Self-interstitial bonding configurations in GaAs and Si

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The charge-state-dependent stable and low-energy metastable states of self-interstitial defects in GaAs and Si are identified via self-consistent pseudopotential calculations. An unconventional type of ⟨110⟩-split-interstitial configuration in which there is essentially no bonding between the split interstitials is found to play an important role in determining the ground-state properties of interstitials for several charge states. Self-interstitials in GaAs are found to be "negative-U" defects. They are characterized by effective U's of -0.2 eV for Ga and -0.7 eV for As interstitials. The large negative-U value for As interstitials may explain why no magnetic resonance identification of As interstitials has been achieved in GaAs.

I. INTRODUCTION

Self-interstitials are among the basic intrinsic defects that are involved in many important solid-state processes in semiconductors such as diffusion. Experimentally there are few and mostly indirect clues on the properties of self-interstitials in Si and GaAs. For example, when Si is irradiated with 1.5–3.0-MeV electrons at 4.2 K, electron paramagnetic resonance (EPR) from isolated vacancies is observed. However, no EPR that can be identified with interstitials or Frenkel pairs is seen.[1,2] Additional experiments on the capture of Si interstitials by impurities lead to the conclusion that these defects must be mobile even at very low temperatures.[2] Several mechanisms, in particular, barrier lowering through cyclic changes in the charge state during migration, have been investigated in detail to explain the athermal diffusion of Si interstitials in Si.[3–6] In the case of III-V semiconductors, no magnetic-resonance identification of any column-V interstitial has been achieved yet. The failure may be explained if the interstitial has negative-U properties which would make states with unpaired spins unstable.[1] Very little is known, however, about the atomic structure of such interstitials. The situation is only slightly better for Ga interstitials. Isolated Ga^{2+} interstitials in GaP and $Al_xGa_{1-x}As$ alloys have been identified in GaAs via optically detected magnetic-resonance experiments but not much is known about their atomic structure for other charge states.[7,8] The charge-state-dependent energies of self-interstitials in GaAs have been examined theoretically for the two inequivalent tetrahedral-interstitial positions.[9,10] Lower symmetry states have not been studied up to now.

In this paper various types of bonding configurations for interstitials are examined. A ⟨110⟩-split interstitial geometry which has quite a different bonding topology than the more common ⟨100⟩ split is found to be important as a result of its low energy. In all, the properties of eight different structures for self-interstitials in GaAs and four different ones for Si interstitials in Si were examined. The total-energy calculations were done for positive, double positive, neutral, and negatively charged states. A 32-atom periodic unit cell was used in the calculations and atomic relaxations were fully taken into account in all cases. The total energies, electronic properties, and structural parameters were determined from *ab initio* self-consistent pseudopotential calculations with a 6.5-Ry cutoff energy for GaAs and 7.0 Ry for Si. The different types of bonding configurations considered in this study are examined in Sec. II and the results of the calculations for Ga, As, and Si self-interstitials in GaAs and Si are discussed in Secs. III–V.

II. INTERSTITIAL BONDING

An interstitial atom can assume one of many different bonding geometries in tetrahedral semiconductors. An important class of geometries is the split-interstitial configuration. A split interstitial can be imagined to result from the "splitting" of an atom at a regular lattice site into two atoms which are then allowed to relax away from each other. Split interstitials are classified as (hkl) splits where (hkl) is along the vector joining the two atoms. A "conventional" type of split-interstitial configuration for a Ga-interstitial atom in GaAs is shown in Fig. 1(a). The As atoms at the corners of the cube are at the vertices of a tetrahedron. The split interstitials correspond to the two central threefold coordinated Ga (shaded) atoms at the center. Each is bonded to the other and to two other As atoms (open circles). The vector joining the two split interstitials in this configuration is along a (100) cubic axis and the structure is, therefore, a ⟨100⟩ split.

A different and, as it turns out, important type of split-interstitial configuration which has not received much attention before is the ⟨110⟩ split. In this configuration the vector from one split interstitial to the other lies along a (110) cubic axis or, in the more general definition used here, it lies in a [110] plane. The bonding topology of a ⟨110⟩ split (for a Ga interstitial) obtained from our energy-minimization calculations is shown in Fig. 1(b). The novel feature of this ⟨110⟩ split is the very weak bonding between the central split-interstitial Ga atoms which results from a relatively large separation of

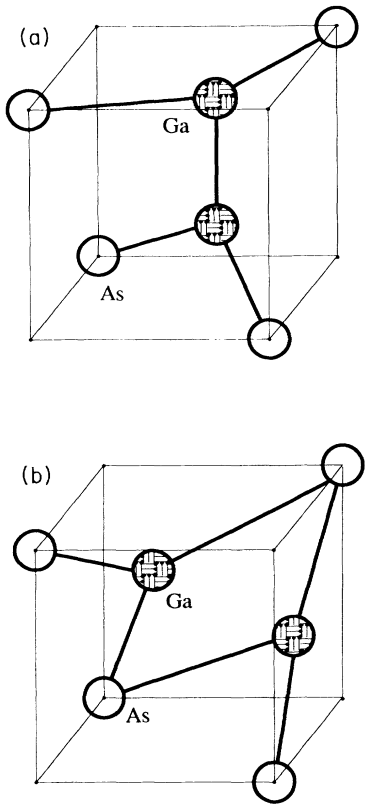

FIG. 1. A ⟨100⟩-type of split-interstitial configuration for Ga is shown in (a). The As atoms at the corners of the cube form a tetrahedral "cage." A ⟨110⟩ split is shown in (b). The bonding between the two Ga atoms of this split interstitial is very weak and is not shown. The two As atoms which make bonds to the two Ga split-interstitial atoms become fivefold coordinated. The Ga bonds to the fivefold coordinated atoms are about 5% longer than a normal Ga-As bond length. The other two bonds are shorter by the same amount.

2.7 Å. The primary bonding of the two Ga split interstitials in Fig. 1(b) is to their surrounding As atoms. Two of these four As atoms become *fivefold* coordinated. These distinguishing features of a ⟨110⟩ split for a Ga interstitial are found to remain unchanged for the corresponding As and Si ⟨110⟩-split interstitials. Despite the usual bonding topology of this center, it is found to play an important role in the determination of the ground- and metastable-state properties of self-interstitials in GaAs and Si for several charge states. The relaxed ⟨110⟩-split configurations are found to have either C_{2v} or C_2 symmetry. The former occurs when the vector joining the split-interstitial atoms is along a (110) cubic axis, the latter when it is in a (11ζ) direction.

Two other split-interstitial configurations for a Ga interstitial can be obtained by replacing the As "cage" atoms in Figs. 1(a) and 1(b) by Ga atoms. The resulting structures are shown in Figs. 2(a) and 2(b). As before, the ⟨100⟩ split results in a strong bond between the two interstitial atoms whereas the ⟨110⟩ split has very weak bonding between these atoms.

Another important type of interstitial binding is shown in Fig. 3. A Ga interstitial breaks a bulk Ga-As bond and forms bridge bonds to the two resulting broken bonds. This type of bonding has a low energy when the interstitial atom has either two or six valence electrons as, for example, for the *positively* charged state of a Ga interstitial or for the *negatively* charged state of an As interstitial. The lone pair nonbonding orbitals of the interstitial are then either completely empty or completely full.

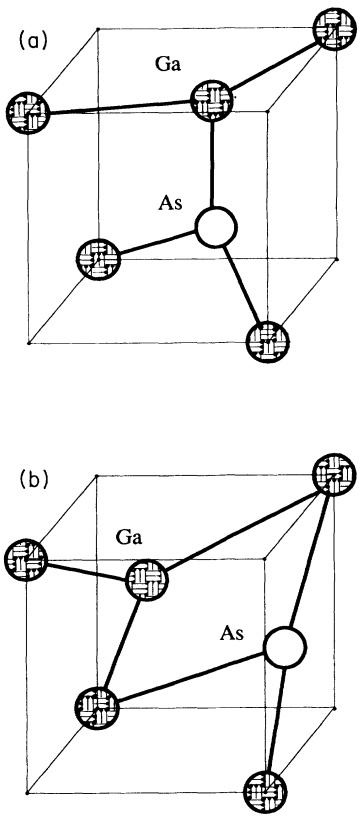

FIG. 2. Two other possible ⟨100⟩- and ⟨110⟩-type split interstitials for a Ga interstitial are shown in (a) and (b), respectively.

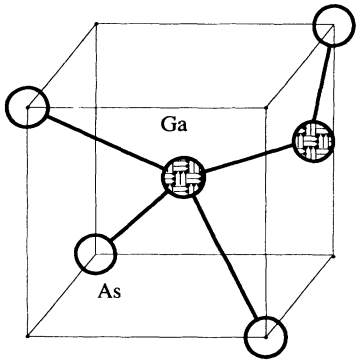

FIG. 3. A twofold coordinated bridge-bond geometry for a Ga interstitial. This configuration has a low energy when the interstitial is positively charged.

TABLE I. The energies (in eV) of a Ga interstitial in various charge states and atomic structures are shown. The reference of energy is taken as the energy of the interstitial in the positively charged twofold coordinated state in Fig. 3. The low-energy states are boldface.

Structure	$E(Q=+1)$	$E(Q=0)$	$E(Q=-1)$
Fig. 3: Twofold Ga	**0.0**	**1.6**	2.9
Fig 1(b): ⟨110⟩ split	**0.2**	**1.2**	**2.2**
Fig. 4: Hexagonal site	**0.1**	1.7	3.2
Fig. 2(b): ⟨110⟩ split	0.5	1.9	3.0
Fig. 2(a): ⟨100⟩ split	0.8	2.1	2.7
Fig. 1(a): ⟨100⟩ split		2.0	3.4

TABLE II. The atomic coordinates of a Ga self-interstitial for its lowest-energy charge-dependent configurations are shown in units of the cubic lattice constant (approximately 5.65 Å). A Cartesian coordinate system is used. The Ga-interstitial coordinates are given on the first line. The remaining coordinates give the positions of the most important nearest-neighbor atoms.

Fig. 3 $Q=+1$	Fig. 1(b) $Q=0$	Fig. 1(b) $Q=-1$
Ga(0.226,0.226,−0.106)	Ga(0.169,0.169,−0.113)	Ga(0.166,0.166,−0.101)
As(0.308,0.308,0.302)	Ga(−0.169,−0.169,−0.113)	Ga(−0.166,−0.166,−0.101)
Ga(−0.096,−0.096,−0.073)	As(0.272,0.272,0.282)	As(0.256,0.256,0.285)
	As(0.259,−0.259,−0.247)	As(0.256,−0.256,−0.241)
	As(−0.259,0.259,−0.247)	As(−0.256,0.256,−0.241)
	As(−0.272,−0.272,0.282)	As(−0.265,−0.265,0.285)

TABLE III. Arsenic-interstitial energies (in eV) for three different charge states and six different bonding configurations are shown. The total-energy reference is taken at the lowest-energy positively charged state which occurs for a ⟨100⟩-like split-interstitial configuration. The low-energy states are boldface.

Structure	$E(Q=+1)$	$E(Q=0)$	$E(Q=-1)$
Fig. 6(a): ⟨100⟩ split	**0.0**	**1.4**	2.3
Fig. 5(b): ⟨110⟩ split	0.8	**1.3**	**1.9**
Fig. 8: Hexagonal site	**0.4**		
Fig. 7: Twofold As	1.2	1.6	**2.0**
Fig. 5(a): ⟨100⟩ split		2.0	2.7
Fig. 6(b): ⟨110⟩ split		2.3	

TABLE IV. The atomic coordinates of an As self-interstitial for its lowest-energy charge-dependent states is shown. The first line gives the coordinates of the As interstitial, the second is split partner, and the remaining four represent the coordinates of the "cage" atoms. The coordinates are in units of the cubic lattice constant of GaAs.

Fig. 6(a) $Q=+1$	Fig. 5(b) $Q=0$	Fig. 5(b) $Q=-1$
As(−0.186,0.090,0.094)	As(0.166,0.166,−0.101)	As(0.153,0.153,−0.080)
Ga(0.198,−0.036,0.032)	As(−0.166,−0.166,−0.101)	As(−0.153,−0.153,−0.080)
As(0.299,−0.280,−0.278)	Ga(0.265,0.265,0.285)	Ga(0.273,0.273,0.288)
As(0.334,0.271,0.276)	Ga(0.256,−0.256,−0.241)	Ga(−0.273,−0.273,0.288)
As(−0.293,0.259,−0.281)	Ga(−0.256,0.256,−0.241)	Ga(0.259,−0.259,−0.251)
As(−0.311,0.281,0.261)	Ga(−0.265,−0.265,0.285)	Ga(−0.259,0.259,−0.251)

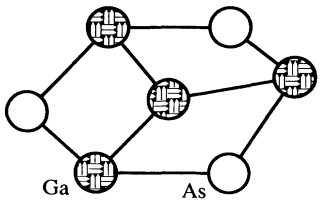

FIG. 4. A hexagonal site bonding configuration of a Ga interstitial (at the center of the sixfold ring of atoms) is shown. The primary bonding is between the Ga atoms and the interstitial induces a very large lattice relaxation.

In addition to the above configurations, three other types of bonding configurations corresponding to the two inequivalent tetrahedral-interstitial sites and the hexagonal-interstitial position, near the center of a sixfold ring of atoms, as shown in Fig. 4, were also examined. The tetrahedral site geometry appears to be most important for the doubly positive charge state of Ga (but not As) interstitials in GaAs. It is nearly as low in energy as the $\langle 110 \rangle$-split configuration for the +2 charge state of a Si interstitial in Si.

The results of the calculations for the charged-state-dependent atomic structures and energies of Ga, As, and Si self-interstitials in GaAs and Si are discussed in the following sections. The relative energies for the different interstitial bonding states and the atomic coordinates for the lowest-energy structures for Ga and As self-interstitials in GaAs given in Tables I–IV. The energies of different structures for Si are shown in Table V.

III. Ga SELF-INTERSTITIALS IN GaAs

A. Ga^{2+} interstitials

The lowest-energy structure for the +2 charge state occurs for the T_{d1} tetrahedral-interstitial site geometry where the Ga interstitial is surrounded by four Ga atoms. The energy of this state is about 0.14 eV lower than the other inequivalent tetrahedral site (T_{d2}) where the interstitial is surrounded by As atoms. The interstitial induced relaxations for the two structures are quite different. For T_{d1}, the Ga interstitial induces an outward relaxation of the neighboring four Ga atoms which lengthens the Ga-Ga distance by 5%. In the T_{d2} structure, the interstitial's distance to its four neighboring As atoms is equal to the normal Ga-As bond length in GaAs. The interstitial induces relaxations, however, on all the neighboring Ga atoms of these four As atoms, increasing the As-Ga bond lengths by about 3.5%. The tetrahedral-interstitial configurations have no acceptor states in the band gap. As a result, interstitial Ga is stable at this site only in a +2 charge state. Binding at the hexagonal interstitial site (Fig. 4) gives a metastable state with an energy 0.54 eV higher than the ground state. The tetrahedral-interstitial configuration for a Ga^{2+} interstitial is consistent with experimental data.[7,8] The (++/+) level is found to be at the valence-band maximum.

B. Stable and metastable states of Ga^{+} interstitials

The lowest-energy state of a positively charged Ga interstitial occurs for the *twofold* coordinated state shown in Fig. 3 in which the interstitial forms a bridge bond between two As and Ga atoms. In this configuration the interstitial has a weak interaction with a distant Ga atom at a separation of 2.64 Å. The atomic coordinates for this structure are given in Table II. There are two electronic states in the gap for this configuration: a doubly occupied As-derived one at $E_v + 0.12$ eV and a Ga-derived (0/+) level at $E_v + 1$ eV.

The energy of a singly ionized Ga^{+} interstitial in the twofold coordinated state is approximately 1 eV higher than that of a doubly ionized Ga^{2+} atom at a tetrahedral-interstitial site. The relative free-energy differences between Ga (or other) interstitials in different charge states can be obtained from

$$\Delta F = \Delta E - \mu \Delta n \ , \tag{1}$$

where E is the total energy obtained from the calculations and shown in Table I, μ is nearly the same as the Fermi energy (measured from the valence-band maximum), and n is the number of electrons on the defect. For the positively charged Ga interstitial, the Ga^{+} state would become more favorable, therefore, than G^{2+} when the Fermi energy is at least 1 eV above the valence-band maximum.

As shown in Table I, there are two metastable states with energies within 0.25 eV above that of a ground state. The first is the threefold symmetric hexagonal site binding state in Fig. 4. The energy of this state is within 0.12

TABLE V. The energies of Si self-interstitials in Si for configurations similar to those examined for Ga (or As) interstitials are shown. The lowest energies for the three charge states shown occur for a $\langle 110 \rangle$-split-interstitial configuration. The hexagonal-interstitial site is very close in energy for the positive and neutral charge states. The atomic structures are very similar to those for the corresponding Ga self-interstitials given above. The low-energy states are boldface.

Structure	$E(Q=+1)$	$E(Q=0)$	$E(Q=-1)$
Fig. 1(b): $\langle 110 \rangle$ split	**0.0**	**0.9**	**2.0**
Fig. 4: Hexagonal site	**0.1**	**1.0**	
Fig. 3: Twofold site	0.3	1.2	2.2
T_d: Tetrahedral site	0.4		
Fig. 1(a): $\langle 100 \rangle$ split	0.9	1.8	2.9

eV of that of the twofold state. The interstitial's primary bonding is to the three Ga atoms of the ring (with a nearly ideal Ga-Ga bond length of 2.47 Å); the bonds to the As atoms are weaker (Ga-As bond lengths of 2.6 Å). The interstitial induces a large 8.5% expansion of the Ga-As atoms on the sixfold ring.

The second metastable state of a positively charged Ga interstitial corresponds to the ⟨110⟩-split configuration shown in Fig. 1(b). It has an energy about 0.24 eV higher than the optimal structure.

C. Neutral Ga interstitials

The lowest-energy state of an interstitial Ga atom in a neutral charge state corresponds to the ⟨110⟩-split-interstitial configuration shown in Fig. 1(b) in which the two Ga split interstitials are surrounded by four As atoms. For the relaxed structure, the vector joining the two central Ga atoms is parallel to a (110) cubic axis. The structure has C_{2v} symmetry, i.e., the coordinate transformations $(xyz)\rightarrow(-x\ -yz)$ and $(xyz)\rightarrow(yxz)$ leave the structure unchanged. As mentioned earlier, the unusual features of this bonding geometry are the fivefold coordination of two of the four surrounding As atoms and a weak Ga-Ga bond of length 2.7 Å or about 10% larger than a normal Ga-As bond length. Each of the two Ga atoms makes bond angles of 117°, 117°, and 106° with its neighboring As atoms. The atomic coordinates of the central six atoms for this model are given in Table II. The defect center has an unpaired electron localized equally on the two Ga atoms at a (0/+) energy level of $E_v=0.6-0.7$ eV where E_v represents the energy of the bulk valence-band maximum. The As_4 environment of the two Ga atoms as well as the spread out nature of the spin active electron seem consistent with the similar experimentally derived conclusions of Kennedy and Spencer[8] from optically detected magnetic resonance although no specific bonding geometry was inferred from the measurements.

The lowest-energy *metastable* state of a neutral Ga interstitial has a twofold coordinated structure shown in Fig. 3. The energy of this state is 0.37 eV above that of the ground state. The metastable state has an unpaired electron localized on the Ga interstitial and its nearest-neighbor Ga atom at an energy of E_v+1 eV.

D. Negatively charged Ga interstitials

Gallium interstitials have generally been considered to be shallow donors in GaAs. This is not difficult to understand since the energy of the valence p electron of Ga lies at approximately 2 eV above the conduction-band minimum of GaAs.[11] The results of our calculations discussed above show that Ga interstitials do indeed behave as donors for a variety of structures. However, we have found several structures in which a Ga interstitial can behave as an acceptor. The energies of the negatively charged states corresponding to the structures in Figs. 1–4 are given in Table I.

The lowest-energy configuration for a negatively charged Ga interstitial is very similar to that for the neutral state, i.e., it has the ⟨110⟩-split-interstitial configuration shown in Fig. 1(b) with a Ga-Ga distance of approximately 2.66 Å. The Ga bonds to the fivefold coordinated As atoms are 5% longer than normal Ga-As bonds in GaAs whereas the bonds to the fourfold coordinated As atoms are 5% shorter. The center has $(xyz)\rightarrow(yxz)$ symmetry and very nearly $(xyz)\rightarrow(-x\ -yz)$ symmetry. The atomic coordinates for this state are listed in Table II.

E. Ga interstitials: A negative-U system

The results of the total-energy calculations on neutral and charged Ga interstitials shown in Table I indicate that these defects form a negative-U system. The charge-exchange reaction

$$2Ga^0\rightarrow Ga^+ + Ga^- \quad (2)$$

is calculated to be exothermic by 0.2 eV. In this reaction, the neutral and negatively charged Ga interstitials have the ⟨110⟩-split structure shown in Fig. 1(b). The positively charged state is in the twofold coordinated configuration shown in Fig. 3. The negative-U nature of the defect may explain the difficulties encountered experimentally in magnetic-resonance identification of neutral Ga interstitials. It may be possible, however, to create a nonequilibrium concentration of neutral centers through optical excitation of Ga^- centers which have a doubly occupied state at approximately 0.7 eV above the valence-band edge.

IV. ARSENIC SELF-INTERSTITIALS

A. Bonding structure

The bonding configurations for As interstitials are very similar to those examined for Ga. An interchange of the Ga and As atoms in Figs. 1–4 leads to the corresponding structures shown in Figs. 5–8. The relative energies of these structures as a function of charge state are examined below and are separately listed in Table III. The atomic coordinates of the most stable states for neutral, negative, and positively charged states of an As interstitial are given in Table IV.

B. Positively charged As interstitial

The lowest-energy state for an As interstitial in either the +1 or +2 charge state is found for a ⟨100⟩-like split-interstitial bonding configuration shown schematically in Fig. 6(a). The lowest-energy structure has no symmetry at all as can be seen from the atomic coordinates in the first column in Table IV. In the +2 charge state, the split-interstitial configuration is significantly more stable than either the hexagonal site geometry (by 0.6 eV) or the two tetrahedral interstitial positions (by 1.5 eV). For the +1 charge state the lowest-energy ⟨100⟩-split configuration gives rise to a doubly occupied state at the valence-band edge and a Ga-derived empty state at 0.8 eV above it.

The lowest-energy metastable state of a singly ionized As interstitial is found to correspond to the threefold

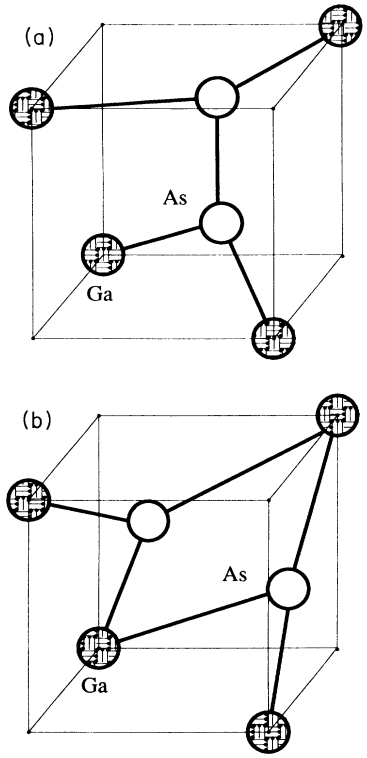

FIG. 5. The ⟨100⟩- and ⟨110⟩-split bonding geometries for an As interstitial atom in GaAs are shown in (a) and (b), respectively. The tetrahedral "cage" at the corners of the cube are Ga atoms.

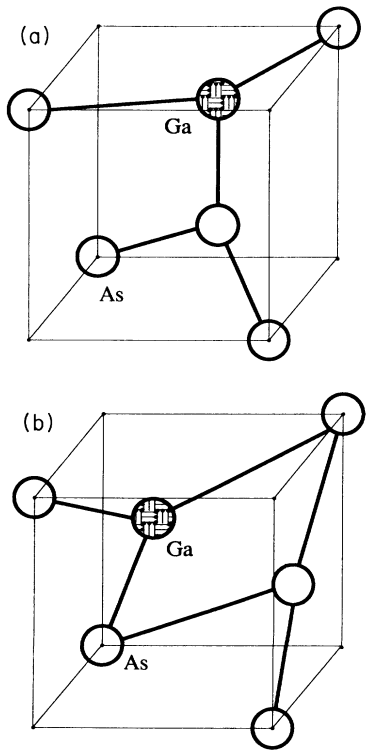

FIG. 6. Two As-interstitial configurations similar to those in Fig. 5 except that the four surrounding "cage" atoms of the As interstitial are As atoms.

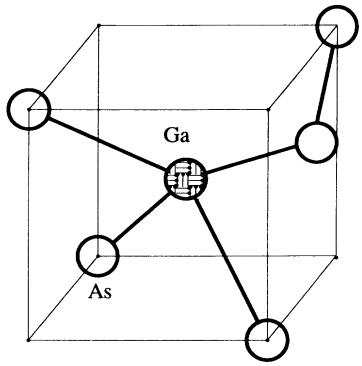

FIG. 7. A twofold coordinated bridge-bond geometry for As. This state has low energy when the As interstitial is negatively charged.

symmetric hexagonal site binding (Fig. 8). This state has a 0.4 eV higher energy than a ⟨100⟩-split interstitial. The As interstitial bonds most strongly to the As atoms of the sixfold ring with an As-As length of 2.45 Å. The interstitial bond to the three Ga atoms of the ring is stretched by 9% compared to the ideal Ga-As value. In addition, the interstitial significantly weakens the Ga-As bonds within the ring, stretching them by about a sizable 0.27 Å.

C. Neutral As interstitial

Neutral As interstitials have three distinct bonding states with nearly equal energies. The lowest-energy state is the ⟨110⟩ split shown in Fig. 5(b) in which the two As split interstitials are surrounded by four Ga atoms and where two of the four surrounding Ga atoms are fivefold coordinated. This is the exchanged Ga↔As analog of the lowest-energy state of a neutral Ga interstitial [Fig. 1(b)]. The energy-minimized structure has only C_2 symmetry since the vector joining the two split-interstitial As atoms lies in a (110) plane but is not along a (110) axis. The As-As bond length in Fig. 5(b) has an elongated value of 2.66 Å. The bond lengths between the fivefold Ga atoms and the two As split-interstitial atoms are stretched by 5% and those between the fourfold Ga's and the two As atoms are contracted by the same amount. The ⟨110⟩ split in Fig. 5(b) is energetically degenerate with the ⟨100⟩-like split shown in Fig. 6(a). The latter structure has an acceptor level at E_v+1 eV and an unoc-

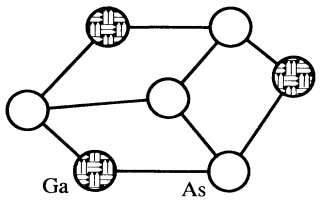

FIG. 8. A hexagonal site binding structure for an As-interstitial atom. The primary bonding is between As and As atoms.

cupied level at $E_v+1.2$ eV. The filled state is localized on a p_y orbital of the Ga atom of the split interstitial. Surprisingly, the twofold coordinated geometry shown in Fig. 7 is only 0.3 eV higher in energy than the most stable state. The hexagonal interstitial site (Fig. 8) acts as a shallow donor.

D. Negatively charged As interstitials

As in the case of Ga, two low-energy structures for which an As interstitial acts as an acceptor were found. The lowest-energy state is the same as for the neutral state as is the ⟨110⟩-split interstitial shown in Fig. 5(b). A 0.1 eV higher-energy state is found for the *twofold* coordinated geometry shown in Fig. 7. In this configuration the As interstitial breaks a bulk Ga-As bond and forms a bridge bond between the two atoms. This type of structure is, from a bonding and electron counting point of view, reminiscent of interstitial *oxygen* in Si. In the twofold coordinated state, there is a strongly localized filled state derived from the As interstitial's p_x+p_y orbitals at 0.4 eV above the valence-band maximum.

E. As interstitials: A negative-U system

The results of the total-energy calculations discussed above and summarized in Table III show that As interstitials form a large negative-U system. The charge-exchange reaction

$$2\mathrm{As}^0 \rightarrow \mathrm{As}^+ + \mathrm{As}^- \quad (3)$$

between As interstitials is exothermic by 0.7 eV. In this reaction the interstitial in the positively charged state is in a ⟨100⟩-like split-interstitial configuration [Fig. 6(a)], the neutral state has either a ⟨100⟩- or a ⟨110⟩-split [Fig. 5(b)] geometry, and the negatively charged state has a ⟨110⟩-split configuration. The large negative-U value for As interstitials may explain why a magnetic-resonance identification of this defect has proved unsuccessful so far. The As^- state has a doubly occupied band at approximately 0.35 eV above the valence-band edge and it may be possible, therefore, to obtain an EPR signal from it via optical excitation with subband gap light.

V. Si SELF-INTERSTITIALS IN Si

The bonding configurations examined were the same as those for Ga self-interstitials in GaAs shown in Figs. 1, 3, and 4 where all atoms are turned into Si atoms. In addition, the tetrahedral interstitial site was also examined. Among these structures the ⟨110⟩-split geometry [Fig. 1(b)] is again found to be the most important structure for Si interstitials in Si. It gives the lowest energy for the $+2$, $+1$, neutral, -1, and possibly the -2 charge states of a Si interstitial. A ⟨110⟩-split geometry for Si interstitials has been previously considered by Bar-Yam and Joannopoulos.[4] For the $+2$ state, the tetrahedral-interstitial site geometry has nearly the same energy. The atomic coordinates (in units of the bulk lattice constant) for the ⟨110⟩ split are very similar to the corresponding ones for the (positively charged) Ga ⟨110⟩ split shown in Table II. The Si-Si bond between the split interstitials is stretched by nearly 10% and is very weak. The interstitial bonds to the two fivefold coordinated Si atoms are stretched by 4% and those to the fourfold Si atoms are contracted by the same amount. The split interstitials are in an intermediate sp^2-sp^3 bonding state with two bond angles of 117° and one of 106°. The total energies of a Si interstitial in Si for positive, neutral, and negatively charged states for several configurations are shown in Table V.

A very interesting property of the ⟨110⟩-split-interstitial geometry is that it gives rise to nearly degenerate single and double *acceptor states* at 1 eV above the valence-band maximum. The $(-/0)$ and $(--/-)$ levels are derived from localized p_x and p_y orbitals of the two Si split interstitials. The threshold energy for optical excitation from the acceptor states into the conduction band is calculated to be 0.5 eV.

The energy of the threefold symmetric hexagonal site geometry is 0.12 eV higher for both a neutral and positively charged states than for the ⟨110⟩ split. The negatively charged state leads to a free electron in the conduction band. The energies of the traditional ⟨100⟩-split-interstitial configuration is consistently higher than the ⟨110⟩ split for all charge states. The energy of a *twofold* coordinated interstitial Si is within 0.4 eV of the optimal value for all three charge states.

VI. CONCLUSIONS

The stable and metastable states of self-interstitials in GaAs and Si for three different charge states were identified using an *ab initio* pseudopotential approach. The ground-state configurations are in many cases different from previously accepted models. In particular, two structures, a ⟨110⟩-split interstitial [Figs. 1(b) and 5(b)], and an off (111) axis twofold coordinated bonding state (Figs. 3 and 7), are found to have the lowest energies in nearly all cases except for the positively charged state of an As interstitial where a traditional ⟨100⟩-split geometry (Fig. 7) is best. Gallium and As self-interstitials in GaAs are each found to form a negative-U defect system. The bonding states examined in this study are expected to be important in the understanding of the electronic properties and stability of interstitial impurities in tetrahedral semiconductors. A ⟨110⟩-split interstitial configuration for an As-derived antisite-interstitial complex has been examined by Delerue and Lannoo.[12]

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[1]For a recent review, see G. D. Watkins, in *Materials Science and Technology*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH, Wernheim, 1991), Vol. 4.

[2]G. D. Watkins, *Radiation Damage in Semiconductors* (Dunod, Paris, 1964), p. 97; G. D. Watkins, Phys. Rev. B **12**, 5824 (1975); G. D. Watkins and K. L. Brower, Phys. Rev. Lett. **36**, 1329 (1976).

[3]G. A. Baraff and M. Schluter, Phys. Rev. B **30**, 3460 (1984); G.

A. Baraff, M. Schluter, and G. Allan, Phys. Rev. Lett. **50**, 739 (1982).

[4]Y. Bar-Yam and J. D. Joannopoulos, Phys. Rev. B **30**, 2216 (1984); Phys. Rev. Lett. **52**, 1129 (1984).

[5]S. T. Pantelides, A. Oshiyama, R. Car, and P. J. Kelly, Phys. Rev. B **30**, 2260 (1984).

[6]R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **54**, 360 (1985).

[7]K. M. Lee, in *Defects in Electronic Materials,* edited by M. Stavola, S. J. Pearton, and G. Davies (Materials Research Society, Pittsburgh, 1988), Vol. 104, p. 449.

[8]T. A. Kennedy, R. Magno, and M. G. Spencer, Phys. Rev. B **37**, 6325 (1988); T. A. Kennedy and M. G. Spencer, Phys. Rev. Lett. **57**, 2690 (1986).

[9]G. A. Baraff and M. Schluter, Phys. Rev. Lett. **55**, 1327 (1985).

[10]S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).

[11]D. J. Chadi, Phys. Rev. B **19**, 2074 (1979).

[12]C. Delerue and M. Lannoo, Phys. Rev. B **38**, 3966 (1988).