Structure of the DX state formed by donors in (Al,Ga)As and Ga(As,P)

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High-resolution Laplace-transform deep level transient spectroscopy has been used to study the influence of the defect local environment on electron emission from the DX centers related to group-IV (silicon) donors in $Al_xGa_{1-x}As$ (0.20 < x < 0.76) and δ -doped GaAs and group-VI (tellurium) donor elements in $Al_xGa_{1-x}As$ (0.25 < x < 0.73) and $GaAs_{0.35}P_{0.65}$. The experimental evidence that substitutional-interstitial atom motion is responsible for DX behavior and for the associated metastability effects is presented. The atom which is subjected to this transition is for DX(Si) silicon itself, as in the spectra only one group of peaks in $Al_xGa_{1-x}As$ is observed, while for DX(Te) it can be either gallium or aluminum, producing two groups of peaks in Al_xGa_{1-x} As and three or four broad emission bands in $GaAs_{0.35}P_{0.65}$. The present results rule out a possibility that the DX-type defect states are formed by a donor atom in a stable substitutional position with a small lattice relaxation or with a fully symmetric large lattice relaxation effect. © 1995 American Institute_of Physics.

I. INTRODUCTION

The unusual properties of deep, localized, energy states introduced by donor doping were first noted in AlGaAs by SpringThorpe,¹ although a similar behavior had been observed previously in other materials.² These centers (called the DX centers) exhibit metastability and the most characteristic phenomenon is known as persistent photoconductivity.

The basic problem related to the properties of these defects is the understanding of the mechanism leading to the metastable behavior. Since the early work of Lang³ 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. Chadi and Chang,⁴ independently Morgan,⁵ and lately Dabrowski, Strehlow, and Scheffler⁶ suggested that a substitutional-interstitial defect reaction may be responsible for the LLR phenomena. A very important consequence of the Chadi and Chang model is such that to stabilize the central atom of the defect in the interstitial position the center must capture two electrons. Therefore the DX center should behave as a so-called negative-U center.⁷ Recently, an alternative model of the DX state formation was presented by Biernacki.⁸ In this model a trigonal distortion in the arsenic sublattice in the first neighbor shell to the donor results in a very strong Jahn–Teller effect on the two-electron T_2 state of the center. In this case the lattice distortion predominantly occurs in the arsenic sublattice (for the silicon donor) while in the Chadi and Chang model the LLR effect is equivalent to the substitutional-interstitial motion of the silicon ion itself. In both cases the DX state formation is associated with the lowering of the defect local symmetry from T_d to C_{3v} and in both cases the defect forms a negative-U system.

The negative-U character of the defect, i.e., the fact that the center in the ground state binds two electrons, has been recently evidenced by numerous experimental results. A detailed analysis of the photoionization of tellurium related DX centers in AlGaAs has revealed that the process goes through two steps,⁹ as one can expect for a defect forming a negative-U system. Deep level transient spectroscopic (DLTS) studies of GaAs crystals codoped with silicon and germanium performed under hydrostatic pressure demonstrated again the two-electron character of the ground state.¹⁰ A similar conclusion has been drawn when investigating transport properties under hydrostatic pressures¹¹ or with photoconductivity effects.¹² Recently, the observation of the electron-hole recombination process on the DX center allowed us to demonstrate that the defect in the ground state indeed forms a negatively charged acceptor state,¹³

A much more complicated issue is to verify experimentally the microscopic mechanism leading to the metastability effects observed for the defects. Most of the local environment sensitive experimental techniques seem to fail in producing unambiguous results (see Ref. 14 for details). The spin pairing for the two electrons bound by the defect in the ground state results in a diamagnetic ground state, and the electron-spin-resonance technique cannot be applied.¹⁵ Extended x-ray-absorption fine-structure (EXAFS) and Mössbauer spectroscopies do not work at the low-excitation regime required to observe the defect in its ground state. These methods lead to unavoidable disappearance of the DX center, either via the photoionization process or recombination with holes. A very important contribution came from the local

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vibrational mode absorption measurements performed under very high hydrostatic pressure for silicon doped GaAs.¹⁶ This experiment revealed the appearance of a new peak in the spectra when the DX defect is in the ground state. However, the link between this new feature and the defect model is still not clear. Recently Sallese *et al.*¹⁷ demonstrated that the position of the DX(Te) level in $Al_xGa_{1-x}As$ extrapolated to x=0 does not correspond to the value found for GaAs under hydrostatic pressure and extrapolated to zero pressure, while such a correspondence is observed for the DX(Si) center in GaAs under pressure and in $Al_xGa_{1-x}As$.¹⁸ This result will be discussed later.

In this work a systematic study of the influence of the local defect environment on the electron emission process observed for the DX centers is presented. The comparison of this process for the defect related to a group-IV donor (silicon), which in Al_rGa_{1-r}As can replace gallium or aluminum, with that observed for a group-VI donor (tellurium), which resides in the arsenic sublattice in $Al_rGa_{1-r}As$ and the arsenic or phosphorus sublattices in $GaAs_{1-x}P_x$, allowed us to deduce the configuration of atoms when the center is in the ground state. Additionally, the silicon-related DX centers were observed in δ -doped binary GaAs crystals. We have examined the existing models of the DX center and concluded that our results can only be interpreted in terms of the DX state formation associated with a lowering of the defect local symmetry from T_d to C_{3v} , which incudes the substitutional-interstitial defect motion postulated in Refs. 4-6.

II. EXPERIMENT

A. Alloy splitting of the DX state—Where is it?

Some authors presented results where the DLTS spectra have a structure which they associate with the presence of the DX states in samples. In some of the cases series of well-separated peaks are observed; sometimes there are only unresolved subsidiary shoulders seen on the main DLTS peak for the center. Similar features have been observed in transport measurements. The conductivity of the AlGaAs layer with DX centers was found not to depend monotonically on temperature. Sometimes a few steps on such curves could be seen. In both types of experiments never more than four such features (for the Si-related DX centers) were observed. Basing on these findings numerous authors concluded that only four different configurations of the DX(Si)state in AlGaAs are possible. This concept apparently agrees with the model of Chadi and Chang, in which after breaking of one of the Si-As bonds the silicon atom moves toward 3 of the 12 surrounding cations. As the cation can be either gallium or aluminum, there are four configurations possible. Each of them should have a slightly different energy; consequently, in different types of experiments one can observe four configurations of the DX state.

To draw any conclusion about the relation between the observed structures and the local configuration of the DX center one has to assume that the AlGaAs crystal is perfectly uniform, i.e., there is a real random distribution of gallium and aluminum atoms among the cation sites, and that the

silicon atoms form isolated centers in the crystal. These assumptions can be, however, seriously questioned when all possible processes occurring during the sample preparation are taken into account. In our study we have examined numerous AlGaAs samples grown by different growth techniques and doped with different elements. Only in the case of low-quality or highly doped samples grown by molecularbeam epitaxy (MBE) on the DLTS spectrum beside the dominant peak, which can be regarded as related to the DXcenters, were there additional features observed (see the Appendix for details). No structure or other features on the DLTS spectra were found for samples grown by liquid phase epitaxy (LPE) or vapor phase epitaxy (VPE). Consequently, the obvious conclusion is that if there is any true alloy splitting effect for the DX state, it has to be hidden in the broad DLTS peak observed for the high-quality samples.

The resolution of the standard DLTS technique is basically insufficient to study fine structure in the emission process. The most obvious reason is the way the spectrum is obtained, i.e., even a perfect defect, with no physical processes causing a broadening of its parameters, produces a broad DLTS line. Any fine structure present for a defect results in additional broadening of the peak, and is practically impossible to resolve unless qualitatively new features appear on the spectrum. In our study we have overcome this problem by using the so-called Laplace-transform DLTS technique which gives orders of magnitude better resolution than the conventional one. A brief description of the method is given in Ref. 19. A report including details of the experimental setup, software numerical tests, and results of measurements performed on simple point defects (e.g., platinumrelated center in silicon, etc.) is presented in Ref. 20. In this method the diode capacitance transients are recorded at constant temperatures $(\pm 0.1 \text{ K})$ 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 less than by a factor of 2.

The validity of the software used for calculations has been thoroughly checked by performing a series of inverse Laplace transforms on computer-generated transients. The purpose of this was to determine the ability of the program to properly reveal a spectrum of emission rates in the transient. It was also necessary to establish the resolution of the method and its sensitivity to noise present in real transients. In these tests extreme conditions where the software still gives reliable results have been defined. We found a general tendency that the noise in the signal effectively reduces the method resolution. However, in practice, for the DX centers rather strong signals are observed (high signal-to-noise ratio). That allowed us to achieve a top resolution offered by the software.

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It is known that in the DLTS measurements there are numerous phenomena which may lead to an occurrence of nonexponentiality in the thermal emission transients even for perfect point defects in homogeneous materials. The most common sources of such nonexponentiality are the facts that (i) defects have higher concentration than shallow centers, (ii) the space-charge region is never abrupt (the Debye tail of carriers), i.e., the defects present close to the border of this region have variable emission characteristics depending on the distance from the neutral region, and (iii) the nonuniform electric field always present in the space-charge region may enhance the emission process due to the Poole-Frenkel or tunneling effects. In our study we found it essential to recognize these effects and minimize their influence on the obtained spectrum by applying special experimental conditions. For each of the cases discussed below these conditions were always established through a long series of measurements until an optimal resolution of the method was achieved.

B. Samples and experimental results

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 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 LPE grown p^+ -*n* diodes. The doping level of the *n*-type material was 10¹⁶ and 5×10¹⁶ cm⁻³ for the samples grown by MBE and LPE, respectively. The Si δ -doped GaAs samples were grown by MBE. As it is known, in GaAs the DX state is resonant with the conduction band. Usually, in order to observe these states in GaAs it is necessary to have highly doped samples. In this case the Fermi level can approach the DX level which results in its partial occupation by electrons. On the other hand, on the highly doped samples good quality Schottky diodes necessary for our type of studies cannot be fabricated. We have managed to overcome this limitation by applying the δ -doping procedure. The sheet of silicon atoms with a high planar concentration was placed within the space-charge region of the Schottky diode. As a consequence, we have achieved locally a very high concentration of donors, while the moderately doped buffer layers allowed us to maintain the good quality of the diodes. For this type of sample DX-like features were only observed for the sample with the highest planar doping level equal to 1.0×10^{13} cm⁻² (see Ref. 21 for details). The sample of GaAs_{0.35}P_{0.65} doped with tellurium was grown by VPE. The conventional DLTS spectra taken for the samples used in our study revealed only one dominant broad peak (see Fig. 1). The DLTS spectrum of the Si δ -doped GaAs sample is presented in Ref. 21.

The Laplace-DLTS spectrum of the δ -doped GaAs sample revealed only one peak which can be attributed to the doping process (Fig. 2). The activation energy for this emission process was found to be exactly the same (0.35 eV) as that derived from standard DLTS measurements.²¹ For the DX(Si) in $Al_xGa_{1-x}As:Si$ (x=0.20, 0.35, 0.44, 0.67, 0.76) the Laplace-DLTS spectra taken at T=205 K are shown in Fig. 3. In the spectra for all alloy compositions there are always three well-resolved peaks which can be unambigu-



FIG. 1. Standard DLTS spectra for three types of samples considered in the study.

ously related to the doping process. The peaks for different alloy compositions can be perfectly aligned for direct bandgap alloys, whereas for the alloys with indirect band gaps there is a slight shift toward higher emission rates. Although the absolute value of the electron emission rate from the DX(Si) center depends on temperature, the ratio of the emission rates seen in the spectra does not change, keeping the distance between the peaks unchanged with varying the alloy composition and temperature. In our previous study²² we demonstrated that from the Arrhenius plot for x=0.35 the activation energy of the thermal emission for each of the peaks is the same within the experimental error and similar to that given by the conventional DLTS technique ($E_e \approx 0.42$) eV). Due to 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. 3), the height of the peak does not represent the true magnitude of each of the emission processes in the transient.

In the Laplace-DLTS spectra for tellurium-doped $Al_xGa_{1-x}As$ crystals up to eight peaks (depending on tem-



FIG. 2. The Laplace-DLTS spectrum of the silicon δ -doped GaAs. The peaks marked by dashed lines are not related to the donor doping procedure. The activation energy for the emission process depicted by the solid-line peak is 0.35 eV and coincides very well with the value inferred from standard DLTS measurements (see Ref. 21).



FIG. 3. The Laplace-DLTS spectra taken at T=205 K for the DX(Si) in Al_xGa_{1-x}As: (a) x=0.20, (b) x=0.35, (c) x=0.44, (d) x=0.67, and (e) x=0.76.

perature and alloy composition) can be observed (Fig. 4). These peaks were found to be closer to each other than in the case of DX(Si), and usually much broader. The patterns of the peaks observed for the DX(Te) defect for different alloy



FIG. 4. The Laplace-DLTS spectra for the DX(Te) in (a) $Al_{0.25}Ga_{0.75}As$ and (b) $Al_{0.73}Ga_{0.27}As$.

compositions and for different temperatures changed slightly, but they were always distinctly different from the patterns observed for DX(Si). It has been recognized that these peaks form two groups, each of them being characterized by a different activation energy of the thermal emission process $(E_{e1} \approx 0.18 \text{ eV} \text{ and } E_{e2} \approx 0.27 \text{ eV})^{.22}$ Figure 5 presents the Arrhenius plots for the spectra shown in Fig. 4. It is seen that for low aluminum composition (x=0.25) the group of peaks with the lower emission energy (E_{r_1}) dominates, while for the sample with high aluminum content (x=0.73) this group is not seen and only peaks characterized by the energy E_{e2} can be observed. In Fig. 4(b) more than four peaks are observed but only for those seen on the right-hand side of the spectrum could the Arrhenius plot be constructed. The remaining two are characterized by an at least three orders of magnitude lower concentration than the other ones. They were found very instable against noise and even small sample temperature fluctuation, making a quantitative analysis impossible.

For the tellurium-related DX center in GaAs_{0.35}P_{0.65} the Laplace-DLTS spectra are very broad approaching the limit when the method still gives reliable results. This fact made a quantitative analysis of the spectra impossible. however, in the spectrum in Fig. 6 at least three very broad peaks can be clearly distinguished.

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FIG. 5. Arrhenius plots of the emission rates for DX(Te) in (a) $Al_{0.25}Ga_{0.75}As$ and (b) $Al_{0.73}Ga_{0.27}As$. The activation energies for each of the processes are indicated.

The identification of the peaks shown in Figs. 3, 4, and 6 with the presence of the DX defects in the samples was further checked by studying the efficiency of the hole capture process. It was already demonstrated by us¹³ in a direct measurement that the DX defect in the ground state forms a negatively charged acceptorlike center. In such a case the defect has a long-range Coulombic potential which makes



FIG. 6. The Laplace-DLTS spectra for the DX(Te) in GaAs_{0.35}P_{0.65}.



FIG. 7. The Laplace-DLTS spectra for DX(Si) in $Al_{0.35}Ga_{0.65}As$ taken without (solid line) and with (dashed line) hole injection. The sensitivity of the defect occupancy to the presence of holes in the space-charge region is a fingerprint of the DX center. This effect allows us to exclude the possibility that other unrecognized defects participate in the thermal emission process studied here.

the hole capture process $(D^- + h^+ \rightarrow D^0)$ very efficient. The Laplace-DLTS spectra taken for the DX(Si) in the hole injection regime (Fig. 7) showed that the defect occupancy can be effectively decreased by the presence of holes in the space-charge region. The latter fact being a fingerprint of the DX center allowed us to exclude the possibility that other unrecognized defects participate in the thermal emission process studied here. A similar behavior was found for the DX(Te) centers in AlGaAs and GaAsP.

In general, the ionization of a negative-U, two-electron defect goes in two steps: $D^- \rightarrow D^0 + e^-$ and $D^0 \rightarrow D^+ + e^-$ and the second process should be faster than the first one (see Ref. 23 for details). Consequently, the peaks for the second ionization process should appear in the spectra at higher emission rates than those for the first one. Such peaks were not observed. Presumably it was due to the limitations of our apparatus, which prevents the observation of processes faster than 10 000 s⁻¹. Thus the spectra presented in the study show only the first step in the ionization process. Further evidence for that comes from the analysis of the hole recombination process observed for the defect.

III. DISCUSSION

In Fig. 3 it is seen that the DX(Si) defect in AlGaAs produces on the Laplace-DLTS spectra a very characteristic sequence of peaks. This pattern can be observed to be unchanged for DX(Si) in different alloy compositions and at a very wide range of temperatures. Each of the peaks is also characterized by the same activation energy for thermal emission. Thus we conclude that the energy barrier for the emission process is predominantly formed by the local energy barrier and has very little to do with the second-neighbor shell of atoms where alloying occurs. In the model in which the DX state is associated with the interstitial-substitutional atom transition,⁴⁻⁶ the energy barrier governing the thermal emission process has an ionic character, i.e.,

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FIG. 8. Configurations of atoms for the DX defect in the ground (DX^{-}) and the ionized (d^{+}) states (see Refs. 4 and 5) for three types of the DX centers considered.

it is the energy necessary to push aside three arsenic atoms when the silicon atom passes from the interstitial to the substitutional position [see Fig. 8(a)]. The total energy calculations performed by Dabrowski *et al.*⁶ support this concept. It was 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.

On the other hand, the second neighbors to the silicon atom may influence the total energy of the defect in the ground state. In the AlGaAs lattice silicon can move into one of the four equivalent (in the $\langle 111 \rangle$ direction) interstitial sites. If they were energetically identical there would be no reason to observe more than one peak, because the process would be fourfold configurationally degenerated. Such a situation would describe the case of DX(Si) observed in δ -doped GaAs. However, if the lattice distortion along one of the $\langle 111 \rangle$ directions lowers the total energy of the defect, then the spatial degeneracy is lifted. Figure 9 shows four examples of different combinations of gallium and aluminum atoms in the second-nearest-neighbor shell. These 12 atoms form four subgroups of atoms gathered along four different (111) directions. In Fig. 9 it is assumed that the energetically favorable $\langle 111 \rangle$ direction for the DX state formation points toward the most aluminum rich location (as proposed in Ref. 24). In order to recognize the actual spatial degeneracy of the DXstate formation process one has to find first the subgroup with the highest number of Al atoms. Then one has to count the number of the (111) directions where this highest number of the Al atoms occurs. This number of occurrences can be, of course, between one and four. If this highest number of the Al atoms occurs only once, then the spatial degeneracy



FIG. 9. Flat diagram showing the silicon donor in AlGaAs with 12 second nearest neighbors. Four examples show how the fourfold spatial degeneracy of substitutional-interstitial motion can be lifted by the fact that the lattice distortion along one of the $\langle 111 \rangle$ directions gives the lowest total energy of the defect. Two upper cases show the examples of the degeneracy equal to one (deg 1); the lower ones illustrate the cases with the spatial degeneracy equal to two (deg 2). The arrows indicate the energetically favorable directions for the DX state formation.

equals one. This is the case of the two upper diagrams in Fig. 9, which are denoted with "deg 1." The arrows there show the favorable $\langle 111 \rangle$ direction. For the two lower examples in Fig. 9 there are two equivalent $\langle 111 \rangle$ directions with the highest number of Al atoms and thus the degeneracy equals two ("deg 2").

Following this procedure one can calculate the probability of a given degeneracy for any alloy composition. Figure 10 shows the result of such calculations where it was assumed that the aluminum rich environment in the second-



FIG. 10. Calculated probabilities of finding a given spatial degeneracy of the DX(Si) state. It was assumed here that the aluminum rich environment in the second-neighbor shell is preferred for the DX state formation. One has to reverse the horizontal axis to get a picture for the case when the gallium rich environment is preferred. The curves denoted from 1 to 4 are the probabilities of finding the spatial degeneracy from one to four, respectively.

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neighbor shell is energetically preferred. One has to reverse the horizontal axis in Fig. 10 to get a picture for the case where the gallium rich environment is preferred. In both cases, for a random distribution of aluminum in the crystal there is a very small probability that a configuration with the degeneracy equal to four will occur for the alloy compositions in the range of 0.2 < x < 0.8. Besides the conclusions derived from an inspection of Fig. 10, there are two other facts which would not favor the observation of the degeneracy equal to four in AlGaAs. First, the probabilities presented in Fig. 10 were calculated assuming that the alloy is perfectly random. However, if this assumption is not valid, i.e., during the crystal growth there are processes which cause the donor atoms to have certain preferences for incorporation into the crystal, there are some strains in the crystal, or, finally, the donors have a tendency to form complexes with other impurities, all of these would result in an effective lifting of the fourfold spatial degeneracy of the DX state formation and, therefore, in a decrease of the concentration of the DX centers in this category. Indeed, the EXAFS measurements for sulfur atoms in AlGaAs clearly showed a compositional enrichment for the sulfur first neighbor shell.²⁵ One can expect that a similar preference may occur for the silicon atoms as well. Second, from numerical tests we have noticed that when a spectrum contains a larger number of peaks the software has a tendency to reveal a too small preexponential amplitude for the most left-hand peak (peaks) in the spectrum, especially when on the right-hand side there are peaks with considerably larger amplitudes.²⁰ The above two arguments (physical and experimental) explain why it is very unlikely that the degeneracy equal to four could be observed in AlGaAs, despite that based on the results presented in Fig. 10 one would expect equal concentrations of degeneracies equal to three and four for x=0.20. Consequently, only three degeneracies, i.e., equal to one, two, and three, will be observed.

These three degeneracies should give a sequence of three emission lines with the respective ratios of 3:1.5:1 and with exactly the same activation energy for the thermal emission process. The three lines observed in the experiment for DX(Si) occur at slightly larger distances which would indicate that, in addition, there are differences in entropy factors for different configurations. Figure 10 also shows that the concentration of the DX centers with a degeneracy factor of unity (right-hand side line in the spectra in Fig. 3) is $3-6\times$ higher than that for degeneracies equal to two or three and this relation does not change significantly for the alloy compositions between 0.2 and 0.7. For x=0.76 the contribution of this line to the total emission is lower [see Figs. 3(e) and Fig. 10]. This is exactly what we observed in the experimental spectra for DX(Si) where the area under the peak is connected to the magnitude of charge exchange. For the DX(Si)in GaAs only one line is observed, which can be related to the spatial degeneracy equal to four, the case which is practically impossible to observe in AlGaAs.

According to the model for DX centers related to the group-VI donors (tellurium) in AlGaAs, it could be either gallium or aluminum which has to go to substitutional position to from the DX state [see Fig. 8(b)]. These two constitu-

ents of the crystal have similar, but not exactly equal, ionic radii (the lattice constant of AlAs is slightly larger than that of GaAs). This small difference in size may result in a substantial difference in energies required to push either aluminum or gallium between the three arsenic atoms. Consequently, one can expect the energy for the emission associated with the motion of aluminum to be larger than that related to gallium. For DX(Te) the Laplace-DLTS spectra indeed consist of two sets of peaks characterized by different activation energies for the thermal emission process. As it is demonstrated in Fig. 5, the relative concentration of the centers with larger emission energy increases with aluminum content in the alloy. Thus we may conclude that for DX(Te)the emission process with the larger activation energy is associated with 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; it is consistent with the lower resolution of the technique and the weighting factor.

These conclusions can be supported by the recent results of Sallese et al.¹⁷ who have shown that the hydrostatic pressure of 1.5 GPa is not sufficient for DX(Te) to emerge from the conduction band to the gap, while even a small aluminum content ensures that the DX(Te) state can be observed in the gap at much lower pressures. This result shows that the state associated with Al-Te bond breaking has a much lower total energy than that produced by the breaking of the Ga-Te bond. On the other hand, in our study we found that for x=0.25 both groups of lines can be observed, while for x=0.73 in the spectra for DX(Te) only lines with larger activation energies could be unambiguously recognized. There is no controversy between these two experiments if one remembers that in the DLTS experiment the filling of the defects with electrons occurs only during a very short period of time, too short to establish equilibrium distribution of electrons among different configurations of the DX defects in the crystal, while in the transport measurement such an equilibrium can be easily reached, resulting in the compensation of one group of the defects (Ga-Te bond breaking) by the other.

The number of peaks within each of the groups found in the case of DX(Te) can again be deduced based on the 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), 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, more peaks can be expected, though with a 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 those of DX(Si), suggesting a possible unresolved structure.

If the microscopic process leading to the DX state formation in tellurium-doped GaAs_{0.35}P_{0.65} is the same, the ionic barrier for the emission process is formed in this case by three atoms for the mixed anion sublattice [see Fig. 8(c)]. Thus, according to the model, one should observe four groups of peaks having different energy barriers for the emission. Moreover, each of the barriers should be split due to possible spatial degeneracy of the atom motion process. Four possible energy barriers for the emission process must result in additional broadening of the Laplace-DLTS spectra in respect to those observed for tellurium in AlGaAs. The spectra for DX(Te) in GaAsP were indeed found to be very broad, making a quantitative analysis impossible. In this case three to four very broad peaks with no fine structure could be observed.

The comparison of the Laplace-DLTS spectra for DX(Si) and DX(Te) in AlAl, $Ga_{1-r}As$ (Figs. 3 and 4) reveals that the number of peaks and distances between them are not what one would expect if the DX center is formed by a donor atom in a stable substitutional configuration. Silicon as a donor in AlGaAs replaces a cation, i.e., gallium or aluminum. Next cations (12 of them) are in the second-nearestneighbor shell, so eventual alloy splitting should give more lines and they should be less separated than those for substitutional tellurium which sits in the arsenic sublattice and has four cations (gallium or aluminum) as nearest neighbors. This is exactly opposite to what we observe. The present results practically rule out the possibility that the DX-type defect is formed by a donor atom in a stable substitutional position, with a small lattice relaxation effect, or with a fully symmetric LLR effect similar to that evidenced for the case of indium in CdF₂.²⁶ Exactly the same arguments can be put forward against the so-called X-S model proposed by Morgan.²⁷ In this model the DX state is formed when a cation and anion close to a donor atom exchange their sites.

The present experimental data led us to the conclusion that the substitutional-interstitial defect reaction is responsible for the DX state formation. However, it should be pointed out here that solely lowering the defect local symmetry from T_d to C_{3v} , i.e., with a less dramatic atom rearrangement (Jahn-Teller effect, e.g., see Ref. 8 for details), would give a similar overall picture of the fine structure observed in the study. However, in this case the independence of the emission barrier of alloy composition seemed to us less obvious. Consequently, we have left this interpretation open until the theory explores this possibility in detail.

IV. CONCLUSIONS

We have compared the Laplace-DLTS spectra of the DX(Si) centers in Al_rGa_{1-r}As and δ -doped GaAs with that of DX(Te) in Al_xGa_{1-x}As and GaAs_{0.35}P_{0.65}, revealing the fine structure caused by the alloy splitting. We have shown that for the DX(Si) defect in $Al_xGa_{1-x}As$ 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 Al_rGa_{1-r}As two groups of peaks are observed and we attribute them to the same process but associated with interstitial-substitutional motion of the aluminum and gallium atoms. For DX(Te) in GaAs_{0.35}P_{0.65} the spectra are very broad, possibly due to a more pronounced influence of alloying on the emission process. The latter fact is predicted by the model for the defect. The lack of structure in the spectrum for DX(Si) in δ -doped GaAs and its presence in $Al_xGa_{1-x}As$ and the apparent broadening of the peaks seen

for $GaAs_{0.35}P_{0.65}$ we relate to the spatial degeneracy of the process for the defect in the different local environments.

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APPENDIX: ALLEGED FINE STRUCTURE OF THE DX CENTERS

Most of the silicon doped AlGaAs samples used for the transport measurements were grown by molecular-beam epitaxy (MBE). For this type of experiment it is convenient to have highly doped samples to avoid high sample and contact resistances at low temperatures. For AlGaAs grown at optimal conditions (good surface morphology, low native defect concentration) the top electron concentration possible to obtain is about 1×10^{18} cm⁻³.²⁸⁻³⁰ This concentration can be increased to about 3×10^{18} cm⁻³ by lowering the growth temperature;²⁸ however, this is accompanied by a dramatic degradation of the surface morphology^{31,32} caused by the reduced surface mobility of the aluminum atoms at lower growth temperatures.^{32,33} Consequently, this effect can lead to formation of local inhomogeneities of the Al content or even aluminum clusters.³³ Lower than optimal growth temperatures may also lead to surface segregation of the Al_xGa_{1-x}As alloy.³⁴ Secondary-ion mass spectroscopy revealed that even for moderate doping levels there is a distinct accumulation of silicon at the sample surface,³⁵ while for higher doping levels a difference in the silicon concentration across the layer can be up to a few orders of magnitude.³⁶

Despite the fact that the DLTS experiment demands much lower doping levels, the relation between the features observed in the spectra and the crystal doping procedure again is in some cases not clear. In one of our previous studies¹³ we reported that the DX states are characterized by a very large hole capture cross section as a consequence of the long-range negative Coulomb potential present for the defect at the ground state. Figure 11 shows the DLTS spectra related to DX(Si) in two Al_{0.35}Ga_{0.65}As layers. One of them (solid line) was prepared in a form of the unsymmetrical p-nheterojunction which allowed injection of holes to the diode depletion region. A majority-carrier filling pulse (zero bias), long enough to fill all the DX centers with electrons, was immediately followed by a short hole injection pulse (forward bias). The amplitudes of the DLTS peaks related to the DX(Si) centers decrease as the hole injection current is increased (see dotted lines in Fig. 11). This is because the electrons trapped by some of the defects during the injection pulse recombine with injected holes, so reducing the occupancy at the start of the emission process. In Fig. 11 an additional distinct peak at lower temperatures is observed

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FIG. 11. DLTS spectra of the silicon-doped $Al_{0.35}Ga_{0.65}$ As taken without (solid line) and with (dotted line) hole injection (see Ref. 13). Dashed line shows the DLTS spectrum for DX(Si) in the high-quality $Al_{0.35}Ga_{0.65}As$. The 0.34 eV peak, which is not reduced by the hole injection process and is absent in the high-quality sample, cannot be identified with the DX center.

with the activation energy of 0.34 eV. As is clearly seen, this peak is not reduced as a result of the recombination process with holes. Consequently, the dramatic difference in the hole capture cross section of this defect and that observed for DX(Si) rules out the possibility put forward by other authors that this defect belongs to a family of the DX centers in $Al_xGa_{1-x}As$.

The final evidence for the idea that the structure seen in some DLTS spectra is not related to the DX centers is gained when the spectrum in Fig. 11 (solid line) is compared with the spectrum of the other sample (dashed line) produced by the same technology with the same alloy composition and doping level. This sample is a high-quality Al Schottky diode prepared *in situ* in the MBE machine.³⁷ It had almost ideal I-V and C-V characteristics which was demonstrated in the previous study.³⁷ In this sample the 0.34 eV peak is missing, indicating that this particular defect had nothing to do with the doping process. It is highly likely that it is generated on the interface between two AlGaAs layers.

In general, samples grown by MBE are characterized by a rather high concentration of defects, presumably as a consequence of nonequilbrium growth conditions or oxygengettering action of aluminum in the MBE chamber. Even high-quality MBE samples used in our study have a substantial number of deep centers of unrecognized structure with a concentration around 10^{15} cm⁻³. Figure 12 shows one of the DLTS spectra of Si-doped Al_{0.20}Ga_{0.80}As samples where eight different features can be recognized. Only one of them we would relate tot he DX(Si) center, which can be observed with the much higher concentration in samples with larger aluminum contents. This assignment could be done due to the fact that the DX centers at different alloy compositions are characterized by the same electron emission rate at corresponding temperatures, the feature which is discussed in detail in the main part of this paper. As a result, the DXpeaks on the DLTS spectra taken for different alloy compositions but with the same rate window can be aligned, and only this particular peak in Fig. 12 aligns with other DX



FIG. 12. The DLTS spectrum of the silicon-doped $Al_{0.20}Ga_{0.80}As$ sample showing numerous defects present in this particular layer. The peak related to the *DX* center is indicated.

peaks for samples with higher aluminum content.

In conclusion, the appearance of a fine structure which is allegedly related by some authors to alloy splitting of the DXstate in AlGaAs is presumably caused by (i) a too high doping level, (ii) very strong segregation of dopants in the layer, (iii) surface segregation of aluminum and gallium in AlGaAs, (iv) clustering of aluminum as a result of nonoptimal growth conditions, (v) creation of defects in the AlGaAs (1)/AlGaAs(2) interface, (vi) oxygen-gettering action of aluminum in the MBE chamber, or (vii) low quality of the Schottky or p-n junctions. The evidence for this conclusion comes from the fact that such a structure *is not* observed when (i)-(vii) do not occur, i.e., in the high-quality Schottky diodes or samples grown at equilibrium conditions (e.g., by LPE).

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