The structure and properties of vacancies in Si nano-crystals calculated by real space pseudopotential methods

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Abstract

The structure and properties of vacancies in a 2 nm Si nano-crystal are studied using a real space density functional theory/pseudopotential method. It is observed that a vacancy's electronic properties and energy of formation are directly related to the local symmetry of the vacancy site. The formation energy for vacancies and Frenkel pair are calculated. It is found that both defects have lower energy in smaller crystals. In a 2 nm nano-crystal the energy to form a Frenkel pair is 1.7 eV and the energy to form a vacancy is no larger than 2.3 eV. The energy barrier for vacancy diffusion is examined via a nudged elastic band algorithm.

Key words: theory, nano-structures, vacancies, diffusion

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1 Background

As the size of micro-electronic devices continues to diminish the devices are approaching the nano-scale \(^{(1)}\). Although scaling improvement is still possible within the traditional micro-electronics paradigm, \(^{(1; 2)}\) there is an effort to move to devices constructed directly from nano-structures \(^{(3; 4)}\). Nano-devices can be constructed that function both to fill the roll of existing technology \(^{(4; 5)}\) and as novel devices whose performance is dependent upon nano-induced properties \(^{(3; 6)}\).

One aspect of device design and manufacture that requires special attention is doping. In micro-electronics the placement and control of dopants has been studied in depth and is continuing to be studied \(^{(7)}\). At the nano-scale dopants behave very differently than in bulk. Quantum confinement limits the possible concentration of some impurities due to an increase in the enthalpy of formation. This is the so-called \textit{self-purification} effect in nano-structures \(^{(8)}\). However, by carefully controlling the growth environment it is possible to create selectively doped nano-structures \(^{(4; 5; 9; 10)}\). It is unclear whether the dopants that are incorporated during the growth process remain in the active region of the nano-structure because they are kinetically limited, or if they are thermodynamically stabilized by a yet unidentified effect.

The diffusion of impurities depends strongly upon their interaction with intrinsic defects, especially interstitial atoms and vacancies. At the nano-scale it is anticipated that quantum confinement will affect the energy of formation.

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and migration of intrinsic defects. In addition, the free surfaces, which can move to reduce internal stresses, will also influence the properties of defects. Understanding diffusion at the nano-scale requires understanding the balance between these two effects.

The density functional theory/pseudopotential methods used here are encoded in the software PARSEC (11, 12). The real space grid is chosen to be 0.5 a.u.\(^1\), which is sufficient for force and energy convergence. Aperiodic boundaries conditions are employed with a vacuum region of greater than 6 Å between the surface of the nano-crystal and the cell boundary. The local density approximation is used for the exchange and correlation functional (13). Troullier-Martins pseudopotentials (14) are used with Si having a valence of 3s\(^2\)3p\(^2\)3d\(^0\) and a cutoff radius of 2.5 a.u. for all angular channels. The hydrogen pseudopotential has a valence of 1s\(^1\) and a 2.0 a.u. cutoff. The pseudopotential is transformed into local and non-local components by the Kleinman-Bylander (15) transformation with the p channel selected as the local component for Si. All atomic structures are optimized until the forces are smaller than 0.04 eV/Å.

To calculate the diffusion barriers a nudged elastic band method is implemented (16). The velocity Verlet algorithm is used to update the images in configuration space. The vacuum region is increased by 2 Å to insure that the nano-crystal does not interact with the boundaries. The spring coefficient of the elastic band is initially set to a large value, to insure the stability of the calculation, but as the elastic band approaches the minimum energy path, the coefficient is reduced to improve the convergence rate.

A 2 nm diameter, hydrogenated, Si nano-crystal (\(Si_{175}H_{116}\)) is examined. The \(^1\) The atomic units of length used here are Bohr radii unless specified otherwise.
The geometric center of the nano-crystal corresponds to an Si atom. Each surface Si is bonded to no more than 2 H. A hydrogen passivated surface represents the situation where the surface is the most capable of relaxation. It is anticipated that replacing the hydrogen with oxygen, polymers, or an Si reconstruction will lead to a slight constriction of the surface. The calculated gap in a defect free Si nano-crystal is 2.04 eV, as shows in Fig. 1.

2 Results and Discussion

A vacancy is placed at sites along the [110] direction from the center of the crystal to the surface. The structures, states, and total energies are calculated for each configuration. When a vacancy is placed in the center of the nano-crystal, the local symmetry of the vacancy is that of the nano-crystal’s point group, $T_d$. The vacancy undergoes a Jahn-Teller distortion similar to that observed in bulk, which results in the $T_d$ symmetry being broken to $D_{2d}$ [17, 18]. The reduction in local symmetry causes a reduction of degeneracies of the electronic states. The $T_d$ configuration has a triply degenerate, partially occupied, state associated with the $t_2$ representation. This splits into a fully occupied state belonging to the $b_2$ representation and an empty, doubly degenerate, state belonging to the $e$ representation of the $D_{2d}$ point group. The states that are localized at the defect are identified in Fig. 1 as well as the representations to which they belong. The energies of each of the structures are presented in Table 1. The geometry of the calculated structures are given in Table 2 using the atomic structure shown in Fig. 2 as a reference.

When the vacancy is located one site from the center, a Jahn-Teller distortion is still present, however, the symmetry of the distortion is different. The local
symmetry of the site depends not only upon the nano-crystal’s point group, but also the location of the vacancy in the nano-crystal. Because the vacancy is positioned along one of the $T_d$ three-fold rotation axis, the local symmetry obeys this three-fold rotation, but most of the other operations of the $T_d$ point-group are destroyed. The local symmetry about the vacancy is $C_{3v}$. The geometry of the vacancy is given by Table 2 and Fig. 2 where the center of the nano-crystal is site A. The defect states are shown in Fig. 1 where the occupied state belongs to the $a_1$ representation and the degenerate, empty, states belongs to the $e$ representation.

If the vacancy is located yet one site farther from the center, in the [110] direction, all of the $T_d$ symmetry operations are absent except for one mirror plane that contains both the center of the crystal and the vacancy site and has a normal in the [110] direction. The vacancy has symmetry $C_s$. The geometry is given in Table 2 and Fig. 2 where the vector $\vec{AC}$ points from the center of the crystal toward the surface, in the [110] direction. Because $C_s$ has no doubly degenerate, irreducible, representations, the defect states, shown in Fig. 1 have no degeneracy.

The energies of the vacancy structures reported in Table 1 are directly related to the energies of the occupied defect states and the local symmetry. This is in agreement with published observations of the importance of symmetry in nano-crystals (19). If the diffusion mechanism for vacancies is limited to site hopping, then in these highly symmetric nano-crystals it is possible to trap vacancies at the center of the nano-crystal. It is also apparent that sites nearer the surface are lower in energy than sites in the interior. When a vacancy is placed within two atomic layers of the surface, around 4 nm, the vacancy is spontaneously pulled to the surface. These calculations are in qualitative
agreement with calculations performed on 3 nm Si nano-crystal. It is predicted that the effect of symmetry on the properties of point defects will also be observed in other nano-structures. In particular it is anticipated that vacancies and other point defects in [111], [001], and [112] nano-wires should differ from one wire to the next.

The energy of formation for a Frenkel-pair is investigated in 1 and 2 nm nano-crystals.Interstitial atoms are placed at tetrahedral sites adjacent to vacancies that have the $D_{2d}$ structure. The energy of formation is calculated to be 0.63 and 1.70 eV for the 1 and 2 nm nano-crystals respectively. The calculated energy of formation for a Frenkel defect, in bulk, is around 7 eV. The bulk calculation uses a vacancy-interstitial separation of 8 Å, but this is not possible in these nano-structures. It is concluded from this calculation that as a nano-structure decreases in size, the energy to spontaneously create intrinsic point defects diminishes. The energies calculated here, are small enough that one expects to find nano-crystals containing Frenkel defects in any reasonable sized ensemble of nano-structures. In principle these Frenkel defects can act to generate vacancy-interstitial pair that may be pulled toward the surfaces, creating an internal stirring within the nano-crystal. Additional studies must be performed to understand the impact of this result on diffusion.

Subtracting the calculated total energy of a nano-crystal with a vacancy from the total energy of a perfect nano-crystal yields the energy of formation for a vacancy plus the energy to add an Si atom to the computational cell. The energy to add an atom is dependent upon the computational method. It is more tractable instead to calculate the relative energy of formation by defining one vacancy structure as the energy zero. By setting the energy of formation for a vacancy in the center of a 1 nm crystal as zero it is determined that the
relative energy of formation for a vacancy in a 2 nm crystal is 1.4 eV. For a 3
nm crystal the relative energy of formation is calculated to be no larger than
2.0 eV. The energy of formation in bulk is around 3.7 eV (21). It is deduced
that the absolute energy of formation for a vacancy can be no larger than 1.7
and 2.3 eV for 1 and 2 nm nano-crystals. These calculations demonstrate the
influence of free surfaces on the energy of formation for point defects in nano-
structures. Although it is known that for some classes of defects the quantum
confinement, self-purification effect is dominant (8), this is not universally
ture.

To study the migration barrier for vacancies, a 2 nm crystal centered on a Si-Si
bond is examined. The nudged elastic band method is employed to determine
the minimum energy path to move a vacancy across the center of the crys-
tal. The end configurations have $C_{3v}$ symmetry. The middle of the transition
corresponds to placing the atom that is exchanging sites with the vacancy
directly in the center of the crystal, creating a six-fold coordinated structure
with $D_{3d}$ symmetry and bond lengths of 2.63 Å. The energy of this structure
is -0.64 eV relative to the $C_{3v}$ structure. The end configurations are only local
minima. The lowest energy configuration is found between the $C_{3v}$ configura-
tion and the $D_{3d}$. The minimum has low symmetry and a relative energy of
-1.24 eV. There is no degeneracy in the defect states and the energy difference
between the empty and full state is 1.1 eV. The vacancy in this configuration
is much nearer to the center of the crystal, and is off of the [111] three-fold
rotation axis. Although this arrangement introduces strain to the surrounding
bonds, the surfaces help to reduce the strain energy. This result suggests that
the vacancy diffusion process may occur through pathways that do not require
the vacancy to sit directly upon atomic sites. The barrier to moving across the
center of the crystal from one minimum to another is 0.6 eV. This is slightly smaller than the literature value for bulk Si, 0.8 eV (22). This indicates that the diffusivity of vacancies in Si nano-structures is enhanced.

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Fig. 1. The electronic states of vacancies with various local symmetries. The occupied states are shown in black and the empty states in red. The representation that each defect state belongs is written to the right of the corresponding state.

Fig. 2. A geometric representation of the local structure around a vacancy.
The energy of defect states and total energy of nano-crystals containing vacancies.

The defect levels are expressed in eV. The highest occupied, non-localized, state is taken to be the valence band maximum (VBM) and is set to zero. The energy gap of a vacancy free crystal is 2.04 eV. The total energy of the vacancy structures are presented in meV and the $D_{2d}$ structure is arbitrarily set to zero.

|       | $D_{2d}$ | $C_{3v}$ | $C_s$ |
|-------|----------|----------|-------|
| **Defect States (eV)** | | | |
| Rep. | Ene. | Rep. | Ene. | Rep. | Ene. |
| $b_2$ | 0.24 | $a_1$ | 0.72 | $a'$ | 0.13 |
| $e$ | 1.47 | $e$ | 0.96 | $a''$ | 1.55 |
|       |       |       |       | $a'$ | 1.81 |
| **Total Energy (meV)** | | | |
| 0 | 853 | -329 |
Table 2

The local structure about vacancies with different symmetries. The reference geometry is shown in Fig. [2] and the details of the orientation is given in the text. Using this computational method the bond-length in the center of a vacancy free nano-crystal is 2.3 Å, and the distance between the segments, is 3.8 Å.

| Segment | $D_{2d}$ | $C_{3v}$ | $C_{s}$ |
|---------|---------|--------|--------|
| $AB$    | 3.4     | 3.4    | 3.6    |
| $AC$    | 2.7     | 3.4    | 2.5    |
| $AD$    | 3.4     | 3.4    | 3.6    |
| $BC$    | 3.4     | 2.9    | 3.4    |
| $BD$    | 2.7     | 2.9    | 2.7    |
| $CD$    | 3.4     | 2.9    | 3.4    |