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Nonexponential photoionization of *DX* centers in Si-doped $Al_xGa_{1-x}As$

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Evidence for the existence of the intermediate neutral *DX* state is most likely to be observed in careful photoionization studies; hence, photoionization measurements were made for Si-doped $Al_xGa_{1-x}As$. Nonexponential optical ionization transients are observed and are shown to be due simply to the sum of single-exponential processes for the individual *DX* levels, revealing the difference of the photoionization cross sections for different *DX* levels. Capacitance-voltage measurements show that the photoionization processes in the depletion region and neutral region are identical. This result rules out the possibility of an observable two-step photoionization process for the *DX*(Si) centers in the temperature range of the experiment, and sets an upper limit of 20 meV to the activation energy of the proposed neutral state of the distorted *DX* configuration.

Among the many models for the *DX* centers in $Al_xGa_{1-x}As$ and related materials, the negative-*U* model proposed by Chadi and Chang[1] has gained wide acceptance. In the negative-*U* model, the ground state of the *DX* center is negatively charged and undergoes a large lattice relaxation. The lattice relaxation involves either a large bond-breaking displacement of a column-IV donor (such as Si) away from a nearest neighbor into a threefold-coordinated interstitial site, or a similar displacement of a nearest-neighbor Ga (or Al) atom away from the column-VI donor (such as S) and into an interstitial site. Many properties of the deep donor level, such as the large Stokes shift between the optical and thermal ionization energies,[2,3] the thermally activated electron-capture cross section,[2] the number of *DX* levels,[4–7] and the pressure dependence of the capture and emission energies,[8] can be readily explained only when a large lattice relaxation is invoked. The validity of the negative-charge hypothesis of the *DX* centers has also been tested by a large number of experiments.[9–15] Among these experiments, most, though not all, have supported the negative-*U* model.

According to the negative-*U* model, it is natural to presume that the donor is left in a neutral excited state of the distorted *DX* configuration, DX^0, after removal of one electron from the DX^- state by photoionization at low temperature. Calculations by Chadi and Chang[1] for the Si- and S-related *DX* centers indicate that the interstitial DX^0 is highly unstable and that there is no barrier for transformations to the fourfold-coordinated substitutional donor (D^0) configuration. However, more recent theoretical calculations by Dabrowski *et al.*[16] predict that the DX^0(Si) state is metastable and will transform to D^0 over a barrier of approximately 0.1 eV. Since a metastable DX^0 configuration may give rise to nonexponential photoemission transients, evidence for its existence is most likely to be observed in careful photoionization studies.

Experimentally, the only claim of finding direct evidence for a stable DX^0 state comes from a photoconductance experiment on Te-doped $Al_xGa_{1-x}As$,[17] in which nonexponential photoemission transients are reported. In the photoconductance experiment, the electron concentration in the $Al_xGa_{1-x}As$ layer was determined indirectly from the effects of series resistance on the measured capacitance of the equivalent circuit of the p^+-n-n^+ diode. In contrast to the above photoconductance experiment, earlier photocapacitance experiments on Si-doped samples have found that the photoionization process is exponential,[18–20] indicating no *observable* effect from the DX^0 state. The main difference between the photoconductance and photocapacitance experiments is that the former probes *DX* levels in the neutral region while the latter probes in the space-charge region. In order to account for the apparent difference between the photocapacitance and the photoconductance results, it has been suggested that the sweeping out of free electrons from the space-charge region prevents the DX^0 state from recapturing a second electron and thus prevents the observation of the DX^0 state in the photocapacitance experiments.[21] However, this suggestion has not been proved experimentally.

Given the contradictory results in both the theory and experiment, the properties of the proposed DX^0 state are not yet clear. Accordingly, in this paper the photoionization processes of *DX* centers are investigated for Si-doped $Al_xGa_{1-x}As$ material for temperatures greater than or equal to 20 K. Capacitance-voltage (*C*-*V*) measurements are used to compare the photoionization process in the neutral-charge region to that in the space-charge region, directly addressing the difference between photocapacitance and photoconductance studies.

The samples used in this study were prepared from an $Al_{0.29}Ga_{0.71}As$ epilayer doped with Si at 1.5×10^{17} cm^{-3} and grown by molecular-beam epitaxy on an n^+-type GaAs substrate. Schottky diodes were made by evaporating Ni dots on top of the epilayers, and Ohmic contacts were formed by indium alloying at 350 °C for 15 min.

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The series resistance of the diodes is sufficiently low even at low temperature, so there is no effect on the measured junction capacitance due to the series resistance. In the optical ionization measurements, light was incident on the $Al_xGa_{1-x}As$ layer from the back side of the GaAs substrates. A tungsten lamp was used along with a silicon wafer as a filter so that only photons with $E_{ph} \leq 1.1$ eV could reach the samples. In order to avoid the distortion due to the large defect concentration, the photoionization transients were measured using the constant-capacitance technique.

The optical ionization transients at four representative temperatures are shown in Fig. 1. All four curves are normalized to unity at $t=0$, the moment illumination started. The *DX* centers were filled at 200 K and the sample was cooled at zero bias. At all measurement temperatures, the *DX* centers are thermally stable. For $T \leq 70$ K, persistent photoconductivity is observed and the recapture of electrons after photoionization is negligible. Unlike the previous results,[18–20] the curves in Fig. 1 are obviously nonexponential, even though the constant-capacitance technique was used. As will be discussed below, however, the nonexponentiality of the photoionization transients cannot be interpreted as a two-step photoionization process due to the successive removal of the two electrons from the DX^- center.[17]

If one of the components were associated with the excitation (thermal and optical) of the second electron from the *DX* center, this component should vanish and the photoionization transients become exponential once the temperature is high enough that the DX^0 state is thermally unstable. As shown in Fig. 1, however, the shape of the photoionization transients remains the same at all the measurement temperatures (except for a slight decrease in the time constants for $T > 70$ K). Thus no component can be assigned to the ionization of the DX^0 state, unless DX^0 is thermally stable even at the highest measurement temperature (i.e., optical emission always dominates).

If it were assumed that the distorted DX^0 state is thermally stable, then this state should efficiently capture a second electron and return to the DX^- ground state once free electrons are provided, because in such a process no large lattice relaxation is involved.[16] To examine this possibility, a filling pulse was applied to the sample after *DX* centers were partially photoionized. No change in the space-charge concentration due to the filling pulse is observed, indicating that no thermally stable DX^0 state exists. Therefore, the nonexponentiality of the photoionization in the space-charge region does not result from a two-step photoionization process.

The question remains as to whether the DX^0 state is detectable in an experiment (e.g., photoconductance) that probes the neutral-charge region. Even if the DX^0 state is unstable, it can still affect the photoionization process in the neutral-charge region as long as its lifetime is at least comparable to the time constant for recapturing a second electron. In the above case, the net photoionization rate of the *DX* center will be lower in the neutral-charge region than in the space-charge region. For the comparison of the photoionization processes in the two charge regions, *C-V* measurements were used to profile the charge density following illuminations to various fluences. The profile results for $T=20$ K are shown in Fig. 2. The photoionization prior to the profile measurements was performed under reverse bias. The constant-capacitance technique was used to maintain a constant space-charge region during the photoionization process. As shown in Fig. 2, the charge density is nearly uniform over the whole measurement region. No step is found near the edge of the space-charge region, indicating that the photoionization rates of the *DX* centers in the two charge regions are identical. The small oscillation in the

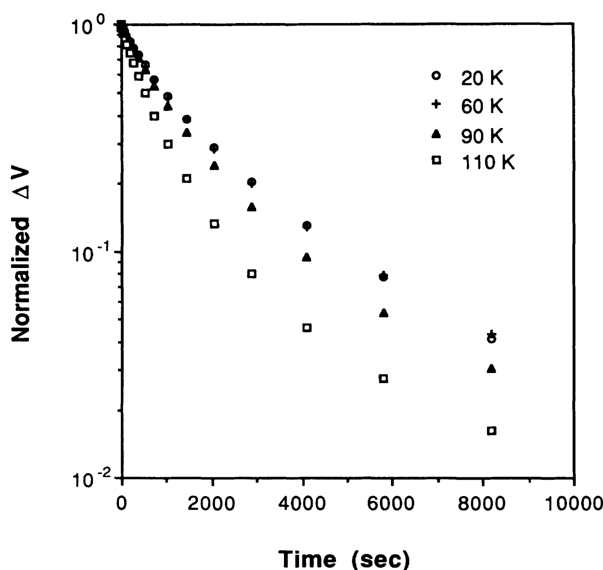

FIG. 1. Normalized photoionization transients of the *DX* center at different temperatures. The constant-capacitance technique was used in the measurements.

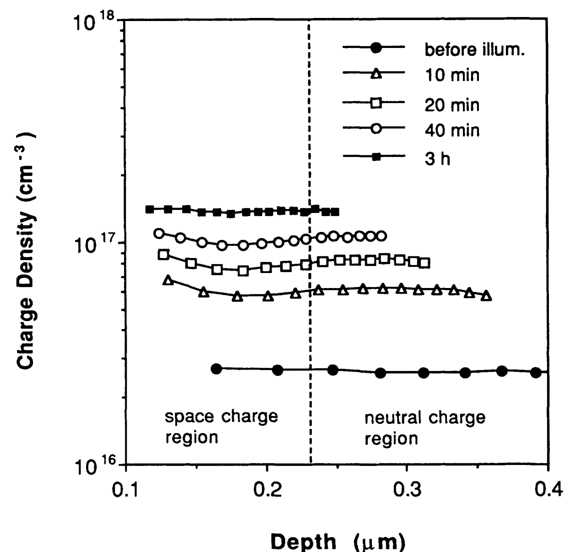

FIG. 2. Profiles of charge density at $T=20$ K after illuminations with various periods of time. The dashed line represents the edge of the space-charge region during the photoionization process.

charge density is due to the standing-wave effect of the incident light for some wavelengths. The observation of the small oscillation demonstrates that the *C-V* measurement is sensitive to small variations of charge density.

Since no evidence has been found for a two-step photoionization process, the nonexponentiality of the photoionization transients must have another origin. It is well known that the thermal-emission kinetics of *DX* centers are also nonexponential.[22] Correspondingly, the deep-level transient-spectroscopy (DLTS) spectra of *DX* centers usually exhibit multiple-peak structures.[6,7] The nonexponential thermal-emission kinetics, as well as the multiple-peak DLTS spectra, have been shown to result from the effect of the local environments of the *DX* centers, i.e., the number of the nearest Al neighbors of the interstitial Si atoms.[5] It will be shown that the nonexponentiality of the photoionization processes is related to the multiple *DX* levels, and thus also originates from the different local environments.

In earlier work[7] it was shown that in the same Si-doped $Al_{0.29}Ga_{0.71}As$ material four *DX* levels can be resolved from window-rate-scan DLTS spectra. A typical spectrum, measured at 148 K with filling for 16 sec, is shown in the inset of Fig. 3. The dotted curves represent peaks of the four individual *DX* levels obtained from a nonlinear least-squares fit. To determine the relationship between the nonexponentiality of photoionization transients and the multiple *DX* levels, photoionization transients have been measured at 30 K with different initial filling conditions. The results are shown in Fig. 3. The procedures for establishing the initial conditions with the *DX* centers are described as follows. In case 1, the sample was cooled to 30 K after filling all of the *DX* levels with a 16-sec fill pulse at 148 K. For case 2, after filling the *DX* centers with a 16-sec fill pulse, the sample was reverse-biased for 30 sec at 148 K, and then cooled to 30 K. According to the inset of Fig. 3, the shallowest level (DX_0) is almost emptied by thermal emission, while the occupancies in other levels change little from the previous case. Case 3 is similar to case 2, except that the sample was held at reverse bias for 1 h at 148 K before cooling. Consequently, all the *DX* levels except the deepest level (DX_3) are nearly empty. As seen in Fig. 3, the photoionization transient tends to be more exponential as fewer *DX* levels are occupied and becomes exponential when only one level (DX_3) is occupied. The difference between the transient curves of cases 1 and 2 (curve 4) represents the photoionization transient from the shallowest *DX* level (DX_0), and is exponential as well. However, the decay time constants for DX_0 and DX_3 differ by a factor of 5. A similar separation of the DX_1 and DX_2 levels is not possible due to the close values of their thermal-emission rates. From the above results, it can be concluded that the photoionization process from a single *DX* level is exponential, and the nonexponentiality of photoionization transients is simply due to the superposition of exponential processes for the individual *DX* levels with different decay time constants. These measurements reveal for the first time that the photoionization cross sections for the different *DX* levels are not the same, i.e., that the photoionization cross section depends on the local environment of the *DX* center.

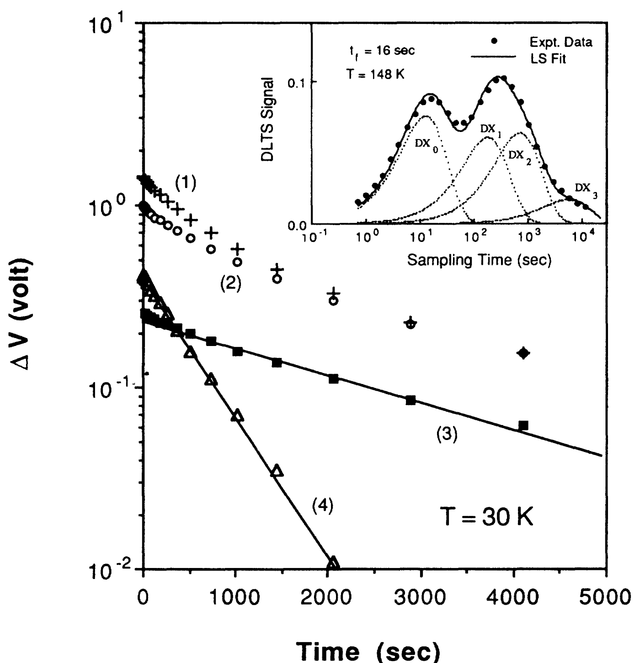

FIG. 3. Optical emission transients at $T = 30$ K with different initial filling conditions as described in the text. The inset shows a window-rate-scan DLTS spectrum of *DX* centers and the four discrete *DX* levels obtained from a nonlinear least-squares fit.

The above data provide no evidence for the observation of a two-step photoionization process for the *DX*(Si) centers. These results do not necessarily conflict with the negative-*U* model, but may instead confirm the Chadi-Chang calculations, suggesting that the intermediate state for the Si-related *DX* center is highly unstable. As mentioned earlier, the validity of the negative-*U* model has been tested by many independent experiments (for both the large lattice relaxation and negative charge state). However, since there is no difference between the net photoionization rates of the *DX*(Si) centers in the two charge regions, the distorted DX^0 state, if it indeed exists, must have an extremely small emission energy. In such a case, the emission rate of the remaining electron, r^0, is much larger than the recapture rate of the second electron, c^0, even at the lowest measurement temperature. Therefore, the DX^0 state has virtually no chance of recapturing the second electron before being further ionized. It is possible to roughly estimate an upper limit for the emission energy E_e^0 of the distorted DX^0(Si) state. Since no large lattice relaxation is involved during the recapture of the second electron by a DX^0 state, the capture coefficient γ^0 is taken to be 10^{-10} cm^3 sec^{-1}, a typical value for a neutral defect in semiconductors. Now $c^0 = \gamma^0 n_c = 10^7$ sec^{-1} when the free-carrier concentration n_c is about 10^{17} cm^{-3}. Given that the emission rate is $r^0 = \nu_0 \exp(-E_e^0/kT)$, where ν_0 is the escape frequency, which is taken to be 10^{12} sec^{-1}, and assuming that $r^0 > 10^0_c$, then E_e^0 must be less than 20 meV, which is much smaller than the theoretical prediction ($E_e^0 \approx 0.1$

eV) made in Ref. 16.

The present results differ from the claim in Ref. 17 that *DX* centers undergo a two-step photoionization process. It may be argued that the properties of the Te-related *DX* centers are not necessarily the same as those of the Si-related *DX* centers, so the results from Si-doped samples cannot, in principle, rule out the possibility of relatively stable DX^0 states in Te-doped samples. However, some problems are found in Ref. 17, including the fact that the free-carrier concentration appears to have been overestimated by 2 orders of magnitude.[23] As a consequence, the previous claim of finding direct evidence for a two-step photoionization of the *DX*(Te) centers is unsubstantiated, and whether relative stable DX^0 states exist in Te-doped $Al_xGa_{1-x}As$ is still an open question.

In summary, nonexponential photoionization transients are reported for *DX* centers in Si-doped $Al_xGa_{1-x}As$. It is shown that the departure from exponential behavior is *not* due to a two-step photoionization process associated with an excited DX^0 state, indicating that the DX^0(Si) state, if it indeed exists, is highly unstable. Rather, the transients are simply the sum of exponential transients from the multiple levels of the *DX* center associated with different local environments, indicating an alloy effect on the photoionization energies. Finally, an upper limit on the activation energy of the theoretically predicted DX^0 state is estimated to be 20 meV.

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