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Tetrahedrally symmetric *DX*-like states of substitutional donors in GaAs and $Al_xGa_{1-x}As$ alloys

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The structural and electronic properties of Si, Ge, Sn, S, Se, and Te substitutional donors in GaAs are examined via self-consistent pseudopotential calculations. Two distinct negatively charged *DX*-like deep donor states are found. The first has a broken-bond atomic configuration while the second arises from a symmetric "breathing-mode" relaxation around the impurity. The energies of the two configurations are especially close for Sn, Se, and Te donors. Experimental data on *DX* centers in $Al_xGa_{1-x}As$ alloys are analyzed within this model.

Substitutional donors in GaAs and $Al_xGa_{1-x}As$ alloys are well known to exhibit very interesting electronic properties as a function of hydrostatic pressure and Al concentration.[1] Column IV or VI dopants generally give shallow effective-mass-like donor levels for hydrostatic pressures[2] of under 20 kbar or for Al concentrations of less than 22%.[3] Above these thresholds the donor level becomes progressively deeper with increasing pressure or Al content. The deep "*DX*" donor levels have the property that their optical ionization energy of approximately 0.75–1.5 eV is many times larger than their thermal ionization energy of 0–160 meV.[4] The underlying mechanism for this and other properties of *DX* centers has been a subject of intense investigation over the last decade.

It is now generally well accepted that the occurrence of *DX* centers is purely an intrinsic property of donor impurities and does not involve, for example, a complexing of the impurity with a defect.[2,5] There is also considerable experimental support[6–15] for a "negative-*U*" model of *DX* centers based on the charge-exchange reaction[16]

$$2d^0 \rightarrow d^+ + DX^- , \qquad (1)$$

where d^0 and d^+ represent neutral and ionized *effective-mass-like* states of a substitutional donor. The atomic structures of a substitutional donor in the d^0 and d^+ states are essentially identical in $Al_xGa_{1-x}As$ alloys because of the small binding energy and large effective Bohr radius of the donor electron. The negatively charged DX^- state in Eq. (1) was earlier proposed to arise from a large bond-breaking lattice relaxation at either the donor site [for Si impurities, as shown schematically in Fig. 1(a)] or at a nearest-neighbor Ga (or Al) sublattice site (for S impurities).[16] The model accounts well for the large Stokes shift between the optical and thermal ionization energies of *DX* centers and for the observation of persistent photoconductivity (PPC). It also yields good results for the pressure, alloying,[17] and local atomic structure dependence of the donor binding energy.[18–20]

The purpose of this paper is to examine the properties of a second type of donor-derived *DX*-like defect [labeled *D* in Fig. 1(b)] with negative-*U* properties. The primary relaxation in *D* is an outward, tetrahedrally symmetric, breathing-mode displacement of the impurity's four nearest neighbors. The electronic properties and total energies of both types of *DX* centers are examined via self-consistent pseudopotential calculations for Si, Ge, Sn, S, Se, and Te dopants in GaAs. It is found that the energies of the D^- and DX^- states are very close for Sn, Se, and Te donor impurities. The primary differences between the two centers are that (i) D^- has a metastable neutral state that can be reached via optical excitation whereas the broken-bond structure for DX^- is unstable in a neutral charge state; and (ii) DX^- has generally a larger optical excitation energy than D^-. Recent experimental re-

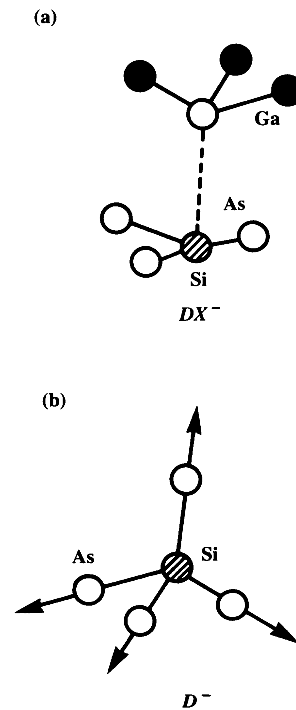

FIG. 1. The DX^- and D^- states for a Si substitutional donor in GaAs are shown in (a) and (b), respectively. The D^- state involves a symmetric breathing-mode distortion around the impurity which is indicated by the arrows.

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sults by Peale *et al.*[14,21] on Te-doped $Al_{0.35}Ga_{0.65}As$ alloys showing the existence of two different *DX*-like centers and separate experimental data[10] on other substitutional donors are shown to be consistent with this picture. For the case of Sn donors, a third metastable state (labeled DX' in Fig. 2) with *DX*-like properties which results from a large bond-breaking displacement on an As *nearest neighbor* of Sn (instead of the donor itself) is found.

The *D* center arises from a radially outward displacement of its four nearest neighbors. The electronic level of this center corresponds to the lowest energy antibonding level of the impurity-host system. The properties of *D* in a neutral charge state have been examined by several authors.[22–26] This state was also an early candidate for the *DX* center.

The stability of the shallow effective-mass state relative to the deep states are determined by considering the energy changes resulting from the reaction given in Eq. (1) and

$$2D^0 \rightarrow d^+ + D^- \tag{2}$$

and

$$d^0 \rightarrow D^0 \,. \tag{3}$$

The distinction between d^0 and D^0 is that d^0 refers to an effective-mass-like state in which the donor electron is loosely bound to the impurity. In contrast, in the D^0 state the donor electron is localized on an atomic scale to the impurity. In the simplest tight-binding picture it arises from a symmetric antibonding combination of the impurity's sp^3 orbitals with the corresponding orbitals of its four nearest-neighbor atoms. The DX^0 state obtained by keeping the atomic structure of the DX^- state intact, but changing the charge state is highly unstable[16] compared to the d^0 state and will not be considered. The d^0, D^-, and DX^- states of a Si donor are shown schematically in Fig. 1.

A three-dimensionally periodic 32-atom cell was used to study the total energies and electronic properties of donors in the d^+ (ionized effective-mass state), DX^- (broken-bond state), D^0, and D^- states. The energy of the d^0 shallow donor state was determined from the relation $E(d^0) \simeq E(d^+) + E_{\text{gap}}$ where E_{gap} is the calculated band gap of GaAs. The atomic configurations were fully optimized via an iterative total-energy minimization scheme based on using Hellmann-Feynman forces to determine the directions of atomic motions. All atoms in the unit cell were allowed to relax. An energy cutoff of 6.5 Ry was used for the plane-wave expansion. At this cutoff the calculated minimum band gap of GaAs is 1.53 eV, close to the experimental value of 1.52 eV at low temperatures.

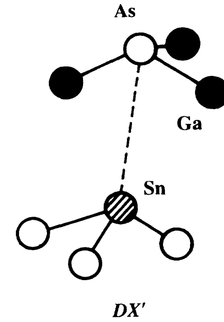

FIG. 2. The DX' state for a Sn donor impurity in GaAs. Unlike the DX^- state, such as the one shown for Si in Fig. 1(a), this center arises from a large atomic relaxation on an As sublattice. Among column IV impurities the DX' state is relevant primarily for Sn. The DX' configuration is stable only in a negatively charged state.

The results of the calculations show that the reaction given by Eq. (2) is always exothermic and that *D* is a negative-*U* defect center. The energy difference between D^- and DX^- and the optical excitation energies for the two states are shown in Table I. For Si- and Ge-doped $Al_xGa_{1-x}As$ alloys we find, in agreement with our previous results,[16–18] that the experimentally observed *DX* center should be identified with the C_{3v} symmetric broken-bond DX^- state. In GaAs the DX^- state is a resonance lying 0.27 ± 0.1 eV above the conduction-band minimum and at high doping levels causes Fermi-level pinning.[27] It becomes a deep center in $Al_xGa_{1-x}As$ for $x > 0.22$. The DX^- center for Si and Ge is calculated to be significantly lower in energy than the D^- center. Experimental data also appear to favor DX^- over D^-. The deep-level transient spectra (DLTS) of the Si-induced *DX* center in GaAs seen under pressure exhibits a *single* peak.[2] This peak is observed to split into four components in $Al_xGa_{1-x}As$ alloys.[1] The splitting is easily understandable if the *DX* center corresponds to the DX^- model shown in Fig. 1(a).[1,18] For an energy difference as small as 0.01 eV between the DX^- and D^- models, as suggested from a cluster calculation,[26] one would expect to see two peaks in the DLTS. Experimental evidence for a relatively *shallow* defect center with a binding energy of

TABLE I. The optical excitation energies (in eV) of Si, Ge, Sn, S, Se, and Te donor impurities in GaAs for the D^- and DX^- states and the total-energy difference between the two states are shown.

Energies \ Donors	Si	Ge	Sn	S	Se	Te
$E_{\text{opt}}(D^-)$	0.3	0.5	0.48	0.57	0.49	0.44
$E_{\text{opt}}(DX^-)$	1.09	0.9	1.15	0.94	0.83	0.79
$E(DX^-)-E(D^-)$	−0.37	−0.2	−0.03	−0.10	−0.04	−0.05

0.03 eV in a Si-doped $Ga_{0.6}Al_{0.4}As$ alloy has been reported.[28] Identification of this center with D^- allows an estimation of its total energy relative to DX^-. The binding energy of DX^- for the alloy is about 0.14 eV. This would indicate an energy difference of 0.11 (0.22) eV between the two states if the *DX* and *D* centers are assumed to be neutral (negatively charged).[16] This value is within 0.15 eV of that calculated for GaAs and shown in Table I.

The energy of the D^- is found to be within 0.05 eV of DX^- for Sn (and also Se and Te) impurities in GaAs. A radially symmetric distortion of approximately 0.35 Å around Sn is calculated for D^-. A *third* type of *DX* center in which the Sn donor has a *small* lattice relaxation was found. In this state, shown schematically in Fig. 2, a nearest-neighbor *As atom* of Sn undergoes a large lattice relaxation that breaks its bond to the impurity. This new DX' center has an energy that is 0.08 eV higher than the "normal" type of *DX* center [shown schematically in Fig. 1(a) for a Si impurity] that results from a large lattice relaxation on Sn. The optical excitation energy for the new center is 0.75 eV. We had previously examined[16] a similar configuration for Si but had found its energy to be much larger than the normal DX^- state in Fig. 1(a) than is found here for Sn. The DX' center is also predicted to exhibit a persistent-photoconductivity effect. The center is stable in the configuration with a large lattice relaxation only when negatively charged. It reverts to the ordinary fourfold-coordinated configuration when its charge is changed, e.g., via optical excitation, to neutral or positively charged. The barrier for bond breaking prevents the formation of DX' and leads to persistent photoconductivity.

Experimental observations of a metastable *neutral* and paramagnetic active state[10] of *DX* in a Sn-doped $Al_{0.39}Ga_{0.61}As$ alloy are consistent only with the assignment of this state to a D^0 center. The predicted closeness of the energies for the D^- and DX^- states is consistent with the experimental observation[29] of two DLTS peaks in Sn-doped GaAs under hydrostatic pressure. The two peaks are seen to occur at nearly the same pressure. Only a single peak is seen for the case of Si. Extended x-ray-absorption fine-structure (EXAFS) experiments[30] can distinguish, in principle, the various types of Sn-derived donor states and such experiments are currently underway.

For S, Se, and Te substitutional donors in GaAs the energy of D^- is calculated to be only $0.05-0.1\pm0.1$ eV higher than the DX^- state. The tetrahedrally symmetric Ga-nearest-neighbor atomic relaxations induced by the D^- centers are found to be nearly 0.25 Å for Se and 0.36 Å for Te. The DX^- center develops into a deep donor in $Al_xGa_{1-x}As$ alloys when $x>0.22$. Assuming that the variation of the binding energy of D^- and DX^- with alloy composition is nearly equal, the D^- state is estimated to become a deep state for $x>0.26-0.29$. This suggests that at higher Al concentrations, there could be two deep negatively charged donor-derived states in the band gap. This situation may explain the observation of *three* S-related vibrational modes (possibly corresponding to the d^+, D^-, and DX^- states) in some S-doped GaAs samples under pressure.[31]

The D^- and DX^- states may also be important in explaining the recently observed properties of Te donors in an $Al_{0.35}Ga_{0.65}As$ alloy where Peale *et al.*[14,21] have found evidence for two different *DX*-like centers with optical excitation energies of 0.6 and 1.5 eV. Both centers were found to be diamagnetic in character, a behavior consistent with that expected from negative-*U* defects. Peale *et al.*[21] used the notations *DX* and PPC2 for the 0.6- and 1.5-eV centers, respectively. They examined the dichroism of the optical-absorption spectra (by using polarized light incident along various symmetry axes) to check the symmetry of the *DX* center. They found no statistically significant effect and concluded that either the dipole matrix elements of the *DX* are accidently very isotropic, or that more likely there is no large symmetry-lowering distortion (e.g., of C_{3v} character) at this center. Although the first conclusion on the diamagnetic nature of this defect was found to be consistent with our previous broken-bond model for the *DX* center, the latter conclusion is in direct conflict with it.

We would identify the 0.6-eV center as the D^- center. Its diamagnetic properties, tetrahedral symmetry, and relatively small optical ionization energy are all consistent with this assignment. In addition, the observation of a metastable neutral state of this center in photoionization experiments[13] is consistent with the creation of a metastable D^0 center and not a DX^0 center since the latter is theoretically found to be highly unstable.[16] Similarly, it is possible that the 1.5-eV center arises from the previously proposed C_{3v} symmetric broken-bond DX^- state. This would be consistent with the much larger optical excitation energy calculated for this state as compared to the D^- state. The observation by Mochizuki and Mizuta[32] that in some samples only the D^--like is found suggests, however, that the 1.5-eV center may be an extrinsic defect center not associated directly with Te donors.

The D^- model for *DX* in group-VI-doped GaAs and Al and $Al_xGa_{1-x}As$ alloys is also consistent with the results of EXAFS experiments on S- and Se-doped samples.[33,34] At extremely high doping levels in GaAs the electrons at the Fermi level have enough energy to form *DX* centers. In this doping regime Sette *et al.*[34] found that S impurities in GaAs had two different substitutional configurations corresponding to two different nearest-neighbor bond lengths. The two configurations were found to have equal concentrations to within 20%. These results are consistent with those expected from Eq. (2). EXAFS data[34] on Se showing that Se atoms do not move upon the formation of *DX* centers are consistent with either the DX^- or D^- models.

In summary, substitutional donors in $Al_xGa_{1-x}As$ alloys are found to have two different negatively charged states with *DX*-like properties. The C_{3v} symmetric broken-bond DX^- state [Fig. 1(a)] is found to be the best candidate for the *DX* center in Si- and Ge-doped alloys. The tetrahedrally symmetric D^- state [Fig. 1(b)] has an energy very close to that of DX^- for Sn, Se, and Te impurities. The D^- state can be distinguished from DX^- by its smaller optical excitation energy and by the presence of a metastable neutral state. It is suggested that the

two DX-like centers seen experimentally[14] in Te-doped $Al_{0.35}Ga_{0.65}As$ may be related to the two different negatively charged states of donors discussed above. A third type of low-energy metastable configuration with an energy 0.08 eV above that of DX was found for Sn. In this structure the donor is not displaced but a nearest-neighbor As atom goes into a threefold-coordinated "interstitial" configuration.

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