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Origin of the nonexponential thermal emission kinetics of *DX* centers in GaAlAs

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Direct evidence has been found, via hydrostatic pressure experiments, that the random distribution of Al and Ga atoms (alloy broadening) is the main cause of the nonexponential behavior of thermal emission processes from *DX* centers in $Ga_{1-x}Al_xAs$ alloys ($0.19 \leqslant x \leqslant 0.74$). Isothermal single-shot emission transients at constant capacitance were used to measure the nonexponential behavior. Experimental values of the degree of nonexponentiality at ambient pressure, as a function of the Al content, are in good agreement with an alloy broadening model. When hydrostatic pressure up to 11 kbar is applied, the nonexponential behavior does not change, confirming its independence from variations in the conduction-band structure.

The donor-related defects, *DX* centers, present in many III-V semiconductors such as GaAlAs,[1-3] GaAsP,[4] InGaAlP,[5] and InGaAsP,[6] are responsible for limitations in the performance of modulation-doped field-effect transistors (MODFET's)[7] as well as in optical devices such as light-emitting diodes (LED's) based on GaAsP and GaAlAs. Such limitations are due to persistent photoconductivity effects[8,9] and short defect-related recombination lifetimes.[4]

Lang *et al.*[1,2] proposed a large lattice relaxation model which explains the experimental results related to *DX* centers. This model has been criticized because it requires an extremely high As vacancy concentration ($\simeq 10^{18}$ cm^{-3}) to explain the complex nature of this center as a donor-V_{As} pair. This objection is overcome by the proposal that the complex involves a self-generated vacancy when the donor is displaced from the substitutional site in the lattice.[10,11] Furthermore, the large lattice relaxation model, together with an alloy-induced disorder effect,[12] explains a very general and striking aspect of *DX* centers, namely, the strong dependence of the nonexponential behavior of the thermal emission and capture processes on the alloy composition. Thermal emission and capture data have been fit with the assumption of an alloy-dependent energy broadening.[6,13-15] However, no direct evidence that the alloy broadening is the main cause of nonexponential thermal emission and capture processes has been shown. This work demonstrates that in Si-doped GaAlAs alloys, the nonexponential behavior of thermal emission processes from *DX* centers depends on fluctuations of the alloy composition and not on the band structure.

MODFET's and Mo Schottky barrier diodes were fabricated in Si-doped GaAlAs layers grown by molecular beam epitaxy (MBE) technique. GaAlAs layers in MODFET's were doped to 10^{18} cm^{-3} and had thicknesses between 500 Å and 700 Å. Schottky contacts were made on 1-μm-thick layers with donor concentrations in the range 5×10^{16} cm^{-3} to 10^{17} cm^{-3}. The Al mole fraction was determined from electron microprobe and photoluminescence measurements with a ± 0.03 accuracy and varied from 0.19 to 0.74.

For hydrostatic pressure measurements, a Cu-Be piston-cylinder-type pressure cell with kerosene as a liquid medium was used with a continuous flow liquid nitrogen cryostat. The pressure was monitored at low temperature by a heavily *n*-doped InSb probe with four contacts, used as a resistor. Because of the dependence of the pressure on temperature and the fact that single shot emission transients are much more sensitive to small variations in the nonexponential behavior than standard deep level transient spectroscopy (DLTS) techniques, we used the former method. A feedback system that adjusts the voltage, keeping the capacitance constant when the thermal emission process takes place, was used for both types of devices. This method eliminates the nonexponential behavior of thermal emission and capture processes due to high trap concentrations.[2] A set of isothermal emission transients, at different temperatures and pressures, was obtained for each sample. Then, a computer-aided fit using two exponential functions was performed and a nonexponential factor, defined as the ratio between the "slow" and "fast" time constants, was calculated.

Due to the high sensitivity to error in this procedure, all transients were performed under identical experimental conditions and their amplitudes were normalized prior to the fitting. Fits were made taking the first 90% of the total transient amplitude in all the samples. In that way, the final slow tails, which produce the most error, were omitted.

The variation of the nonexponential factor with the Al mole fraction, at ambient pressure, has been measured. It clearly follows the expected behavior, according to the alloy broadening model[12] (Fig. 1). The spread of the values of the nonexponential factor arises from several measurements on the same sample at different temperatures.

It is well known that hydrostatic pressure changes the relative position of the different conduction-band minima, in almost the same way as the increase of the Al mole fraction does,[16] for direct band-gap compositions. Accordingly, the application of hydrostatic pressure to a sample of a given Al content will show the influence of the conduction-band structure on the nonexponential factor.

Figure 2 shows the variation of the nonexponential factor with pressure, for samples with Al mole fractions corresponding to direct and indirect gap regions. Figure 3 shows a

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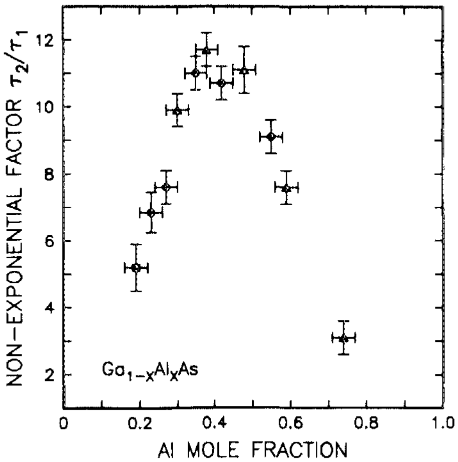

FIG. 1. Dependence of the nonexponential factor τ_2/τ_1 on Al mole fraction. (○) MBE MODFET, (▲) MBE Schottky barrier, (■) MBE MODFET at 5 kbar.

similar result obtained from the normalized emission transients with and without pressure, for a sample with $x = 0.35$. Note that in Fig. 3 the transients have been fit by three exponential functions. That provides enough accuracy to show that both the ratio between equivalent time constants and the amplitudes remain unchanged when pressure is applied. From our experimental results we conclude that the nonexponential behavior of thermal emission transients depends on the alloy composition and not on the conduction-band structure.

Si-related *DX* centers in GaAlAs are barely detected in samples with $x \simeq 0.2$.[9] Because the nonexponential factor does not change with pressure, we have included the data corresponding to the lowest applied pressure (5 kbar), for $x = 0.19$ samples, in Fig. 1.

Optical emission transients from *DX* centers, when stimulated with monochromatic light, behave almost like single exponential processes, regardless of the mole fraction, the photon energy, or the ternary alloy under study.[2,4,17] In fact, if a constant capacitance technique is used, the optical emission transients are perfect single-exponential processes,[2] as seen in Fig. 4, from a sample with $x = 0.35$.[18]

In Fig. 1, the maximum value of the nonexponential factor occurs at Al compositions close to crossover, around $x = 0.4$, rather than the expected value of $x = 0.5$, if an alloy broadening is considered. However, the results from the pressure experiments rule out the possibility of any effect due to the conduction-band structure.

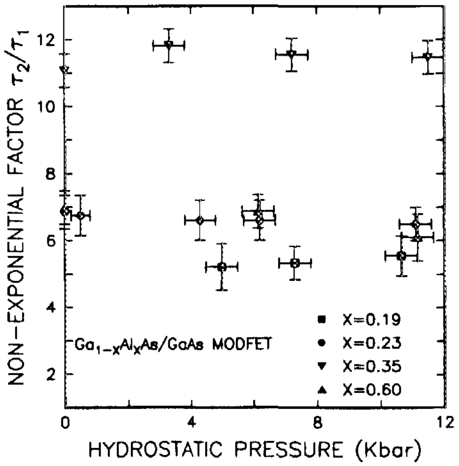

FIG. 2. Dependence of the nonexponential factor τ_2/τ_1 on hydrostatic pressure for different alloy compositions.

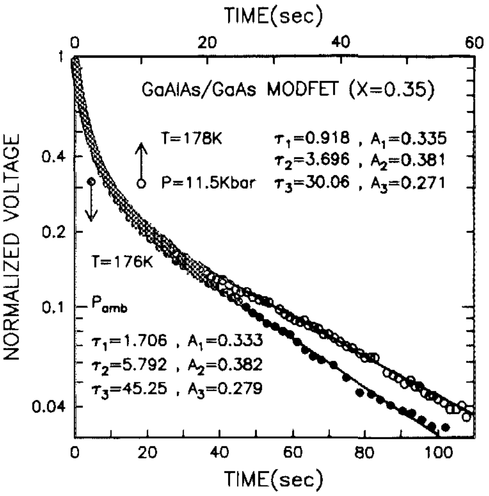

FIG. 3. Thermal emission transients at constant capacitance. Open and full circles correspond to the experimental values from the same sample at 11.5 kbar and at ambient pressure, respectively. Solid lines show the best fit obtained with three exponential functions, whose amplitudes and time constants are indicated.

This discrepancy arises from an artifact of the fitting method used, together with an asymmetric energy distribution due to the alloy broadening for samples with $x \neq 0.5$.[12] A fitting method, using only two exponential functions, will give a higher nonexponential factor in samples that exhibit higher slow tail amplitudes, as was the case for those with $x \leqslant 0.5$.

It has been established that the alloy broadening will produce a spread in the thermal capture barrier and emission energies of *DX* centers. Some values have been obtained for this energy spread in different alloys, such as InGaAsP,[6] GaAsP,[13] and GaAlAs,[14,15] derived from both emission and capture experiments. A general result, describing this energy spread as a Gaussian distribution with a full width at half-maximum (FWHM) between 35 and 60 meV, is found.

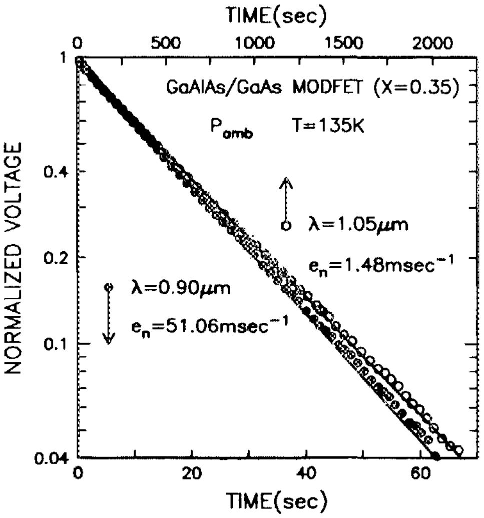

FIG. 4. Optically excited emission transients from *DX* centers at constant capacitance. Open and full circles represent the experimental data for two different photon energies. Solid lines are the least-squares fits that give a single time constant for each transient (Ref. 18).

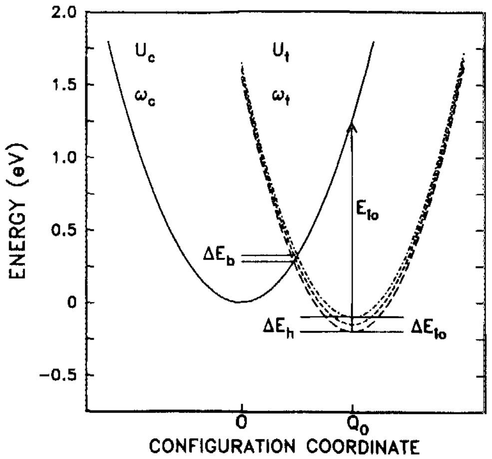

FIG. 5. Configuration coordinate diagram for the *DX* center in Si-doped GaAlAs. A 50-meV spread in the capture barrier energy, ΔE_b, when the spring constant and the coordinate Q_0 are fixed, produces a strong variation in the Hall energy and predicts a nonexponential behavior in the optical emission transients. The same spread in the capture barrier energy is obtained when a 25% change in the relaxed state spring constant is allowed. Then, a single exponential behavior for the optical emission transients as well as a single Hall energy value is found.

If we consider a large lattice relaxation model,[1,2] the effects of such an energy spread can be explained with a configuration coordinate diagram. A 50-meV spread in the capture barrier height produced by means of a shift in the binding energy, as shown in Fig. 5 (the spring constant and the coordinate Q_0, remaining fixed), accounts for the nonexponential behavior in thermal processes. However, it will require a 110-meV spread (ΔE_h) in the Hall energy, that has never been reported. This picture also predicts a strong nonexponential behavior in the optical transients, since a change in the optical cross section of about an order of magnitude is expected when the photon energy is varied by 110 meV.[2,3] It is also clear that a spread of the relaxed state configuration coordinate Q_0 is not consistent with the single exponential behavior of the optical transients.

If a spread of the relaxed state spring constant is allowed, thermal emission and capture processes can be nonexponential with similar energy spreads, as found experimentally. Simultaneously, a single value will be obtained for both the Hall energy and the optical threshold energy, E_{io}. For this case, $\Delta E_h = \Delta E_{io}$, shown in Fig. 5, would be zero.

Because the effect of the alloy broadening will be much more important when the electron is localized, only the curve that represents the electronic plus the vibrational energy of the relaxed state, U_t, will show a spread in the spring constant. If we consider that the lowest energy at Q_0 is mainly determined by the strong lattice relaxation, the alloy broadening being a second order effect in this case, this energy will not show any spread. As the donor atom moves toward its centered position in the lattice, the alloy broadening effect becomes more important and an energy spread at the crossing point between curves U_c and U_t (the capture barrier height) will occur.

Now, a 50-meV spread in the capture barrier energy ΔE_b will require a 25% change in the relaxed state spring constant. Due to a lack of experimental data it is difficult to judge if this value is reasonable. Note that the spring constant is a rather sensitive parameter. For example, the spring constant value that is found when Sn is used as a donor in GaAlAs is only 25% of the one corresponding to the Si donor.[3] Also in Te-doped alloys, a 25% relative change is found between GaAsP[4] and GaAlAs[3] alloys. In a recent paper, Takikawa[14] concludes that the spring constant for Si donors in AlGaAs may be weakly affected by the atoms surrounding the defect, because of the similar atomic radii of Al and Ga. However, if the covalent radii are considered, the difference between the values for Ga and Al atoms could account for a spread in the spring constant.

It has been shown that alloy broadening is the main origin of the nonexponential behavior of the thermal emission processes due to *DX* centers in Si-doped GaAlAs alloys. The application of hydrostatic pressure to the samples, which produces a change of the conduction-band structure, without changing the local environment of the Si atoms, has no effect on the nonexponential behavior of these processes. These results stand for both direct and indirect gap compositions and we suggest that they apply also to thermal capture processes as well as to other alloy systems. Furthermore, the variation of the nonexponential behavior with the alloy composition, at ambient pressure, agrees well with an alloy broadening effect due to the different configurations of the atoms surrounding the defect.

Interpreting these results in terms of the large lattice relaxation model, we propose that a spread in the spring constant of the relaxed state is produced by the alloy broadening. This spread accounts for the nonexponential behavior of thermal emission and capture processes as well as for the single exponential behavior found in optical emission transients.

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