Direct evidence for the negative-U nature of the DX center in $Al_xGa_{1-x}As$

Subhasis Ghosh and Vikram Kumar
Department of Physics, Indian Institute of Science, Bangalore 560012, India
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Photoemission-deep-level transient spectroscopy with 1.38-eV light reveals a new level with a thermal activation energy of 0.2 eV for the DX centers in silicon-doped $Al_xGa_{1-x}As$ ($x=0.26$). The observation of this level directly proves the negative-U properties of DX centers and the existence of a metastable state DX^0, which is also confirmed by transient photoconductivity experiments.

The defect that gives rise to a deep level in n-type $Al_xGa_{1-x}As$ alloys doped with group-IV (Si, Ge, Sn) and group-VI (S, Se, Te) dopants for $x \geq 0.22$ is commonly known as the DX center.[1] This deep level is also observed[2] in n-type GaAs at pressures greater than 20 kbar and when the dopant concentration[3] is more than 10^{19} cm^{-3}. Recently it has been suggested that the DX center might have negative-U properties by Chadi and Chang via a simple theoretical model and *ab initio* self-consistent pseudopotential total-energy calculations.[4] A defect has negative-U properties if it can trap two electrons with the second bound more strongly than the first. In this model, the defect must capture two electrons to form the DX ground state which should be negatively charged (DX^-) and the whole system should possess a negative Hubbard correlation energy. Hence the capture process will be

$$DX^+ + e^- \rightarrow DX^0; DX^0 + e^- \rightarrow DX^- .$$

In this system the neutral DX^0 state should be thermodynamically unstable. The evidence cited by Chadi and Chang[4] for the two-electron capture by DX^+ states and, hence, the existence of two energy levels, one donor ($0/+$) and one acceptor ($-/0$), include (i) the absence of an EPR signal related to the DX center in darkness and (ii) the large Stokes shift observed with the 5.5-meV (Ref. 5) phonon mode involved in lattice relaxation upon electron capture.

In this paper we present a demonstration of the negative-U properties of the DX center and conformation of the proposition of Chandi and Chang by photoemission deep-level transient spectroscopy (DLTS) and transient photoconductivity experiments.

The $Al_xGa_{1-x}As$ ($x=0.26$) samples in our experiments were grown by molecular-beam epitaxy on a semi-insulating GaAs substrate with silicon doping of 2×10^{18} cm^{-3}. The active $Al_xGa_{1-x}As$ layer is separated from the semi-insulating GaAs substrate by an undoped spacer layer. The particular composition $Al_{0.26}Ga_{0.74}As$ has been chosen for these experiments to avoid carrier freeze-out at low temperatures, which has been verified by Hall, and capacitance measurements down to 50 K. Samples with $x>0.3$ suffered from carrier freeze-out below about 100 K and were not suitable for DLTS measurements at low temperatures. These observations are consistent with earlier reports.[6] Schottky contact is made by evaporating silver and Ohmic contact by Au-Ge alloys. For photoconductivity measurements, Ohmic contacts are also made by evaporating Au-Ge alloys. The DLTS system uses a Boonton 72B capacitance meter and the double-boxcar window scheme. For both photo-DLTS and photoconductivity experiments, a 600-W quartz halogen lamp with a quartz focusing lens and an interference filter were used as a monochromatic excitation source for 1.38-eV light. The temperature is scanned from 10 to 300 K using a closed-cycle helium refrigeration system and a computer-controlled temperature programmer.

The DLTS measurements carried out in the dark showed only one peak at about 195 K labeled A in Fig. 1. The position and shape of this peak are typical of the DX center related to silicon in $Al_xGa_{1-x}As$. This peak has thermal activation energy of $E_{TA}=0.46$ eV, in general agreement with earlier results,[7,8] and a capture barrier of 320 meV is obtained, which is also in general agreement with an earlier result.[9] The DLTS experiment is repeated in the presence of intense 1.38-eV light during emission. A new majority-carrier peak is seen at about 50 K and labeled B in Fig. 1. These photo-DLTS spectra are taken for time constants over 70–560 ms and thermal activation energy $E_{TB}=0.2$ eV is obtained and a capture barrier of 150 meV is obtained.

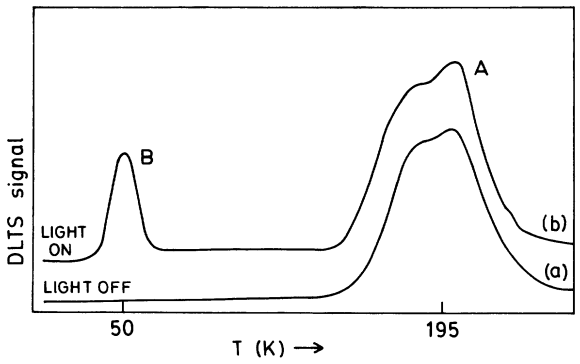

FIG. 1. DLTS spectra in (a) darkness and (b) illuminated with 1.38-eV light. Note that the new peak B is seen only in the presence of light. Both spectra are taken with a time constant of 70.8 ms.

The observed photo-DLTS spectra can be accounted for within the framework of the Chadi and Chang model of DX centers with negative U. For a normal type of defect (with positive correlation energy), after two-electron capture, one should observe an acceptor level $(-/0)$ at low temperature followed by a donor level $(0/+)$ at high temperature during emission of electrons. Now let us consider why only one level with an emission energy of 0.46 eV is observed in normal DLTS and why the new level with an emission energy of 0.2 eV, which can be observed in photo-DLTS, is not observed in dark DLTS spectra. This apparent contradiction can be explained if the level with thermal activation energy, 0.46 eV (peak A), is an acceptor level ($DX^- \rightarrow DX^0 + e^-$) in the inverted negative-U ordering below the new donor level ($DX^0 \rightarrow DX^+ + e^-$) (Ref. 10) with the thermal activation energy 0.2 eV (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 $DX^0 - e^- \rightarrow DX^+$, 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 (0.46-eV) 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 observe. 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 state DX^0. This difficulty of observing the DX^0 state has been 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 for the DX^0 state by tuning the DLTS spectrometer with the thermal-emission time constant of the donor level $(0/+)$. Hence, during each trap-filling pulse, the DX^+ state captures two electrons to be in the DX^- state and the subsequent emission proceeds by

$$DX^- \xrightarrow{h\nu} DX^0 + e^- \xrightarrow{0.2\ \text{eV}} DX^+ + 2e^- .$$

The subband-gap light energy is chosen such that no communication of DX^- or DX^0 with the valence band is possible. Sufficiently high intensity of light is necessary to observe this photoinduced level in DLTS spectra. The intensity of light is chosen such that photoionization of DX^- (e_1^0) is more than the thermal-emission rate (e_2^t) of DX^0, otherwise not enough DX^0 will be available to observe this metastable peak in DLTS spectra. The thermal emission rate of the DX^0 state (e_2^t) is more than its optical emission rate (e_2^0) around 50 K which is verified by photoconductivity experiment.

It is clearly seen from the DLTS spectra that the amplitude of peak B is half that of peak A. This proves that two electrons are emitted in the high-temperature emission process, whereas a single electron emission gives rise to peak B. This is similar to the observation of Harris, Newton, and Watkins[10] regarding the negative-U character of interstitial boron in silicon. The negative-U ordering of the two levels and correlation between peak A and peak B can be further verified by the dependence of peak heights of A and B with filling pulse widths. The amplitude of peak B showed an initial increase with increasing filling pulse width up to 1 ms, but after 1 ms it started decreasing. This decrease in peak height with filling pulse width would be an anomalous result for a normal level in DLTS spectra, but is a direct signature of metastability and a defect with negative correlation energy. In this case the longer filling pulse allows more time for the capturing of the second electron, which will produce more defects in the DX^- state and, hence leave fewer defects in the DX^0 state. This dependence of peak height with filling pulse width shows the complementary behavior between the photoinduced metastable level (peak B) and the deep level (peak A). The capture cross-section measurements for peak B poses some difficulties due to anomalous behavior of this peak with increasing filling pulse width. Thus, a doubt remains about its saturation value, which is required for determining capture cross section. However, if the maximum height reached at about 1-ms pulse width is used, a capture barrier of 150 meV is obtained. If this value is used, the ionization energy of peak B would be 50 meV. Due to inherent technical difficulty we wish to treat this only as a preliminary result.

There are few claims[11,12] about a photoinduced shallow level in Si-doped $Al_xGa_{1-x}As$. In these papers, a little hump is very clearly seen at the same position (around 130 K) where an increase in DLTS peak height is observed under photoexcitation with white light. It is also widely reported[8,13] that the DX center consists of more than one peak in DLTS. We believe that occupancy of one of the levels would increase due to photoexcitation. Those authors could not observe a 50-K peak due to the total freeze-out of the carriers. We have avoided this difficulty by choosing the right composition.

Further support for the negative-U properties of DX centers and the existence of the metastable state DX^0, which plays an important role in all capture and emission processes as an intermediate state, comes from the photoconductivity growth experiment. In our detailed analysis of the photoionization process of DX centers on the same epitaxial layer for different temperature, we have observed a two-step photoionization that provides us with a desired proof of the existence of an intermediate state. Photoionization measurements are performed between 10 and 150 K. The sample is cooled down in the dark. When the required temperature is achieved, the sample is illuminated with 1.38-eV light. The photocurrent is measured by applying a 20-mV bias across the sample. The initial condition is reestablished by heating the sample up to the room temperature. Figure 2 shows the typical nonexponential transient observed in our experiments which is the sum of two exponentials. The photoionization transients have been simulated by a set of coupled differential equations

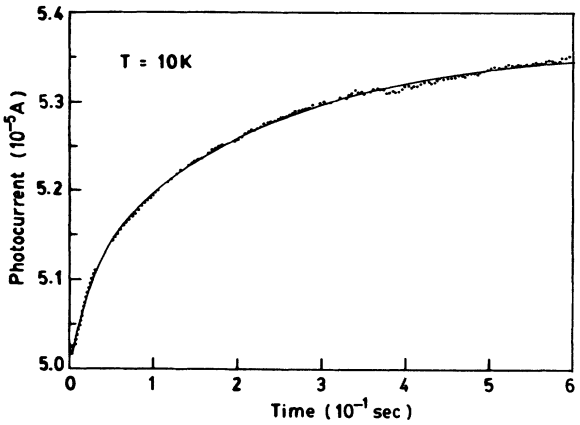

FIG. 2. Photoconductivity growth at 10 K observed in the experiments. The solid line is a fit of the model described in the text with $e_1^0=4.60\ s^{-1}$; $e_2^0=41.55\ s^{-1}$. The capture coefficients c_1 and c_2 strongly depend on temperature and almost vanish at 10 K compared to e_1^0 and e_2^0, and, hence, are neglected for fitting.

$$\frac{dn_T^-}{dt}=-e_1n_T^-+c_1n_T^0\ ,$$

$$\frac{dn_T^0}{dt}=e_1n_T^--e_2n_T^0+c_2n_T^+-c_1n_T^0\ ,$$

$$\frac{dn_T^+}{dt}=e_2n_T^0-c_2n_T^+\ ,$$

$$n=N_D-n_T^0-2n_T^-\ ,$$

where n_T^-, n_T^0, and n_T^+ are the concentrations of the DX centers in the negative, neutral, and positive charge states, respectively. N_D is the net donor concentration, n is the free-electron concentration. c_1 is the capture rate for the process $DX^0+e^-\rightarrow DX^-$, and c_2 is the capture rate for the process $DX^++e^-\rightarrow DX^0$. e_1 corresponds to the emission rate for the process $DX^-\rightarrow DX^0+e^-$ and e_2 corresponds to the emission rate for the process $DX^0\rightarrow DX^++e^-$. The emission rates e_1 and e_2 are the sum of optical and thermal-emission rates. But at 10 K the optical emission rate dominates over thermal-emission rate. The experimental data are nicely fitted with the sum of two exponentials, which are the solutions of the above equations with negative-U initial condition

$$n_T^-(t=0)=\frac{N_D}{2},\quad n_T^0(t=0)=n_T^+(t=0)=0\ .$$

We have fitted our experimental data at 10, 15, and 27 K. We have found that the time constants remain the same at these temperatures if the intensity of the light is kept constant, but depends sensitively on the intensity of light. So we can rule out any contribution in emission time constant from thermal emission. The ratio of two preexponential factors remains constant for different intensities of light at these temperatures, as expected in this model. Our analysis shows that the two exponentials are coming from the same defect, i.e., from the two charge states of the same centers and not from the excited state of the same center. At a higher temperature ($T>80$ K), the photoionization can be fitted with a single exponential that corresponds to the emission $DX^-\rightarrow DX^0+e^-$, since it is not possible to observe the emission from DX^0 to DX^+ in photoconductivity growth because the thermal-emission rate (e_2^t) for this transition is faster than the optical emission rate (e_2^0), which is also consistent with the DLTS experiment described above. Similar two-step photoionization is also observed[14] in Te doped $Al_xGa_{1-x}As$.

An experiment that should determine the charge state of the DX center is electron paramagnetic resonance (EPR). In the case of a silicon donor, the neutral-state DX^0 is paramagnetic. If the ground state is negatively charged DX^- after capturing two electrons, it is diamagnetic and one should not observe an EPR spectrum. To our knowledge, until today there has been no report regarding the observation of an EPR signal from a DX center in the dark, which indirectly supports the negative-U property of the DX center. Recently, it has been reported[15] that an EPR signal is observed upon photoexcitation with light of $h\nu>0.9$ eV at 4 K with the conclusion that the EPR signal is coming from a metastable state. We believe that in this experiment the EPR signal is coming from the metastable DX^0 state, which is photoexcited from the DX^- state with light $h\nu>0.9$ eV, which is consistent with the photo-DLTS experiment reported above.

In conclusion, we have unambiguously and directly demonstrated that there are two levels in the gap, an acceptor level ($DX^--e^-\rightarrow DX^0$) and a donor level ($DX^0-e^-\rightarrow DX^+$) DX center in $Al_{0.26}Ga_{0.74}As$. In this system the acceptor level ($-/0$) lies inverted below the donor level ($0/+$). 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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