defects with similar electronic properties as EL2 in GaAs have been observed using dark capacitance methods in GaInAs,[14] AlGaAs,[15–17] and in GaInAsP.[18] To the best of our knowledge, no EL2 photocapacitance quenching effect in any alloy or any material other than GaAs has been reported so far. Since the center behaves similarly in GaAs and $GaAs_{1-x}P_x$ (for $\lesssim 0.3$) it seems most likely that the effect also exists in other alloys, at least for small values of x.

The similarity of the optical cross section, the thermal regeneration rate, and the electron-induced regeneration rate of EL2 in $GaAs_{1-x}P_x$ alloys and in GaAs suggests that the microscopic nature of the defect is similar. Assuming the existence of an intermediate state for the $EL2^0 \rightarrow EL2^*$ transition the absorption coefficient for the intercenter transition given in Ref. 13 then corresponds to the absorption between $EL2^0$ and the intermediate state. This absorption coefficient and the one for the ionization process are of the same magnitude in GaAs (≈ 1 cm^{-1} in a GaAs sample with [EL2]$\approx 2\times 10^{16}$ cm^{-3}).[13] The ratio between the optical cross section for ionization and the optical cross section for the $EL2^0 \rightarrow EL2^*$ transition, is estimated from our photocapacitance measurements to be ≈ 100 (the ratio between τ_2 and τ_1 in Fig. 1). As already noted in Ref. 13 this observation suggests that the intermediate state acts as a branching state for the $EL2^0 \rightarrow EL2^*$ transition. Furthermore, since the ratio of the probability, for optical ionization of $EL2^0$ and population of $EL2^*$ (τ_1 and τ_2 in Fig. 2) in $GaAs_{1-x}P_x$ is similar to that observed in GaAs, it is reasonable to assume that

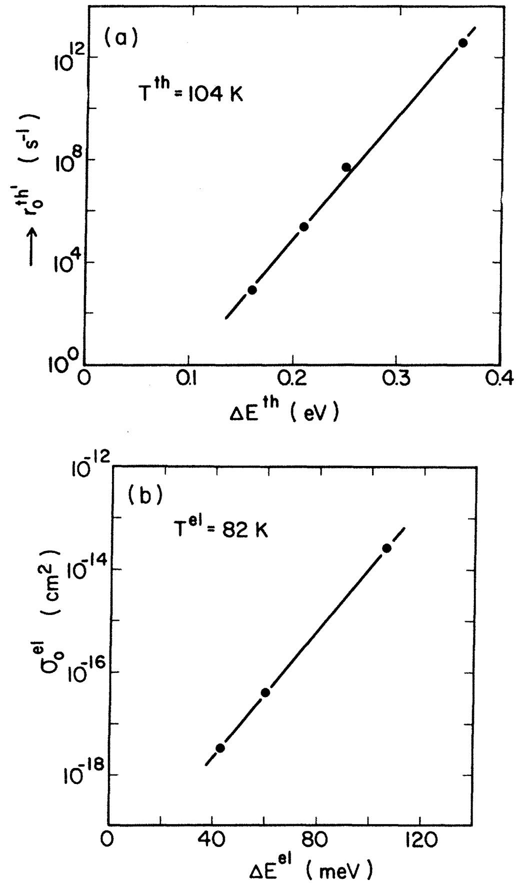

FIG. 8. (a) Logarithm of the prefactor of the thermal regeneration rate, $r_0^{th'}$ [see Eq. (3)] in the alloy system plotted as a function of ΔE^{th}. (b) Logarithm of the cross section for the electron-induced regeneration rate, σ_0^{el} [see Eq. (3)] in the alloy system plotted as a function of ΔE^{el}.

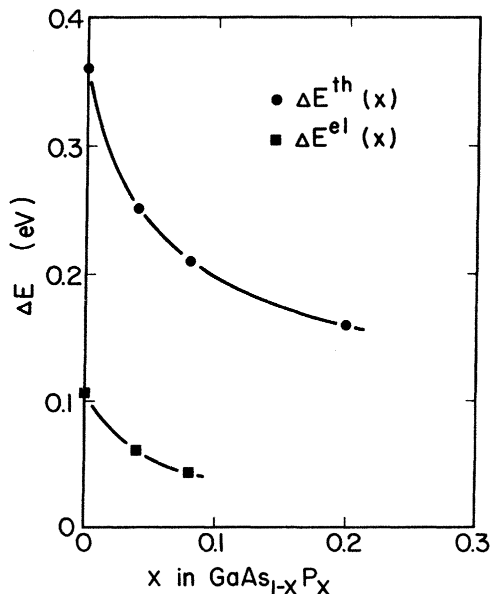

FIG. 7. Activation energies for thermal regeneration, ΔE^{th}, and electron-induced regeneration, ΔE^{el}, plotted vs the alloy composition.

the intermediate state also acts in $GaAs_{1-x}P_x$ as a branching state for the $EL2^0 \rightarrow EL2^*$ transition.

The nonexponential behavior of the thermal regeneration rate measurements (Fig. 4) is interpreted as an alloy effect, i.e., different EL2 centers having different local surroundings resulting in a distribution of time constants. The activation energy, which does not depend on the definition of rth (see Sec. III D), decreases with increasing phosphorous concentration in the alloy (see Fig. 7). This decrease is also observed for the electron-induced activation energy ΔE^{el}. Our results can be summarized in an empirical expression for the thermal and electon-induced regeneration rates valid for the investigated part of the alloy system (see Fig. 8),

$$r(x,T)=2\times 10^{-5}\exp\left[\frac{-\Delta E^{th}(x)}{k_B}\left[\frac{1}{T}-\frac{1}{T^{th}}\right]\right] +9\times 10^{-21}n\langle v_{th}\rangle\exp\left[\frac{-\Delta E^{el}(x)}{k_B}\left[\frac{1}{T}-\frac{1}{T^{el}}\right]\right], \quad (5)$$

where $T^{th}=104$ K [from Fig. 8(a)], $T^{el}=82$ K [from Fig. 8(b)], $\langle v_{th}\rangle$ is the thermal velocity in cm/s, and n is the

free-carrier concentration in the conduction band (cm^{-3}). The reason for disappearance of the photocapacitance quenching effect for $x \gtrsim 0.3$ may be due to the lowering of the activation energy ΔE^{th}. Changes in the energy position of the EL2* level relative to the $EL2^0$ level may thus make the metastable state energetically unfavorable. Alternatively, increasing (decreasing) the P (As) concentration may reduce the probability of producing the microscopic aggregate responsible for the metastable properties.

V. CONCLUSIONS

The photocapacitance quenching effect, typical for EL2 in GaAs, is observed for the corresponding defect in the $GaAs_{1-x}P_x$ alloy system. The spectral distribution of the optical transition rate for the population of the metastable state has been studied for different values of x, yielding remarkably constant spectral shapes. In GaAs the spectrum has been found to be temperature dependent. This temperature dependence has been discussed in terms of splitting either of the ground state or of an excited state.

The thermal regeneration rate ($EL2^* \rightarrow EL2^0$) is thermally activated with an activation energy decreasing from 0.36 eV (GaAs) to 0.16 eV ($x = 0.20$). The electron-induced regeneration rate shows a similar reduction in activation energy. The metastable properties seem to disappear for $x \gtrsim 0.3$. It is also shown that the regeneration rate (thermal and electrical) can be expressed in one single formula valid for the investigated part of the alloy system.

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