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Orthorhombic symmetry *DX* centers in S-doped GaSb, GaAs, and $Al_xGa_{1-x}As$

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We identify a different type of deep donor *DX* center with orthorhombic C_{2v} symmetry in III-V semiconductors. The center is predicted to occur only for anion site dopants, especially S. Its atomic structure, obtained from *ab initio* calculations, is characterized by cation-cation dimer-bond formation. Experimental data on S-doped GaAs and GaSb are shown to provide support for this type of *DX* structure. Theoretical results for *DX* centers with orthorhombic and trigonal symmetries in S-, Se-, and Te-doped GaSb, GaAs, and $Al_xGa_{1-x}As$ alloys are examined. [S0163-1829(96)52240-X]

Deep donor *DX* centers have been extensively studied in connection with problems encountered in the doping of zinc-blende semiconductors.[1,2] Two key features exhibited by these centers are persistent photoconductivity (PPC) and a large Stokes shift between thermal and optical ionization energies. Shallow to deep transition of donor levels with pressure or alloying have also been associated with the formation of *DX* centers in a number of III-V and II-VI compounds.[3,4]

DX centers were first seen in $GaAs_{1-y}P_y$ and $Al_xGa_{1-x}As$ alloys doped with a variety of impurities. Lang and Logan proposed a configuration-coordinate diagram with two minima in the total energy to explain the PPC and the Stokes shift between thermal and optical ionization energies.[5] Theoretical studies based on *ab initio* total-energy calculations confirm this picture.[6] A tetrahedrally coordinated substitutional impurity usually gives an effective-mass type of donor level.[7] This structure is either stable or metastable with respect to a deep donor state arising from a large trigonal distortion [Fig. 1(a)] at an impurity. In the latter configuration the atomic relaxations are sufficiently large as to cause bond breaking.[6] The bond breaking is accompanied by the capture of two electrons making the *DX* center negatively charged. In the following we will refer to this model as the broken-bond (BB-*DX*) model to distinguish it from a different structure discussed below.

The trigonal symmetry BB-*DX* model explains the phenomena of PPC, the Stokes shift between optical and thermal excitation energies, and the pressure and alloy dependence of binding energies for donor impurities in AlGaAs alloys.[6] The splitting of the binding energy of *DX* centers into four components in going from Si-doped GaAs to $Al_xGa_{1-x}As$ provides strong evidence in favor of the trigonal symmetry of the BB-*DX* state.[8,9] The splitting results from second-nearest-neighbor interactions of the displaced Si atom with different combinations of Al or Ga atoms. For the case of an anion-substitutional impurity such as S, the model predicts that a nearest-neighbor Ga or Al atom of the impurity undergoes a large displacement. In this case an eightfold splitting of the *DX* energy is expected in an alloy system and seen experimentally.[8]

Even though the BB-*DX* model is successful in explaining many properties of *DX* centers for both cation and anion substitutional site impurities, a number of experimental observations are not explained by this model.[10–14] As discussed below, the problems are most pronounced for substitutional S impurities and occur in both GaAs and GaSb and most probably in other III-V semiconductors.

In GaAs, it is well known that *DX* centers set a limit to the free carrier density obtained from doping. This occurs when the Fermi level crosses the *DX* resonance in the conduction band.[1,6,4] In the case of heavy S doping where many of the donors are in a *DX* state, x-ray fine-structure spectroscopy (EXAFS) measurements[10] show a 0.23-Å broadening of nearest-neighbor distances around S instead of the large 1.3-Å bond length change predicted by the BB-*DX* model.[15]

In GaSb, sulfur is the only impurity that gives a deep donor *DX* center.[11,16,17] The *DX*-related PPC effect in GaSb:S is qualitatively different, however, from that in $Al_xGa_{1-x}As$:Si. In particular, photosensitivity to 0.66 eV light and PPC become gradually quenched after repeated illumination cycles and are recovered only after heating to room temperature.[12] The results in GaSb can be explained if a transfer of electrons from one deep center to another with a larger optical excitation threshold is assumed to occur.[11,12]

Since S-induced *DX* centers in GaSb and heavily doped GaAs occur at atmospheric pressure and there are no complications associated with either alloy broadening or level splitting, these systems are ideal ones for experimental and theoretical investigations on the properties of *DX* centers.

The main purpose of our paper is to report on the identi-

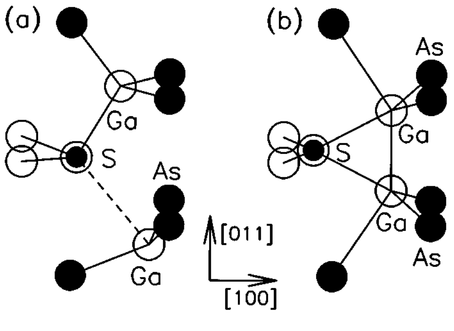

FIG. 1. Schematic atomic structures of (a) the trigonal broken bond (BB-*DX*) configuration and (b) the cation-cation bonded (CCB-*DX*) state for a S substitutional impurity in GaAs are shown in a [011] plane.

fication of a new type of *DX* center in III-V semiconductors, in particular, in S-doped GaAs and GaSb. The center has orthorhombic C_{2v} and its structure is characterized by dimer bond formation between two of the nearest-neighbor cations of an anion-site substitutional impurity [see Fig. 1(b)]. In the following, we will refer to this structure as a cation-cation-bonded *DX* center (CCB-*DX*).[18] From the results of *ab initio* total-energy calculations we find that the CCB-*DX* structure has a lower energy than the trigonally symmetric BB-*DX* state [Fig. 1(a)] for S impurities in GaAs and GaSb. We also compare the binding energies of Se and Te impurities in GaAs and GaSb for the BB-*DX* and CCB-*DX* models. The CCB-*DX* center is shown to provide a satisfactory explanation for the EXAFS data in GaAs:S and the two types of *DX* centers provide an explanation for the quenching of PPC in S-doped GaSb.

The first-principles pseudopotential total-energy calculations[19] are based on the local-density-functional approximation.[20] Norm-conserving nonlocal pseudopotentials[21] were generated by the scheme of Troullier and Martins,[22] and the Kleinman-Bylander type of fully separable pseudopotentials were constructed.[23] Brillouin zone summations were done with four special k points[24] in a three-dimensionally periodic 32-atom bcc supercell. Total-energy minimization was achieved by a Davidson-type self-consistent diagonalization method.[25]

The results of our calculations show that the CCB-*DX* center, like the BB-*DX* state, is stable or metastable only in a negatively charged state. Charge disproportionation in the presence of *DX* centers can be described by the following negative-U-type reaction:[6]

$$2d^0 \rightarrow DX^- + d^+, \tag{1}$$

where *DX* represents either a BB-*DX* state [Fig. 1(a)] or a CCB-*DX* state [Fig. 1(b)], and *d* denotes a tetrahedrally coordinated substitutional impurity.

The formation of the CCB-*DX* state involves a large lattice relaxation. For GaAs:S, two nearest-neighbor Ga atoms of the impurity are each displaced by 0.73 Å along a [011] axis to form a dimer bond [Fig. 1(b)]. The Ga-Ga distance is reduced from an initial value of 3.98 to 2.53 Å. The total electronic charge density and the charge density of the highest occupied electronic state associated with this state (Fig. 2) clearly show the formation of a covalent bond. The CCB state is stabilized by two electron occupancy at a deep CCB level the electronic charge density for which is shown in Fig. 2(b). As mentioned above, the CCB state is stable only in a negatively charged state. In a neutral or positively charged state the cation-cation bond becomes too weak to overcome the elastic strain energy needed to stabilize the CCB geometry.

A S impurity in CCB-*DX* is moved by 0.53 Å in a [100] direction. The displacement compresses two cation-impurity bonds; the strain is accommodated best by impurities with covalent radii *smaller* than the anions they replace. Substitutional S impurities, and in some cases oxygen atoms,[26] are found to be conductive to the generation of this type of structure. For each Ga atom of the dimer, one Ga-As bond length becomes stretched by 21%. This is to be compared to a 57% bond length extension for a trigonal type of *DX* center.[15]

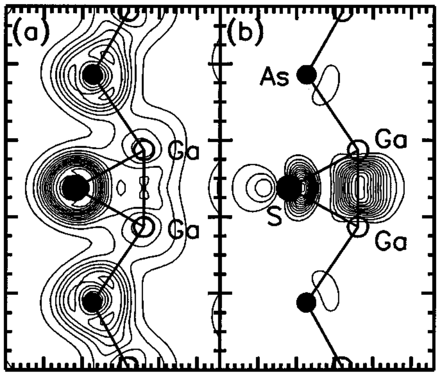

FIG. 2. (a) Total electronic charge density, and (b) the charge density for the highest occupied state of the CCB-*DX* configuration of S in GaAs.

We note that unlike our previous BB-*DX* model, the formation of the CCB state does not lead to a large change in the nearest-neighbor distance around an *impurity* in comparison with the tetrahedrally coordinated substitutional geometry. This occurs despite a very large lattice relaxation in the vicinity of the impurity. For the CCB-*DX* state in GaAs:S we obtain two S-Ga distances differing by 0.24 Å : 2.57 Å when the S atom is bonded to the dimerized Ga atoms, and 2.33 Å for the other two S-Ga bonds. The S-Ga bond length for the tetrahedrally coordinated d^+ is 2.46 Å. The lengthening of two of the S-Ga bonds in the CCB-*DX* state arises because the charge density between the dimerized Ga atoms and the central S atom is antibonding in character [Fig. 2(b)]. Overall, the bond length changes of 0.11–0.13 Å around the mean are an order of magnitude smaller than those in the BB-*DX* state where one bond is stretched by about 1.3 Å.[15]

The relatively small bond length changes in CCB-*DX* provide an explanation for EXAFS data on S-related *DX* centers in GaAs.[10] The data indicate that the width of the first-neighbor-shell peak in the Fourier transform function $F(r)$ of the EXAFS signal from S is 0.23 Å wider than that from Ga or As in pure GaAs and is 0.13 Å wider than the second- and third-neighbor-shell widths. The x-ray data was previously interpreted in support of a small lattice relaxation model for *DX* centers,[13] an interpretation in conflict with the large Stokes shift between the optical and thermal ionization energies. The data can now be explained more satisfactorily by the CCB-*DX* model which combines a large lattice relaxation with small bond length changes around S.

For Se-doped GaAs, we find that the bond length changes in the CCB-*DX* state are within 0.09 Å of the tetrahedrally coordinated substitutional value. Experimentally, the nearest-neighbor bond length deviation between the shallow state and *DX* is estimated to be about 0.04 Å in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys.[13]

The binding energies of BB-*DX* and CCB-*DX* states for S, Se, and Te impurities in GaAs are listed in Table I. The magnitude of the binding energy is defined here as one-half of the reaction energy in Eq. (1), since the *DX* level is occupied by two electrons. A negative binding energy implies that the *DX* state is unbound relative to the shallow donor state. Consistent with experimental data we find that when the Fermi level is taken to be at the conduction-band mini-

TABLE I. *DX* binding energies in eV for S, Se, and Te donor impurities in GaAs. Negative values indicate a metastable *DX* state.

	S	Se	Te
CCB-*DX*	−0.09	−0.23	−0.36
BB-*DX*	−0.18	−0.19	−0.10

mum, neither of the two types of *DX* centers is bound relative to the shallow donor state. For Se, the energy difference between the CCB and BB structures is very small. The BB-*DX* configuration is calculated to be only 0.04 eV more stable than CCB-*DX*. For Te, BB-*DX* is 0.26 eV more stable than CCB-*DX*. It is noteworthy, however, that the CCB configuration for S is 0.09 eV more stable than the BB-*DX* state. The trends in the binding energies are correlated with the ionic bonding radii of the impurities.

The relatively small value of −0.09 eV for the binding energy of S in GaAs (as compared to −0.22 eV for Si) indicates that doping saturation should occur at doping densities near $10^{18}/\mathrm{cm}^3$ for S instead of $10^{19}/\mathrm{cm}^3$ for Si. In the highly S-doped GaAs specimen used for the EXAFS study,[10] a large fraction of the *DX* states are expected, therefore, to be of the CCB-*DX* type. The sulfur-CCB-*DX* state is also expected to be the dominant type of *DX* center in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys.

For GaSb, the trends in the stability of the CCB configurations relative to the BB-*DX* states are similar to those in GaAs. The calculated binding energies for the two types of *DX* centers for S, Se, and Te impurities are shown in Table II. For S we find that the formation of CCB-*DX* is slightly exothermic and its energy is 0.1 eV lower than BB-*DX*. The CCB-*DX* and BB-*DX* states are found to be metastable with respect to the shallow donor states for Se and Te impurities. These results are consistent with experimental data which show that in GaSb, *DX* centers occur only for S doping.[16,17] In addition to GaAs and GaSb, S has recently been shown to be a negative-*U* *DX* center in $\mathrm{GaAs}_{0.6}\mathrm{P}_{0.4}$ at ambient pressure.[27]

The key feature of *DX* centers, i.e., PPC can also be explained within the CCB-*DX* model. Optical excitation of an electron from the CCB state into the conduction band is found to lead to a breaking of the cation-cation bond and a transformation to the tetrahedrally coordinated configuration which gives shallow donors. In GaAs:S, the CCB-*DX* optical level is calculated to be at $E_v+0.25$ eV, where E_v is the energy of the valence-band-maximum (VBM). The thermal barrier for electron capture from the shallow state back to the CCB-*DX* state is found to be 0.2 eV. In comparison, for BB-*DX*, the optical level is at $E_v+0.63$ eV.[28] For Se and Te, the CCB-*DX* optical levels are at $E_v+0.18$ eV while the BB-*DX* levels are at $E_v+0.5$ eV. In all cases the optical ionization energies are significantly larger than the thermal binding energies.

TABLE II. *DX* binding energies in eV for S, Se, and Te substitutional donor impurities in GaSb.

	S	Se	Te
CCB-*DX*	0.06	−0.08	−0.21
BB-*DX*	−0.01	−0.09	−0.07

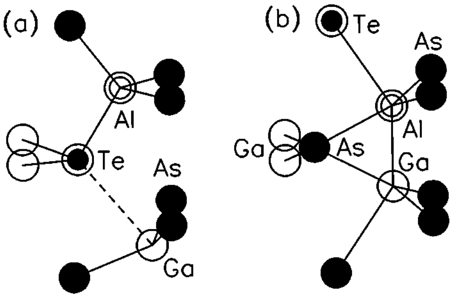

FIG. 3. Atomic structures for the most stable configurations of (a) the trigonal BB-*DX* state, and (b) the CCB-*DX* state when a Te donor impurity is surrounded by Al atoms in an $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloy.

As mentioned above the quenching of PPC in S-doped GaSb (Ref. 12) points to the occurrence of at least two types of deep donor centers, a result consistent with separate deep-level-transient-spectroscopy (DLTS), capacitance, and Hall measurements.[11,16] From the results of our calculations we find that the CCB-*DX* optical level (i.e., highest occupied electronic level) lies 0.11 eV *below* the VBM while for the BB-*DX* state it is at $E_v+0.13$ eV. This means that CCB-*DX* state cannot be photoionized by subband-gap light. Photoexcitation of electrons from the BB-*DX* state into the shallow donor state and their capture into the CCB-*DX* state will lead, therefore, to a gradual quenching of the PPC. The experiments were carried out at relatively high temperatures of 83–100 K where retrapping of electrons into the *DX* centers can occur thermally.

It is well known that in GaAs *DX* centers become stabilized with respect to the shallow donor state under pressure. Previous theoretical work has demonstrated this effect for the BB-*DX* state.[6] We find that the CCB-*DX* state also becomes more stable under pressure, and that a shallow to deep transition occurs. The pressure derivatives of the *DX* binding energy are calculated to be 11.52 meV/kbar and 10.45 meV/kbar in GaAs:Se for the CCB and BB-*DX* states, respectively. The BB to CCB transition is calculated to occur at a pressure of 26 kbar.

Our theoretical results indicate that the CCB-*DX* state is 0.53 eV less stable in the total energy than the BB-*DX* in Te-doped GaAs because of the large atomic size of Te. However, we find that much-lower-energy CCB-*DX* structures are possible in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys. At low Al concentrations, the most stable BB-*DX* and CCB-*DX* structures for a Te donor in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ are shown in Fig. 3. For the CCB structure, an Al-Ga dimer bond occurs next to the smaller sized As atom instead of the Te atom. The energy differences between the BB-*DX* [Fig. 3(a)] and the metastable CCB-*DX* state [Fig. 3(b)] is lowered to 0.2 eV. At high Al concentrations when all nearest neighbors of a Te atom are Al atoms, the CCB-*DX* state is found to be 0.12 eV *more* stable than the trigonal BB-*DX* state. Therefore, both CCB-*DX* and BB-*DX* structures are expected to occur in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$:Te. The observation of orthorhombic defect centers in Te-doped $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ in ballistic phonon attenuation experiments is consistent with the CCB-*DX* state.[14]

In summary, a new type of deep donor *DX* state resulting from cation-cation bond formation in the presence of chalcogenide substitutional impurities in III-V semiconductors is identified. The state is most favorable when the ionic bonding radius of the impurity is smaller than that of a host anion. Sulfur impurities in GaAs, GaSb, and $Al_xGa_{1-x}As$ alloys are predicted to preferentially form this type of CCB-*DX* center. Structural parameters from EXAFS measurements in S-doped GaAs is explained more satisfactorily by the CCB-*DX* state than by a trigonal symmetry BB-*DX* model. We suggest that the quenching of PPC in GaSb involves a transfer of electrons from the BB-*DX* to the CCB-*DX* state. The new CCB-*DX* center is found to be the most favorable *DX* state even for Te impurities in $Al_xGa_{1-x}As$ alloys when the impurity is surrounded by Al atoms.

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