RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 43, NUMBER 14 15 MAY 1991-I

Deep center in $Al_{0.3}Ga_{0.7}As$

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(Received 11 February 1991)

We report the observation of a new trapping center in $Al_{0.3}Ga_{0.7}As$. The center becomes active under a hydrostatic pressure of ~45 kbar, and has an unusually deep emission barrier. It quenches all radiative transitions and causes a hysteresis in the photoluminescence intensity, which we interpret via a lattice relaxation model. It is neither the DX nor the SD center, and is probably related to a donor.

Substitutional group-IV and group-VI dopants in $Al_xGa_{1-x}As$ gives rise to two types of electronic states:[1] a shallow effective-mass level and a more localized level DX, arising from lattice distortion near the donor. The relative stability of the two states depends on alloy composition. Below $x=0.22$, the localized level is a resonance above the conduction-band (CB) minimum. Above $x=0.22$, DX becomes a bound state, more stable than the shallow donor state. The application of hydrostatic pressure for $x<0.22$ can move DX from a resonant to a stable state.[2-4] This shallow-to-deep transition occurs between 20 and 30 kbar in GaAs.

We report the observation of a *new* localized state in $Al_{0.3}Ga_{0.7}As$ under hydrostatic pressure, which is in some ways reminiscent of the DX center. It is resonant above the X CB below 40 kbar. At higher pressures it becomes stable and captures all electrons that are photoexcited into the X CB, causing a *sharp drop in the intensity* of radiative transitions. Upon reducing the pressure, the intensity does *not recover* despite thermal cycling to room temperature, indicating an *unusually deep emission barrier,* much deeper than that of DX. The intensity finally recovers at low pressures (~10–20 kbar).

We have repeatedly seen both the decline in intensity and the hysteresis in bulk $Al_{0.3}Ga_{0.7}As$ ($\sim 2\times10^{15}$ Si cm^{-3}) and in a $GaAs/Al_{0.3}Ga_{0.7}As$ (40 Å/90 Å) multiple-quantum-well (MQW) sample. At pressures above the Γ-X crossover, radiative recombination is observed from the X CB of $Al_xGa_{1-x}As$ barriers to the valence band (VB) of the GaAs wells.[5,6] The initial states of the electron are the same for this staggered transition as in bulk $Al_xGa_{1-x}As$, and, as expected, they show behavior similar to the bulk.

Samples were molecular-beam-epitaxy grown on a GaAs substrate. Photoluminescence (PL) was excited at 15 K using principally 5145-Å radiation from an Ar^+ laser. Measurements under pressure were made in a diamond anvil cell with argon as the pressure medium and ruby fluorescence as the *in situ* manometer. The pressure was changed at 300 K, and after an overnight pumpdown, the cell was cooled. Measurements were performed over the next several hours.

$Al_{0.3}Ga_{0.7}As$ is a direct-gap semiconductor. Under pressure, the energy of the Γ CB increases while that of the X CB decreases, crossing ~13 kbar. At 1 bar a sharp, intense peak due to the neutral donor bound exciton BE^{Γ}, and weaker peaks due to donor-acceptor recombination, DA^{Γ}, are observed. Around 9 kbar, new peaks appear below BE^{Γ}. These peaks exhibit bowing around crossover,[7] indicative of Γ-L-X mixing, and then decrease in energy with a pressure coefficient of −1.6 meV/kbar. The peak energies of all observed transitions are shown in Fig. 1(f). A typical spectrum in the indirect regime is shown in Fig. 1(a). The high-energy peak A is the exciton bound to the X CB BE^{X}, while the broad peaks B, C, and D are due to DA^{X}. The peaks are intense up to about 45 kbar. The intensity drops steeply beyond 45 kbar, decreasing by more than 2 orders of magnitude at ~65 kbar [Fig. 2(a)].

The unusual feature occurs when the pressure is reduced. The intensity of the PL spectrum *does not recover* at the same pressure at which it declined. An example is seen in Figs. 1(d) and 1(e), where we show the spectrum at almost the same pressures as in Figs. 1(a) and 1(b), but for *decreasing* pressure (downstroke). Pressurizing the sample to 70 kbar and decreasing the pressure reduced the intensity by a factor of 17 at 44 kbar, though the peak positions and PL line shape remain similar. The ratio improves to a factor of 6 at 31 kbar, and is about a factor of 2 at very low pressures of ~6 kbar (for BE^{Γ}). The intensities of the staggered transitions in the MQW show a similar hysteresis [Fig. 2(b), inset]. In contrast, the heavy-hole exciton in the GaAs well E_{1h}^{Γ} also loses intensity at 70 kbar, but recovers its intensity on the same path. This clearly indicates that the behavior occurs in $Al_xGa_{1-x}As$.

Three common causes for a decrease in PL intensity are level crossings, dislocations, and trapping centers. A well-known example of a level crossing is the Γ-X crossover:[8,9] when the bands cross, electrons scatter preferentially to the X CB, and the Γ-VB PL intensity decreases by several orders of magnitude, as in the low-pressure region of Fig. 2(a). Another example is the crossing of the nitrogen deep levels in GaAs,[10] with the X CB near 70 kbar. When the N levels become resonant with the X CB, their intensity drops. In both cases, however, the transitions *reappear* upon decreasing the pressure with the same

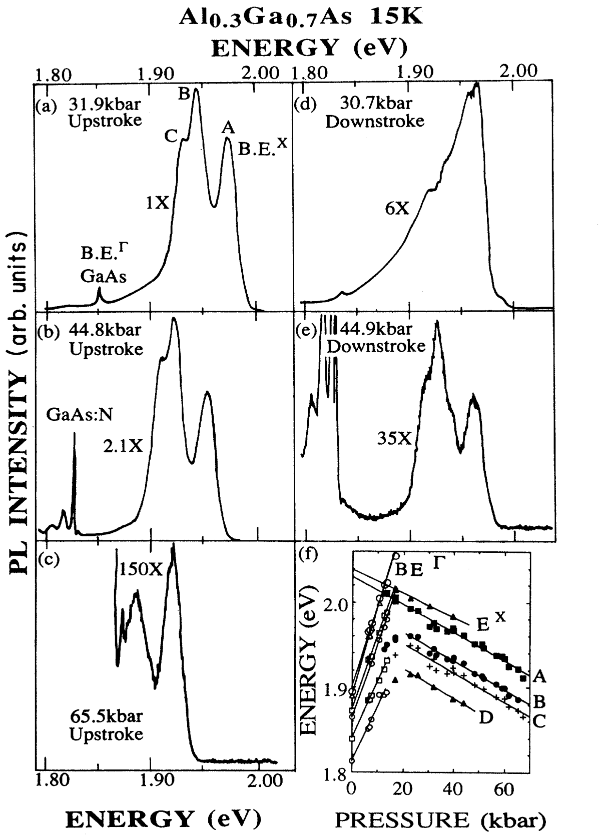

FIG. 1. PL spectra at selected pressures in $Al_{0.3}Ga_{0.7}As$ for both increasing and decreasing pressures. Note the decline in intensity in the downstroke. Shown in (f) are the energies of the radiative transitions as a function of pressure.

intensity and at the same pressure as in the upstroke, unlike the levels we observe.[11] The hysteresis in the intensity, then, rules out a simple level crossing.

Dislocations occurring near a structural phase transition quench PL intensity, as in CdS (Ref. 12) and CdTe.[13] In $Al_xGa_{1-x}As$, the phase transition takes place at ~150 kbar,[14] and is unlikely to cause dislocations at 70 kbar. Dislocations do not allow the PL intensity to recover upon releasing the pressure; since we find an almost total recovery near 10 kbar, we conclude that dislocations do not cause the effect we observe.

The simplest model that describes the effect we observe is a trapping center with lattice relaxation. Since the hysteresis is large, we use the model for large lattice relaxation. A schematic model is shown on a configuration coordinate diagram in Fig. 3. The minimum in the potential energy for the localized center (U_T) is displaced from that of the electron delocalized in the X CB (U_X). Scattering to U_T can occur thermally via the capture barrier E_B or via an intermediate state[15] as postulated for the DX center. Our data do not make it possible to differentiate between the two. For simplicity we assume a level E_m, which mediates the transfer of electrons from U_X to U_T (either the intermediate state or the energy defining E_B), whose separation ΔE from the bottom of U_X varies linearly with pressure.

At low pressures (20–30 kbar) U_T is high above U_X, as is E_m. $\Delta E \gg kT$ ($T = 15$ K, the temperature at which electrons are photoexcited into X), no electrons scatter to U_T, and strong recombination is seen [Fig. 3(a)]. At slightly higher pressures (say, ~40 kbar), although the minima of U_T and U_X line up, a situation akin to level crossing without lattice relaxation, there is still no transfer of electrons to U_T because $\Delta E > kT$ [Fig. 3(b)]. At still

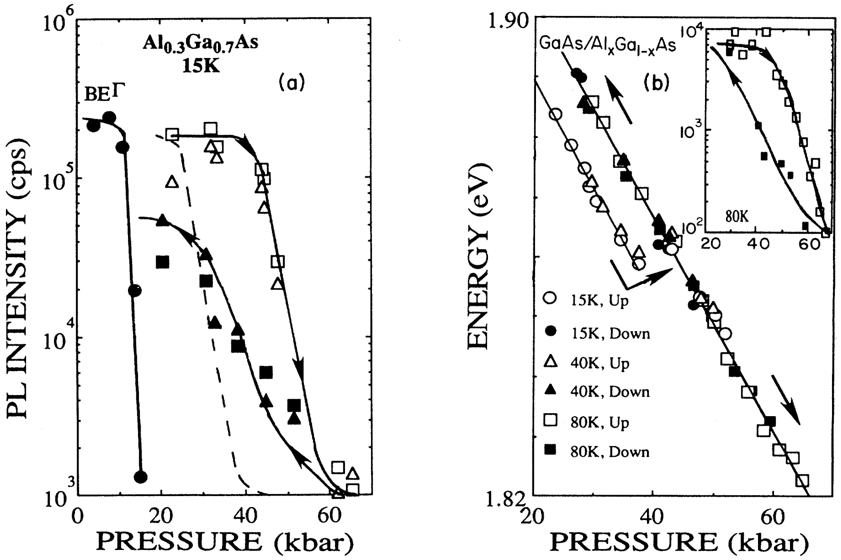

FIG. 2. (a) PL intensity in $Al_{0.3}Ga_{0.7}As$ for up- and downstrokes (open and solid symbols, respectively), showing the hysteresis in the intensity between 30 and 70 kbar. The fits are described in the text. The triangles and squares refer to peaks A and B, respectively. The circles refer to BE$^\Gamma$. (b) Energies of the staggered high-energy X-related peak in the MQW sample at 15, 40, and 80 K for up- and downstrokes. Inset is the intensity of the peak as a function of pressure.

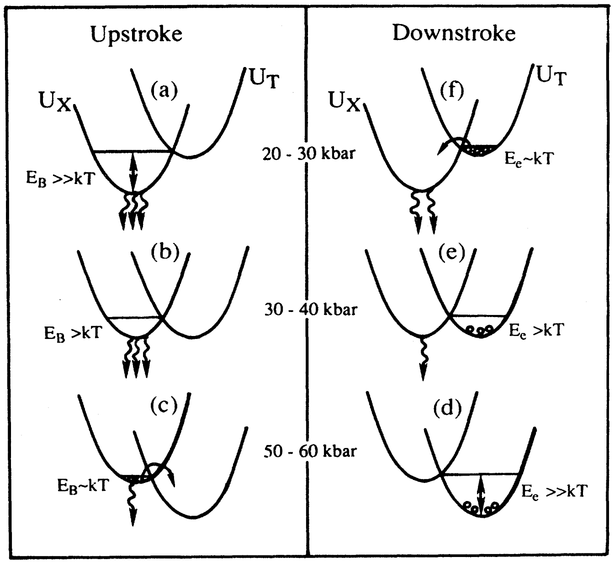

FIG. 3. A schematic configuration coordinate diagram for the electron delocalized in the X CB, U_X, and the new center, U_T.

higher pressures (~50 kbar), U_T is below U_X, $\Delta E \approx kT$, electrons transfer to U_T, and PL intensity decreases sharply [Fig. 3(c)]. When all electrons transfer to U_T (~65 kbar), PL intensities fall below experimentally detectable levels.

We fit the upstroke PL intensity I as a function of pressure P to the function[8,9]

$$I(P)=\frac{I_0}{1+Ae^{\Delta E/kT}}+I_{\min}\,, \tag{1}$$

where $\Delta E=(\alpha_X-\alpha_m)(P-P_T)$ is the energy separation between the mediating level and U_X, α_m, and α_X are their respective pressure coefficients, P_T is the crossover pressure, defined by the pressure at which the energy difference between E_m and the minimum of $U_X \approx kT$. I_0 and $I_{\min}$ are the high- and low-intensity plateaus, respectively. Fitting the upstroke data to this equation (solid line through the open symbols in Fig. 2), we obtain $P_T=45$ kbar, and $\alpha_X-\alpha_m=0.8\pm0.1$ meV/kbar, giving $\alpha_m=-2.4\pm0.3$ meV/kbar, since[16] $\alpha_X=-1.6\ \pm0.2$ meV/kbar. Similar fits to the MQW sample yield $P_T=47\pm1$ kbar, and $\alpha_m=-3.5\pm0.3$ meV/kbar, values from two different samples that are within two standard deviations of each other. If linearly extrapolated from the α's obtained, E_m is about 60 ± 25 meV above the X CB at ambient pressures. In analogy with Eq. (1), as used for the Γ-X crossover,[9] $I_{\min}/I_0$ is the ratio of the scattering time $(U_X \rightarrow U_T)$ and the radiative lifetime, which from our data is about 10^{-2}.

On the downstroke, when the pressure is reduced to where the intensity initially decreased [~50 kbar, Fig. 3(d)], few electrons are present in U_X, making for low PL intensity. At 40 kbar, where previously the PL intensity was high, since the electrons could not enter the trap, now the reverse is true: most of the electrons are in the trap, and the emission barrier $E_e > kT$, preventing strong recombination [Fig. 3(e)]. Finally, at ~10–20 kbar [Fig. 3(f)], $E_e \approx kT$, the center empties, and PL intensity recovers to close to prepressurizing levels.

This scenario would yield a sharp recovery curve [as indicated by the dashed line in Fig. 2(a)] if the temperature was held at 15 K while the pressure was reduced. However, we cycle the temperature to 300 K to change the pressure, which allows some trap emptying to occur. Above 45 kbar, a few electrons transfer out of U_T into U_X and the VB. These electrons are photoexcited into U_X at 15 K, where most of them transfer back to U_T, but a few undergo radiative recombination. This makes the downstroke curve smoother than the upstroke. Below 45 kbar, the photoexcited electrons do not transfer back to U_T, since they have too high a barrier E_B to scatter into the trap;[17] however, because some electrons are still in U_T, PL intensity has not yet recovered. Our data are not sensitive enough to separate the competing processes above 45 kbar, so we assume the dominant process of trap emptying and fit the downstroke data to Eq. (1), with $\Delta E=\Delta\alpha(P-P_R)$ and $T=300$ K, where P_R is the downstroke crossover pressure. We obtain $P_R=30\pm3$ kbar for the two samples, consistent with the qualitative picture of the hysteresis.

If the center is an efficient trap of electrons, one expects that in a heavily doped sample, effects due to doping should abruptly disappear close to 45 kbar. This phenomenon is seen in the MQW sample, which had a center-doped GaAs well (10^{18} Si cm^3). When E^{Γ}_{h} and Al$_x$Ga$_{1-x}$As X bands cross, electrons spill into the Al$_x$Ga$_{1-x}$As and recombine with holes in GaAs via a staggered transition. We find that the energy of the leading peak of the staggered transitions is affected by the trapping process, shown in Fig. 2(b) for 15, 40, and 80 K with open (solid) symbols for up (down) strokes. In the upstroke at 15 and 40 K, the high-energy peak E_1 shifts at a typical rate of −1.6 meV/kbar, but is observed *only* up to ~40 kbar. Above 40 kbar, E_1 abruptly disappears, and a new peak at a slightly higher energy, E_2, appears. E_2 continues to shift at −1.6 meV/kbar, and is visible up to 50 kbar, beyond which it is masked by the GaAs:N levels. Pressure was increased to 70 kbar and then reduced. On the downstroke, E_2 emerges from the GaAs:N levels near 50 kbar, but *continues* to follow the E_2 path to pressures of 30 kbar. E_1 was never recovered, even at pressures at which it had been seen in the upstroke. In contrast, at a higher temperature of 80 K, E_1 is the only level that can be observed, both in the up- and downstrokes.

It is reasonable to assume that at 80 K, E_2 is the free exciton associated with the confined level in the X CB. Its energy is consistent with previous studies[5] at 80 K of other undoped MQW samples. When corrected for the temperature shift of the band gaps, E_1 at 15 K is ≈ 24 meV below E_2 at 80 K. At low temperatures and below 40 kbar it is likely that the large number of electrons makes viable a transition whose energy is lowered by screening effects,[18] E_1. When the electrons are trapped near 45 kbar, the level is no longer available, and only a higher-energy, free-excitonic transition E_2 occurs. In the downstroke, the free exciton E_2 is still the only one available until detrapping takes place (< 30 kbar). At 80 K, the thermal smearing of the Fermi sea makes the free exciton

E_2 the only viable state both in the up- and downstrokes.

The energy behavior is consistent with the hysteresis in the intensity and suggests that a donor state is involved in the trapping process. This is reinforced by the fact that its crossing with the CB determines the decline in intensity, both in bulk and MQW samples. We conclude that the new center arises from an energy level that is *above* the X CB at ambient pressures, and crosses to come below it at higher pressures. If it were below the X CB at low pressures, it would trap electrons efficiently at low pressures, and PL intensity would rise when it crossed the X CB at high pressures, which is contrary to our experimental observations. This new center does not have the characteristics of the normal DX center; the DX is below the X CB at all pressures,[19] and its emission barrier is sufficient to empty[20] it at 300 K. Moreover, DX can be optically emptied with the 2.4 eV excitation we use for PL. We conclude that this new center is not the DX, and that its E_e is > 300 K at high pressures. A level that does cross X at high pressures is the recently observed shallow donor (SD) level.[21,22] However, its E_e is less than that of the DX center, which rules it out as this new center.

Our discussions have assumed that the new center is an electron trap. Low-temperature PL is affected by hole trapping,[23] causing a PL transient that saturates in ~ 10 sec (for 10^{18} Si cm^3). While one cannot *a priori* rule out hole trapping as the cause for this new center, it would require a time constant of the order of a few hours, as well as an identical turn-on pressure in GaAs and $Al_xGa_{1-x}As$. The channel switching of energies in the MQW sample is more easily understood from the point of view of electron rather than hole trapping. We also note that the shape of the hysteresis may depend on the time scales for the relaxation of carriers. These time scales are not known at present.

In summary, we have observed a new center in $Al_{0.3}Ga_{0.7}As$ under hydrostatic pressure. This center has lattice relaxation, probably large, and forms an efficient electron trap. It produces a hysteresis in the PL intensity, which recovers at low pressure. The hysteresis rules out a simple level crossing, and the recovery of PL rules out dislocations. It is neither the DX nor the SD center. The microscopic origin of the center is not known at present. Annealing experiments and investigations of samples with other Al compositions are currently under way.

This work was supported by U.S. Army Research Office under Grant No. DAAL03-86-K0083, the U.S. Department of Energy under Grant No. DE-FG02-89ER45402, and the University of Missouri Research Council.

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