

Structural Transformation in the Formation of H-Induced (111) Platelets in Si

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On the basis of first-principles calculations, we present a structural model for the formation of H-induced (111) platelets in Si, which involves a structural transformation from a double-layer- H_2^* configuration of H_2^* aggregates into an H-saturated internal (111) surface structure. This reaction process preferably occurs at high H plasma treatment temperatures and subsequently generates H_2 molecules in the platelet voids, consistent with experiments. Our model also reveals the important features observed in (111) platelets, such as high-resolution transmission electron microscopy images, step structures, lattice dilation lengths, and H vibrational frequencies.

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Hydrogen in Si has been studied extensively because of its scientific and technological importance. The major role of hydrogen is the passivation of both shallow and deep impurities or other defects through the formation of complexes [1]. In high concentrations, hydrogen, incorporated either by H-plasma treatment or H-ion implantation, is known to create extended planar defects, called platelets, along the crystalline planes of (100) and (111) [2,3]. Based on experimental results, it has been established that the platelets consist of Si-H bonds. In H-plasma treated samples, the (111) platelets have been observed predominantly, while the (100) platelets are superior to the (111) in ion-implanted samples [2,4]. In H-ion implanted Si(100) wafers, the (100) direction parallel to the wafer axis is most preferential for the platelets [5]. The high density of H_2 molecules in the voids created by platelets results in high internal pressure along the wafer direction. This building up of internal pressure ultimately leads to cracking. This is known as the Smart-Cut™ process, especially used in silicon-on-insulator device fabrication [6].

The (111) platelets have been mostly studied experimentally and theoretically, and several models have been suggested. One of the suggested models is the H-saturated internal (111) surface structure $([2Si-H]_n)$, i.e., the configuration that each Si-Si bond on an (111) plane is replaced by two Si-H bonds with the H atoms positioned at the bond-center sites [7,8]. Theoretically, it was shown that the $[2Si-H]_n$ structure is unstable against the formation of hydrogen molecules at tetrahedral (T_d) sites [7,9], while high-resolution transmission electron microscopy (HRTEM) images [8] suggested an atomic structure where H atoms saturate the broken bonds between adjacent (111) planes. Zhang and Jackson studied various models for the (111) platelets based on H_2^* complexes [10]: single-layer- H_2^* ($[H_2^*]_n^S$), staggered- $[H_2^*]_n^S$, and double-layer- H_2^* ($[H_2^*]_n^D$) structures [11]. They found that the $[H_2^*]_n^D$ structure is lowest in energy, and its stability increases as the number of H_2^* 's increases, and thus they suggested the $[H_2^*]_n^D$ structure for the (111) platelets. Based on recent experiments on the dependence of platelet concentration on the position of the Fermi level [12], it

has been proposed that H_2^* aggregates, which are easily formed in *n*-type samples, are involved in the formation of the microstructure seen in the (111) platelets. However, there have been no direct experiments so far confirming the existence of the $[H_2^*]_n^D$ structure. Reboredo and his co-workers suggested large planar VH_4 aggregates, called V platelets [13]; for the (111) platelets, an (111) monolayer of Si vacancies is decorated by H atoms ($[VH_4]_n$). They also proposed an H-saturated (111) double vacancy layer ($[V_2H_2]_n$). In H-ion implanted samples [4], sharp vibrational lines observed at 1930, 2025, 2161, 2182, and 2208 cm^{-1} indicated the existence of vacancies. However, vacancies are unlikely to be involved in the formation of the (111) platelets, because the (111) platelets have been observed in H-plasma treated samples, in which vacancy concentrations are very low; vibrational frequencies lie in a wide range of 2050–2150 cm^{-1} [2,14,15].

In this Letter, we propose a structural model for the formation of (111) platelets based on first-principles calculations. The $[H_2^*]_n^D$ structure, which is the most stable configuration of H_2^* aggregates in the perfect Si lattice, is more stabilized due to strain release, as the lattice is dilated. For further lattice dilations, this configuration eventually turns into the $[2Si-H]_n$ structure with the upper bound of 1.8 eV for the activation energy, accompanied with the formation of H_2 molecules in the interstitial region of platelets. The formation model reveals the important features of (111) platelets, such as HRTEM images, step structures, dilation lengths, H vibrational frequencies, and the formation of H_2 molecules in platelet voids.

Our calculations are based on the first-principles pseudopotential method within the local-density-functional approximation [16]. Norm-conserving nonlocal pseudopotentials are generated by the scheme of Troullier and Martins [17] and then transformed into a separable form of Kleinman and Bylander [18]. The Ceperley-Alder expression for the exchange-correlation potential is used [19]. The wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff of 25 Ry, which ensures the total energy convergence for H in Si. Testing a higher kinetic energy cutoff of 64 Ry and the generalized-gradient

approximation (GGA) for the exchange-correlation potential, we find the energetics of various platelet structures to remain unchanged. We employ an orthorhombic supercell containing 72 host atoms which has six Si layers along the [111] direction.

The formation energies for various platelet structures are calculated as a function of lattice dilation along the [111] direction. The energy of an H_2 molecule at a T_d site in Si is chosen for the reference energy. With zero dilation, the $[H_2^*]_n^D$ structure [see Fig. 1(a)] is found to be the lowest energy configuration among the three H_2^* aggregates considered, as shown in Fig. 2. The energies for the $[H_2^*]_n^S$, staggered- $[H_2^*]_n^S$, and $[H_2^*]_n^D$ structures are in general agreement with previous calculations [11]. The $[H_2^*]_n^D$ structure is lower in energy by 0.3 eV per H pair, as compared to the staggered- $[H_2^*]_n^S$, and this structure is even more stable by 0.1 eV per H pair than an interstitial molecular hydrogen. The stability of the $[H_2^*]_n^D$ structure was in fact shown to be enhanced as the number of H_2^* aggregates increases [11]. We also examine the $[VH_4]_n$ and $[V_2H_2]_n$ structures with H decorated vacancy layers and find their energies to be nearly independent of dilation length (see Fig. 2), similar to previous calculations [13]. At zero dilation, the $[V_2H_2]_n$ structure is more stable by about 0.4 eV than the $[H_2^*]_n^D$ structure, while this structure is energetically unfavorable as the dilation length increases. Moreover, the formation of the vacancy-related platelets was shown to have very high activation energies of 2.5–5 eV per H pair [13]. Since the energy barriers for H_2 and H_2^* migrations in Si lattice are about 1 eV [10], the $[H_2^*]_n^D$ structure is considered to be more favorable at the initial stage of platelet formation.

On the other hand, without lattice dilation, the H-terminated internal (111) surface structure is very unstable, because there is not enough space to accommodate H atoms in forming Si-H bonds. This $[2Si-H]_n$ structure can be stabilized by dilating the lattice along the [111] direction, as shown in Fig. 2. In the equilibrium geometry at a dilation of about 2.3 Å, the separation of the two

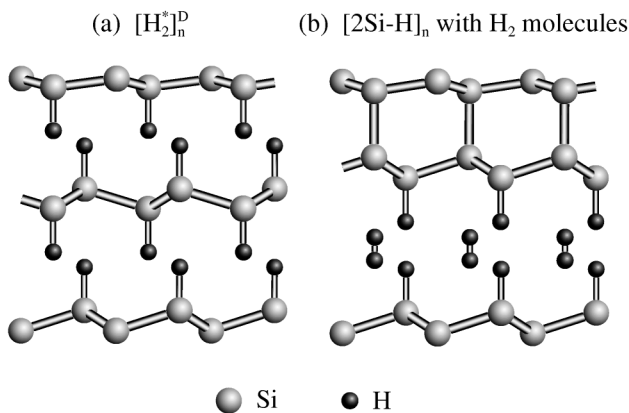


FIG. 1. The atomic geometries of the (a) $[H_2^*]_n^D$ and (b) $[2Si-H]_n$ (with H_2 molecules) structures are shown.

hydrogenated internal planes is 1.9 Å. Thus, repulsive interactions between the two H planes are almost removed, and the $[2Si-H]_n$ structure has the minimum energy quite close to that of the $[H_2^*]_n^D$ structure at about 2.3 Å, similar to previous theoretical calculations [11]. Nevertheless, the $[2Si-H]_n$ structure is still unstable with respect to the $[H_2^*]_n^D$ structure for dilation lengths above 2.7 Å. We investigate the other $[2Si-H]_n$ structure with H_2 molecules inserted in the interstitial region of the platelet structure, which is shown in Fig. 1(b). This configuration is generally lower in energy, as compared to the $[2Si-H]_n$ structure without H_2 molecules. For lattice dilations above 1.7 Å, the $[2Si-H]_n$ structure with H_2 molecules is found to be the lowest energy configuration; thus, a structural transformation is expected to occur as the lattice is expanded.

On the basis of our calculational results, we suggest a structural model for the formation of (111) platelets. At the early stage of the platelet formation, where no lattice dilation exists, the $[H_2^*]_n^D$ structure is more preferably formed, compared with the $[2Si-H]_n$ structure either with or

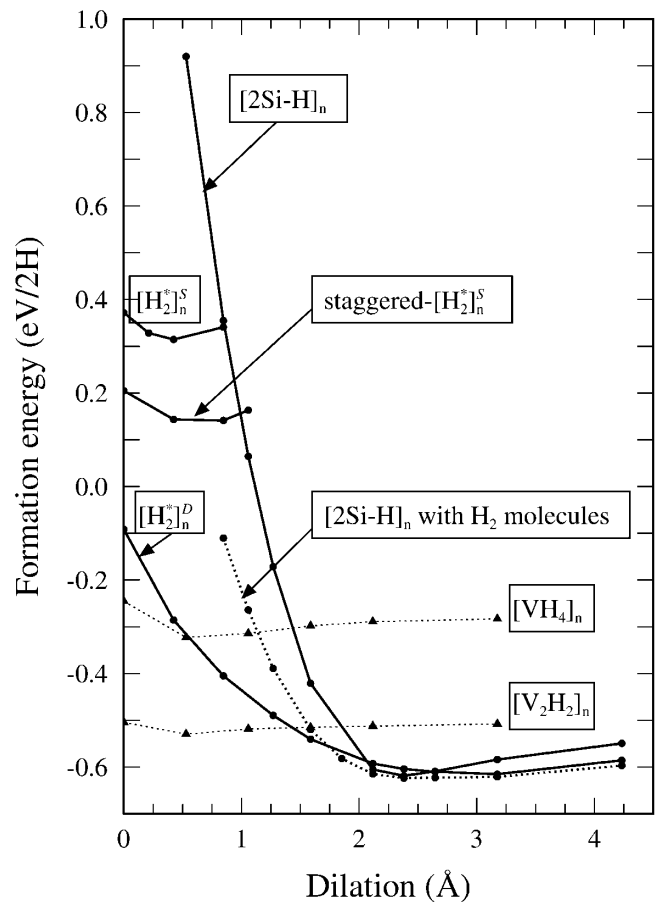


FIG. 2. The formation energies of various structures for H-induced (111) platelets are plotted as a function of lattice dilation, which is defined as the dilation length from the perfect Si lattice along the [111] direction. The chemical potential of bulk Si is used for the Si chemical potential.

without H_2 molecules. As the $[H_2^*]_n^D$ structure grows laterally after the nucleation, the dilation is expected to be increased, because the repulsion between the inner surfaces of the $[H_2^*]_n^D$ is enhanced, and the edge effect acting against the lattice expansion is relatively reduced. With increasing of the dilation, the $[2Si-H]_n$ structure with H_2 molecules becomes energetically favorable against the $[H_2^*]_n^D$ structure. Here we point out that the $[H_2^*]_n^D$ structure has the same number of hydrogen atoms as the $[2Si-H]_n$ structure having one H_2 molecule per two Si-H bonds.

Next we calculate the activation energy for the transformation of the $[H_2^*]_n^D$ structure into the $[2Si-H]_n$ structure with H_2 molecules. Among various reaction paths considered, the lowest energy path is shown in Fig. 3. In each step, one or two atoms are shifted, while the other atoms are fully relaxed. In the initial $[H_2^*]_n^D$ configuration, a Si-H bond in the central layer, which is labeled as Si_{II} - H_{II} in Fig. 3(a), approaches to the bond-centered H atom (H_I) of

the H_2^* unit. In this process, the H_I atom is shifted toward the Si_{III} atom, so that new Si_{III} - H_I and Si_I - Si_{III} bonds are formed, as shown in Fig. 3(b). This transition state has an energy of 1.8 eV above the initial $[H_2^*]_n^D$ configuration, and without any energy barrier it easily transforms into an intermediate metastable structure [see Fig. 3(c)], whose energy lies only 0.74 eV above that of the initial configuration. In the metastable configuration, the two H atoms denoted by H_I and H_{II} are positioned between the Si_{II} and Si_{III} atoms, and the formation of the Si_I - Si_{III} bond represents the recrystallization of one of the two broken (111) layers in the $[H_2^*]_n^D$ structure. Because the $[2Si-H]_n$ has only a single broken layer, such a recrystallization should be involved in the structural transformation. Because of the strain remaining in the Si backbonds, further relaxations take place, recovering the Si_{II} - Si_{III} bond. Then, released H_I and H_{II} atoms form an H_2 molecule in the interstitial region, as shown in Figs. 3(d) and 3(e). In this relaxation process, an energy barrier of 1.02 eV is found. In a similar way, recrystallization will occur for neighboring H_2^* complexes, which produces interstitial H_2 molecules. From the configuration with one H_2 molecule [see Fig. 3(e)], it costs an energy of about 1.0 eV to recover two additional Si-Si bonds and thus to form two more H_2 molecules. However, by changing the positions of three H atoms at the antibonding sites between the three new Si-Si bonds to the bond-center sites, we can reduce the energy by about 1 eV, recovering the energy in Fig. 3(e). Repeating such a recrystallization process, we can obtain the final $[2Si-H]_n$ configuration containing H_2 molecules [see Fig. 1(b)], with an energy gain of 0.54 eV from the initial configuration.

Since the reaction path considered here is somewhat specific, our calculations reveal only the upper bound of the energy barrier. In our calculations, the dilation length is fixed at 2.1 Å. Since the dilation length in the real reaction process will be relaxed to follow the lowest energy path, the actual activation energy will be lower. Moreover, when H_2 molecules are accumulated in one void region of the $[H_2^*]_n^D$ geometry, the central layer can be shifted toward the other void region; then, the activation energy can decrease again.

Recent HRTEM measurements for (111) platelets exhibited the structure of atomic ledges on the (111) plane with broken bonds [8]. The atomic ledges were found to be in a single layer and symmetric for both the sides of platelets. This image is consistent with the $[2Si-H]_n$ structure with H_2 molecules. In our model, one of the two broken layers in the $[H_2^*]_n^D$ geometry is recrystallized during the formation of the $[2Si-H]_n$ structure. If the recrystallization occurs in different broken layers in different regions, a step structure will be naturally formed. This step structure in (111) platelets was in fact observed by HRTEM experiments [8]. We can estimate the pressure built up in platelets from the derivative of the total energy with respect to dilation length. For the $[2Si-H]_n$ structure with

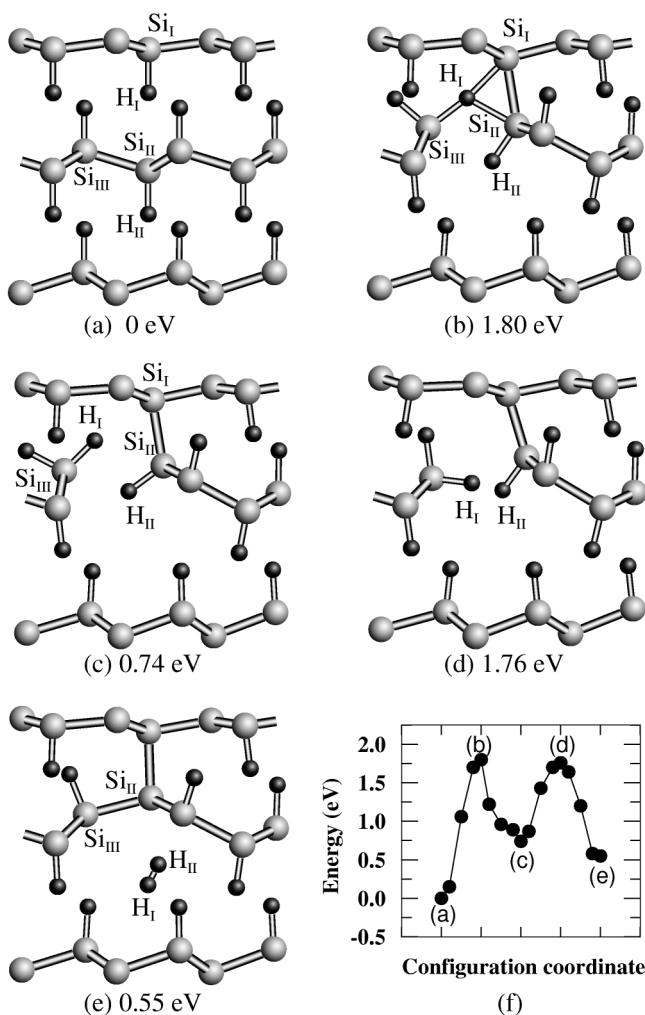


FIG. 3. (a)–(e) The recrystallization process for the formation of one Si-Si bond and an H_2 molecule in the interstitial region. Energies are given relative to the $[H_2^*]_n^D$ configuration in (a), and the energy variation during the reaction is drawn in (f).

H₂ molecules, we find a pressure of 1 GPa when the dilation is 2.2 Å. Electron microscopy studies combined with continuum elasticity theory showed that applied stress is 1.05 GPa for dilation lengths of 3 ± 1 Å [8]. If the density of H₂ molecules in the platelet void is higher than that considered in our calculations, the dilation length increases. In HRTEM measurements [2,8], the dilation length was shown to be smaller than 1 Å. This small dilation length may be due to the extraction of H₂ molecules from the void and other possible edge closing effects, when samples are cut for measurements.

We calculate the H vibrational frequencies for the [2Si-H]_n structure with H₂ molecules using the GGA for the exchange-correlation potential and the kinetic energy cutoff of 64 Ry, which give accurate vibrational frequencies for Si-H and H-H bonds [20]. Here only the H atoms are allowed to move, while the other host atoms are fixed. Previous calculations showed that the errors caused by this approach are within a few percent, compared with the dynamical matrix method [20]. For the dilation lengths of 1.59 and 3.18 Å, we estimate the vibrational frequencies of the Si-H bonds to be 2076 and 2095 cm⁻¹, respectively, while 4132 and 4243 cm⁻¹ for the H₂ molecules. The results for the Si-H bonds are consistent with experimentally measured values of 2050–2150 cm⁻¹, which are the characteristic frequencies of H-induced (111) platelets in Si. The calculated frequencies for the H₂ molecules are also in good agreement with the observed value of 4158 cm⁻¹ [21], which is recently assigned to the H₂ molecules trapped in the voids created by platelets [22]. From infrared and Raman studies, Heyman *et al.* found 2065 (I), 2075 (IIa), 2095 (IIb), and 2125 cm⁻¹ (III) lines [14]. Their annealing studies further showed that the predominant line changes from line I to line II with increasing of temperature, indicating the existence of a structural transformation. Although our calculations cannot resolve such small differences in frequencies, the frequencies of the Si-H bonds for the dilations of 1.59 and 3.18 Å are found to lie in the range of 2056–2100 cm⁻¹ in the [H₂]_n^D structure and 2076–2095 cm⁻¹ in the [2Si-H]_n structure with H₂ molecules, close to the measured values. The trigonal and inversion symmetries of the [2Si-H]_n structure are also consistent with polarized Raman measurements [14].

Our model further explains the net conversion of H atoms from Si-H bonds into H₂ molecules in the platelet voids, which can be measured by infrared absorption spectroscopy and forward recoil scattering experiments [4]; the former gives the concentration of Si-H bonds, while the total amount of H in a sample is obtained from the latter. In ion-implanted samples, although there is a possible conversion from vacancy- and interstitial-H complexes to H₂ molecules, the structural transformation from [H₂]_n^D to [2Si-H]_n should also be involved for (111) platelets. On the other hand, in H-plasma treated samples, the relative

formation profiles of Si-H bonds and H₂ aggregates depend on plasma treatment temperature; at low temperatures around 150 °C, the formation of Si-H bonds is dominant, while H₂ molecules are preferentially formed in the range of 200–300 °C [15]. In support of this interpretation, we suggest that (111) platelets favor the [H₂]_n^D structure at low temperatures; then, increasing plasma treatment temperature induces lattice dilation and subsequently H₂ molecules are generated by the formation of the [2Si-H]_n structure.

In conclusion, we have presented a structural model for the formation of H-induced (111) platelets in Si; the aggregation of H₂^{*} complexes induces the [H₂]_n^D structure as a precursor, and it is structurally transformed into the [2Si-H]_n structure with generating H₂ molecules in the voids. This model reveals all the features of the (111) platelets, such as HRTEM images, step structures, dilation lengths, H vibrational frequencies, and the formation of H₂ molecules in platelet voids.

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- [1] *Hydrogen in Semiconductors*, edited by J.I. Pankove and N.M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic, New York, 1991).
 - [2] N.M. Johnson *et al.*, Phys. Rev. B **35**, 4166 (1987).
 - [3] G.F. Cerofolini *et al.*, Phys. Rev. B **46**, 2061 (1992).
 - [4] M.K. Weldon *et al.*, J. Vac. Sci. Technol. B **15**, 1065 (1997).
 - [5] S. Romani and J.H. Evans, Nucl. Instrum. Methods Phys. Res., Sect. B **44**, 313 (1990).
 - [6] M. Bruel, Electron. Lett. **31**, 1201 (1995).
 - [7] P. Deak *et al.*, Physica (Amsterdam) **170B**, 223 (1991).
 - [8] S. Muto *et al.*, Philos. Mag. A **72**, 1057 (1995).
 - [9] C.G. Van de Walle *et al.*, Phys. Rev. B **39**, 10791 (1989).
 - [10] K.J. Chang and D.J. Chadi, Phys. Rev. Lett. **62**, 937 (1989).
 - [11] S.B. Zhang and W.B. Jackson, Phys. Rev. B **43**, 12 142 (1991).
 - [12] N.H. Nickel *et al.*, Physica (Amsterdam) **273B–274B**, 212 (1999).
 - [13] F.A. Reboredo *et al.*, Phys. Rev. Lett. **82**, 4870 (1999).
 - [14] J.N. Heyman *et al.*, Phys. Rev. B **45**, 13 363 (1992).
 - [15] A.W.R. Leitch *et al.*, Phys. Rev. Lett. **81**, 421 (1998).
 - [16] M.L. Cohen, Phys. Scr. **T1**, 5 (1982).
 - [17] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
 - [18] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
 - [19] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
 - [20] Y.-S. Kim *et al.*, Semicond. Sci. Technol. **14**, 1042 (1999).
 - [21] K. Murakami *et al.*, Phys. Rev. Lett. **77**, 3161 (1996).
 - [22] A.W.R. Leitch *et al.*, Solid State Commun. **105**, 215 (1998).