

# Hydrogen above Saturation at Silicon Vacancies: H-Pair Reservoirs and Metastability Sites

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We propose that hydrogen-passivated multivacancies which appear to be fully saturated with H can actually capture additional H in electrically inactive sites. In silicon, first-principles total energy calculations show that splitting an ( $m \geq 2$ ) multivacancy into a mono- and an ( $m - 1$ ) vacancy provides a low-strain pairing site for H, 0.4 eV per H lower than any known bulk pairing site. This monovacancy ejection mechanism is an excellent candidate for the H reservoir found both in crystalline and amorphous Si. A distinct H pairing on the fully saturated  $m$  vacancies, by forming an internal surface Si-Si dimer, provides the final state of light-induced metastable degradation of hydrogenated amorphous silicon.

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Hydrogen is an important accidental impurity and intentional additive in all forms of silicon [1]. H can reduce electrical activity of point and extended defects, including grain boundaries and threefold-coordinated Si dangling bond (DB) defects. H can enhance the diffusivity of impurities such as oxygen and split crystalline Si ( $c$ -Si) by forming platelets. In hydrogenated amorphous Si ( $a$ -Si:H), H mediates defect and dopant thermal equilibration and is believed responsible for the deleterious metastable degradation caused by illumination [2]. The effectiveness of many of these processes depends critically upon sites where H can be trapped and released without creating DBs or other gap-state defects. Though paired H configurations are obvious candidates, the microscopic identities of these electrically inactive H sites are the subject of intense debate, despite many years of study.

In  $a$ -Si:H, Zafar and Schiff [3] proposed that only a reservoir of electrically inactive paired H can explain the phenomenology of both DB equilibration above 200 °C and the growth of DB density during H evolution. Their model comprises a 1.9-eV-deep isolated Si-H bond and a shallower paired H configuration, 1.6 eV per H below the transport level for mobile H [4]. This paired state equilibrates with the isolated Si-H sites and the DBs. Branz [5] postulated a metastable paired H configuration about 1 eV deep that explains the phenomenology of light-induced metastability in  $a$ -Si:H. Distinct equilibration and metastability pairing sites are implied by these phenomenological models, but no convincing microscopic models were proposed.

In  $c$ -Si, H passivation experiments depend upon a reservoir of electrically inactive H. Plasma hydrogenation or H implantation produces H densities [6] as high as  $10^{20} \text{ cm}^{-3}$  in a surface layer 10–100 nm deep [6,7]. Further annealing drives the H into the sample bulk during H passivation treatments. Thermal stability studies of mesa-etched Si diodes with plasma-H passivated surfaces [8], and Mössbauer spectroscopic studies of Sb-H complexes [9] in H-implanted  $c$ -Si, also indicate an active H reservoir. Remarkably, H diffuses from the surface reservoir without leaving a deleterious density of electronic defects.

The energetics of various H configurations has been studied extensively [10]. In  $c$ -Si, individual H and odd-numbered clusters of H are generally higher in energy because they create gap states, usually by the formation of DB-like defects. Paired H configurations such as  $\text{H}_2$  molecules and  $\text{H}_2^*$  [11] and H platelets [12] are also predicted and observed. However, none of these structures can provide the required H reservoirs because: (1) calculations showed that the  $\text{H}_2$  and  $\text{H}_2^*$  molecules are not sufficiently stable; and (2) although platelets would be more stable, their nucleation and growth requires specially designed hydrogenation and anneal treatments in  $c$ -Si.

In this paper, we propose that “ $m$  vacancies” of  $m$  missing Si atoms (the term includes monovacancies and multivacancies), which are fully terminated with Si-H bonds to eliminate DBs and strained Si-Si bonds, provide the H-pair reservoir and metastability sites in Si. H-rich Si normally contains hydrogenated  $m$  vacancies of various sizes. Positron annihilation spectroscopy (PAS) reveals hydrogenated multivacancies near the surface of plasma-treated  $c$ -Si [7]. In  $a$ -Si:H, PAS [13], multiple-quantum nuclear magnetic resonance [14,15] and H evolution [16] experiments indicate multivacancies of  $m = 2$  to 7 missing Si atoms passivated by H. Carlson linked H capture at vacancies to  $a$ -Si:H metastability [17], but  $m$  vacancies have not previously been seriously considered as a candidate for the H reservoir. Any H trapping or emission would have been expected either to lead to the formation of dangling bonds or to require transport of Si atoms to and from surfaces or dislocations via high-formation-energy defects such as Si interstitials. We find, however, two H-pairing sites 0.8 and 1.4–1.5 eV deep on fully hydrogenated  $m$  vacancies, which lead to H above saturation at the  $m$  vacancies. The capture and release of the H pairs from these sites does not create gap states, nor do they require any long-range Si or monovacancy transport. Our proposals thus provide a unified  $m$  vacancy model for H reservoirs in hydrogenated Si and metastable H pair sites formed during illumination of  $a$ -Si:H.

We performed *ab initio* pseudopotential total energy calculations, as detailed elsewhere [18]. To study the

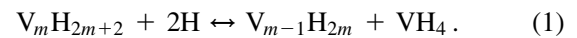
hydrogenated  $m$  vacancies, we used a 128-atom  $c$ -Si supercell, a 20 Ry cutoff energy, and  $k$  points that are equivalent to the 10 special  $k$  points for bulk Si. Zero-point energies for H are included by adding the values from Ref. [10] to our results. We relaxed all the atoms to their equilibrium positions by force minimization. To make an  $m$  vacancy, we removed  $m$  Si atoms, hydrogenated their  $(2m + 2)$  neighbors, and relaxed the structure. The overall uncertainty of the calculations is estimated to be less than 0.05 eV per H. The Drabold-Fedders (DF)  $a$ -Si:H model of 61 Si and 10 H atoms [19] was used to compute the energies of isolated Si-H configurations.

**Energies of proposed H-pair sites.**—Figures 1a and 1b show the energetics for H pairing at or near Si  $m$  vacancies in two configurations which we describe in detail, below. Energies are referenced to “mobile” H in a distant bond-center (BC) site, which is the saddle point in the lowest energy H transport path in undoped  $c$ -Si. Thus, Fig. 1 shows the energies per H captured from the BC mobile level to the various Si-H bonding sites (equivalently, the energies required to excite the bonded H to the mobile H level). The calculations were done in the  $c$ -Si supercell. Fig. 1a shows the energy per H for the capture of H pairs by a “monovacancy ejection” process in which a single  $m$  vacancy splits into a smaller  $(m - 1)$  vacancy and the monovacancy. Figure 1b shows the relevant energies for capture of H pairs by the formation of Si-Si “ $m$ -vacancy surface dimers.” In both cases (Figs. 1a and 1b), H emission takes place in pairs because the second H costs little or no energy. In other words, the H atoms are negatively correlated [3]. Studies of other H-pair sites in Si showed that  $H_2^*$  and  $H_2$  are about 0.4 eV/H shallower than the

monovacancy ejection while fully dilated  $H_2^*$  platelets are about 0.1 eV/H deeper.

For reference, we also calculated the H energies of an isolated Si-H bond in  $a$ -Si:H. In  $c$ -Si, isolated Si-H bonds (which are also not adjacent to any DB) cannot exist, but in  $a$ -Si:H, isolated H-passivated Si bonds are abundant. The energy depends strongly upon the local geometry. At one typical site, we found that H was 2.2 eV below the transport level, but the highly strained flipped configuration can be as little as 1.6 eV deep [20].

**Monovacancy ejection.**—Figure 2a shows the ejection of a monovacancy by an H-saturated  $V_2H_6$  divacancy upon capture of two additional H atoms. The divacancy has split into two H-saturated monovacancies,  $VH_4$ , that are second nearest neighbors. Monovacancy ejection can occur on any  $m$  vacancy with  $m \geq 2$ , according to



Equation (1) also indicates the reverse process of monovacancy recapture. The calculated H energies are 1.35 and 1.49 eV/H for  $m = 2$  and 5, respectively. From Fig. 2a, we see that both the initial and final states of the monovacancy ejection pathway involve only sixfold rings of Si atoms. Capture of 2H atoms results in two additional, strong, Si-H bonds on low-strain Si rings. As such, the H binding energy in Fig. 1a is significantly greater than that of  $H_2$ ,  $H_2^*$  and small  $H_2^*$  aggregates where local strain significantly lowers the H binding energy.

Equilibration times for H in this site are determined by the mobile H density and by the activation barriers for H-pair capture and emission. The barriers to the reactions of Eq. (1) depend on the number of mobile H involved. In an unlikely but instructive H capture scenario, three incoming mobile BC H atoms could break three Si-Si bonds in the initial divacancy configuration to mobilize one of the Si-H pairs. As shown in Fig. 2, the bonds from Si(1) to Si(3), Si(4), and to a third Si (not shown) are broken. The mobilized Si(1) then hops one lattice site to form the Si(1)- $H_2$  dihydride (Fig. 2b). Two strong Si-H bonds are formed and one H is returned to a BC transport site. In this case, the barrier is small since cutting the Si-Si bonds by the mobile BC H literally costs no energy. However, convergence of three mobile H at the  $m$  vacancy is unlikely: Instead, we expect bond-center H to arrive singly or in pairs. Our crude estimate puts the activation barrier for the two-H assisted process at  $\sim 2$  eV per pair, the energy required to break one normal Si-Si bond without H assistance. The actual capture barrier will be smaller because the Si atom hops only one lattice site and the H atom capture repairs any DBs before they are fully formed.

The activation barrier for reemission of the H pair also depends upon the number of mobile H that assist the process. The Si(1) is a dihydride (Fig. 2b) and will be mobilized without a significant barrier when two mobile H cut its Si-Si backbonds. Trapping of a single H at a backbond

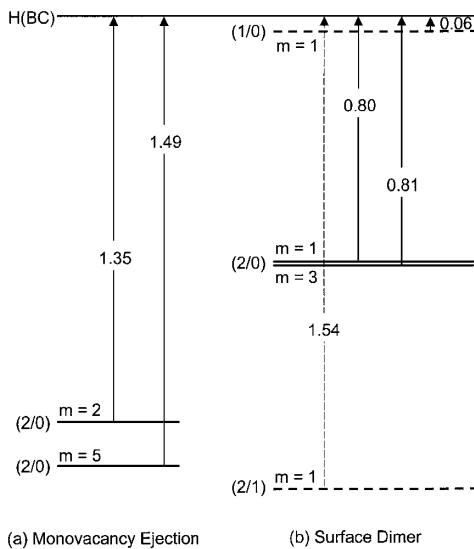


FIG. 1. Total energies (eV) per H for H pair emission (solid) and for single H emission (dashed) from (a) paired monovacancy ejection sites [Eq. (1)] with  $m = 2$  and 5, and (b) internal surface dimer sites [Eq. (2)] with  $m = 1$  and 3. Initial (i) and final (f) H occupations are indicated by (i/f).

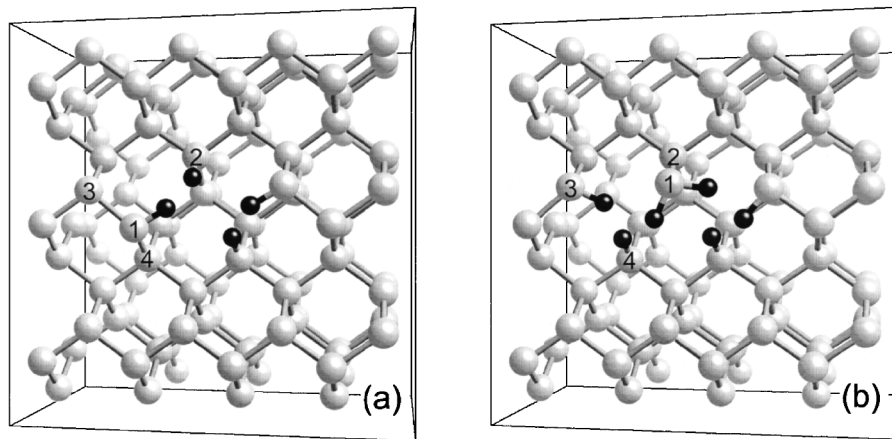


FIG. 2. Monovacancy ejection from a divacancy in *c*-Si [Eq. (1)]. (a)  $V_2H_6$  and (b) two  $VH_4$  formed by capture of 2H and the Si(1) hop. For clarity, we exclude two Si-H from each panel.

to form Si(1)-H<sub>3</sub> should be exothermic because of the freedom to rotate the trihydride to a configuration with minimum H-H repulsion energy. Si(1) could then be mobilized with less than the Si-Si bond-breaking energy ( $\sim 2$  eV) or by arrival of a second mobile H. In these scenarios, the assisting mobile H and the two bound H are returned to transport as the monovacancies coalesce. We do not know of any experiments directly measuring the equilibration time of the reservoir H.

*m*-vacancy surface dimer formation.—Figure 3 shows the formation of a Si-Si dimer on a monovacancy “internal surface” when an H-saturated  $VH_4$  captures two additional H atoms. Two incoming BC H atoms cut two back bonds of the Si atoms adjacent to the vacancy (along a zigzag chain which includes the missing Si). These bonds are indicated by “X” in Fig. 3a. This allows the two second-neighbor Si atoms to form the Si(1)-Si(2) bond shown in Fig. 3b. We call this structure an “*m*-vacancy surface dimer” because the local atomic structure resembles that of a hydrogenated Si-Si dimer on the Si(001) surface [21]. These internal surface dimers can be formed by a H-pair capture process on any *m* vacancy, according to:



Equation (2) also indicates the reverse process of dimer bond breaking and H release. The calculated H energy is 0.80 and 0.81 eV/H for  $m = 1$  and 3. In contrast to the monovacancy ejection mechanism, formation of an *m*-vacancy surface dimer creates a fivefold ring of Si atoms. Strained Si-Si bonds are created by the H-pair capture. As a result, the *m*-vacancy surface dimer H binding energy (Fig. 1b) is smaller than the monovacancy ejection binding energy (Fig. 1a) by 0.54–0.68 eV per H, and is smaller than that of  $H_2^*$  by 0.2 eV per H.

The H capture process of Eq. (2) is qualitatively different from the monovacancy ejection process of Eq. (1). Only two mobile H atoms are needed to initiate low-barrier formation of the Si-Si dimer bond. In fact, our *c*-Si calculation showed that even one mobile H can initiate barrierless dimer formation as it is trapped 0.06 eV deep (Fig. 1b). In *a*-Si:H, we expect that trapping of a single mobile H in the dimer precursor site can be deeper ( $\sim 0.2$  eV), because the *a*-Si:H network adapts more readily to the creation of a fivefold ring than does our *c*-Si model.

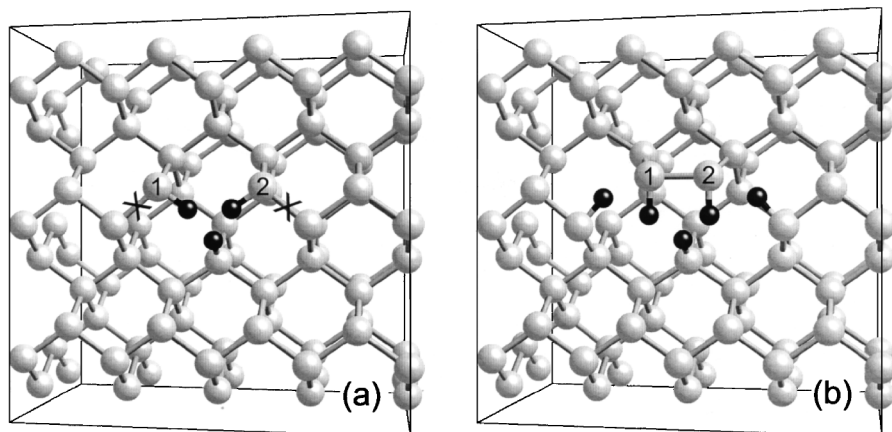


FIG. 3. Internal surface dimer formation in *c*-Si [Eq. (2)]. (a)  $VH_4$  and (b)  $VH_6$  with a dimer, after capture of 2H at the bonds marked (X) in the left panel. For clarity, we exclude one Si-H from each panel.

Our calculations thus demonstrate two mechanisms of H pair capture and release by  $m$  vacancies in Si which were already fully passivated by H. Neither mechanism creates electronic gap levels or dangling bond defects near the  $m$  vacancy. The monovacancy-ejection pathway creates only sixfold rings; there is little strain and the Si-H bonds are stronger. The H pairs are trapped deeper than at any of the bulk pairing sites. The  $m$  vacancy dimer pathway creates fivefold rings; there is some local strain and the Si-H bonds are weaker.

*Unified model for H reservoir and metastability.*—Our H-pairing mechanisms and energies meet the requirements of the H-related phenomenological models [3,5] for  $a$ -Si:H. We propose that the metastable paired H state [5] of light-induced degradation is the  $m$ -vacancy surface dimer. An  $m$  vacancy first captures a single light-induced mobile BC H to form the dimer precursor state. When a second mobile H arrives, the  $m$ -vacancy surface dimer forms, as in Fig. 3. Neither H capture has a significant energy barrier, so the H pair can even be captured during illumination at low temperatures. The calculated binding energy per H is 0.80–0.81 eV in  $a$ -Si:H, only slightly below the experimental annealing activation energy of light-induced metastability for  $a$ -Si:H. Unlike the previously proposed  $H_2^*$  model for the metastable H pair [22], our pairing site forms at an  $m$ -vacancy surface and thus explains the correlation between light-induced defect density and the  $2100\text{ cm}^{-1}$  infrared absorption [23]. We interpret this infrared mode as Si-H at an internal surface [24]. We also propose that the H-pair reservoir for defect equilibration is at  $m$  vacancies which undergo the reconfiguration of Eq. (1). H pairs are captured by ejecting monovacancies and are emitted by coalescence of a monovacancy and a neighboring  $m$  vacancy. By splitting  $(m + 1)$  vacancies during growth, excess pairs may create  $m$  vacancies which have neighboring monovacancies. Although there is a barrier to monovacancy ejection, this low-energy reservoir for H pairs can be accessed during equilibration above  $200^\circ\text{C}$ . The reservoir energy depth is 1.4–1.5 eV per H. H in isolated Si-H is deeper; between 1.6 and 2.2 eV, depending upon local strain. These energies are consistent with the  $a$ -Si:H equilibration model [4].

The H ejection mechanism can play as important a role in heavily hydrogenated  $c$ -Si as in  $a$ -Si:H. During plasma hydrogenation or implantation of  $c$ -Si, H-pair capture by monovacancy ejection maximizes the incorporation of H. Coalescence of the monovacancies into larger  $m$  vacancies during subsequent annealing would emit the H atoms exploited for defect passivation. Similar processes may occur in other tetrahedrally coordinated solids, such as Ge, SiGe, C, and SiC. However, detailed analyses are outside the scope of this work.

In summary, we propose two electrically inactive paired configurations of additional H at Si  $m$  vacancies already

saturated with H. First-principles total energy calculations show that these sites are excellent candidates for the H-pair reservoirs in both  $c$ -Si and  $a$ -Si:H and for the metastable H-pair site occupied during illumination of  $a$ -Si:H.

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