Large- versus small-lattice-relaxation models of the *DX* centers in $Ga_{1-x}Al_xAs$

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The first observation of a metastable delocalized bound state of *DX* centers in $Ga_{1-x}Al_xAs$:Te pinned to the *X* minimum of the conduction band is reported. *DX* centers are therefore the first defects in covalent semiconductors that bind carriers in two barrier-separated states which are either strongly localized or delocalized. This validates the general Toyozawa model of extrinsic self-trapping for covalent materials, as well as the large-lattice-relaxation model of these centers.

It is well known that $Ga_{1-x}Al_xAs$ doped with either group-VI or group-IV elements produces medium-depth donors, called the *DX* centers, exhibiting various persistency effects. Since their discovery[1] in 1977, numerous authors[2–5] have proposed various microscopic models of them, but until now, no consensus has been reached. *DX* centers are characterized by a large difference between thermal and optical ionization energies, thermally activated carrier capture and emission, and by an immeasurably low capture cross section of ionized DX^+ centers at low temperatures (usually below 50 K). The last property, distinguishing the *DX* centers from most deep defects, manifests itself by the existence of persistent photoconductivity observed in low-Al-content ($0.2<x<0.4$) samples cooled in darkness,[6] and then illuminated by light of energy above the *DX*-center photoionization threshold. Photoinduced metastable conduction-band filling can last without quenching for an immeasurably long time at low temperatures. The only way of restoring a previous state of the *DX* center is to heat a photoconverted sample to about 100–150 K (for a more detailed summary of the physics and chemistry of the *DX* centers in semiconductors see the recent review by Lang[7]).

Quite similar behavior was reported even earlier for some donor states in such small-gap semiconductors as InSb or GaSb (see Refs. 7 and 8 for a review). Truly intense interest in this type of center was stimulated by their detection in $Ga_{1-x}Al_xAs$ mixed crystals doped with Te, S, and Se, and later on, with the group-IV elements.[1,2] Since these centers are unavoidable (at least at present) when preparing *n*-type $Ga_{1-x}Al_xAs$ and are efficient lifetime controllers, a general interest in unravelling their nature is obvious.

To account for the atypical properties of the *DX* centers Lang and Logan[1,2] postulated very strong coupling of these defects to the lattice, resulting in a large difference in the equilibrium lattice arrangement around the defect in its neutral (highly localized) and ionized states. A configuration-coordinate diagram (Fig. 1) was used to describe this large coupling, called the large-lattice-relaxation (LLR) phenomenon.[8] The metastability is a consequence of the presence of a barrier resulting from a shift of the equilibrium positions of the lattice for these two states.

The LLR model of the *DX* centers has recently been contested.[3,4] The key argument for such a reinterpretation came from near-gap donor-acceptor luminescence seemingly involving silicon-originated *DX* donors.[3] The emission itself does not exhibit a pronounced phonon structure, and thus excludes strong defect-lattice coupling for a donor participating in the recombination. Among other alternative explanations, the potential-fluctuation model[9] may account at least for persistency effects seen in *DX* centers in $Al_xGa_{1-x}As$. This model explains the bulk persistency effects by the occurrence of electrostatic barriers resulting from doping inhomogeneities and local composition fluctuations in the ternary compounds. The key argument against this model comes, however, from the fact that various technologies of material preparation and doping (from bulk-crystal growth via liquid-phase epitaxy, or metal-organic

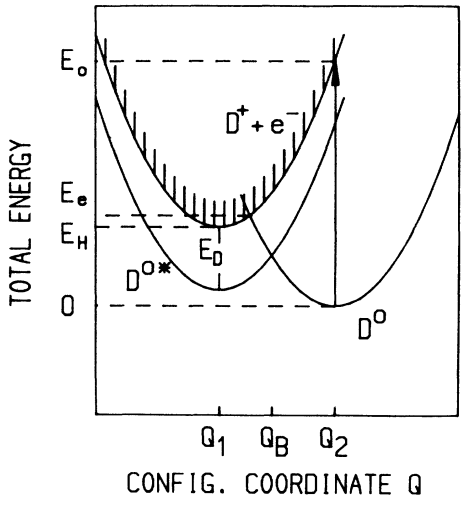

FIG. 1. Configuration-coordinate diagram of donors *D* exhibiting large lattice relaxation.

chemical-vapor deposition to molecular-beam epitaxy produce virtually the same results. Recent discovery of *DX*-type behavior of *n*-type GaAs subjected to either high hydrostatic pressures[10] or high electric fields producing hot electrons,[11] adds a strong argument in favor of association of all the peculiar properties of a *DX* center with real donors, and not with extended-potential fluctuations.

Meanwhile Toyozawa,[12] extending the intrinsic self-trapping problem extensively studied for excitons and polarons in ionic lattices to cover defects, was able to prove that common action of the local defect chemical potential and acoustic phonons may result in localization of an electron on a donor. These short-range interactions must always be weighted, however, against long-range Coulomb-type attraction (due to optical phonons and the impurity Coulomb-potential tail), which tends to favor extended effective-mass states. From an analysis of the most general defect Hamiltonian, he finally concluded that an electron can be bound by a defect either in a strongly localized atomiclike state or in a delocalized effective-mass one. Which of them is deeper is a specific defect property (in many case the localized state may simply be unobservable, being resonant with band states). If the ionization energies (in a thermodynamic equilibrium sense) of these states are comparable, they should be separated by a potential barrier. A similar barrier must exist between a localized state and a continuum of band states. Since carrier localization is directly related to the electron-phonon coupling strength,[13] the configuration-coordinate diagram depicted in Fig. 1 provides a somewhat equivalent description. These general conclusions are independent of the type of bonding, which may only enter through numerical values of the coupling strength parameters.[5,8,12]

The large Stokes shift of the ionization processes for the *DX* ground state[1,2] and the magnitude of the inhomogeneous broadening due to alloy composition fluctuations in $Ga_{1-x}Al_xAs$, seen in deep-level transient-spectroscopy (DLTS) experiments,[14] indicate its highly localized nature. If other properties of the *DX* centers were defect-specific, the Toyozawa model should also be applicable to this kind of center. Therefore one should expect to detect the metastable delocalized bound states of the *DX* center pinned to the nearby conduction-band minima. Their existence would provide the final proof of the LLR model of *DX* centers and prove that all the major properties of these centers are truly defect-specific.

Such a proof was recently given by us for In and Ga donors in highly ionic CdF_2 crystals.[15] We showed the presence of LLR in the ground state of these donors and its absence in the first excited metastable, delocalized, bound polaronlike state. These two states are separated by a vibronic barrier, thus exhibiting all the characteristic features of Toyozawa's extrinsic self-trapping model of defects. We then attempted the same kind of observation on the *DX* centers in the much more covalent $Ga_{1-x}Al_xAs$. For simplicity, Te was chosen as the dopant, mainly because of the amphoteric behavior of group-IV elements. For small Al content (below that of the Γ-*X*-*L* conduction-band crossover[16] at about $x=0.4$) the effective-mass bound states associated with the Γ minimum should be the lowest. Because of the very small effective mass m^* at Γ, an impurity band is formed even for very low doping levels. In order to look for the excited effective-mass metastable states of the *DX* center it was thus necessary to look for them in samples with Al contents around and above the crossover at $x=0.4$. It should be noted, however, that Theis *et al.*[17] have observed a photoinduced *DX*-related far-infrared absorption in lightly doped (but still very close to the Mott transition for a Γ-like donor) $Al_xGa_{1-x}As$:Si, $N_{Si}=(2-3)\times10^{16}$ cm^{-3}. The authors have suggested the $1s$-$2p$ Γ-like donor character of the transition, and certain experimental arguments were given to connect this donor state with the *DX* centers themselves. The spectrum was measured at 4.2 K only. Because of that, as well as a much smaller value of the ionization energy of this state compared with a known *DX*-center capture barrier, its metastable character could not be proved.

Te-doped samples of $Ga_{1-x}Al_xAs$ were grown by liquid-phase epitaxy (LPE) on (100)-oriented semi-insulating GaAs(Cr) substrates. Since the intended Te concentration was in the range of $10^{15}-10^{16}$ cm^{-3}, fairly thick layers had to be grown. This, in turn, yielded some gradient in Al content along the growth axis, which was measured by an electron microprobe (depicted by the x error bars in Fig. 3). The relevant sample parameters are

TABLE I. Sample parameters of $Ga_xAl_{1-x}As$:Te layers of thickness d, in which the photoionization spectrum shown in Fig. 2 was seen: Carrier concentration, as obtained from Hall-effect measurement at 300 K, n_{300}, the photoionization threshold energy, E_D, and the empirical constants A and B. E_D, A, and B are obtained by fitting the expression $\alpha=C(\hbar\omega-E_D)^A\hbar\omega^{A+B}$ for the absorption coefficient to the experimental data of Fig. 2.

x (%)	d (μm)	n_{300} (cm^{-3})	E_D (meV)[a]	A[a]	B[a]
23±5	52	2.3×10^{16}			
26±4	45	3.8×10^{16}			
35±3	40	1.0×10^{16}	49	1.5	2.3
42±2	45	1.4×10^{16}	43	1.8	2.6
47±1	19		39	1.6	2.5
57±1	28	2.6×10^{16}	42	1.3	2.7

[a]The estimated root-mean-square deviation of the fitting parameters E_D, A, and B are 5 meV, 0.4, and 0.2, respectively.

summarized in Table I. All low-Al-content samples have exhibited persistent photoconductivity typical of *DX* centers in $Ga_{1-x}Al_xAs$.[7] For larger Al contents, a notable freezeout, similar to that reported for $Ga_{1-x}Al_xAs$: Si,[6] is seen.

Infrared absorbance was measured after cooling the samples in darkness down to 10 K, using a fast-scan DIGILAB Fourier spectrometer. The metastable, light-induced absorption αd depicted in Fig. 2, for various samples of different compositions, has been recorded after tungsten-halogen lamp sample illumination and corrected for the "dark" absorbance. After the pumping light is switched off the spectra remain stable during a one-day measurement run, thus proving metastability of the photoinduced absorption. The absorption which is metastable at $T=10$ K disappears when the temperature of the sample is raised above about 100 K, and later on the whole experimental procedure can be repeated with the same result. In the same temperature range the other metastability effects[7] are quenched, thus proving that we are dealing with the same barrier and the same center. The photoinduced ir absorption decreases with a decrease of $Al_xGa_{1-x}As$ thickness changed by a layer etching. It is also observed on samples with a GaAs substrate removed, thus finally proving a bulk origin of the observed transition.

The most remarkable feature of the photoinduced absorption is the fact that the position of its peak and the low-energy cutoff are almost independent of composition. The shape of the photoinduced metastable absorption, similar to impurity photoionization in GaP (Ref. 18), indicates its impurity photoionization origin. Similar unstructured absorption was also seen for donors exhibiting persistency effects in more heavily doped CdF_2.[19] Although the almost constant maximum position of the photoinduced absorption band indicates constant ionization energy of the metastable bound state, to be more quantitative, we have performed a fit of a quite general form of impurity photoionization absorption cross section, $\alpha=C(\hbar\omega-E_D)^A/\hbar\omega^{A+B}$, to the experimental data. The fitting parameters are summarized in Table I. They are well in accord with the postulated shape of hydrogen-like donors originating from the *X* conduction-band minimum, as proposed for GaP by Kopylov and Pikhtin.[18] The values of the *A* and *B* exponents in the photoionization spectrum, the effective pinning of the photoinduced state to the *X* conduction-band minimum (Fig. 3) as well as the value of the ionization energy itself,[5] strongly indicate its *X*-like effective-mass origin. It is worth noting that Dingle *et al.*[20] have observed that for $Al_xGa_{1-x}As$:Te ($x>0.6$) a donor level participating in a donor-acceptor photoluminescence has a constant depth of about 40 meV and concluded it was an *X*-like state. Although its identity with the one observed by us remains to be proven, it is most likely that both are identical.

All these observations indicate that the *DX*-center-related properties in $Ga_{1-x}Al_xAs$:Te are truly defect-specific and the Te-related *DX* donor possesses at least two bound states separated by a barrier. The ground state of the *DX* center is strongly coupled to the lattice, while the slightly higher, effective-mass state—derived from the nearby conduction-band minimum—is not. *DX* centers are therefore the first defects in covalent semiconductors for which the possibility of binding carriers in

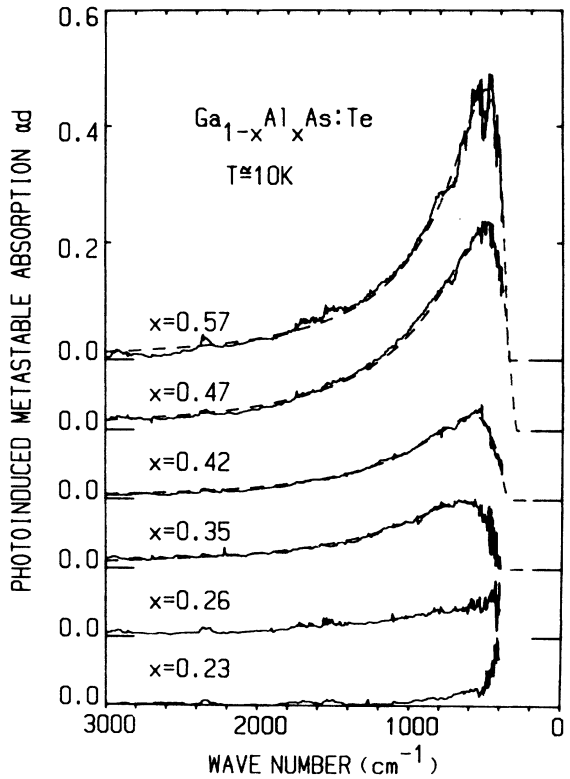

FIG. 2. Photoinduced metastable absorption in $Al_xGa_{1-x}As$:Te. The dashed line gives the photoionization-spectrum fit discussed in the text.

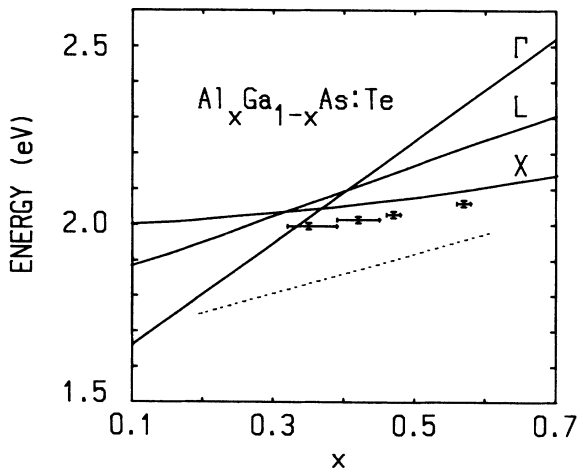

FIG. 3. Conduction-band minima and *DX* donor levels in $Al_xGa_{1-x}As$. The points denote the optical ionization energy of the metastable photoinduced state of the Te *DX* center. The dotted line shows a typical compositional dependence of the thermal ionization energy of *DX* centers, as obtained from Hall-effect measurements; the thermal emission activation energy as obtained; e.g., from DLTS experiments follows much more closely the nearby conduction-band minimum (Ref. 7).

two barrier-separated states, either strongly localized or delocalized, has finally been proved. This extends the validity of the general Toyozawa model of extrinsic self-trapping to covalent materials and finally proves the correctness of the large-lattice-relaxation model of these centers. The upper, hydrogenlike state of a *DX* center may participate in radiative recombination and its depth determines the amplitude of persistent photoconductivity. The ground state governs all the transport properties at high temperatures. The energetic proximity of these two states is most likely the source of the recent controversies.

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