Hydrogen adsorption and diffusion around Si(001)/Si(110) corners in nanostructures

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Abstract
While the diffusion of hydrogen on silicon surfaces has been relatively well characterized, both experimentally and theoretically, diffusion around corners between surfaces, as will be found on nanowires and nanostructures, has not been studied. Motivated by nanostructure fabrication by Patterned Atomic Layer Epitaxy, we present a density functional theory study of the diffusion of hydrogen around the edge formed by the orthogonal (001) and (110) surfaces in silicon. We find that the barrier from (001) to (110) is approximately 0.3 eV lower than from (110) to (001), and that it is comparable to diffusion between rows on a clean surface, with no significant effect on the hydrogen patterns at the growth temperatures used.

Keywords: nanostructure, PALE, DFT

(Some figures may appear in colour only in the online journal)

1. Introduction

Historically, bulk silicon chip fabrication has been a planar process based on repetitive optical lithography. The progressive reduction in device surface area has impaired switching characteristics, leading to the introduction of three-dimensional structures (e.g. finFETs) that can be realized in planar processes. This trend has prompted interest in other ways of engineering three-dimensional silicon growth [1], such as Patterned Atomic Layer Epitaxy (PALE) [2, 3]. PALE utilizes chemical vapour deposition (CVD) to create silicon features without the conventional lithography and masking steps. In this paper we use density functional theory (DFT) to consider how hydrogen diffusion around feature edges affects the growth process.

In PALE a hydrogen-passivated Si(001) substrate can be patterned by selective removal of the hydrogen atoms using an STM probe in UHV conditions [2–4]: the exposed dangling bonds provide adsorption sites for Si fragments deposited from disilane gas admitted into the STM chamber, a form of UHV-CVD. In principle, an atomically-precise three-dimensional structure, of any height, could be grown by successive depassivation and deposition steps. In practice, the quality of the layers grown depends critically on the effectiveness of the depassivation process, which tends to fall as growth proceeds. This leads to surface roughening and the eventual breakdown of epitaxial growth [4].

CVD reactions are complex, with multiple pathways through the adsorption, deposition and desorption phases [5, 6]. On the clean Si(001) surface, the disilane molecule dissociates into SiH2 groups with accompanying atomic hydrogen. When these groups occur on adjacent surface sites they form monohydride dimers [5, 7] which grow into strings and islands upon further disilane deposition. The hydrogen is adsorbed directly onto the substrate and slowly desorbs into molecular gas. The ad-dimers and atomic hydrogen compete for unreacted substrate sites, whose availability determines the overall reaction rate. Conventional low-pressure CVD is conducted at relatively high (around 1000 K) temperatures and the growth rate is determined by precursor throughput. With PALE the ambient temperature cannot exceed 550 K, otherwise the passivating H-layer is destabilized. At this temperature, desorption is incomplete...
and atomic hydrogen remains bound to the substrate, preventing completion of the first monolayer. Now the surface is saturated with a variety of Si–H configurations and further depassivation is necessary. Completion of the first layer typically occurs after three or four depassivation and deposition cycles [4].

Surface coverage is also affected by hydrogen diffusion at the prevailing temperature. H adatoms have been shown to diffuse along trenches in the (0 1 1) surface, with an energy barrier of the order 1 eV [8]. Other theoretical calculations on the (0 0 1) surface predict somewhat larger barriers, i.e. 1.6 eV [9] to 1.7 eV [10, 11], in agreement with experiment [9]. In this study, we use DFT to study H adatoms on the top and side walls of a notional PALE nanostructure, a simple pillar with a horizontal (0 0 1) growth surface. The sidewalls are assumed to have (1 1 0) orientation, a surface of technological interest due to its high carrier mobility. We investigate whether diffusion pathways around the corners would inhibit growth, increasing the number of depassivation/deposition cycles required per monolayer and thus rendering PALE impractical.

We used a chevron-shaped supercell with a 28Å×8Å cross section, with a vertical perpendicular in the (1 1 2) direction (figure 1). This orientation exposes approximately equal (0 0 1) and (1 1 0) surface areas at the apex. A vacuum spacing of 14 Å was interposed and terminating H atoms added between periodic images. We used the experimental bulk Si lattice parameter (5.431 Å), which is in good agreement with the calculated value for this DFT setup. The supercell depth was determined empirically by adding base layers until the change in energy decrement \( \Delta E \) was less than 0.01 eV. The Monkhorst–Pack sampling grid was established in a similar way and set to 6 × 2 × 1. The final structure had a depth of 50 Å and contained 350 Si atoms. A reconstruction of the apex region is shown in figure 2 (lower).

All coordinate files are available on figshare [22].

2.3. Finding H adsorption sites and diffusion pathways

The H adsorption sites are likely to be three-coordinate on the (1 1 0) surface or dimers on the (0 0 1) surface. In both cases a single dangling bond is exposed and its replacement by a covalent Si–H bond causes a reduction in the total energy. We placed an H atom 1.5 Å above each potential adsorption site on the reconstructed surface (in the direction of the dangling bond) and re-optimized the structure. Total structure energy was typically reduced by approximately 4 eV when compared to the clean surface.
structure. Binding energies of the adsorbed hydrogen atom were calculated with respect to the energy of a gaseous $H_2$ molecule:

$$E_b = E_{\text{ads}} - E_{\text{clean}} - 1/2E_{H_2},$$

where $E_{\text{ads}}$, $E_{\text{clean}}$ and $E_{H_2}$ represent the total energy of the optimized structure with the adsorbed H atom, the optimized energy of the clean Si reconstruction and the total energy of gas-phase hydrogen molecule, respectively. A negative binding energy indicates an energy gain on adsorption; a positive binding energy indicates an energy loss. A diffusion pathway will be formed between two adjacent adsorption sites provided that the energy required to surmount any intervening energy barriers is comparable with the thermal energy acquired by the mobile atom. We select the lowest energy sites close to the step edge and use the NEB climbing-image optimizer to find the diffusion barriers. We then use the Arrhenius equation to estimate the diffusion rate across the edge.

3. Results and discussion

3.1. Reconstruction and characterization

As the (001) surface normal swings through a right-angle in the (110) direction it passes through a number of intermediate surface planes e.g., [114], [113], [111], [331] [23]. Each of these surfaces has its own reconstruction strategy but all contain the prototypical 3-coordinate surface atom found on the bulk-truncated (111) surface. Consequently, we can expect the reconstruction of the apex region to include the hexagonal pattern seen on the (111) unreconstructed surface. This can be seen in figure 2 (upper), while the relaxed structure can be seen in figure 2 (lower), which also shows the extended bond lengths expected in the presence of delocalized electrons. Away from the apex, the figure shows characteristic dimerization and buckling on the (001) surface and out-of-plane buckling of the zig–zag rows of the (110) surface. Distortion in the bulk structure is greatest in the region beneath the apex and extends to a depth of 20 Å. These observations suggest that the reconstruction is plausible, offering a sensible basis for the calculation of a model potential energy surface. An exhaustive characterization of the step edge reconstruction would require examination of larger structures in multiple orientations and is beyond the scope of this work.

3.2. The potential energy surface

We investigated 16 possible adsorption sites on the reconstructed surfaces. Six of these gave total energies falling within a 0.3 eV range while the remainder was at least 1 eV higher and not considered further (an increment of 1 eV reduces the adsorption probability by a factor of $\approx 10^4$). These values are shown in table 1 and the sites depicted in figure 3.

| Site | Relative energy | Binding energy |
|------|-----------------|----------------|
| 1    | 0.29            | −1.65          |
| 2    | 0.06            | −1.88          |
| 3    | 0.00            | −1.95          |
| 4    | 0.02            | −1.92          |
| 5    | 0.29            | −1.65          |
| 6    | 0.13            | −1.81          |

Table 1. Stability of H adsorption sites on the chevron surface. All values are in eV. Site labels are those shown in figure 3 (upper).

Figure 2. (Upper) the apex of the 350-atom unoptimized chevron slab viewed from the (112) direction, showing the (100) and (110) surfaces. (Lower) optimized structure, showing (red) buckled (111)-like hexagonal patterns with extended bond lengths (Å). The bond length in bulk Si is 2.35 Å.

Figure 3. (Upper) a composite representation of the six most stable absorption sites from 16 surveyed. Si atoms and H atoms are yellow and blue, respectively. (Lower) approximate path followed by the diffusing H atom (red) in NEB climbing image simulations.
Each is analogous to the kinetics of a chemical reaction with a single transition state corresponding to the highest saddle point in the potential energy landscape and lying between the end points. The climbing image variation of NEB returns the energy at the highest saddle point and so a single-image NEB calculation per hop suffices in this case. Additional images can provide further points on the reaction path corresponding to the route taken by diffusing atoms, although the computational cost is considerable. Since we are interested only in relative barrier heights, we elect to perform single-image calculations.

These results of the NEB calculations values are shown in table 2 and represented graphically in figure 4. Figure 3 (lower) gives a rough indication of the actual diffusion path. The effective barrier for the path is the greater of the hop barriers and is asymmetrical, due to the differing starting energies. Diffusion from the top of the pillar (the (0 0 1) surface) to the side of the pillar (the (1 1 0) surface) has a comparable barrier to diffusion on the Si(0 0 1) surface, while diffusion in the (1 1 0) to (0 0 1) direction.

### Table 2. End-point and NEB barrier energies for a two-hop diffusion pathway around the chevron apex. All values are in eV.

| End-point | Energy | $\Delta E_{(1 1 0 \rightarrow 1 1 0)}$ | $\Delta E_{(0 1 1 \rightarrow 1 1 0)}$ |
|-----------|--------|-----------------|-----------------|
| 3 barrier | −1947.01 | 1.57 | 1.55 |
| 4 barrier | −1945.44 | 1.99 | 1.72 |
| 5 barrier | −1946.98 | 1.72 | 1.99 |

The actual diffusion rate $\nu$ (s$^{-1}$) can be estimated from the energy barrier by the Arrhenius equation

$$\nu = \nu_{\text{hop}} \times \exp \left[ -\frac{\Delta E}{k_B T} \right],$$

where $\nu_{\text{hop}}$ is the attempt frequency, $\Delta E$ is the energy barrier, $k_B$ the Boltzmann constant and $T$ the ambient temperature. $\nu_{\text{hop}}$ is generally found to lie in the range $10^{12} - 10^{13}$ s$^{-1}$ and, since the rate expression is dominated by the negative exponential energy term, we can take $\nu_{\text{hop}} = 10^{13}$ s$^{-1}$ to get an upper bound on the rate. If we assume a PALE process temperature of 550 K, and adsorption sites are assumed to be occupied with a probability of one, then we could estimate a rate of $1.7 \times 10^{-3}$ s$^{-1}$ or approximately one diffusion event every 10 min off the nanopillar. The reverse process would be 300 times less frequent at 550 K.

We can extrapolate from this single event to an entire nanopillar, under the conditions used in PALE. A pillar with a side of 5 nm would have 100 edge sites available, generating a diffusion event off the pillar every 5 or 6 s, assuming that there was an empty site to reach. The reverse process produces a diffusion event every half hour. These results indicate that there would be net hydrogen migration off the pillar, which is a desirable outcome in PALE terms. There is little reason to be concerned about higher temperatures, as the process temperature of 550 K is chosen to avoid desorption of the hydrogen resist (it begins to show mobility at temperatures exceeding 600 K).

Although sidewall hydrogen diffusion may not be a critical issue in a PALE manufacturing process other obstacles remain. Chief amongst these is the formation of anti-phase boundaries (APBs) in the growth surface, due to the collision of islands with different registry. These APBs can trap hydrogen beneath the surface, leading to a reduction in the depassivation yield from subsequent STM lithography. The reduction in yield can be mitigated by adjusting the STM parameters prior to each depassivation step, but the residual hydrogen causes cumulative surface damage, which halts epitaxial growth after two or three monolayers. The remediation of APBs and improvement of the quality of the silicon is the subject of ongoing research.

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**Figure 4.** Diffusion barriers for a hydrogen atom traversing the PES in the apex region of the chevron slab. The adsorption sites are labelled as in figure 3 and the barrier energies derived from two NEB climbing-image calculations. The curve is a spline fit to the data points. Zero energy at adsorption site 3 corresponds to a calculated value of $\approx 1947.01$ eV. Distance travelled increases in the (110) → (100) direction.

-30$^\circ$C
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References

[1] Martin C 2014 Nat Nano 9 89
[2] Lyding J W, Abeln G C, Shen T C, Wang C and Tucker J R 1994 J. Vac. Sci. Technol. B 12 3735
[3] Shen T C, Wang C, Abeln G C, Tucker J R, Lyding J W, Avouris P and Walkup R E 1995 Science 268 1590
[4] Owen J H, Ballard J, Randall J N, Alexander J and Von Ehr J R 2011 J. Vac. Sci. Technol. B 29 06F201
[5] Owen J H G, Miki K, Bowler D R, Goringe C M, Goldfarb I and Briggs G A D 1997 Surf. Sci. 394 79
[6] Owen J H G, Miki K, Bowler D R, Goringe C M, Goldfarb I and Briggs G A D 1997 Surf. Sci. 394 91
[7] Bowler D R 2003 Phys. Rev. B 67 115341
[8] Brázdová V and Bowler D R 2011 Phys. Chem. Chem. Phys. 13 11367
[9] Owen J H G, Bowler D R, Goringe C M, Miki K and Briggs G A D 1996 Phys. Rev. B 54 14153
[10] Bowler D R, Fearn M, Goringe C M, Horsfield A P and Pettifor D G 1998 J. Phys.: Condens. Matter 10 3719
[11] Dürr M and Höfer U 2013 Prog. Surf. Sci. 88 61
[12] Kohn W 1999 Rev. Mod. Phys. 71 1253
[13] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 169
[14] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 8865
[15] Blöchl P E 1994 Phys. Rev. B 50 17953
[16] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[17] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[18] Bitzek E, Koskinen P, Gähler F, Moseler M and Gumbsch P 2006 Phys. Rev. Lett. 97 170201
[19] Henkelman G, Uberuaga B P and Jonsson H 2000 J. Chem. Phys. 113 9901
[20] Sheppard D, Terrell R and Henkelman G 2008 J. Chem. Phys. 128 134106
[21] Klimes J, Bowler D R and Michaelides A 2010 J. Phys.: Condens. Matter 22 074203
[22] Smith R L and Bowler D R 2014 Hydrogen diffusion around a Si (001)/Si (110) corner Figshare
[23] Battaglia C, Gael-Nagy K, Monney C, Didiot C, Schwier E F, Garnier M G, Onida G and Aebi P 2009 J. Phys.: Condens. Matter 21 013001