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Theoretical study of hydrogen stability and aggregation in dislocation cores in silicon

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The interaction between hydrogen and a dislocation in silicon has been investigated using first-principles calculation. We consider 30° and 90° partial dislocations with both single and double periodic structures and nondissociated screw dislocation starting from the case of one single H to a fully H-filled dislocation line. In the case of a single H atom, H is preferentially located in a bond-centered-like site after a possible breaking of a Si–Si bond. In case of two H atoms, the molecular H_2 can be stable but is never the lowest energy configuration. If initially located in a bond-centered site, H_2 usually spontaneously dissociates into two H atoms and breaks the Si–Si bond followed by the passivation of resulting dangling bonds by H atoms. When additional H atoms are inserted into partial dislocation cores, they first induce the breaking of the largely strained Si–Si bonds in the dislocation core, then passivate the created dangling bonds. Next the insertion of stable H_2 near the dislocation core becomes favorable. A maximum H density is determined as 6 H atoms per length of Burgers vector and the largest energy gain in energy is obtained for a 90° single periodic partial dislocation. Our calculations also suggest that the presence of few hydrogens could have a non-negligible influence on the dislocation structures, inducing core reconstructions. The mobility of H along the dislocation line is briefly addressed in the case of the 90° single periodic partial dislocation core.

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I. INTRODUCTION

The research on hydrogen in silicon has attracted a lot of interest for a long time. As a common impurity in semiconductors, hydrogen is known to exist in large variety of forms such as an isolated interstitial, or interacting with other impurities or native defects and so on (see for example Ref. 1). The potential ability of hydrogen to activate inert impurities or defects and to passivate acceptors or donors is especially interesting for technological applications. Besides, massive hydrogen implantation in silicon could lead to the formation of finite planar defects in the form of platelets. They can be used in the ion-cutting process for building silicon-on-insulator systems and other heterostructures, which require atomically sharp interfaces between layers.[2]

A lot of experimental and theoretical studies were performed for investigating the behavior of hydrogen in silicon. There are general agreements among the following results. Hydrogen is highly mobile and fast diffuser in Si with low-activation energy.[3–8] As for monatomic H, the lowest energy configuration is obtained when it is located in a bond-centered (BC) position.[6,9] However, the H_2 molecule located in a tetrahedral interstitial site is the more favorable form of hydrogen in Si,[10,11] while another metastable configuration, called H_2^*, is also reported by Chang and Chadi.[5] The existence of interstitial H_2 molecules has been confirmed by Raman and infrared absorption experiments.[12,13] In the vicinity of strained Si–Si bonds, the H_2 molecule is expected to dissociate into two single H atom with a substantial gain in energy.[14] This suggests that a strong interaction occurs between hydrogen and defects such as vacancies and self-interstitials in Si. Largely strained Si–Si bonds are also common in highly distorted and reconstructed configurations such as dislocation cores,[15–21] which should lead to a similar interaction as observed for point defects.

Dislocations are known to interact with many kind of defects such as vacancies, interstitials and impurities. Understanding the interactions between dislocations and impurities is especially important for semiconductor technologies because the transport properties of dopant impurities are affected by the strain field associated with dislocation. So far the effects of dopants, such as oxygen,[22–24] nitrogen,[25,26] arsenic,[26–28] on the structural, electronic and dynamic properties of dislocation cores in Si were investigated. Regarding the interaction between hydrogen and dislocation in Si, available studies were essentially focused on the influence of hydrogen on the mobility of dislocations. Hence, a large reduction of the activation energy for partial dislocations glide, the so-called hydrogen enhanced dislocation glide effect, were investigated both experimentally[29] and theoretically.[30–32] In the latter works, it was shown that a large gain in energy is obtained when one or two hydrogens are located in the single period reconstructed core of a 90° partial dislocation, compared to bulk configurations. This result suggests an exceptional stability of hydrogen in dislocation cores. We have recently obtained a similar result in the case of hydrogen interacting with a nondissociated screw dislocation.[33] But since only two core configurations were examined, it would be premature to conclude about a general effect. Additional investigations focusing on all possible dislocation core structures are therefore required.

Besides the need to check this improved stability, other intriguing aspects concern the mobility of hydrogen along a dislocation line, as well as a possible tendency for hydrogen to aggregate in the dislocation core. As far as we know, little is known about such issues. Finally, previous studies were focused on the determination of the relative stability of single and double period reconstructed core for the 90° partial dislocation.[16,34–37] one may wonder whether the presence of hydrogen in the dislocation core could have an effect on the core structure, favoring one reconstruction over the other.

In this paper is reported the results of first-principles calculations that we have performed for answering the preceding questions. 30° and 90° partial dislocation with both single and double period structures, and nondissociated screw dislocation were considered for determining the interaction of hydrogen with dislocation cores, starting from the case of one single monatomic H, to a fully H-filled dislocation line. In particular we show that the improved stability of hydrogen into dislocation cores is a general statement in silicon. The energy gain is large enough for a spontaneous dissociation of a H_2 molecule to occur in certain cases. We also determined the optimal filling of hydrogen atoms into the dislocation cores.

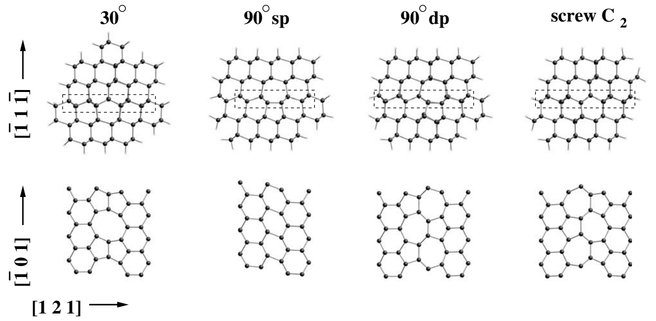

FIG. 1. Ball and stick representation of the systems used in our calculations. From the left to right, 30° partial, 90° single periodic partial, 90° double periodic partial and screw dislocation in glide set. In the top row, the systems are projected onto $(\bar{1}01)$ plane, i.e., along $[\bar{1}01]$ dislocation line. In the bottom row, the regions surrounded by dashed lines in the top row are projected onto $(\bar{1}1\bar{1})$ plane, i.e., along $[\bar{1}1\bar{1}]$ axis. Silicon atoms and hydrogen atoms are represented by big black spheres and small white spheres, respectively.

II. CALCULATION

A. Methods

Our calculations are based on density functional theory with generalized gradient approximations, which is implemented in the SIESTA code.[38–40] Spin polarization was taken into account in the case of monatomic H. We have used the Perdew, Burke, and Ernzerhof (PBE)[41] functional to compute exchange and correlation energy contributions. This functional does not allow a good description of van der Waals interactions which could occur for some configurations including several H_2 molecules. However, these interactions are expected to be rather low with respect to the formation energies reported below, and can be safely neglected here. Norm conserving pseudopotentials were used to describe ionic interactions. Wave functions are described with a generalized version of linear combinations of atomic orbitals, which include multiple-zeta orbitals and polarization states. For the H atoms saturating the dangling bonds of surface Si atoms, we have used single-zeta basis sets. For silicon atoms and hydrogen atom(s) located in the dislocation core, more accurate double-zeta plus polarized basis sets were employed. The charge density is projected onto a real-space grid with an equivalent cutoff of 40 Ry.[40] The Brillouin zone is sampled at the Γ point only because of the large size of our computational systems. Within these conditions, the optimized lattice constant a_0 is equal to 5.484 Å.

All calculations were done using a cylinder-shape cluster with periodic boundary conditions in all directions. Along the cylinder axis, the supercell and the cluster have the same length of $4|\boldsymbol{b}|$, with $\boldsymbol{b}=(a_0/2)[\bar{1}01]$, thus yielding an infinite system in this direction. The length of supercell edges along the two other directions is $5a_0$, ensuring a minimum vacuum separation of 8 Å between periodic images of the cluster. The dangling bonds of silicon atoms at the cluster surface are passivated with hydrogen atoms. Dislocations are introduced in the center of the cluster using anisotropic elasticity theory, the dislocation line being orientated along the cylinder axis. Such a procedure yields an infinite straight dislocation along this orientation. The length of the system along the dislocation line appears sufficient to ensure that an inserted H atom is not interacting with its periodic images.

All the dislocation core structures that we investigated in this paper are shown in the Fig. 1. Our computational system includes a few hundreds of atoms. The number of atoms varies depending on the system: from 264 atoms (C_2 screw dislocation) to 304 (30° partial dislocation) atoms. The cluster except for Si atoms at the surface and H atoms for dangling bonds saturation is relaxed by minimizing the forces on all atoms using conjugate gradient method. Optimization of the ionic positions is allowed to proceed until the maximum atomic force is less than 0.005 eV/Å. Note that surface silicon and passivating hydrogen atoms are fixed during relaxations, in order to maintain the anisotropic elastic displacements field. Finally a variable number of hydrogen atoms is introduced into the dislocation cores at chosen locations. Although it is obviously difficult to assert that we always found the most stable state for a given hydrogen concentration, a total number of 310 configurations were investigated in this work, in order to make the search as exhaustive as possible. The effect of the charge on the stability was not considered in this work.

B. Formation energy

Since the geometry near the dislocation core can be very different from the ideal lattice, a systematic search for all stable configurations of hydrogens is required to obtain the most stable configurations. Such an investigation was started with a single H atom up to 32 H atoms in all the dislocation cores. The first case corresponds to an isolated H atom in the dislocation core, whereas the last one results in a dislocation core filled with as much as 8 H atoms per $\boldsymbol{b}$. As in the case of our previous work,[33] for each relaxed configuration, the defect formation energy $E_F^{nH/\perp}$ defined as follows is computed:

$$E_F^{nH/\perp} = E_\circ^{nH/\perp} - E_\circ^{\perp} - nE_H. \tag{1}$$

Here $E_\circ^{nH/\perp}$ is the total energy of the relaxed system including both the dislocation and n hydrogen atoms, and $E_\circ^{\perp}$ is the total energy of the dislocation alone in the same computational system. The last term of the right hand side of Eq. (1) is the reference energy for a single H atom and is defined as

$$E_{\mathrm{H}} = \frac{1}{2}[E_{\circ}^{\mathrm{H}_2} - E_{\circ}], \quad (2)$$

where $E_{\circ}^{\mathrm{H}_2}$ denotes the total energy for H_2 located in a tetrahedral site in the center of a bulklike system and $E_{\circ}$ denotes the total energy of the same system but without hydrogen. Using this formalism and reference, we found that the formation energy of one H atom relaxed in a BC site in bulk silicon is 1.07 eV.

III. RESULTS

A. Bare dislocation cores

Figure 1 shows the four different dislocation cores considered in this study. In the top row, the systems are projected onto $(\bar{1}01)$ plane, i.e., along $[\bar{1}01]$ dislocation line. In the bottom row, the regions surrounded by dashed lines in the top row are projected onto $(\bar{1}1\bar{1})$ plane, i.e., along $[\bar{1}1\bar{1}]$ axis. In the case of the 30° partial dislocation, the computational system contains 304 (204 Si and 100 H) atoms. The lowest energy configuration is obtained for a double period reconstructed core, in agreement with previous calculations.[42] At the dislocation center, a pair of pentagons and an octagon are alternatively present along the dislocation line. In the case of the 90° partial dislocation, it is well known that two possible cores, single periodic (sp) or double periodic (dp), can be obtained after relaxation, with very close core energies.[43] Using systems including 288 (200 Si and 88 H) atoms, we obtained both core configurations (Fig. 1). For the 90° sp system, distorted hexagons are present along the dislocation line. For the 90° dp system, the core exhibit a double period reconstruction, leading to alternating pairs of a pentagon and a heptagon along the dislocation line. The total energy differences between both core configurations is 0.484 eV, i.e., $0.121\ \mathrm{eV}/|\boldsymbol{b}|$ or $30\ \mathrm{meV}/\mathrm{Å}$, in favor of the dp configuration, in very good agreement with available data.[35] Finally, we also investigated the nondissociated screw dislocation, for which several stable core structures are possible.[17,19,21] In a previous work, we considered one of them, characterized by the dislocation centered at the intersection of two (111) planes of the shuffle set.[33] Another stable configuration, with the lowest energy, is obtained when the center of the dislocation is located at the intersection of two (111) planes of the glide set, with a double period reconstruction along the dislocation line.[19] Here we have investigated the latter, labeled C_2, using a system containing 264 (184 Si and 80 H) atoms (Fig. 1). Again, the relaxed structure is similar to available data.[19,21]

B. Monatomic hydrogen in the dislocation core

We aimed at determining the lowest energy configurations for a single H atom into a silicon dislocation core. Since the structure of dislocation cores can be quite complicated with a low symmetry, there are a large number of possible locations to be investigated in each case. To find low-energy configurations, we have sampled many configurations with different initial H locations. Those were selected either randomly or by analogy with H in bulk silicon, for which monatomic hydrogen can be located in high-symmetry positions such as the tetrahedral and BC sites.[6,9]

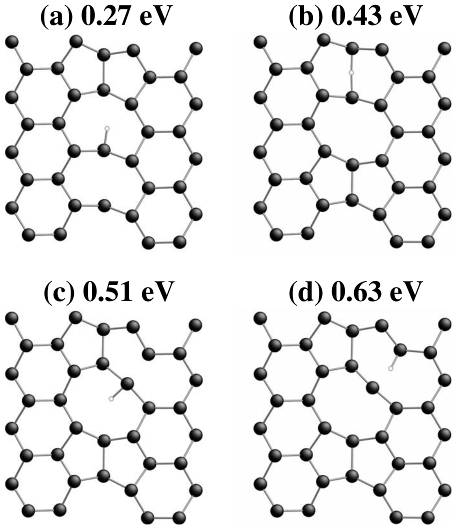

FIG. 2. Low-energy configurations and corresponding formation energies for one H atom in a 30° partial dislocation in Si, projected onto the $(\bar{1}1\bar{1})$ plane. Same graphic convention as in Fig. 1.

In Fig. 2, we show four representative low-energy configurations for monatomic H within the 30° partial dislocation in Si. The most stable configuration, with a formation energy of 0.27 eV, is shown in upper left part of the figure. In this configuration the H atom is located in the close vicinity of the dislocation line, inside an octagon. It forms a bond with a Si atom, with a bond length of 1.55 Å. Due to the large space in the octagon, the accommodation of the H atom appears easier than in other locations close to the dislocation line. Nevertheless, H insertion leads to the breaking of one neighbor Si–Si bond defining a pair of pentagons. Another configuration with the formation energy of 0.43 eV is obtained when a H atom is inserted in the middle of this Si–Si bond [see Fig. 2(b)]. The relaxed structure is very close to the BC configuration in bulk, since the H atom forms bonds with both Si atoms, the Si–H bonds lengths being 1.70 Å and 1.76 Å (1.65 Å in bulk silicon). The separation between the two Si atoms was initially 2.47 Å, and reached 3.46 Å after H insertion. At this point, it is important to emphasize that bond analysis is made solely on the basis of a distance criterion. The examination of all our relaxed configurations suggests that H is bonded to Si when the Si–H distance is lower than about 1.8 Å. This distance criterion is used for drawing bonds in the figures. Two other stable configurations have been obtained when H is interacting with Si atoms next to the dislocation line [Figs. 2(c) and 2(d)]. For both, a Si–Si bond is broken after H insertion. Depending on the position of H, the resulting formation energies are 0.51 and 0.63 eV. The relaxed Si–H distance is 1.58–1.59 Å, close to the value corresponding to the H-passivation of a Si dangling bond.

For the 90° single periodic partial dislocation, we were able to find several low-energy configurations, almost degenerate in energy, when H is located in the center of the dislocation core. These configurations are described in Fig. 3.

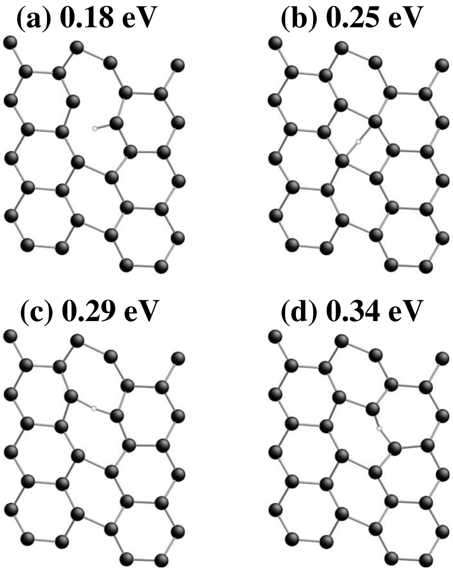

FIG. 3. Low-energy configurations and corresponding formation energies for one H atom in a 90° single periodic partial dislocation in Si, projected onto $(\bar{1}1\bar{1})$ plane. Same graphic convention as in Fig. 1.

Three of these configurations (with formation energies of 0.25, 0.29, and 0.34 eV) are obtained when the H atom is located in an asymmetric BC-like position, between opposite atoms in central hexagons [Fig. 3(b)], or between atoms forming the edges of the hexagon [Figs. 3(c) and 3(d)]. Si–H distances range from 1.64 to 1.77 Å, and the initial Si–Si separations are increased up to 3.34 Å. When a H atom is accommodated at an initially longer Si–Si bond, the formation energy becomes lower. The configuration shown in Fig. 3(c) has already been proposed by Scarle and Ewels.[32] In their work, they determined a formation energy of 1.07 eV relative to H in a bulk BC site. With the same reference, we computed a lower formation energy of 0.78 eV. Nonetheless, our investigations indicate that this configuration is not the most stable one. In fact, the lowest energy structure, albeit very close in energy to the previous ones, is obtained when the H atom is located approximately in the middle of an hexagon, and forms a single bond with a Si core atom, the bond length being 1.53 Å [Fig. 3(a)].

In Fig. 4, we show four representative configurations for monatomic H within the 90° double periodic partial dislocation in Si. The most stable configuration, whose energy is 0.38 eV, is obtained when the inserted H atom breaks the Si–Si bond shared by a heptagon and a pentagon, which are aligned parallel to the dislocation line [see Fig. 4(a)]. The H atom forms a bond with a Si atom, whose length is 1.56 Å. The Si–Si bond length accommodating the H atom is increased from 2.45 to 3.79 Å. Another configuration is obtained when a H atom is put in a BC-like position at the Si–Si bond between a heptagon and a hexagon [see Fig. 4(b)]. The H atom moves slightly inward from the exact BC position. Si–H separations after relaxation are 1.67 Å and 1.72 Å. In a third configuration, a H atom is located inside one of the heptagon, which is distorted due to the presence of the H atom. The latter has a bond with one of the Si of the heptagon [Fig. 4(c)] with a length of 1.53 Å. Finally, a fourth configuration corresponds to H located at another asymmetric BC-like structure in the vicinity of the dislocation line [Fig. 4(d)]. The H atom forms bonds with neighbor Si atoms, with lengths of 1.65 and 1.77 Å.

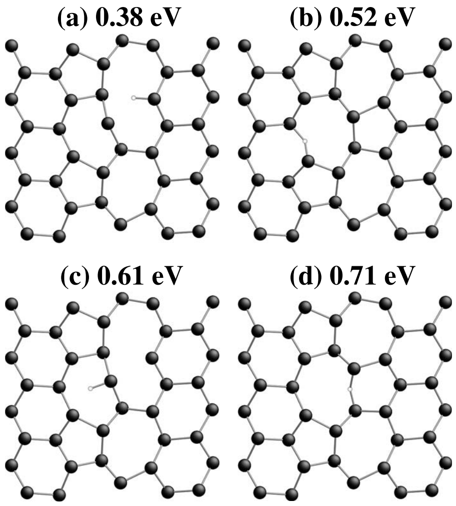

FIG. 4. Low-energy configurations and corresponding formation energies for one H atom in a 90° double periodic partial dislocation in Si projected onto $(\bar{1}1\bar{1})$ plane. Same graphic convention as in Fig. 1.

Finally, in Fig. 5, we report four low-energy configurations for monatomic H within the screw C_2 configuration in Si. When a H atoms is located in a BC site in the center of a Si–Si bond shared by a pentagon and a hexagon near the dislocation line, the most stable (0.14 eV) configuration is obtained [Fig. 5(a)]. In this case, the relaxed structure is quasi symmetric, with final Si–H distances of 1.74 and 1.75 Å. The Fig. 5(b) shows the second best configuration with an energy of 0.57 eV. Here a H atom is inside a heptagon and has a bond with a Si atom, whose bond length is 1.57 Å. We obtained a third configuration with an energy of

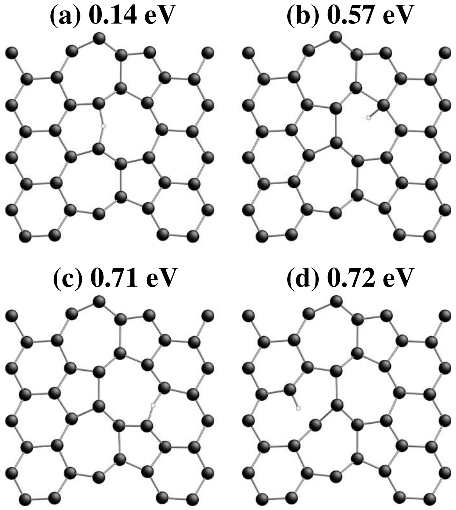

FIG. 5. Low-energy configurations and corresponding formation energies for one H atom in a C_2 screw dislocation in Si, projected onto $(\bar{1}1\bar{1})$ plane. Same graphic convention as in Fig. 1.

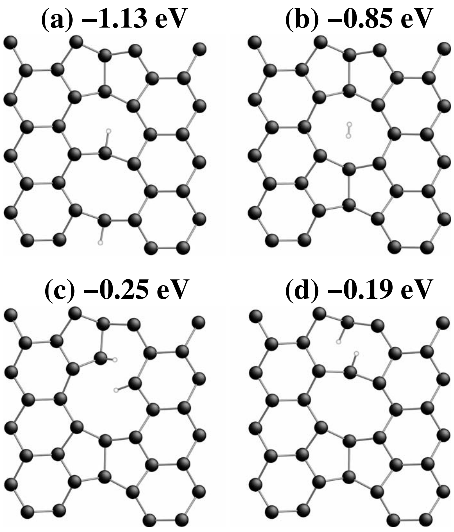

FIG. 6. Low-energy configurations and corresponding formation energies for two H atoms in a 30° partial dislocation in Si. Same graphic convention as in Fig. 1.

0.71 eV, where a H atom is located in a symmetric BC-like position at a Si–Si bond between a heptagon and a hexagon [see Fig. 5(c)]. The distance of the Si–Si bond increases from 2.42 Å to 3.30 Å, H being equidistant to both Si atoms with a separation of 1.67 Å. Finally, another configuration with a close formation energy is obtained when a H atom is located at the center of a Si–Si bond between a pentagon and a hexagon [Fig. 5(d)]. The H atom is singly bonded with one of the Si atoms, with a length of 1.58 Å. The Si–Si separation is increased from 2.40 to 3.38 Å.

C. Two hydrogen atoms in the dislocation core

Next we have investigated the stability of two H atoms in the dislocation core, either as molecular hydrogen or as two distant H atoms. Compared to the previous situation involving only a single H atom, it becomes increasingly difficult to explore all possible configurations. Our strategy for determining low-energy configurations was (1) start with a H_2 molecule located in various positions, either with high symmetry or in regions with enough available space to accommodate the molecule (2) combine the previously determined low energy configurations for a single H atom. Nevertheless, despite a large number of investigated configurations, it is not possible to claim that our search was exhaustive.

In Fig. 6, four representative low-energy configurations of two H atoms in a 30° partial dislocation are shown. The most stable one is obtained when the two H atoms are put in separate octagons, with a formation energy of −1.13 eV. Each H atom has a bond with a Si atom on the dislocation line with a bond length of 1.54 Å. This configuration can be viewed as the H-passivation of the structure depicted in the Fig. 2(a). We found that molecular H_2 is stable inside an octagon, with a formation energy of −0.85 eV [Fig. 6(b)]. The bond length between the two H is 0.80 Å, i.e., the same value as in the bulk. However, when a H_2 molecule is put on one of the Si–Si bonds between a octagon and a pentagon, it spontaneously dissociates into two H atoms separated by 2.24 Å [Fig. 6(c)]. The two H atoms passivate the dangling bonds resulting from the breaking of the initial Si–Si bond. The same mechanism, i.e., spontaneous dissociation and Si–Si bond breaking, also happens when a H_2 molecule is put on a Si–Si bond between two adjacent pentagons [Fig. 6(d)]. In this case the relaxed distance between the two H atoms is 2.05 Å.

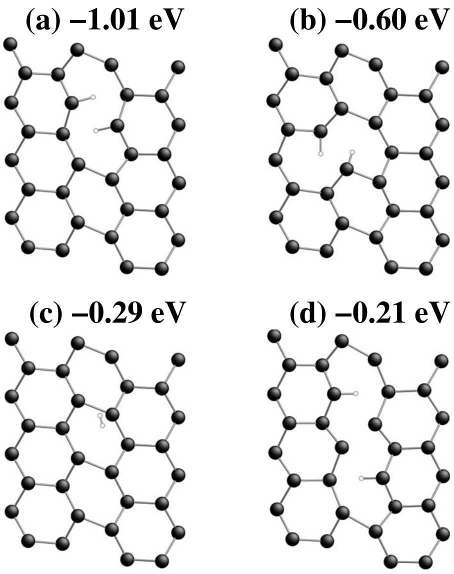

FIG. 7. Low-energy configurations and corresponding formation energies for two H atoms in a 90° single periodic partial dislocation in Si. Same graphic convention as in Fig. 1.

A similar procedure was employed in the case of the 90° sp partial dislocation. In Fig. 7, we show the four best low-energy configurations when two H atoms are present in the dislocation core. As in the case of the 30° partial dislocation, when a hydrogen molecule is put at the center of a Si–Si bond, it spontaneously dissociates into two separated H atoms [Figs. 7(a) and 7(b)]. In the case of configuration (a), which is the most stable configuration with a formation energy of −1.01 eV, the final distance between two H atoms is 2.26 Å and each H atom forms a bond to a Si atom with lengths of 1.52 Å and 1.53 Å, respectively. This configuration can also be viewed as the combination of structures shown in Figs. 3(a) and 3(b). Scarle and Ewels also proposed this configuration, called H_{2BC} in their paper,[32] with a formation energy of 2.70 eV relative to two H atoms in bulk BC sites. Using the same reference, our computed formation energy is 3.15 eV, in good agreement. In the second case, shown in Fig. 7(b), the formation energy is higher (−0.60 eV). The final separation between two H atoms is 2.13 Å and each H atom has a bond with a Si atom with lengths of 1.53 Å and 1.54 Å. Figure 7(c) represents the lowest energy configuration where the molecular form of hydrogen is retained. The H_2 molecule is not located in the plane of the figure, but rather in the center of the large heptagon clearly visible in the $(\bar{1}01)$ projection of the 90° sp core (upper row of Fig. 1). The bond length is 0.80 Å, i.e., the same value as in the bulk. Finally, in Fig. 7(d), we show a low-energy configuration for which the two H atoms are

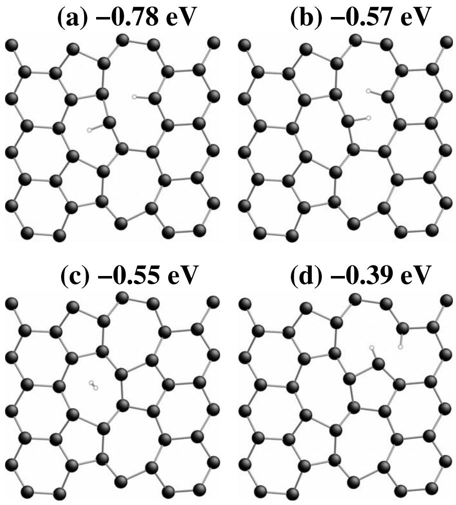

FIG. 8. Low-energy configurations and corresponding formation energies for two H atoms in a 90° double periodic partial dislocation in Si. Same graphic convention as in Fig. 1.

clearly not in interaction. Both H atoms form bonds with the neighbor Si atoms, with lengths of 1.52 Å. This geometry is obtained by the combination of two times the configuration described in Fig. 3(a).

For the dp reconstruction of the 90° partial dislocation, we found that the lowest energy (−0.78 eV) is obtained by combining the configuration shown in Figs. 4(a) and 4(c), i.e., one H atom is located at the BC site between a heptagon and a pentagon and the other H atom is located inside a heptagon [Fig. 8(a)]. In this geometry, a Si atom is located in between the two H atoms, seemingly like the H_2^* configuration in bulk silicon. When a H_2 molecule is initially located in the center of one Si–Si bond, the H_2 molecule spontaneously dissociates, the Si–Si bond being broken and the two H atoms passivating the created dangling bonds. The relaxed configurations are shown in Figs. 8(b) and 8(d), whose energies are −0.57 and −0.39 eV, respectively. However, an H_2 molecule initially positioned at the center of one heptagon is determined to not dissociate [Fig. 8(c)]. The formation energy is computed to be −0.55 eV.

Finally, we also explored configurations including 2 H atoms in the core of the C_2 screw dislocation. The most stable ones are reported in Fig. 9. When one H atom is located on a Si–Si bond parallel to the dislocation line between a pentagon and a heptagon and the other H is inside a neighbor heptagon, the most stable configuration is obtained with an energy of −0.92 eV. Each H atom forms a bond with a Si atom with lengths of 1.54 and 1.55 Å, respectively. As in the case of Fig. 8(a), in this geometry a Si atom is located in between two H atoms and this can be considered as a kind of H_2^* configuration. This is also true for the configuration shown in Fig. 9(c), where after relaxation, a Si atom is between the two H atoms. When a H_2 molecule is positioned on a Si–Si bond parallel to the dislocation line between a pentagon and a heptagon, it spontaneously dissociates, leading to the formation of two Si–H bonds with lengths 1.53 Å [Fig. 9(b)]. The separation between the H atoms is 2.04 Å. Finally, the lowest energy configuration for which the molecular hydrogen is stable is obtained when the molecule is initially located in the center of a heptagon, the formation energy being −0.39 eV [Fig. 9(d)].

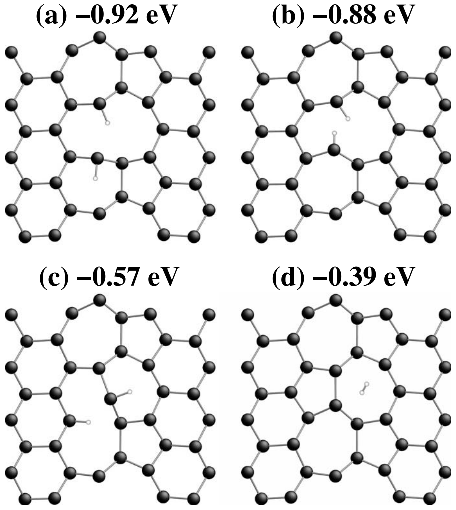

FIG. 9. Low-energy configurations and corresponding formation energies for two H atoms in a C_2 screw dislocation in Si. Same graphic convention as in Fig. 1.

D. Optimal H filling of the dislocation core

Finally we have investigated the modification of core dislocation structures containing an increasing number of hydrogen atoms. The remarks made previously about the difficulty of fully exploring the configuration space obviously hold in this case. Due to the large number of possible structures, we focus on three dislocations cores, the 30°, 90° sp, and 90° dp partial dislocations. We also only considered configurations for which the hydrogen atoms are located in the center of the dislocation core.

Figure 10 represents the lowest energy configurations corresponding to different H fillings in the 30° partial dislocation core. For 4 H atoms in our computational system, the most stable configuration is obtained when each H atom is bonded to a Si atom, the bond length being 1.54∼1.55 Å [Fig. 10(a)]. The relaxed dislocation core now exhibits a single period structure formed by octagons including a H atom inside. This geometry is easily obtained by repeating the most stable configuration for a single H atom in the 30° core [see Fig. 2(a)]. Adding a single H_2 molecule near the core of the previous structure yields the lowest energy configuration in the case of six H atoms [see Fig. 10(b)]. The H_2 molecule is not exactly located in the same plane as the other H atoms, and fills one of the hexagons visible in the $(\bar{1}01)$ projection of the 30° core (upper row of Fig. 1). This configuration has a −2.49 eV formation energy.

The most stable 12 H configuration is very easily obtained by adding three more interstitial H_2 molecules, periodically repeated along the dislocation line, to the configuration (b). The final geometry is shown in Fig. 10(c) for two different projections. One can see that H_2 molecules are located at the largest open space near the dislocation core, and stacked along the dislocation line. Adding four more H_2 molecules in

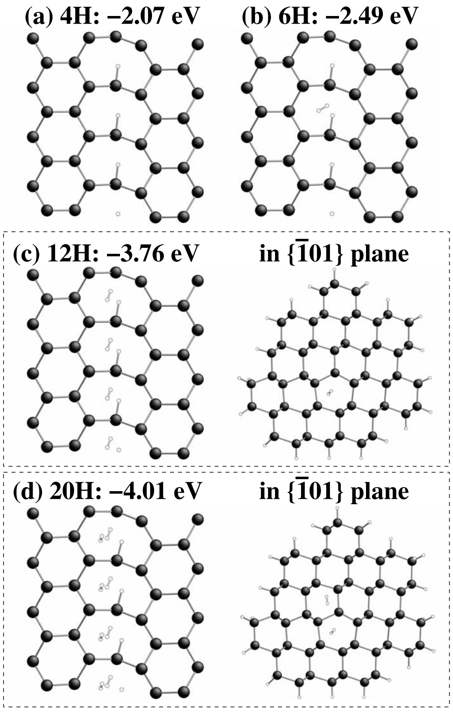

FIG. 10. Low-energy configurations and corresponding formation energies for 4, 6, 12, and 20 H atoms in a 30° partial dislocation in Si. Same graphic convention as in Fig. 1.

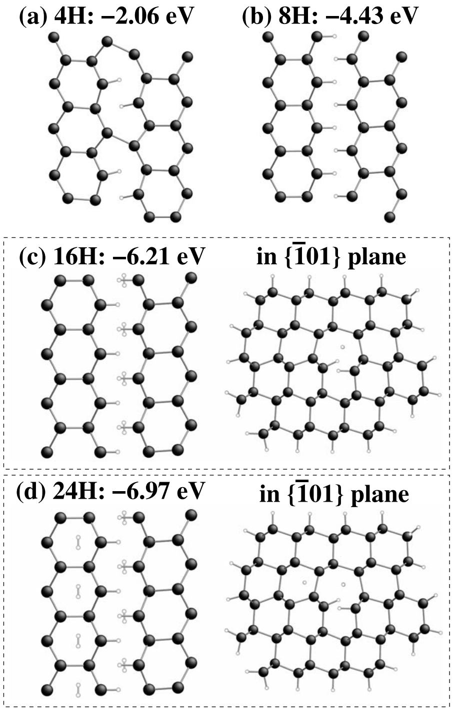

FIG. 11. Low-energy configurations and corresponding formation energies for 4, 8, 16, and 24 atoms in a 90° single periodic partial dislocation in Si. Same graphic convention as in Fig. 1.

another hexagon close to the dislocation line, allows to further decrease the energy to −4.01 eV [Fig. 10(d)]. This last case corresponds to the optimal filling of the dislocation core. In fact, adding more H or H_2 molecule leads to an increase of the energy.

In Fig. 11, representative configurations of the 90° sp partial dislocation containing 4, 8, 16, and 24 H atoms are shown. The configuration depicted in Fig. 11(a) is the most stable one in the 4 H case, with a formation energy of −2.06 eV. The dislocation geometry is characterized by pairs of H atoms, passivating Si core atoms, separated by one remaining Si–Si bond. These hydrogen pairs result from spontaneous dissociation of H_2 molecules at BC sites. The distance between H atoms in each pair is 2.26 Å. Note that this structure can be viewed as the generalization of the configuration shown in the Fig. 7(a) along the dislocation line, with approximately twice the formation energy. Adding more H atoms leads to the breaking and subsequent passivation of the remaining Si–Si bonds in the core, yielding a well ordered relaxed structure, periodically repeated along the dislocation line [Fig. 11(b)]. The formation energy is −4.43 eV. Each hydrogen has a bond with its nearest Si atom with a length of 1.52 Å, perpendicular to the dislocation line. The most stable configuration with 16 H atoms located around dislocation core is shown in Fig. 11(c). The formation energy is −6.21 eV. This geometry is obtained by adding four H_2 molecules in the open space near the dislocation core relatively to the previous configuration. These additional H_2 molecules tend to be oriented along the [$\bar{1}$01] axis, with H–H bond lengths equal to 0.79 Å. Finally, the optimal H filling is reached for a total of 24 H in the vicinity of the dislocation core [Fig. 11(d)], the formation energy being −6.97 eV. This configuration is obtained by adding 4 additional H_2 molecules in another available space near the dislocation core to the previous configuration. Newly added H_2 molecules are again oriented along the [$\bar{1}$01] axis, with H–H bond lengths equal to 0.79 Å. For the 90° sp partial dislocation, we did not find a configuration including more H atoms and further decreasing the formation energy at the same time.

Finally, we have determined the optimal H filling in the case of the 90° dp partial dislocation. Figure 12(a) represents the most stable configuration when 4 H atoms are present near the dislocation line. This geometry is a generalization by periodic repetition of the most stable configuration for 2 H in the core [see Fig. 8(a)]. The formation energy of −1.67 eV is about twice the one of the 2 H structure. The lowest energy configuration with 8 H is shown in Fig. 12(b). Here, the relaxation lead to the breaking of Si–Si bonds and the spontaneous dissociation of H_2 molecules, followed by the passivation of those bonds by pairs of H atoms. The structure shown in Fig. 12(c) is the most stable configuration when 16 H atoms are included near the dislocation line. This is obtained by adding 4 H_2 molecules to the previous 8 H configuration, in available open spaces. These added H_2 molecules are stable and tend to be slightly misoriented with respect to the dislocation line. We determined the optimal H filling to be reached when 24 H atoms are present in the system [Fig. 12(d)]. Starting from the previous configuration, the final structure is obtained by adding 4 more H_2 molecules in another available open space in the vicinity of the dislocation core. This structure appears to be the optimal one, since extra H atoms do not allow to lower the formation energy.

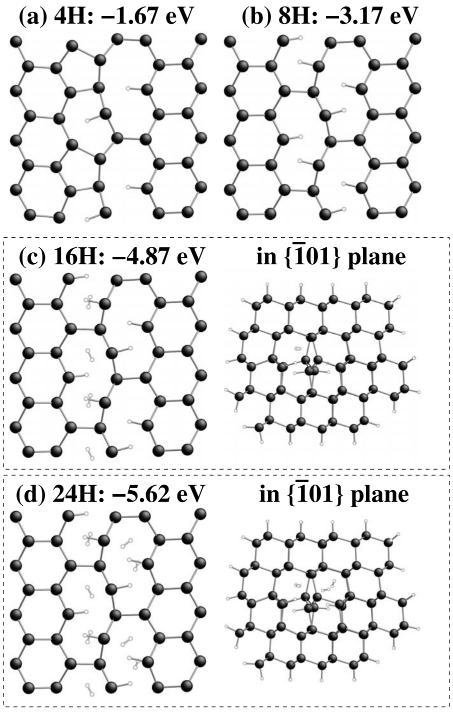

FIG. 12. Low-energy configurations and corresponding formation energies for 4, 8, 16, and 24 H atoms in a 90° double periodic partial dislocation in Si. Same graphic convention as in Fig. 1.

IV. DISCUSSION

We have computed a large number of stable configurations for different dislocation cores interacting with a variable number of hydrogen atoms (Table I). It would be now useful to extract general behaviors from all this information, whenever possible. First, we focused on the local environments of H atoms in the dislocations cores. In all cases, we found that only two different structures are obtained after relaxation. In the first one, the H atom interacts with two Si atoms, initially bonded together. This structure is similar to the BC configuration, which is the most stable for neutral H in silicon bulk. In dislocation cores, Si–Si bonds are stretched and distorted compared to the bulk, which allows an easier accommodation of H between the two Si atoms. In fact, for all configurations, we found that the formation energy is lower than the one corresponding to one H atom relaxed in a BC site in bulk silicon (1.07 eV). Si–Si bonds distortion in dislocation cores also explains why the H atom is usually slightly displaced from the ideal location. The second possible geometry for a single H atom in the dislocation core corresponds to the formation of single Si–H bond. This H-passivation mechanism is not favored in bulk silicon, but has been shown to occur in the vicinity of point defects.[14] Here, we found that it can require the breaking of a Si–Si bond [see Fig. 4(a)], thus leaving one undercoordinated Si atom, but not always [see Fig. 5(b) for instance]. Obviously, the already mentioned bonds distortions in dislocation cores are largely responsible for the large energy gain associated with this configuration. However, we found that when H is initially positioned in a large available volume in the dislocation core, it is never stable. This is in striking contrast with the metastability observed when H is located in a low-electronic density region such as the tetrahedral site in bulk silicon. We found that the H-passivation mechanism and the H adsorption in a BC-like site are often close in energy. The former is favored in 30° and 90° partial dislocations, whether the latter is more stable in screw with C_2 and A cores.[33] However, the differences in energy are not significant enough to draw general conclusions.

TABLE I. Energies of the most stable configurations for each core structure with given number of H atoms in units of eV.

Number of H	30°	90° sp	90° dp	Screw C_2
1	0.27	0.18	0.38	0.14
2	−1.13	−1.01	−0.78	−0.92
4	−2.07	−2.06	−1.67	
6	−2.49			
8		−4.43	−3.17	
12	−3.76			
16		−6.21	−4.87	
20	−4.01			
24		−6.97	−5.62	

In the case of H_2, three different configurations have been identified. In the most simple one, the H_2 molecule is conserved [see Fig. 6(b)], and tends to remain in the middle of open spaces available in dislocation cores. This situation is equivalent to H_2 in bulk silicon, for which the most stable configuration corresponds to the tetrahedral site, a location with a low electronic density. A second stable geometry is obtained when a Si atom is passivated by one H, and also interact with the other H [see for instance Fig. 9(a)]. Although the relaxed geometries are not fully symmetric due to bond distortion in dislocation cores, it seems to be equivalent to the H_2^* configuration, which is known to be metastable for H_2 in bulk silicon.[1,11] Finally, the third possible structure results from a H-passivation mechanism. A Si–Si bond is broken, and the two H passivate the silicon atoms. Again, this mechanism does not occur in bulk silicon, but is favored here due to the large amount of stress stored in reconstructed dislocation cores. After relaxation, the two H atoms are separated by at least 2 Å. In most of the cases where an H_2 molecule is initially located close to a Si–Si bond, this H passivation is observed in association with a spontaneous dissociation of the molecule. We determined that all three final identified configurations are possible in the investigated dislocation cores, with negative formation energies. However the H_2 molecule is never the most stable state for two H atoms into a dislocation core in silicon, and either a H_2^*-like configuration or the H-passivation mechanism are favored.

We have also determined the optimal hydrogen numbers that can be accommodated in the case of partial dislocation cores. This optimal filling is defined as the hydrogen quantity for which the formation energy is decreasing. Also, in the following, we introduced normalized values for the number of H atoms and the formation energy. Since our system encompasses 4 elementary layers of width $|\boldsymbol{b}|=|(a_0/2)[\bar{1}01]|$

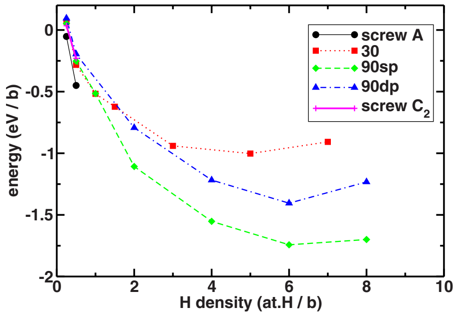

FIG. 13. (Color online) Variation of the normalized formation energy as a function of the H density for all dislocation cores.

along the dislocation line, the normalized hydrogen number, i.e., the H density (in H atoms/$|\boldsymbol{b}|$ or at. H/$|\boldsymbol{b}|$), and the formation energy (in eV/$|\boldsymbol{b}|$) are easily obtained as one fourth of the original quantities. For all three dislocation cores, a similar process is found when the number of H atoms increases. The first H atoms form bonds with silicon atoms, after the breaking of Si–Si bonds in the dislocation core. These bonds are usually largely stretched and distorted, and their rupture results in a large release of stored elastic energy. At a given H quantity, the dislocation core is appears to be saturated, and it becomes energetically too expensive to break further Si–Si bonds. This situation happens for a H density of 1 at. H/$|\boldsymbol{b}|$ for the 30° partial, 2 at. H/$|\boldsymbol{b}|$ for the two possible cores of the 90° partial. At this point, the structure of the cores is completely modified by the presence of the H atoms. In the case of the 30° partial, the double periodicity is removed, whereas it is retained in the case of the 90° dp core. Next, extra H atoms are best accommodated in the form of H_2 molecule which tends to be located in the available open spaces in the vicinity of the dislocation core center. Optimal H densities as high as 5 at. H/$|\boldsymbol{b}|$ for the 30° partial, and 6 at. H/$|\boldsymbol{b}|$ for the two possible cores of the 90° partial, are obtained. It has been suggested that dislocations act primarily as recombination centers for atomic hydrogen.[30] Our calculations suggest that this is indeed the case as soon as the dislocation core is saturated with Si–H bonds. However, before this state is reached, the dislocation act as a dissociation center for H_2 molecules.

Figure 13 shows the variation of the normalized formation energy as a function of the H density for all dislocation cores. The graph also includes data for the A core of the screw dislocation, which was investigated in a previous work.[33] Focusing on low-density values, i.e., one or two H atoms in the dislocation core, formation energies seem to be in a narrow range of values. The only exception is the screw A core for which the formation energy is about 0.1–0.2 eV/$|\boldsymbol{b}|$ lower. A possible explanation is based on the structure of the dislocation core, and will be proposed in the following. For high H density, marked differences appear although the optimal H density is approximately the same for all partial dislocation cores. The best energy gain is obtained for the sp core of the 90° partial, followed by the dp core, and the 30° partial dislocation. It is difficult to give a definite explanation for these results. Nevertheless, a simple examination of the different H-passivated dislocation core structures suggests that in the case of the 90° sp core, the hydrogen atoms has helped to remove all bonds distortion, thus minimizing the core strain energy to a large extent. Interestingly, this H-passivated 90° sp dislocation core has already been used for investigating the formation of H-induced platelets in association with dislocation dipole.[44,45]

There have been many theoretical studies trying to determine which of the sp or dp reconstructed 90° core was the most stable one.[16,34–37] Most of the first-principles calculations indicate that the dp core is slightly more stable than the sp core, a well reproduced feature in our calculations (the dp core being 0.121 eV/$|\boldsymbol{b}|$ lower in energy). The energy difference is small and at finite temperature and in a real material containing defects, it is likely that both kind of cores could co-exist. It is therefore interesting to investigate whether the energy balance could be modified due to the presence of hydrogen. The formation energy variation shown in Fig. 13 suggests that the energy lowering is larger for the sp core than the dp core. For a H density of 1 at. H/$|\boldsymbol{b}|$, the energy difference between both cores drops to 0.023 eV/$|\boldsymbol{b}|$, still in favor of the dp reconstruction.[46] However, when the H density is increased up to 2 at. H/$|\boldsymbol{b}|$, the sp core becomes energetically favored, with an energy difference of 0.194 eV/$|\boldsymbol{b}|$. Finally, for the highest density, the energy difference increases up to 0.216 eV/$|\boldsymbol{b}|$. This result suggests that in presence of hydrogen, the sp reconstructed core should be favored over the dp core. Another case to be examined concerns the screw dislocation, for which two stable core structures A and C_2 have been proposed.[17,19,21] The C_2 core is more stable, the energy difference being rather large [0.54 eV/$|\boldsymbol{b}|$ (Ref. 19)]. Our previous calculations showed that very low formation energy (−1.80 eV, i.e., −0.45 eV/$|\boldsymbol{b}|$) is obtained when two H atoms are relaxed in the screw A core.[33] This value has to be compared with the lowest formation energy of −0.92 eV (−0.23 eV/$|\boldsymbol{b}|$) obtained for two H in the screw C_2 core, which would suggest that the presence of H could eventually modify the stability ordering for higher H density. But a careful examination of the configuration obtained for two H in the A core [compare Fig. 3(b) of Ref. 33 with Fig. 9(a) of the present paper] reveals that the inserted hydrogen atoms induce a modification of the structure of the A core, which is partially transformed in a C_2 structure. Therefore, our calculations point out that a core transformation can occur because of the presence of hydrogen. This is especially interesting in the case of the core transformation $A \rightarrow C_2$ since it has been recently shown to be associated with a very large activation energy barrier.[47]

Finally, we are discussing the mobility of hydrogen along the dislocation core. It is usually expected that diffusion in dislocation core is enhanced, a phenomenon which has been experimentally evidenced.[48] Investigating the mobility of hydrogen along the various dislocation cores in silicon, either by molecular dynamics or by using transition state determination methods would be highly appealing, but nonetheless beyond the scope of the present paper. However, one could use the large number of investigated configurations in order to get some information. The most simple case is the 90° partial dislocation with the sp core. It is conceivable that the diffusion of H along the dislocation would proceed along the first three low energy configurations shown in Fig. 3. The H diffusion path is here very straight and simple, and does not imply significant modifications of the silicon structure. We have performed simple calculations in which the hydrogen atom is constrained along the path from Fig. 3(b) to Fig. 3(c), Fig. 3(a) being an intermediate step. From these simulations, we determined an activation energy for H diffusion along the 90° dislocation line equal to 0.1 eV. This is lower than in the bulk.[1] It is likely that H will diffuse very easily along the dislocation until it encounters defects such as an antiphase defect[30] or kinks. For the other dislocation cores, it is much more difficult to draw conclusions. The reconstructed nature of the dislocation cores leads to various possible H configurations, usually with a significant local modification of the dislocation core structure, such as Si–Si bond breaking for instance. It is therefore difficult to compute simulation paths with simple constrained methods, or to explore all the possible diffusion paths.

V. CONCLUSION

The effect of the presence of a variable number of hydrogen atoms in dislocation cores in silicon was investigated using first principles calculations. We considered the 90° partial dislocation, both with sp and dp reconstructed cores, the 30° partial dislocation, and the nondissociated screw dislocation. We especially focused on the case of one and two H atoms in dislocation cores, inserted as monatomic or molecular hydrogen. Then a systematic search for the optimal H filling, corresponding to a still decreasing formation energy, was performed. In all cases, several low-energy configurations were determined.

In the case of a single H atom, it is found that H is more stable in dislocation cores than in the bulk. H can be located in a bond-centered-like site, or forms a Si–H bond in the dislocation, after a possible breaking of a Si–Si bond. In case of two H atoms, we found that the molecular form H_2 can be stable, but is never the most stable state. If initially located in a bond-centered site, H_2 usually spontaneously dissociates, leading to the formation of a configuration similar to H_2^* in bulk, or to the separation and passivation by H of two initially bonded Si atoms. Considering an increasing number of H atoms inserted into partial dislocation cores, the following scenario is always observed. The first H atoms induces the breaking of the largely strained Si–Si bonds into the core, and passivates the created dangling bonds. As soon as the core is fully passivated, the insertion of stable H_2 becomes favorable. We determined a maximum H density of 6 at. $H/|\boldsymbol{b}|$. The largest gain in energy is obtained for a 90° sp partial dislocation.

Our calculations also suggest that the presence of few hydrogens could have a non-negligible influence on dislocation core structures. Adding hydrogen atoms in the 90° partial dislocation core change the stability ordering of the two possible reconstructions, the sp core becoming more stable than the dp core. Also, in the case of the screw dislocation, adding hydrogen atoms is enough to initiate the transformation from the shuffle A core into the glide C_2 core. We have also determined the mobility of H along the dislocation line in the case of the 90° sp partial. We estimate the activation energy barrier to be equal or lower than 0.1 eV, which suggests that H diffusion would be easier in dislocation cores than in the bulk. Note however that a generalization of this result requires devoted investigations.

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