Microscopic theory of diffusion on the Ga sublattice of GaAs: Vacancy-assisted diffusion of Si and Ga

J. Dąbrowski
Institut für Halbleiterphysik, Walter-Korsing-Strasse 2, D-15230 Frankfurt (Oder), Germany

John E. Northrup
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304
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Ga vacancies are believed to mediate self-diffusion of Ga and diffusion of substitutional impurities residing on the Ga sublattice in GaAs. We present results of first-principles calculations for the vacancy-mediated diffusion of Si and Ga. We show that a *DX*-like mechanism facilitates the migration of lattice site atoms into the interstitial region and that the dangling bonds of a second-nearest-neighbor vacancy assist migration through the interstitial region. Due to these two mechanisms vacancy-assisted diffusion of both Ga and Si occurs with a low-energy barrier.

In the past few decades there has been much work devoted to understanding the diffusion of substitutional dopants in semiconductors. Of special interest is the diffusion of Si in GaAs, which occurs in a variety of technologically important processes such as epitaxial growth and impurity induced-lattice disordering. A large number of experiments[1-8] indicate that Si diffusion and Ga self-diffusion in GaAs are enhanced under As-rich conditions and by *n*-type doping. Because the concentrations of the Ga vacancy and the Si_{Ga}-V_{Ga} complex are also enhanced under such conditions, these results support models in which charged Ga vacancies play an important role in mediating diffusion.[9,10] Models have been proposed in which Si diffusion occurs via the migration of a Si_{As}-Si_{Ga} nearest-neighbor pair[5,6] or as a Si_{Ga}-V_{Ga} donor-vacancy complex,[7,8] but in each scenario vacancies are assumed to be present and mediate the diffusion.

The viability of vacancy-mediated diffusion is predicated on the assumptions that vacancies are abundant and mobile. Recent calculations of the formation energy of the $(Si_{Ga}$-$V_{Ga})^{2-}$ pair indicate than it is one of the most abundant species in Si-doped GaAs under As-rich conditions.[11] Here we attempt to show that the donor-vacancy complex, in addition to being abundant, is also mobile and may function as a vehicle for Si diffusion. We present a detailed study of the migration pathway for $(Si_{Ga}$-$V_{Ga})^{2-}$ based on the first-principles total-energy calculations performed for a large number of intermediate configurations of the migrating complex. Our results indicate that the initial step in the migration is closely related to the local structural instability of donors which apparently gives rise to the *DX* center in III-V alloys.[12-14] When this instability occurs for a donor which is paired with a Ga vacancy, the donor may effectively switch lattice sites with the vacancy. This, as we will show, leads to the migration of the Si donor with a migration energy of approximately 1.5 eV.

To study the migration paths, parameter-free total-energy calculations were performed using fully nonlocal pseudopotentials of Kleinman-Bylander form[15] and the local-density approximation with Perdew and Zunger's parametrization[16] of Ceperley and Alder's electron-gas data.[17] The infinite crystal was modeled by a periodic repetition of a supercell containing 53 atoms and one vacancy as in previous work.[13]

Mobility of the complex requires that two distinct steps may occur readily. First the Si and vacancy must be able to switch sites. Second, the vacancy must be able to move to a new site, so that the next Si jump does not simply return the complex to its original configuration. To describe the sequence of atomic configurations which defines the $Si_{Ga} \leftrightarrows V_{Ga}$ site switching pathway we divide the path into seven configurations: initial, plane, *DX*, interstitial, *DX*, plane, and final. The path is symmetrical about the intersititial configuration, so we need only consider the first four steps which are illustrated in Fig. 1. In the initial configuration [Fig. 1(a)] a donor-acceptor pair consisting of Si_{Ga}^{+} and V_{Ga}^{3-} is present. In the first step of the migration the Si donor leaves the substitutional site and passes between three of its arsenic neighbors, as displayed in Fig. 1(b). It then enters the interstitial region and converts to a *DX*-like configuration,[12,13] as shown in Fig. 1(c). As previous calculations[13] have shown, an isolated Si_{Ga} donor can move quite easily to this position, provided that it captures two electrons. In the present case the two electrons needed to facilitate this displacement may be provided by the nearby vacancy V_{Ga} or captured from the conduction band. Next, a defect complex which may be described as a "silicon interstitial plus two Gallium vacancies" is formed as shown in Fig. 1(d). We will refer to this complex as V_{Ga}-Si_i-V_{Ga}. The conversion of an isolated Si donor to an interstitial plus vacancy configuration is energetically very unfavorable. However, for a donor-vacancy pair, as the Si atom moves into the interstitial region it begins to interact strongly with the As dangling bonds of the Ga vacancy. This rebonding allows the silicon atom to move through

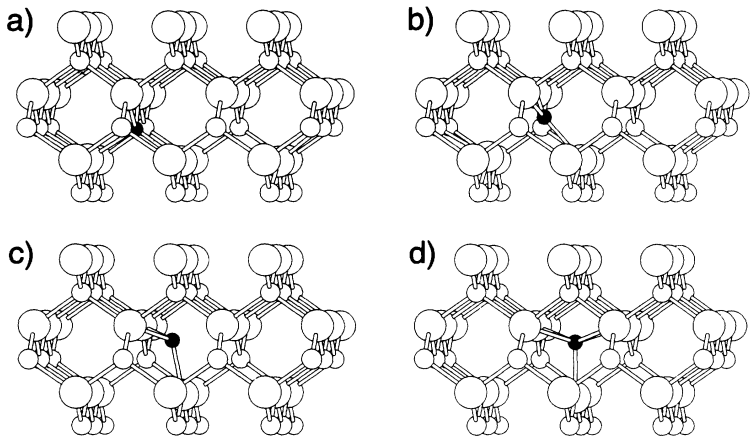

FIG. 1. Fundamental atomic configurations which define the diffusion pathway: (a) initial (Si_{Ga}-V_{Ga}), (b) planar, (c) *DX*, and (d) interstitial (V_{Ga}-Si_i-V_{Ga}). The larger circles are As atoms, the smaller circles are Ga atoms, and the small black sphere is the Si impurity.

the interstitial region and switch places with the Gallium vacancy.

In Fig. 2 we show the total-energy surface calculated for such a migration process. The migrating atom moves along the path *a-b-c-d-c-b-a*. To leave the substitutional region (point *a* in the left side of Fig. 2) the silicon atom must overcome a barrier of only about 1 eV. The Si atom then sees a flat valley leading through the interstitial region toward the vacancy site in the right side of Fig. 2. The total-energy surface shown in Fig. 2 was obtained with all Ga and As atoms occupying their lattice sites. We verified that the relaxation of the nearest neighbors has no effect on the shape of the energy surface, though it moderately changes the numerical values. The energies quoted in the text below were calculated with the nearest neighbors relaxed from their lattice sites.

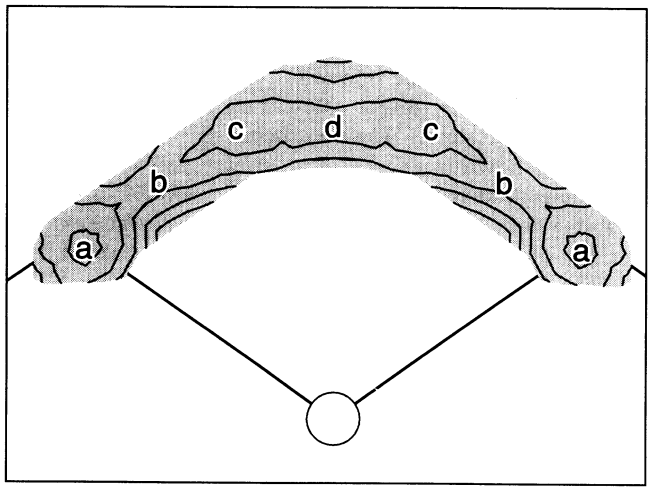

FIG. 2. Contour plot of the total-energy surface for the migration pathway for $Si_{Ga} \leftrightarrows V_{Ga}$ site switching. The (110) plane is shown. The solid lines indicate the Ga-As-Ga bond chain in the (110) plane. In the initial state the Si atom is located on a substitutional Ga site (point *a* on the left). The migration proceeds along the path *a-b-c-d-c-b-a*. The first energy contour is drawn at 0.1 eV above the energy of $(Si_{Ga}$-$V_{Ga})^{2-}$ and the contour spacing is 0.5 eV. The results correspond to zero temperature, and lattice relaxation is not included. Calculations were performed on a grid of points located within the gray area.

In the following, we will explain in detail the origin of two essential features of this migration path: (1) the appearance and low energy of the saddle point at the border between substitutional and interstitial regions (point *b*), and (2) the appearance and flatness of the valley (point *d*). The keys to understanding these features are the individual properties of the Gallium vacancy and the substitutional silicon donor. In a Ga vacancy the four dangling bonds of the four As neighbors form a nondegenerate a_1 resonance in the valence band and a triply degenerate t_2 orbital in the forbidden gap. A neutral Ga vacancy has three electrons occupying the t_2 orbitals. In an *n*-type sample the t_2 orbitals are fully occupied with six electrons and the vacancy is in a triply negative charge state. The Ga-vacancy orbitals of the complex originate from the t_2 gap state split by the local perturbation as shown in Fig. 3. In the $(Si_{Ga}$-$V_{Ga})^{2-}$ complex these three orbitals are fully occupied.

The isolated silicon donor uses three of its four electrons to complete four bonds with its As neighbors and introduces two resonances of a_1 and t_2 symmetry in the conduction band. Thus the fourth electron of Si is donated to the conduction band and the Si atom is positively charged. When this atom is moved toward the interstitial site, as shown in Fig. 1(b), the t_2 state splits and its fully symmetric components (a_1) decreases in energy. This state can be described as a Si dangling bond orbital pointing toward the interstitial site and is denoted Si-sp_{111}. It is empty for a positively charged donor but is doubly occupied for a negatively charged *DX* center.[12] In the latter case, the decrease in energy of the two dangling-bond electrons helps to overcome the increase in elastic energy. Eventually, another total-energy minimum appears, with the Si atom in a configuration similar to that of Fig. 1(c). The Si atom is located in the interstitial region, and bound only to three As neighbors. This behavior is a general property of substitutional *sp* donors in III-V alloys, and is the essence of microscopic models for the *DX* center[12,13] and *EL*2 center[18–20] in GaAs.

During the migration the single-particle orbitals of the complex evolve as shown schematically in Fig. 3. For the

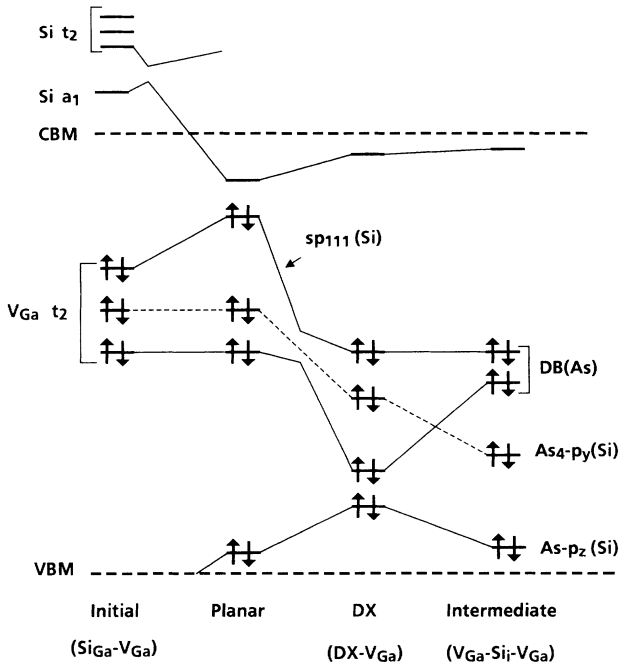

FIG. 3. Schematic representation of the evolution of the single-particle orbitals during the Si migration. The four configurations are illustrated in Fig. 1.

undistorted Si_{Ga}-V_{Ga} pair the lower of the conduction-band resonances corresponds to the a_1 state of the isolated Si_{Ga}, while the upper three resonances originate from the t_2 states. These four states are empty for the 2− charge state of the complex. The lowest-energy components of the t_2 group drops in energy and evolves into a dangling bond as it does for the isolated silicon donor. This state is initially empty, but around the border of the substitutional tetrahedron it obtains electrons either from one of the vacancy states or from the conduction band. As in the case of *DX*, this results in a decrease of total energy when the interstitial region is entered. At the border of the substitutional tetrahedron there appears a saddle point in the total-energy surface (Fig. 2). The height of the energy barrier depends on the charge state of the complex: In the 2− charge state the barrier is found to be approximately 1.4 eV. In this case the electrons which occupy the Si-sp_{111} orbital are obtained from the vacancy. For the 4− charge state the barrier is 0.7 eV. In this case the Si-sp_{111} orbital are obtained from the vacancy. For the 4− charge state the barrier is 0.7 eV. In this case the Si-sp_{111} orbital is occupied from the beginning and the complex remains in the 4− charge state during migration. One might therefore expect that when the Fermi energy is sufficiently high, the defect temporarily captures electrons from the conduction band, and the migration proceeds with a lowered barrier. However, the $(Si_{Ga}$-$V_{Ga})^{2-}$ complex is negatively charged and there is an additional, electrostatic barrier for the electron capture. This may stabilize the diffusion close to the height of 1.4 eV.

The appearance of a low-energy saddle point between the substitutional and interstitial regions, is thus due to the same mechanism which is responsible for the structural metastability of *sp* donors in III-V alloys. However, this mechanism cannot account for the flatness of the energy surface in the interstitial region. To understand what happens there it is helpful to examine the bonding in the V_{Ga}-Si_i-V_{Ga} complex [Fig. 1(d)]. In this configuration the Si atom is bonded to five As atoms. The Si p_z orbital (the z axis is chosen vertical in Fig. 1) is responsible for the bond with the As atom which is directly below the Si atom in Fig. 1(d). The p_x and p_y orbitals of Si form rather complex bonds with the dangling-bond orbitals of four coplanar As atoms, two from each vacancy. The p_y derived state is in the band gap as shown schematically in Fig. 3. The p_x orbital forms a resonance about 3 eV below the top of the valence band. Thus, when the Si atom moves from the *DX* to the V_{Ga}-Si_i-V_{Ga} configuration, two of the As-Si sp^3 bonds do not simply stretch but evolve into the two complex bonds between the Si and the four coplanar atoms. The opposite takes place when the Si atom moves on towards the right side of Fig. 2. Due to this bond-passing mechanism there exists a low-energy migration path joining the two *DX*-like configurations of the complex.

Is it plausible that the same two mechanisms work for self-diffusion of Gallium? In this case one of the second-nearest neighbors of a Ga vacancy follows the Si migration path to switch sites with the vacancy. There is no apparent reason why the bond-passing mechanism should not work. On the other hand, the *DX* mechanism is due to a Si sp_{111} hybrid that splits off from the t_2 resonance introduced by the donor. This t_2 resonance has a large contribution from the conduction states around the *X* minimum, and one may expect that a similar Ga sp_{111} hybrid is split off from the *X* minimum when a Ga lattice atom moves toward the interstitial region. This expectation is confirmed by direct calculation for a Ga vacancy in the -3-charge state. However, because the Ga sp_{111} hybrid moves down in energy more slowly and starts from higher energy than its Si analog, there is no *DX*-like metastability for Ga. For Ga the total-energy surface exhibits a flat plateau corresponding to a barrier of about 1.5 eV. The plateau height agrees well with the value (1.3 eV) obtained by Wei, Zhang, and Zunger[21] for the energy difference between undistorted GaAs and GaAs with one Ga atom moved to the substitutional-interstitial border along the [111] direction.

The total activation energy for Ga self-diffusion is the sum of the vacancy formation energy and the migration barrier, $Q=\Omega+E_{\text{barrier}}$. The formation energy for V_{Ga}^{3-} may be expressed as[11]

$$\Omega\ (\text{eV})=5.26-3\mu_e+\Delta\mu/2,$$

where $\Delta\mu/2$ is related to the difference between the As and Ga chemical potentials and varies between −0.5 eV for As-rich conditions and 0.5 eV for Ga-rich conditions, and μ_e is the Fermi level, which varies between 0 and 1.5 eV. For high temperatures and intrinsic material it is reasonable to assume that the Fermi level is close to

midgap: $\mu_e = 0.75$ eV. Using the present calculation of $E_{\text{barrier}} = 1.5$ eV, we obtain a range of values, $4 < Q(\text{eV}) < 5$. The low end of the range corresponds to the As-rich, limit while the upper end corresponds to the Ga-rich limit. The earliest measurement of Q is due to Goldstein,[22] who obtained 5.6 eV, and recent measurements appear to confirm this result.[23,24] Considering that the theoretical estimate for Q is made for $T = 0$, whereas the diffusion experiments are performed at high temperatures, the level of agreement between the two is satisfactory. Rouviere *et al.*[24] measured a value for E_{barrier} equal to 1.7 eV, which is reasonably close to the value of 1.5 eV obtained here.

In summary we have shown that the energy barrier for $\text{Si}_{\text{Ga}} \leftrightarrows V_{\text{Ga}}$ site switching is approximately 1.4 eV. The low value for the barrier is traced to two mechanisms: (1) the *DX* mechanism, and (2) the bond-passable mechanism. We have also found that the same physics is at work when an isolated Ga vacancy migrates via a similar mechanism: $\text{Ga}_{\text{Ga}} \leftrightarrows V_{\text{Ga}}$. The diffusion barrier was found to be virtually the same as for the $\text{Si}_{\text{Ga}} \leftrightarrows V_{\text{Ga}}$ site switching. As we are not aware of any physical mechanism arising from the presence of a nearby silicon donor which could lead to a significant increase in the Ga self-diffusion barrier, we believe that we have also shown that the vacancy-assisted diffusion of silicon donors is characterized by a low-energy barrier (about 1.5 eV) and proceeds by the Si migration through the interstitial region into the vacancy site, followed by a similar migration of one of the Gallium atoms into the vacancy left behind the Si atom. We believe that this is a general description of vacancy-assisted self-diffusion on the group-III sublattice of III-V compounds.

Note added in proof. We have learned very recently that Chen, Zhang, and Bernholc have found a similar value for the migration energy of the Si_{Ga}-V_{Ga} pair.[25]

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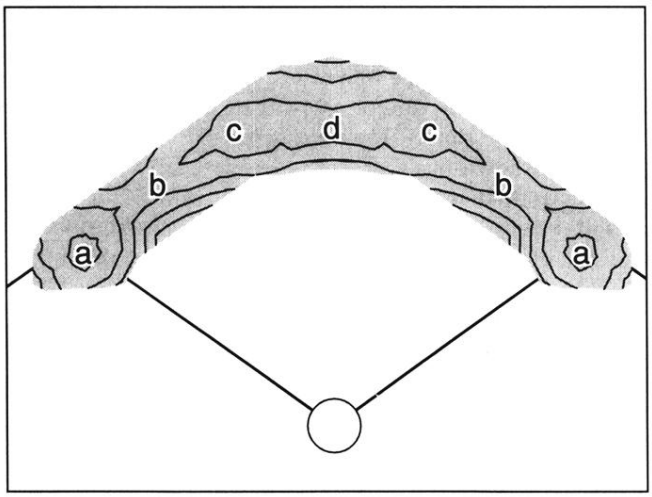

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