Evidence for Substitutional-Interstitial Defect Motion Leading to *DX* Behavior by Donors in $Al_xGa_{1-x}As$

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A high-resolution Laplace-transform deep-level-transient spectroscopy has been used to study electron emission from the *DX* centers related to group-IV (silicon) and group-VI (tellurium) donor elements in $Al_xGa_{1-x}As$ ($0.25 < x < 0.76$). This provides experimental evidence that substitutional-interstitial atom motion is responsible for *DX* behavior and for the associated metastability effects. The atom which is subjected to this transition is, for *DX*(Si), silicon itself, and so only one group of peaks is observed in the spectra; while for *DX*(Te), it can be either gallium or aluminum, producing two groups of peaks.

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Deep localized defects called *DX* centers [1] are observed in GaAs under high hydrostatic pressure, in $Al_xGa_{1-x}As$ for $x > 0.2$, and in some other semiconductors. They are directly related to the process of donor doping of these materials. The distinctive feature differentiating these states from normal donors is that they do not recapture photoexcited carriers when photoionized at low temperatures, resulting in the phenomenon of persistent photoconductivity. The fundamental problem related to the properties of *DX* centers is understanding the mechanism for the metastability of these defects. Since the early work of Lang and co-workers [2] this has been thought to be due to the large lattice relaxation (LLR) following electron capture by the *DX* state. However, the problem of the microscopic structure of these centers, namely, the type or symmetry of the lattice relaxation, is less certain. The computations of Chadi and Chang [3], and of Morgan [4], support the early suggestion by Langer [5] that a substitutional-interstitial defect reaction may be responsible for LLR phenomena. Chadi and Chang calculated that to stabilize such a configuration of atoms in the lattice the defect must capture two electrons to form the *DX* state. Consequently, the ground state of the *DX* center should be negatively charged and the whole system should possess a negative electron correlation energy U ($U < 0$) [6].

In a negative-U system the neutral D^0 state must be thermodynamically unstable, but obviously will play a role in all carrier capture and emission processes as an intermediate state ($D^- \leftrightarrows D^0 + e^- \leftrightarrows D^+ + 2e^-$) [7]. The existence of such an intermediate DX^0 state, and consequently the negative-U character of the defect, has been already demonstrated by a detailed analysis of the photoionization process of the *DX*(Te) centers in $Al_xGa_{1-x}As$ [8] and the thermal ionization process of sulfur-related *DX* centers in GaSb [9].

However, there have been many difficulties in experimentally verifying the microscopic mechanism leading to the metastability effects. The use of electron spin resonance (ESR) does not produce any spectrum related to the ground state of the defect [10] due to a lack of paramagnetism used by a spin pairing effect for the two electrons bound to the defect. Extended x-ray-absorption fine-structure (EXAFS) and Mössbauer spectroscopies give ambiguous results, since both techniques require a high concentration of *DX* centers (some clustering and compensation are then inevitable). Very recently an alternative approach was attempted. The local vibrational mode (LVM) absorption observed under very high hydrostatic pressure for silicon-doped GaAs revealed the appearance of a new peak in the spectra when the *DX* defect is in the ground state [11]. Unfortunately, the link between this new feature and the defect model is still not clear.

In the present study experimental evidence is presented which can only be interpreted in terms of substitutional-interstitial defect motion being responsible for the *DX* state formation. It is based on the detailed observation of the influence of the defect local environment on the electron thermal emission process from *DX* centers in $Al_xGa_{1-x}As$. The direct comparison of this process for the *DX* center related to a group-IV donor (silicon), which can replace gallium or aluminum, with that observed for a group-VI donor (tellurium), which resides in the arsenic sublattice, allowed us to deduce the configuration of atoms when the center is in the ground state. Our experiments were possible because of a newly developed Laplace-transform isothermal deep-level-transient spectroscopy (DLTS) technique [12] which gives orders of magnitude better resolution than the conventional DLTS method.

Samples of $Al_xGa_{1-x}As$:Si ($x = 0.20, 0.30, 0.35, 0.44, 0.67, 0.76$) used in our study were grown by molecular-beam epitaxy (MBE) either with epitaxial aluminum Schottky diodes deposited in the MBE system or in the form of asymmetric p^+-n junctions. The samples of $Al_xGa_{1-x}As$:Te ($x = 0.25, 0.35, 0.45, 0.55, 0.73$) were liquid-phase-epitaxy (LPE) grown p^+-n diodes. The doping level of the n-type material was 10^{16} and 5×10^{16} cm^{-3} for the samples grown by MBE and LPE, respectively. The conventional DLTS spectra taken for both types of samples revealed only one dominant broad peak. This was associated with the *DX* center and did not have the additional structured features reported for heavily doped $Al_xGa_{1-x}As$ with silicon [13].

The diode capacitance transients were recorded at constant temperature (± 0.1 K) after excitation by a filling pulse. To extract a spectrum, i.e., a sequence of the emission rates in the process, an inverse Laplace transform of the recorded transient is made. The result of such a procedure is a spectrum in a form of one deltalike peak for a perfectly exponential decay, a series of deltalike peaks for multiexponential transients, or a broad spectrum with no fine structure for a continuous distribution. In this method it is not necessary to make any *a priori* assumptions about the number of peaks or the functional shape of the spectrum. Using this approach it is possible to distinguish emission rates differing by a factor of less than 2. A brief mathematical description of the method is given in Ref. [12]; a detailed report will be published elsewhere.

The Laplace-DLTS spectrum of the *DX*(Si) defect in $Al_{0.35}Ga_{0.65}As$ is presented in Fig. 1(a). In the spectrum there are four well-resolved peaks. Only three of them (at the higher emission rates) are associated with the *DX*(Si) centers. The fourth [dashed line in Fig. 1(a)] can be related to an unrecognized defect whose concentration increases with the aluminum content in the crystal; even for $x = 0.74$ its concentration is orders of magnitude lower than that of the *DX* centers. Because of the way we calculate the plot it is the area under the peak which is proportional to the magnitude of the charge exchange associated with each component; consequently, when the emission rate is presented on a logarithmic scale (as in Fig. 1), the height of the peak does not represent the true magnitude of each of the emission processes in the transient.

Although the absolute value of the electron emission rate from the *DX*(Si) center is dependent on the temperature, the ratio of the emission rate does not change, being approximately equal to 20:3:1. The Arrhenius plot for $x = 0.35$ and for all peaks associated with *DX*(Si) is shown in Fig. 2(a). The activation energy of the thermal emission for each of the peaks is the same within experimental error and is similar to that given by the conventional DLTS technique. The same pattern of peaks (with minor modifications) was observed for *all* alloy compositions investigated.

In the Laplace-DLTS spectra for tellurium-doped

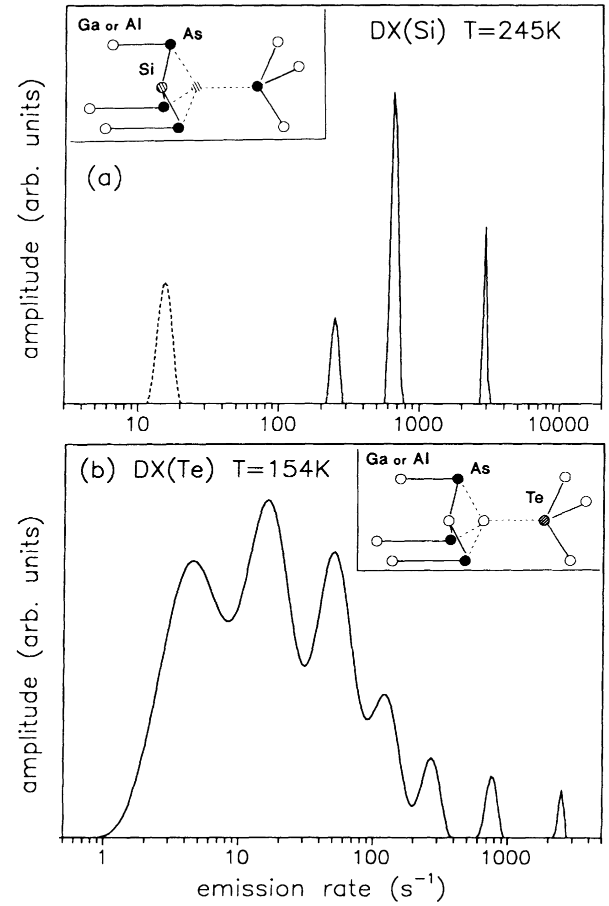

FIG. 1. Laplace-transform DLTS spectra of (a) *DX*(Si) and (b) *DX*(Te) in $Al_{0.35}Ga_{0.65}As$. Insets: Configuration of atoms for the *DX* defect in the ground and the ionized (dashed lines) states. The model is as in Ref. [3].

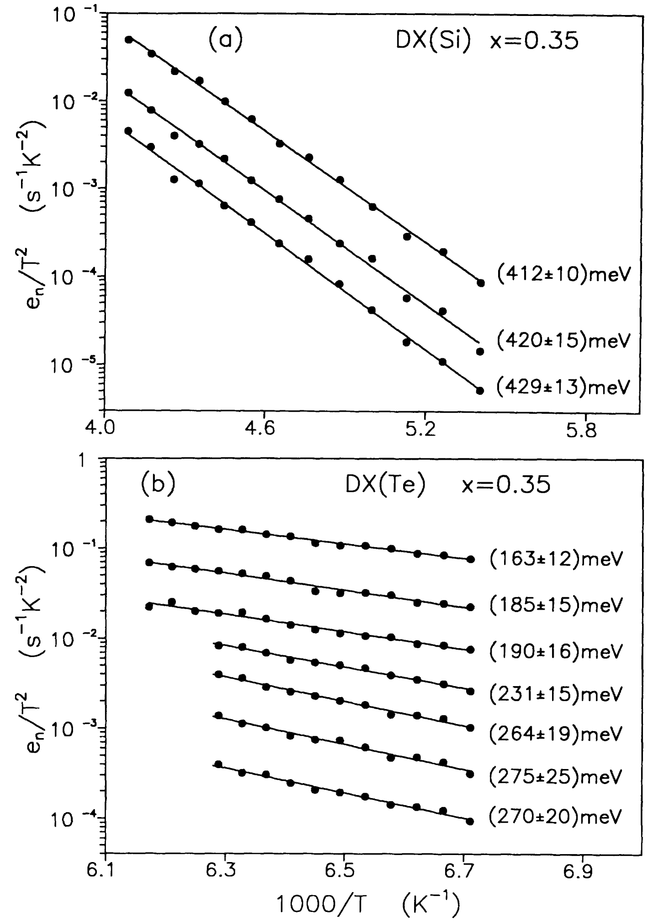

FIG. 2. Arrhenius plots of the emission rates (e_n) for (a) *DX*(Si) and (b) *DX*(Te). Measurements were taken at 5- and 1-K steps, respectively. The activation energies for each of the processes are indicated.

$Al_xGa_{1-x}As$ crystals up to eight peaks (depending on temperature and alloy composition) can be observed [Fig. 1(b)]. These peaks were found to be less separated from each other than for the case of *DX*(Si), and usually much broader; this will be discussed later. The patterns of peaks observed for the *DX*(Te) defect for different alloy compositions and for different temperatures changed slightly, but was always dramatically different from that observed for *DX*(Si).

The Arrhenius plot for *DX*(Te) in $Al_{0.35}Ga_{0.65}As$ taken in 1-K steps is shown in Fig. 2(b). It is seen that the peaks observed on the spectra for *DX*(Te) form two distinct groups differing in the activation energy of the thermal emission process. The activation energy of the peak which is in the middle of the spectrum has an activation energy intermediate between the two groups. Its position in the spectrum can be strongly affected by both groups of neighboring peaks. For temperatures higher than 160 K these two groups start to overlap, approaching the limit of resolution of the method. Above this temperature the total number of peaks and their positions could not be determined with complete certainty.

These results are explained by a situation where the defect ground-state formation is associated with substitutional-interstitial atom motion [3,4]. In this model the energy barrier which governs the thermal emission process has an ionic character, i.e., it is the energy necessary to push aside three arsenic atoms when the cation [silicon for *DX*(Si) and gallium or aluminum for *DX*(Te)] passes from the interstitial to the substitutional position (see Fig. 1 insets). The total energy calculations performed by Dabrowski, Strehlow, and Scheffler [14] support this concept. They found that the defect with two electrons has the lowest total energy for a long range of lattice distortions and becomes unstable only when the central atom approaches the substitutional position. In such a model the energy barrier governing the emission process is only very weakly dependent (or not at all) on the alloy composition.

The activation energy of three emission processes we observe for *DX*(Si) is the same, and it does not change with the alloy composition. Thus we conclude that the energy barrier for the emission process is predominantly formed by the ionic energy, having very little to do with the second-neighbor shell of atoms. On the other hand, these second neighbors may influence the total energy of the defect in the ground state. The silicon atom has four equivalent ⟨111⟩ directions which enable it to go into the interstitial position. If these were energetically identical then for *DX*(Si) there would have been no reason to observe more than one peak, because the process would be fourfold configurationally degenerate whatever the alloy composition. However, if one assumes that the lattice distortion along one of the ⟨111⟩ directions gives the lowest total energy of the defect then the spatial degeneracy is lifted. This energetically favorable ⟨111⟩ direction may be towards the location with either the most aluminum (similarly to the idea of Ref. [15]) or the most gallium as second nearest neighbors (see Fig. 1 inset). For both of the cases it can be easily shown that for a random distribution of aluminum in the crystal a degeneracy equal to 4 will practically never be observed for the alloy compositions $0.2 < x < 0.8$; therefore, only three degeneracies, i.e., equal to 1, 2, and 3, will be observed. These three degeneracies should give a sequence of emission lines 3:1.5:1 with exactly the same activation energy for the thermal emission process. The full details of this analysis will be presented elsewhere. The sequence of three lines observed in the experiment (20:3:1) would indicate that in addition there are slight differences in entropy factors. Calculations also show that the concentration of the *DX* centers with a degeneracy factor of unity is 3 to 6 times higher than that for degeneracies equal to 2 or 3. This relation does not change significantly for the alloy compositions between 0.2 and 0.8, and this is exactly what we observed in the spectra for *DX*(Si) when the area under the peak is connected to a charge exchange magnitude.

For the *DX* centers related to the group-VI donors (tellurium), the atom which is subjected to the substitutional-interstitial motion could be either gallium or aluminum (see Fig. 1 inset). The ionic radii of these two constituents of the crystal are similar, but not exactly equal. The lattice constant of AlAs is slightly larger than that for GaAs; however, this small difference in sizes may result in a substantial difference in energies required to push either aluminum or gallium between the three arsenic atoms. Consequently, one can expect that the energy for the emission associated with the motion of the aluminum is larger than that related to gallium. For *DX*(Te) the Laplace-DLTS spectra indeed consist of two sets of peaks characterized by the different activation energies for the thermal emission process. Moreover, the relative concentration of the centers with larger energy for the emission increases with the aluminum content in the alloy. Thus, we may conclude that for *DX*(Te) the emission process with larger activation energy is associated with the aluminum motion and the other one with gallium. The conventional DLTS technique gives for *DX*(Te) an activation energy close to the value of 0.27 eV found for the aluminum motion in our study consistent with the lower resolution and weighting factor.

In the case of *DX*(Te) the number of peaks within each of the groups can be again deduced based on an analysis of configurational degeneracies. If one assumes that in this case only the first nearest neighbors (aluminum or gallium) are relevant (second nearest neighbors are not changing) then one can expect four peaks for the Te-Al bond breaking process and the same number for Te-Ga giving a maximum of eight peaks. If the third nearest neighbors play any role then many more peaks can be expected though with much reduced separation. In the present study never more than eight peaks were observed; however, for *DX*(Te) the individual peaks were found to be much broader than for the case of *DX*(Si), suggesting a possible unresolved structure of each of them.

In conclusion, we have compared the Laplace-DLTS spectra of the *DX*(Si) and *DX*(Te) centers and shown that for the *DX*(Si) defect in a wide range of alloy compositions only one group of peaks is observed. These peaks we attribute to the *DX*(Si) defect ionization process associated with interstitial-substitutional motion of the silicon atom. In the case of the *DX*(Te) center in the spectra the peaks form two groups and we attribute them to the same process but associated with interstitial-substitutional motion of the aluminum or gallium atoms. The structure of peaks seen within the group we relate to different spatial degeneracies of the process for the defect in different local environments. These observations give for the first time experimental evidence of the *DX*-type state microscopic structure. The number of observed peaks and splitting between them rule out the possibility that this energy state is either an attribute of a stable configuration of a donor in a substitutional position with fully symmetric LLR effect similar to that evidenced for the case of indium in CdF_2 [16] or caused as a result of exchange of sites (*X*-*S*) by cation and anion close to a donor atom (this model was recently proposed by Morgan) [17].

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