

## Negative Charge State of the $DX$ Center in $Al_xGa_{1-x}As:Si$

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We present experimental data for the thermally activated capture of electrons on Si-induced impurity states in  $Al_xGa_{1-x}As$  in the strong-lattice-relaxation regime ( $DX$  centers). Experiments have been performed after photoionization in the region of transition from the normal to the metastable state of the defect, using hydrostatic pressure up to 8 kbar. An analysis of the isothermal as well as the thermally stimulated capture kinetics strongly supports the hypothesis of the negative charge state of the  $DX$  center.

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The  $DX$  centers associated with  $n$ -type substitutional impurities in many III-V semiconductors constitute a class of defects characterized by the dominant role of the lattice relaxation in capture and emission transitions.<sup>1</sup> It has been recognized that the substitutional impurity is, in itself, responsible for the existence of the defect. In spite of this apparent structural simplicity, and of the general nature of the defect, no definitive model for its description has been proposed to date. A point of particular controversy is the charge of the defect in the ground state: Is it neutral ( $DX^0$ ) or negatively charged ( $DX^-$ )?<sup>2-7</sup>

Chadi and Chang's<sup>2</sup> pseudopotential calculations for substitutional donors in GaAs described a metastable resonant state associated with a large lattice relaxation. In the same work, they predicted that  $DX$  is a negatively charged center with a negative Hubbard correlation energy; i.e., in its ground state it binds two electrons. The lack of an EPR signal has been advanced as a confirmation of the negative- $U$  character of substitutional donors in Al-Ga-As and Zn-Cd-Te by Khachatryan, Weber, and Kaminska.<sup>3</sup> These authors also used the arguments of Toyozawa's self-trapping theory and Anderson's theory of the electron pairing due to strong lattice relaxation (see Ref. 3) to show that the centers showing self-trapping and persistent photoconductivity are expected to possess a negative- $U$  character. Various attempts were made to discriminate between the  $DX^0$  and the  $DX^-$  model by interpreting mobility,<sup>4</sup> Hall density,<sup>5</sup> or capture<sup>6</sup> results, without conclusive success until now. In a recent paper, Khachatryan *et al.*<sup>7</sup> showed that the  $DX$  centers are paramagnetic and concluded from their measurements that the ground state of the defect is neutral ( $DX^0$ ). Recently, Katsumoto *et al.*<sup>8</sup> carried out similar experiments in Te-doped  $Al_xGa_{1-x}As$  and found that the amount of paramagnetism was significantly less than that claimed by Khachatryan *et al.*<sup>7</sup> In addition, Fockele, Spaeth, and Gibart<sup>9</sup> presented magneto-optical and optically detected magnetic-resonance

data in Sn-doped  $Al_xGa_{1-x}As$ , giving evidence for the existence of a paramagnetic singly ionized state  $Sn^0$  which implies a negative ground state  $DX^-$ . To discriminate between the  $DX^0$  and  $DX^-$  hypotheses, we study the thermally activated capture of electrons on Si-impurity states.

The samples investigated were Si-doped  $Al_xGa_{1-x}As$  layers, grown in a dedicated molecular-beam-epitaxy (MBE) setup used for industrial production of Si-doped material. All sources are 99.9999%-purity grade. This precludes the possibility for other  $DX$ -like levels originating from other species. The active layer is separated from the semi-insulating GaAs substrate by a large undoped spacer to avoid any 2D effects. The Al mole fraction  $x$  ( $x=0.28$  for sample 1 and  $0.33$  for sample 2) was checked by double x-ray diffraction. The effective doping density  $N_D - N_A$  was checked at 300 K by the  $C-V$  method using a Polaron profiler. Its value amounts to  $3.0 \times 10^{18} \text{ cm}^{-3}$  for sample 1 and  $1.2 \times 10^{18} \text{ cm}^{-3}$  for sample 2. A helium-gas compressor allowed us to perform temperature rampings at constant pressure.

The experimental procedure is the following: The high-pressure cell containing the sample is cooled down to 4.2, 65, or 77 K. The carrier density, as measured by the Hall effect, first decreases from the room-temperature value, and stabilizes as soon as the metastability temperature is attained. The same behavior is observed when the sample is cooled down under pressure, though with a lower value for the metastable carrier density. This proves that the remaining carriers do not originate from another hypothetical shallow ( $\Gamma$ -bound) impurity.<sup>10</sup> Once the lowest temperature has been attained, the sample is illuminated with a light-emitting diode (LED). At 4.2 K, the carrier density increases rapidly up to the value of the effective doping density  $N_D - N_A$ . At 65 or 77 K, the steady-state Hall concentration under illumination is slightly lower than  $N_D - N_A$ . It decreases as the applied pressure increases, but it is independent of the illumination. This effect can be

related to the trapping on the lowest shallow (hydrogenic) level.<sup>11</sup> This leads to a thermal energy  $E_H - E_\Gamma \approx 105$  meV for the  $x=0.28$  samples and 55 meV for the  $x=0.33$  samples at zero pressure, together with a pressure shift of  $-11 \pm 1$  meV/kbar. These values are consistent with those reported by several authors.<sup>11</sup> After switching the LED off at 4.2 K, no change is observed in the free-carrier density over very long periods of time. However, at 65 or 77 K, the carrier density shows a strongly nonexponential decay (Fig. 1).

The capture kinetics on the relaxed ground state depends on its charge state. If the ground state localizes two electrons, the transition  $D^+ + 2e^- \rightarrow DX^-$  most likely occurs through an intermediate excited  $D^{*0}$  state.<sup>6</sup> The capture into the  $DX$  center can then be represented by the Shockley-Read equation

$$dn_{DX^-}/dt = a_n e^\eta n_{D^+}^0 - e_n n_{DX^-}, \quad (1)$$

in which  $\eta = (E_F - E_\Gamma)/kT$ ,  $E_F$  being a quasi-Fermi level which describes the equilibrium between the conduction band and the unrelaxed excited levels. The activation terms originating from the barrier for capture and emission are hidden in the factors  $a_n$  and  $e_n$ .

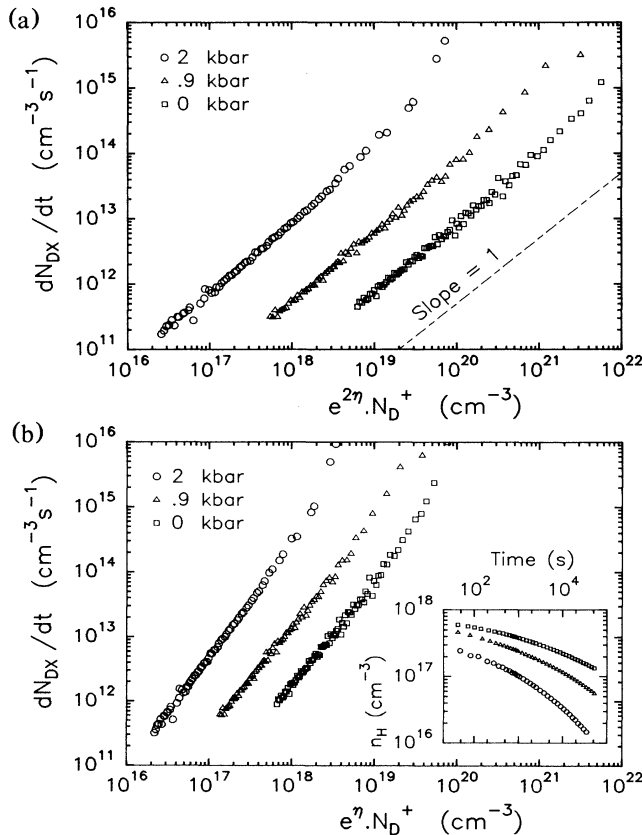


FIG. 1.  $dN_{DX}/dt$  calculated point by point from isothermal capture Hall data [inset in (b)] at 77 K for sample 2 ( $x=0.33$ ): (a) assuming  $DX$  is negatively charged [cf. Eq. (3)]; (b) assuming  $DX$  is neutral [cf. Eq. (4)].

In the model of Chadi and Chang,<sup>2</sup> the excited intermediate state does not give rise to an important lattice distortion. It can thus be considered to be in thermodynamical equilibrium with the conduction band at temperatures where the disappearance of the persistent photoconductivity occurs in a finite time. The concentration  $n_{D^+}^0$  of donor atoms in the intermediate state  $D^{*0}$  is thus related to  $\eta$  and  $N_D^+$  by standard statistical considerations:

$$n_{D^+}^0 = g_0 N_D^+ e^\eta \exp[-(E_{D^+} - E_\Gamma)/kT]. \quad (2)$$

Neglecting for the moment the reemission from the  $DX$  state, Eq. (1) can then be formally rearranged as

$$dn_{DX^-}/dt = a_n' e^{2\eta} N_D^+. \quad (3)$$

For a neutral ground state, the capture equation is

$$dn_{DX^0}/dt = a_n'' e^\eta N_D^+. \quad (4)$$

In the case of capture through an intermediate excited state  $D^{*0}$ , it reads

$$dn_{DX^0}/dt = a_n''' N_{D^+}^0, \quad (5)$$

which reduces to Eq. (4) by applying Eq. (2). Equations (3) and (4) are analogous to a mass action law for the reaction  $D^+ + 2e^- \rightarrow DX^-$  or  $D^+ + e^- \rightarrow DX^0$ .

Several reasons make it impossible to integrate Eq. (3) or (4) analytically: the degeneracy of the conduction band, the possibility of compensation by acceptor impurities, in concentration  $N_A$ , and the ubiquity of the Si-induced defect which gives rise to shallow as well as deep ( $DX$ ) levels.<sup>11</sup> However, one can see from Eqs. (3) and (4) that the capture rate has essentially an  $e^{2\eta}$  dependence in the  $DX^-$  case ( $N_D^+$  can at most vary between  $N_D$  and  $N_D/2$  in this case), whereas it may have either an  $e^{2\eta}$  dependence (for  $n \gg N_A$ ) or an  $e^\eta$  dependence (for  $n \ll N_A$ ) in the  $DX^0$  case. Thus, this dependence can be used to discriminate between the negative and the neutral charge states of the  $DX$  center, provided one has enough information about the acceptor compensation rate.

This information is given by the analysis of the Arrhenius plot of the free-electron density.<sup>12</sup> Indeed, neutral donors partly compensated by acceptor impurities at sufficiently low temperature (such that  $n < N_A$ ), as well as donors with negative  $U$ , give rise to an activated free-electron density with an activation energy equal to the ionization enthalpy  $E_T$ . In addition, for neutral donors only, the activated electron density will behave as  $\exp(E_T/2kT)$  at intermediate temperatures, if the condition  $N_D \gg n > N_A$  is fulfilled.

An Arrhenius plot of the free-carrier density in sample 2 was presented in Ref. 13. It shows a well-defined single slope from  $n > 10^{17}$   $\text{cm}^{-3}$  down to  $n \approx 2 \times 10^{13}$   $\text{cm}^{-3}$ . Thus, if  $DX$  centers are assumed to be neutral, the residual compensation  $N_A$  must be either larger than  $10^{17}$   $\text{cm}^{-3}$  or lower than  $2 \times 10^{13}$   $\text{cm}^{-3}$ . This latter

value is much lower than the residual carbon concentration (a few  $10^{15} \text{ cm}^{-3}$ ), which originates from the graphite heater and is mainly responsible for the  $p$ -type unintentionally doped MBE layers grown in the same conditions. The probability for these carbon atoms to be exactly matched (within  $2 \times 10^{13} \text{ cm}^{-3}$ ) by a further shallow or resonant donor is far too low to be seriously invoked. Therefore, the only logical possibility left open by the activated behavior of the free-carrier density is that if the ground state is neutral, then  $N_A$  is larger than  $10^{17} \text{ cm}^{-3}$ . Thus, the mechanism of capture *must* have an  $e^\eta$  dependence if the  $DX$  ground state is neutral.

The following differential approach can thus be used to test the  $e^\eta$  or  $e^{2\eta}$  dependence of the capture rate. At any time, the quasi-Fermi-level position can be obtained from the instantaneous experimental free-carrier concentration. One can then access the concentration of frozen donors  $n_{DX}$  and of ionized donors  $N_D^+$  by resolving simultaneously the electroneutrality equation and the species conservation equation. In the latter equation, one has to include the number of centers  $n_H^0$  trapping an electron on the lowest excited level, which is related to  $E_F$  and  $N_D^+$  by a relation similar to Eq. (2). Finally, the  $n_{DX}(t)$  resulting from the above procedure are differentiated with respect to time.

The resulting  $n_{DX}/dt$  is plotted in Fig. 1(a) for sample 2 at different pressures as a function of  $e^{2\eta}N_D^+$  [cf. Eq. (3)]. The logarithmic slope is approximately 1 over almost 4 decades. On the other hand, the same procedure under the neutral-donor assumption ( $dn_{DX}/dt$  vs  $e^\eta N_D^+$ ) leads to a slope roughly equal to 2 [Fig. 1(b)]. This latter plot was obtained by using a compensation value  $N_A = 10^{17} \text{ cm}^{-3}$  compatible with the condition previously established. Therefore, the  $e^{2\eta}$  behavior of the capture kinetics clearly demonstrates that electron capture on  $DX$  centers involves a two-electron process.

In order to access the capture barrier height, as well as its pressure and composition variations, we performed thermostimulated capture experiments after photoionization at 65 K using well-controlled constant-temperature sweep rates (typically 1 K/min). For a quantitative analysis, one needs to explicitly define the coefficient  $a_n'$  in Eq. (3).

From general statistical considerations, the population of the negative  $DX$  center at equilibrium is related to the concentration of empty donors by<sup>12</sup>

$$n_{DX}^- = g_{DX} N_D^+ e^{2\eta} \exp[-(\mathcal{E}_{DX} - 2E_\Gamma)/kT]. \quad (6)$$

Here, the energies  $\mathcal{E}_i$  refer to a two-electron system. The emission coefficient  $e_n$  is

$$e_n = A_n \exp[-(\mathcal{E}_B - \mathcal{E}_{DX})/kT]. \quad (7)$$

$\mathcal{E}_{DX}$  is the thermal energy of the relaxed  $DX^-$  center with two bound electrons, and  $\mathcal{E}_B$  is the energy of the saddle point between the relaxed and the unrelaxed state, such as that appearing in a configuration diagram.<sup>6</sup>  $A_n$

may show a slight temperature dependence, but is not thermally activated. The preceding equations, combined with the kinetics equations (1)–(3) in the case of thermal equilibrium, lead to the expression of the *observed* capture coefficient  $a_n'$ :

$$a_n' = g_{DX} A_n \exp[-(\mathcal{E}_B - 2E_\Gamma)/kT]. \quad (8)$$

Thus, the activation energy for capture depends only on the energy of the saddle point.

The procedure used for the isothermal free-carrier decay can then be applied to the thermostimulated  $n(T)$  data for both samples 1 and 2 to get an Arrhenius plot of  $(T^2 e^{2\eta} N_D^+)^{-1} dN_{DX}^-/dt$ , as shown in Fig. 2. Here, the justification of the  $T^{-2}$  prefactor is to permit a comparison of the present results with available deep-level transient spectroscopy and capture data. We neglect in this discussion possible saturation effects of the multiphonon-emission mechanism.<sup>1</sup> This is justified by the nonoccurrence of trapping at 4.2 K within a finite time. The results from Fig. 2 are consistent with the assumption of a negatively charged donor, and are also in agreement with data of other authors. Indeed, the same preexponential factor,  $10^{7.5 \pm 1} \text{ s}^{-1} \text{ K}^{-2}$ , is found at each pressure and for both samples. This value compares well with values from Ref. 14. The capture activation energies, 420 meV for sample 1 and 290 meV for sample 2, fit the values reported by Mooney *et al.*<sup>15</sup> in the 0.22–0.35 composition range. These authors found that the capture barrier height decreases by  $-230$  meV for an Al-mole-fraction increase of 0.10 in the direct-band-gap region. This value is almost twice as large as the direct-

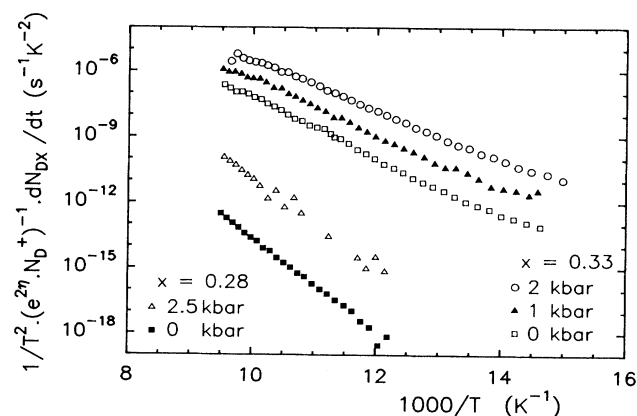


FIG. 2. Arrhenius plot of  $(e^{2\eta} N_D^+)^{-1} dN_{DX}^-/dt$  [cf. Eqs. (3) and (8)] in the region where the reemission from the  $DX$  centers is negligible. Depending on the pressure, the free-carrier concentration decreases from a value close to  $N_D - N_A$  at the beginning of the thermostimulated transient, to  $5 \times 10^{17}$ – $1.4 \times 10^{18} \text{ cm}^{-3}$  (sample 1) or  $2 \times 10^{15}$ – $5 \times 10^{16} \text{ cm}^{-3}$  (sample 2) at  $T \approx 100$  K. The curves for  $x = 0.28$ ,  $p = 6$  kbar (8 kbar) superimpose on those for  $x = 0.33$ ,  $p = 0$  kbar (2 kbar) and thus are not presented.

band-gap variation, and remained unexplained until now. However, it becomes quite natural if the final trapped state is a bound electron pair. The same holds for the pressure coefficient for the capture barrier height, which amounts to  $-17 \pm 1.5$  meV/kbar. This value can be derived either directly from Fig. 2 or from the pressure-induced shift of the capture rate in Fig. 1(a).

Thus, both isothermal as well as capture kinetics are consistent with a negatively charged ground state of Si donors in Al-Ga-As, but they are hard to reconcile with a neutral ground state.

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*Note added.*—Very recently, Dobaczewski and Kaczor<sup>16</sup> deduced from the analysis of photoionization measurements in AlGaAs:Te the conclusion that the ground state of the DX center should be negatively charged. Their method relies on the fitting of transient signals using a set of coupled nonlinear differential equations, under different experimental conditions.

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