Charge of the DX ground state in $Ga_{1-x}Al_xAs$

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(Received 19 December 1991; revised manuscript received 8 September 1992)

We discuss three different types of experiments that provide direct evidence that the ground state of the DX center is neutral, thus demonstrating that this center cannot be a negatively charged isolated donor. The evidence is based on the magnitude of the electron-capture cross section, the sensitivity of electron emission on the electric field, and the modification in the universal conductance fluctuations of a mesocopic system induced by ionizing DX centers.

As evidenced by the numerious studies still devoted to the DX center in $Ga_{1-x}Al_xAs$, the question of the identification of this defect is not settled. This defect, known to be associated with the isolated donor impurity D (for a review of the properties of this defect, see Ref. 1), is often said to be a distorted configuration of the donor state D^0 induced by a large electron-photon interaction when this state traps an additional electron, i.e., becomes D^-.[2] The main experimental arguments in favor of this model come from electron paramagnetic resonance (EPR) and related techniques: the DX ground state being not detected,[3,4] it is concluded that it must be nonparamagnetic. The detection of a hyperfine interaction associated with a Sn-related center after photoionization of this ground state[5] is presented as supplementary evidence that even the ionized state is associated with a strongly localized wave function ψ, since the Fermi contact term, directly proportional to $|\Psi_0|^2$ where ψ_0 is the wave function on the donor site, is not small as it should be for a shallow donor state. However, there are cases (such as Ge) in which the existing donor states are not detected by EPR; there are also cases in which a shallow donor state gives rise to a hyperfine interaction characterized by a value of the Fermi contact term (As in Si, for instance) considerably larger than expected for a shallow effective-mass state.[6] Moreover, it has not been demonstrated that the Sn-related EPR spectrum is due to the DX center and not a defect complex involving Sn.

Thus, there is not yet any direct experimental evidence that the DX ground state is a strongly localized D^- state. On the contrary, the only experimental evidence is for the existence of a very shallow D^- state[7,8] which is not related to the DX ground state. The aim of this paper is to propose three different tests and their results, already published, which provide unambiguously the charge state of the DX center. They are based on (i) the magnitude of the electron-capture cross section, (ii) the sensitivity of electron emission to an electric field, and (iii) the electron-scattering properties of the ground state and the ionized state of this center, respectively.

According to Ref. 2 the ground state of the DX center is a D^- state which exhibits negative U behavior. This means that the ionization of this state, to form a D^+ state, is characterized by the emission of the first electron, since the second one is emitted with a faster rate (this is due to the fact that, first, the energy level associated with the D^--D^0 transition is deeper than that of the D^0-D^+ transition and, second, the cross section for electron trapping on a positive center is larger than that on a neutral one). On the contrary, the capture of electrons on the D^+ state to form the D^- state is limited by the capture of the second electron whose cross section is smaller. Consequently, if the DX center is a negative U state, the capture and emission processes observed correspond to the D^--D^0 transition.

We first consider the electron-capture process. As already mentioned, the magnitude of the associated cross section σ obviously depends on the potential induced by the ionized defect. For instance, for a simple shallow donor, the Coulomb attraction between the D^+ state and the electron lead to a giant cross section which is known to be of the order of 10^{-12}–10^{-14} cm^{+2}.[9] For a neutral state σ is, of course, considerably smaller. As for the cross section for electron capture on DX centers, it has been carefully studied and it is now well accepted[10] that it can be written as

$$\sigma=\sigma_0 \exp\left[\frac{-B}{kT}\right],$$

where the associated capture barrier B varies with the alloy composition x. It is often argued that the existence of this barrier is a consequence of a large electron-phonon interaction, the capture occurring then through a multiphonon emission process. However, this cannot justify why B varies versus x, like the difference between the bottom of the conduction band (L or X) and the L band.[10] On the contrary, if one assumes that the electron must first reach the L band in order to recombine on the DX center,[11] then the variation of B versus x is fully justified and the capture cross section is σ_0. The magnitude of σ_0, which is reported (see, for instance, Fig. 1), is in agreement with the capture cross section of a simple shallow donor. This, therefore, indicates that the DX ionized state is, as for a donor, positively charged and that the transition involved in the capture is the D^+-D^0 one. The reason why an electron must reach the L band in order to get captured on the DX center is simple: the recombination occurs *via* the excited states of the L band (through the so-called cascade mechanism) because the excited

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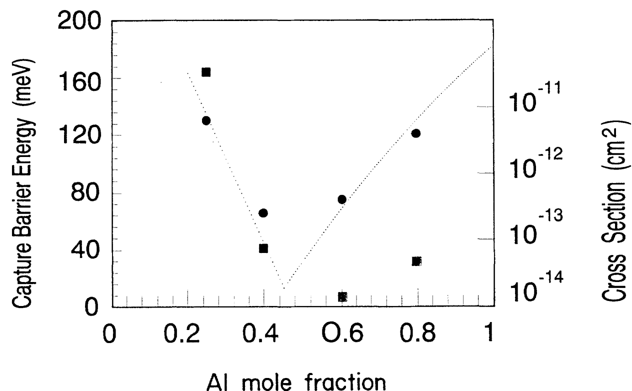

FIG. 1. Variation of the capture barrier B (●) and cross section σ_0 (■) vs the alloy composition x for the DX center in Te-doped liquid-phase-epitaxy $Ga_{1-x}Al_xAs$.

states at the bottom of the conduction band cannot be filled at the temperature (100–200 K) at which the capture is monitored.[12]

Su and Farmer[13] argue that, when one considers the complete transient capture regime, the experimental data are only consistent with a process involving the capture of two electrons *via* an intermediary state. They say that the kinetics for a one-electron capture model cannot describe the complete capture transient. Unfortunately, they do not take into account in the kinetics equation that the free-electron concentration n_c is equal to (or at least of the same order of magnitude as) the DX concentration N_i. This implies[14] that n_c cannot be considered as constant during the capture process: it varies as $n_c(t)=N_i-n_i(t)$ where n_i is the concentration of the trapped electrons. Consequently, in the kinetics equation, dn_i/dt is proportional to $(N_i-n_i)^2$ and not to N_i-n_i.[14] In order to distinguish between a one-electron or a two-electron capture, one has to be in the condition $n_i(t)$ small so that n_c can be considered as constant, i.e., at the beginning of the capture transient. When this is done[15] it clearly appears that dn_i/dt is proportional to n_c and not to n_c^2.

We now come to the question of the enhancement of the electron emission rate induced by the electric field. For deep defects electron emission is not sensitive to the electric field, at least when the field is below a critical value above which phonon-assisted tunneling emission can take place.[16] Electron emission from the DX center is field sensitive as noted by several authors.[17–19] All the data which have been published so far, and in particular the detailed study recently presented,[20] find a variation of the emission rate versus the magnitude of the field and temperature. It is clearly demonstrated that this variation is not a consequence of a phonon-assisted tunneling process but is due to a Poole-Frenkel effect. Such an effect implying the existence of an attractive potential between the ionized state and the electron means again that the emission process observed corresponds to the D^0-D^+ transition, i.e., that the ionized state is D^+ and, consequently, that the ground state is D^0. Of course, a two-electron emission process could also exhibit a Poole-Frenkel behavior. However, the slope of the linear variation of the ionization energy versus the square root of the electric field (2.3×10^{-4} eV $V^{-1/2}cm^{1/2}$) is practically equal to the theoretical value (2.15×10^{-4} eV $V^{-1/2}cm^{1/2}$) assuming a one-electron transition. For a two-electron transition this slope should be two times higher, i.e., beyond experimental accuracy.

Finally, electron scattering is another way to probe the charge state of a defect: electron mobility at low temperature possesses a temperature dependence which depends directly on the nature of the scattering potential, i.e., on the defect charge state. Many studies of electron mobility have been undertaken,[21–26] but they lead to contradictory results and interpretations because the studied materials contain, in addition to DX centers, other defects whose contributions cannot be neglected.[27] Thus, the way to probe the scattering is to use another phenomenon, involving electrons of a two-dimensional (2D) layer in a pure material (GaAs) adjacent to the ($Ga_{1-x}Al_xAs$) layer containing the DX centers. Obviously, if the DX centers are neutral, i.e., characterized by a short-range potential, they will not play a role on the scattering process in this 2D layer; on the contrary, if they are charged, the electrons in the 2D layer will be sensitive to the long-range Coulomb potential of the DX centers located in the vicinity of the interface. The electron mobility cannot be expected to be sensitive enough to detect a change due to a change of the DX charge state (induced by photoionization), because only a small fraction of DX centers close to the interface, within the potential range, act as scattering centers. But electron transport effects involving quantum phase coherence, such as universal conductance fluctuations in diffusive mesoscopic systems, can be used because of the sensitivity of the conductance to the existence of single scatterers. Such measurements have been performed recently:[28] a change in the elastic-scattering configuration is detected after the DX centers have been ionized through conductance fluctuations of a two-dimensional electron gas adjacent to a $Ga_{1-x}Al_xAs$ layer. This experiment demonstrates that photoionization of a DX center is equivalent to adding one elastic scatterer. This therefore implies that photoionized DX centers are charged while the DX ground state is neutral. Since photoionizing the DX center results in electron emission in the conduction band, this means that the DX ground state is D^0 and not D^-.

In conclusion, we have discussed three pieces of direct experimental evidence indicating that the DX ground state is a neutral state and not, as commonly accepted, a negatively charged state.

We thank P. Debray (Orme des Merisiers, Gif-sur-Yvette, France) for introducing us to the question of conductance in mesoscopic systems. This work was supported by a European Economic Community Basic Research contract (No. 3168).

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