

Inverted order of acceptor and donor levels of the Si-related DX center in $Al_xGa_{1-x}As$

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We have demonstrated the inverted ordering of the acceptor level ($-/0$) and the donor level ($0/+$) of the Si-related DX center in $Al_xGa_{1-x}As$ by photoemission deep-level transient spectroscopy (DLTS). The new photoinduced DLTS peak has been observed at low temperature (60 K) in $Al_{0.26}Ga_{0.74}As$ and at high temperature (140 K) in $Al_{0.35}Ga_{0.65}As$. Activation energies for emission and capture for acceptor level and metastable donor level have been determined in both samples with different AlAs mole fractions. The observation of this metastable level of the DX center proves the inverted ordering of the energy levels that reveals an effective negative correlation energy (negative U) with the existence of a thermodynamically unstable DX^0 state. [S0163-1829(97)02107-3]

An impurity or any other simple point defect in a semiconductor can introduce several stable charged states depending on the position of the Fermi level. A typical defect can be in either positive, neutral, or negative charge states and accordingly two electrical levels, an acceptor level and a donor level, can exist inside the band gap of the semiconductor. The acceptor level is expected to be above the donor level because the second electron experiences a repulsion due to Coulomb interaction with the first electron. This Coulomb repulsion energy is defined as U Hubbard correlation energy,^{1,2} and is the difference between donor and acceptor levels. In the case of positive U , ordering of levels mean that each of the three charge states are thermodynamically stable depending on the position of the Fermi level. Hence the donor and acceptor levels can be determined either by Hall or deep-level transient spectroscopy (DLTS). But negative- U properties for a defect mean that the energy levels due to defect in semiconductor are inverted from their usual order, with the acceptor level below the donor level. In this case neutral charge state is no longer a thermodynamically stable charge state. Two simple point defects, in crystalline silicon (interstitial boron and lattice vacancy) have been confirmed experimentally³⁻⁵ and theoretically⁶ to have negative- U properties. Recently it has been suggested that the DX center in GaAs and $Al_xGa_{1-x}As$ might have negative- U properties using *ab initio* self-consistent pseudopotential total-energy calculations.⁷⁻¹¹ According to this model, DX center traps two electrons with the second bound more strongly than the first and the ground state should be negatively charged (DX^-) and the whole system should possess negative Hubbard correlation energy. Hence the capture process will be $d^+ + e^- \rightarrow DX^0 + e^- \rightarrow DX^-$, where d represents the normal fourfold-coordinated donor and DX represents the broken bond configuration of the donor. In this system, the intermediate donor state (DX^0) is thermodynamically unstable. Recently it has been shown¹⁰ that DX^0 is a localized metastable donor state that arises from a symmetric antibonding combination of the impurity sp^3 orbitals with the corresponding

orbitals of its four nearest-neighbor atoms. DX^0 is not an effective-mass-like state of the substitutional donor.

Recently we have shown that there are two energy levels with inverted ordering in the band gap, an acceptor level ($DX^- \rightarrow DX^0 + e^-$), and a donor level ($DX^0 \rightarrow DX^+ + e^-$) of silicon-related DX center in $Al_{0.26}Ga_{0.74}As$ by photoemission DLTS (Ref. 12) and transient photoconductivity.¹³ Li *et al.*¹⁴ have raised the question regarding the interpretation of our experimental results with a not yet fully resolved issue. In this paper we clarify the points raised by Li *et al.* Finally, we present our recent experimental results as corroboration of our arguments and our interpretation of the experimental results. This work completes the preliminary results published earlier.¹²

Regarding the objection raised by Li *et al.*, we like to argue that there is large-scale controversy regarding the capture cross-section parameter of the DX center. In literature, there is very wide scattering in the values of the capture cross section and the capture activation energy. For example, capture activation energy varies from 250 to 340 meV for $x=0.30$.^{15,16} There are two reasons behind this scattering. First, the capture kinetics of the DX center is heavily nonexponential and the conventional pulse-filling DLTS technique for determination of the capture cross section always assumes exponential capture and emission kinetics of the deep centers. Second, it is a well-known fact that there is a large capture barrier for the DX center. So it is very difficult to find out the saturations of DLTS peak height with filling pulse width that is needed for calculating the capture cross section and hence capture cross-section activation energy. These two facts introduce a considerable amount of error in determining capture cross section by the conventional method. We have measured¹⁷ the capture activation energy directly by a deep-level spectroscopic technique and found that the capture barrier is distributed over 50 meV. Incidentally, it is clearly shown that the optical ionization of the Si-related DX center in $Al_xGa_{1-x}As$ is composed of two components; the first one is a ‘fast’ component which is followed by a second ‘slow’ component.^{18,19} We have also

found both in capacitance transient during capture¹⁷ and decay of persistent photoconductivity²⁰ that capture transient is composed of two components, an initial component characterized with “fast” decay, followed by a “slow” decay. Most of the measurements of capture cross section were done on this slow part of the transient. There are few attempts^{16,21} to determine the capture cross section separately from the fast decay part and the slow decay part. Zhou *et al.*¹⁶ have observed that the capture cross section determined from the fast and slow part differ by two to three orders of magnitude. We have also observed²² the difference can vary sometimes by four to five orders of magnitude. So we strongly argue that capture cross section (10^{-30} cm²) at 77 K is heavily underestimated, which is quoted in Ref. 14. We have seen capture cross section at 60 K from the fast decay part is around 10^{-25} cm² and 10^{-28} cm² from the slow part. We believe that capture of the *DX* center at low temperature (50–80 K) is coming from the fast decay part and to enhance the capture at low temperature we have sometimes used a pulse of infrared light during the filling pulse in DLTS. To observe a DLTS peak it is of course not necessary for all of the *DX* center to capture electrons. In our DLTS system we can detect a DLTS signal even when $N_T/N_D \sim 10^{-5}$, where N_T is the concentration of electron traps and N_D the concentration of donors.

The *DX* center in negative charge state (DX^-) cannot ionize at low temperature ($E_i \sim 460$ meV) to observe the emission from the DX^0 state ($E_i \sim 210$ – 280 meV). At high temperature when DX^- can ionize to the DX^0 state, due to the metastable nature of DX^0 it immediately ionized to a d^+ state, so the limiting process is the first electron emission and one can only observe the acceptor level at 460 meV, which will be elaborated in the following discussion. Finally, we present our recent studies regarding the photoinduced DLTS peak in another AlAs mole fraction ($x=0.35$). In this respect, we like to point out that the whole objection raised by Li *et al.*,¹⁴ against our interpretation of the photoinduced DLTS peak is not valid in this case, because a new photoinduced DLTS peak has been observed at relatively higher temperature (140 K).

The $Al_xGa_{1-x}As$ ($x=0.26, 0.35$) samples in our study were grown by molecular-beam epitaxy (MBE). The active $Al_xGa_{1-x}As$ layer is separated from the semi-insulating substrate by an undoped spacer layer. The samples are doped with silicon, with 10^{18} – 10^{17} cm⁻³ concentration. Doping concentration was found by the capacitance-voltage method and secondary ion mass spectroscopy (SIMS). We have not detected any other donor species above the detection limit of SIMS. In some samples oxygen and carbon concentration were high. We have selected the samples with minimum concentration of oxygen and carbon. Schottky contact was made by evaporating silver and Ohmic contact by Au-Ge alloys. The DLTS system uses a Boonton 72B capacitance meter and double boxcar window scheme. For photoinduced DLTS a 600 W quartz halogen lamp with a quartz focusing lens and an interference filter were used as a monochromatic excitation for 1.38, 1.23, and 1.13 eV light. At low temperature to enhance the capture of electrons from the conduction band, we have used a pulse of infrared light (0.5–0.7 eV) during filling pulse in DLTS. The temperature was scanned from 10 to 300 K using a closed-cycle helium refrigerator.

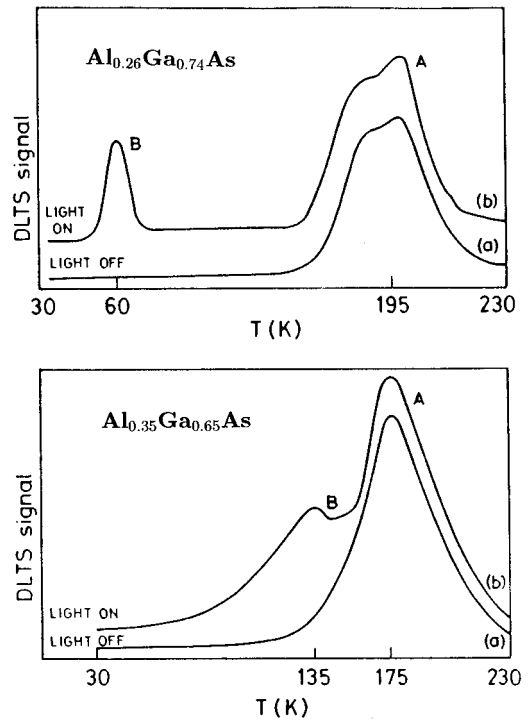


FIG. 1. DLTS spectra of the Si-related *DX* center in $Al_xGa_{1-x}As$ in (a) dark and (b) illuminated with 1.38 eV light for two AlAs mole fractions ($x=0.26, 0.35$). Note that peak B is seen only in the presence of light. Both spectra are taken with a time constant of 70.8 ms.

The DLTS measurements carried out in the dark showed typical double peak at about 200 K labeled as A in Fig. 1 for $x=0.26$ and 0.35. The position and shape of the peak are typical of the *DX* center related to silicon in $Al_xGa_{1-x}As$. This peak has a thermal activation energy of 460 meV for all x values and a capture barrier of 350 meV for $x=0.26$, 260 meV for $x=0.35$. The DLTS experiment was repeated in the presence of intense 1.38 eV light during emission of electrons to the conduction band. The photoinduced DLTS experiment was repeated with 1.23 and 1.13 eV light also. A majority carrier peak was seen at about 60 K for $x=0.26$, and at about 140 K for $x=0.35$ and labeled B in Fig. 1. Thermal activation energies of 210 meV for $x=0.26$ and 280 meV for $x=0.35$ were obtained for a photoinduced peak. Arrhenius plots are given in Figs. 2 and 3. Capture barrier of 150 meV for the $x=0.26$ sample and 180 meV for the $x=0.35$ sample were obtained.²³ We have observed neither peak A nor the photoinduced peak B in undoped $Al_xGa_{1-x}As$ with the same AlAs mole fractions grown by the same MBE machine. We have also observed the photoinduced peak B in MBE-grown Si-doped $Al_xGa_{1-x}As$ from different sources.

For a normal type of point defect with positive correlation energy (positive U), one should observe an acceptor level ($-/0$) at low temperature followed by a donor level ($0/+$) at relatively high temperature in DLTS spectra during emission of electrons. In the case of a point defect with negative correlation energy (negative U), the situation is opposite and in this case one should observe the donor level ($0/+$) at low temperature and the acceptor level ($-/0$) at high temperature. But, to observe the donor level we have to have transition

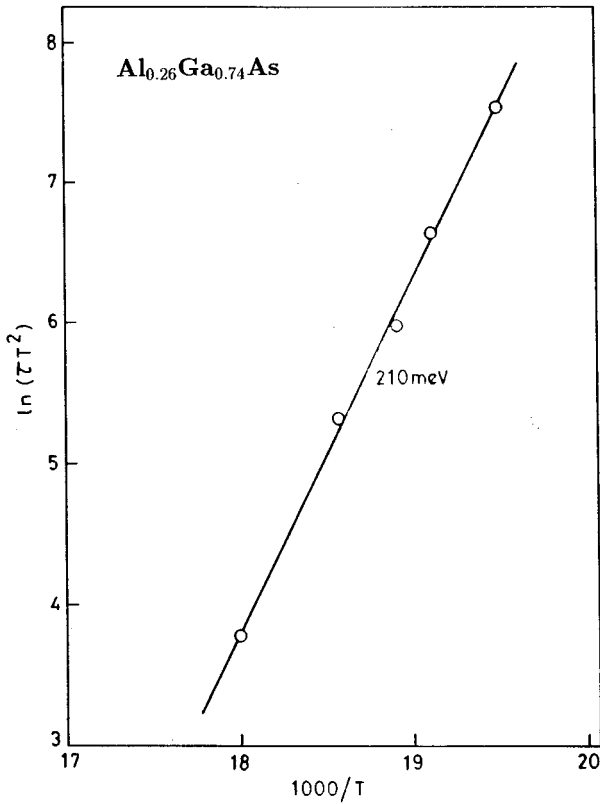


FIG. 2. Arrhenius plot of the photoinduced peak for the DX center in $\text{Al}_{0.26}\text{Ga}_{0.74}\text{As}$.

from the ground state (DX^-) to the neutral state (DX^0), which is not possible at low temperature, because the emission activation energy for the acceptor level is more than that for the donor level in the case of the negative- U system. So one should observe only the acceptor level at relatively high temperature in the case of the negative- U system. Now let us consider why only one level with an emission energy of 460 meV is observed in normal DLTS and why the level with an emission energy of 210 meV (or 280 meV) is observed in photoinduced DLTS, but not in dark DLTS spectra. This apparent contradiction can be explained if the level with thermal activation energy, 460 meV (peak A), is an acceptor level ($DX^- \rightarrow DX^0 + e^-$) in the inverted negative- U ordering below the new donor level ($DX^0 \rightarrow d^+ + e^-$), with the thermal activation energy 210 or 280 meV (peak B). In normal DLTS, the observed peak is due to the emission of electrons from the DX^- state, i.e., $DX^- - e^- \rightarrow DX^0$ transition, quickly followed by the second electron emission $DX^0 - e^- \rightarrow d^+$, since the DX^0 state is thermodynamically unstable. For the negative- U defect, the electron involved in the first ionization is bound more strongly than the second electron. As the deeper (460 meV) DX^- states cannot emit electrons at the low temperature required to observe the DX^0 donor-level emission, these negatively charged centers are essentially removed from the experiment. Effectively, the limiting process is the first electron emission. With repetitive pulses by DLTS, all the centers rapidly accumulate in the negatively charged (DX^-) state, leaving none in the neutral state (DX^0) to be observed. Hence peak B was not observed in the normal DLTS experiment. Now, to observe the donor level (0/+), we have to have emission from the metastable

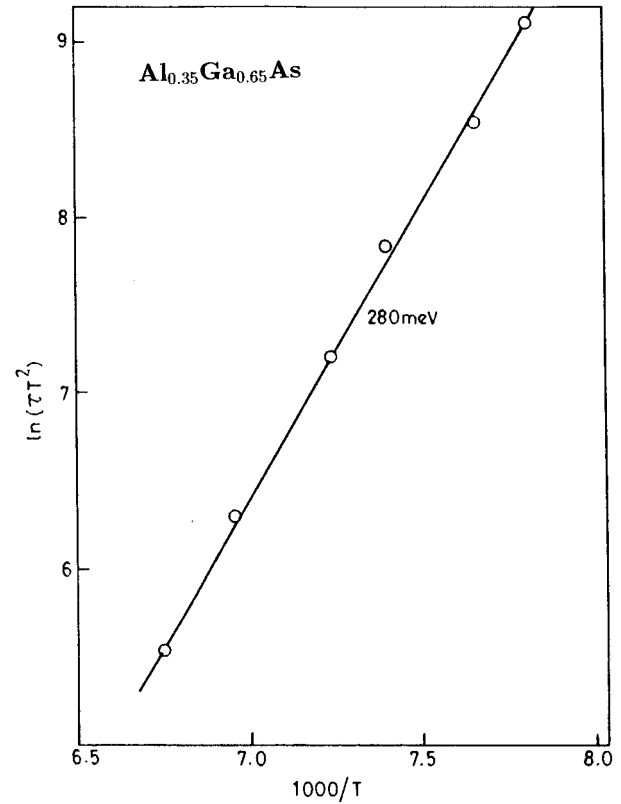


FIG. 3. Arrhenius plot of the photoinduced peak for the DX center in $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$.

state DX^0 . This difficulty of observing the DX^0 state is overcome by simultaneously illuminating the sample with subband-gap light to photoionize the DX^- . Essentially, we have created the DX^0 state from the DX^- state and monitored the thermal emission of the donor level (0/+): Hence, during each trap-filling pulse, the d^+ state captures two electrons in the DX^- state and the subsequent emission proceeds by $DX^- \rightarrow DX^0 + e^- \rightarrow d^+ + 2e^-$.

The choice of light is determined by two factors: first, it should be more than the optical threshold for optical ionization of DX center and second any communication between the valence band and DX^- or DX^0 has to be avoided. The photoionization of DX^- to DX^0 can be adjusted by varying the light intensity. To observe and monitor the thermal emission from the DX^0 state the light intensity has been adjusted such that the photoionization rate is two to three orders of magnitude less than the thermal emission rate. We have adjusted the trap filling pulse to make sure that the maximum number of DX centers are in the positive charge state before the next trap-filling pulse. But after each trap-filling pulse, a few DX centers might be in the neutral charge (DX^0) state and most of the DX centers are in the negative charge (DX^-) state. As the DX^0 state is thermodynamically unstable, the DX^0 state to d^+ state transition takes place very "fast." Although the DX^0 state is a metastable state, it takes place in all capture and emission processes. Hence all capture and emission processes will have this fast component. Our observation²² shows that the fast and slow components are correlated and coming from the same center in contradiction with the observation in Ref. 18.

The intensity of peak *B* gradually increases with the light intensity and saturates at a height where the intensity is half that of peak *A* (Fig. 1). This proves that two electrons are emitted in the high-temperature emission process, whereas single-electron emission gives rise to peak *B*.⁵ The thermal ionization energy of peak *A* (acceptor level) is 110 meV for the $x=0.26$ and 200 meV for the $x=0.35$ sample. The thermal ionization energy of peak *B* (donor level) is 60 meV for the $x=0.26$ and 100 meV for the $x=0.35$ sample. Hence, the negative correlation energy for the Si-related *DX* center becomes 50 meV for $\text{Al}_{0.26}\text{Ga}_{0.74}\text{As}$ and 100 meV for $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$. The variation of negative correlation energy might be due to the separation²⁴ between the donor and nearby cation that depends on the AlAs mole fraction.

In conclusion, we have unambiguously and directly demonstrated that there are two levels in the gap, an acceptor level ($DX^- \rightarrow e^- + DX^0$) and a donor level ($DX^0 \rightarrow e^- + d^+$), of Si-related *DX* center in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ by photoemission DLTS. In this system the acceptor level ($-/0$) lies below the donor level ($0/+$). This is an unambiguous signature of the negative-*U* nature of the Si-related *DX* center in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. In this case, the second electron, which is required to form the DX^- state, is more strongly bound than the first electron, which is required to form the DX^0 state. This inverted ordering of the energy level reveals an effective negative correlation energy with the existence of a thermodynamically unstable DX^0 state.

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