Nature of the DX center in Ga$_{1-x}$Al$_x$As

M. Zazoui, S. L. Feng, and J. C. Bourgoin

Groupe de Physique des Solides de l'Université Paris 7, Tour 23, 2 place Jussieu, 75251 Paris CEDEX 05, France

Comparing the magnitude and temperature dependences of the cross section for electron capture on the ionized donor state D^+ and on the DX center, and the dependence of the capture rate on the free-electron concentration, we demonstrate that the DX center cannot be a neutral donor state D^0 which has trapped an additional electron and, consequently, that the DX center is not a deep D^- state exhibiting a negative-U behavior.

Although it now appears widely accepted that the DX center[1] is a deep state of the donor impurity D exhibiting a negative-U behavior,[2] there is apparently no decisive experimental demonstration, as evidenced by the numerous efforts still made to reach this conclusion. What is missing is a direct experimental test showing that when the doping impurity is located on a donor site in Ga$_{1-x}$Al$_x$As, for an alloy composition $x > 0.2$, it gives rise to a deep state by trapping an additional electron. The binding of an extra electron on the neutral donor state D^0 corresponds to a $D^- \rightarrow D^0$ transition which, because it is observed experimentally to be located below the $D^0 \rightarrow D^+$ transition, implies that the D^- state exhibits a negative-U behavior.[3] If this is not the case the DX center is then an effective-mass state simply deepened by some kind of central cell correction[4] which corresponds to a $D^0 \rightarrow D^+$ transition.

Experimental indications that the DX center is a deep defect come principally from studies performed using electron paramagnetic resonance (EPR) and related techniques.[5] Arguing that the ground state of the center is not observed but only the X effective-mass state of the donor impurity after photoexcitation in direct-band-gap materials, it is concluded that is it not paramagnetic, i.e., not the D^0 state. Although the effective-mass state of the donor is observed at equilibrium in indirect-band-gap materials, and although the EPR spectra of other impurities than Sn do not exhibit after photoexcitation any hyperfine interaction, the existence of this hyperfine interaction[6,7] for one of the ionized states associated with the Sn impurity (another ionized state is the X effective-mass state) is used to conclude that the wave function of the DX ground state must be strongly localized. However, magnetic-susceptibility (MS) experiments[8,9] detect paramagnetic centers without photoexcitation. Moreover, combined secondary ion mass spectroscopy and MS in the heavily Sn-doped materials used for EPR studies strongly suggest[10] that the Sn-associated spectrum must be ascribed to a Sn-related defect complex rather than to the isolated donor.

Among the indications that the DX wave function is not so strongly localized are the facts[11] that the associated energy level depends neither on the nature of the doping impurity nor on the lattice site (Ga or As) it occupies and that electron emission is enhanced by an electric field, this enhancement following the Poole-Frenkel law predicted for a neutral state (i.e., a $D^0 \rightarrow D^+$ transition). Moreover, D^- states exist as shallow states[12] which can now be observed at equilibrium[13] when the electron concentration is larger than the donor concentration.

The aim of this communication is to present a very simple test which should allow us to decide if the DX center is a D^- negative-U defect or a D^0 state. It is based on a comparison of electron capture cross sections on D^+, D^0, and DX states, which are all known. There are three possible mechanisms by which electron trapping on D^+ states can give D^- states. The first one is the following: a first electron has to be trapped on D^+, with a cross section σ^+, and then a second one on D^0, with a cross section σ^0. Since there are as many free electrons as donors, in order to produce D^- states, σ^0 has to be larger than σ^+ since otherwise D^0 states are first formed and there are no more electrons available to create D^- states. Consequently, the condition to be fulfilled, if this first mechanism is taking place, is that σ^0 is larger than σ^+. This is obviously not the case since σ^+ is known to be "giant,"[14] i.e., of the order of 10^{-12}–10^{-14} cm^2 (electron capture occurring by a cascade process from the excited states of the shallow donor D^0), while the cross section σ^0 which then corresponds to electron capture on the DX center (i.e., for the $D^0 \rightarrow D^-$ transition in this first mechanism) is small. Indeed, as demonstrated by many studies (see, for instance, Ref. 15 and the references it contains) σ^0 is thermally activated,

$$\sigma^0 = \sigma_\infty \exp\left[-\frac{B}{kT}\right], \qquad (1)$$

with $\sigma_\infty \sim 10^{-14}$–$10^{-15}$ cm^2, where the barrier B varies with the nature of the impurity and the alloy composition. This is illustrated in Table I which provides values of σ^0 and B versus alloy composition for electron capture on DX centers in Te-doped materials, which we measured using deep-level transient spectroscopy (DLTS). Because B is in the range 50–500 meV, σ^0 is indeed smaller than σ^+ (by factor of $\sim 10^4$ as shown in Table I) at the temperature where the DX centers trap electrons.

The second possible mechanism for the $D^+ \rightarrow D^-$ transition is that D^0 states are first formed and subsequently two neighboring D^0 states exchange electrons to

TABLE I. Variation of the preexponential factor σ_∞ and barrier height B associated with the electron capture cross section in Te-doped materials of various alloy compositions x. σ^0 is a value of this capture cross section measured at the temperature at which the DX associated deep-level transient spectroscopy peak occurs (145 K), i.e., a temperature located in the range where the capture process is measured.

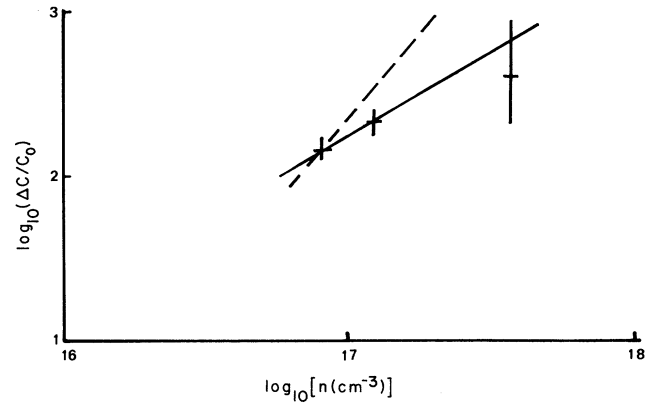| x	σ_∞ (cm^2)	B (meV)	σ^0 (cm^2)
0.25	4.0×10^{-11}	130	1.3×10^{-16}
0.40	7.7×10^{-14}	65	4.2×10^{-16}
0.60	1.1×10^{-14}	75	2.7×10^{-17}
0.80	6.8×10^{-14}	120	4.6×10^{-18}

FIG. 1. Variation of the initial rate of electron capture on DX centers (provided by the relative capacitance change $\Delta C/C_0$, where C_0 is the reverse bias capacitance, induced by a 1-μs duration of the filling pulse) vs the free-carrier concentration in Te-doped, $x = 0.21$, materials. The full line indicates a slope 1, i.e., the linearity between the capture rate and n. The dashed line corresponds to a two-electron capture mechanism.

give a more stable pair of D^+ and D^- states. Such a transformation should occur through electron tunneling by a process called hopping capture, which has recently been developed and experimentally studied.[16] In this case the capture rate has to be replaced by a tunneling probability, which is a temperature-independent process. Since the observed DX capture rate is strongly temperature dependent as a result of Eq. (1), it cannot be ascribed to such a hopping capture.

Finally, the third possible mechanism is that two electrons are captured simultaneously on D^+ states to form directly the D^- states. In this process, the capture rate is proportional to n^2, the square of the free-electron concentration. We therefore measured this rate versus n. For this, experimental conditions are chosen carefully so that the capture kinetics are not distorted by the fact that n varies as capture takes place. This is done using a filling pulse duration very short to ensure that the concentration of filled DX centers remains negligible compared to n. The beginning of the capture kinetics, where the concentration of filled centers is very small compared to n, is monitored at a given temperature (145 K) in a set of Te-doped materials ($x = 0.21$) in which the free-carrier concentration at room temperature varies from 6.8×10^{16} to 3.8×10^{17} cm^{-3}, as determined by capacitance-voltage measurements at room temperature. These materials have been grown by MOCVD (thickness 2 μm) on n^+ GaAs substrates on which the Ohmic contacts are made while Schottky barriers (200-μm diam) are made on the top of the layer by gold evaporation. The capture kinetics is monitored by DLTS through the variation of the amplitude ΔC of the DX associated peak versus the filling pulse duration t_p. The variation of the slope $\Delta C(t_p)$ for

short durations (t_p up to 1 μs), which is the capture rate, is monitored in Fig. 1 as a function of the free-carrier concentration n. The uncertainty, although large in the highest doping case, allows us to make the distinction between a one-electron or a two-electron capture mechanism (full and dashed lines, respectively, in Fig. 1). The uncertainty increases with the doping n because the emission rate cannot be neglected in front of the capture rate (in this material the capture barrier is high) and the filling factor decreases as the capture rate, i.e., as n, increases. In any case, Fig. 1 shows clearly that the capture rate varies as n and not as n^2, allowing us to conclude that electron capture on the DX center does not involve a two-electron process.

In conclusion, the facts that (i) the cross section for electron trapping on D^+ states is by far greater than the capture cross section on the DX center, (ii) the DX center cross section is temperature dependent, and (iii) the initial capture rate is proportional to n and not to n^2, rule out the possibility that this DX center is a D^- state.

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