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Molecular hydrogen evolution from bulk crystalline silicon pretreated with thermal hydrogen atoms

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Temperature-programmed desorption (TPD) from Si(100), preexposed to gas-phase atomic hydrogen at substrate temperatures (T_s) of 415 and 635 K, exhibits a new H_2 peak (α_1) at 850 K in addition to the well-known β_1 (780 K) and β_2 (670 K) H_2 peaks. Dosing with D atoms after H atom exposure shows that H in the β_1 and β_2 states, but not α_1, is replaced by D atoms, suggesting that the α_1 H_2 peak arises from the crystalline bulk. Large H exposures at $T_s=635$ and 415 K produce 3.2 and 4.2 ML hydrogen, respectively, in TPD, which in combination with LEED data supports a model involving concomitant H atom diffusion into the crystalline bulk and surface etching. [S0163-1829(99)02120-7]

INTRODUCTION

Hydrogen chemistry on and in silicon, of great scientific and technological importance, has been studied extensively for the past two decades.[1–3] Electronic-grade amorphous silicon hydride (*a*-Si:H) is obtained when dangling bonds in *a*-Si are H-saturated. *a*-Si:H is used in large-area applications such as thin-film transistor/active-matrix liquid crystal displays (TFT/AMLCD's),[4] solar cells,[5] and image scanners.[3] H incorporation in crystalline silicon (*c*-Si) deactivates or passivates both donor and acceptor dopants and can lead to embrittlement,[2] such properties can have a negative impact on sub-0.1 μm silicon device characteristics.

Hydrogen has been intentionally introduced into *c*-Si by H plasma, by implantation of $\sim 10^2$ keV H^+ ions, and by high-temperature (>1200 °C) treatments in $H_2(g)$.[2] Diffusion of H atoms within *c*-Si occurs rapidly with relatively low energy barriers, 0.2–1 eV,[2] depending on dopant and defect concentrations. Diffusion into silicon followed by recombination to H_2 at tetrahedral (T_d) interstitial sites has long been favored theoretically[6,7] and experimentally.[2,8–12] Calculations predict that molecular H_2 at T_d sites is favored over two neutral interstitial H atoms by 1–2 eV.[7] Deuterium concentrations above that of the dopants have been measured using secondary ion mass spectrometry (SIMS), and the *excess* deuterium, immobile at $T_s \leqslant 400$ °C and electrically and optically inactive, is generally attributed to trapped D_2.[2] The reported diffusion barriers for molecular H_2 are much higher than those for atomic hydrogen and vary from 1.22 to 2.7 eV.[8,13,14] Recently, H_2 stretches at ~3600 cm^{-1} (Ref. 15) and 4158 cm^{-1} (Refs. 15 and 16) have been identified using Raman spectroscopy, suggesting two binding sites. The lower frequency is in the range of some, but not all,[13,14] theoretical calculations for H_2 located in T_d sites.[17–19] To account for the higher frequency, H_2 trapped in microvoids formed in *c*-Si by energetic plasma ions has been proposed.[20,21] H plasmas that contain >15 eV ions severely damage sub-surface ($\sim 10^3$ Å deep) regions of *c*-Si.[15,22] Within the damaged layer, H atoms can recombine to form molecular H_2 and local pressures in voids can rise to $\sim 10^9$ Pa, high enough to exfoliate silicon layers.[23,24]

The formation and stability of molecular H_2 at interstitial sites in void-free *c*-Si motivated the work reported here. We present temperature-programmed desorption (TPD), low-energy electron diffraction (LEED), and D-for-H isotope exchange evidence consistent with the penetration of thermal H atoms into *c*-Si at $T_s = 400-700$ K, the recombinative trapping of H as molecular H_2 at interstitial sites in *c*-Si, and the gas-phase H_2 evolution of this trapped H_2 ($\alpha_1 H_2$) at a temperature ~70 K higher than that derived from H atoms bound to surface Si atoms ($\beta_1 H_2$).

EXPERIMENT

Lightly P-doped ($\sim 2\times 10^{14}$ cm^{-3}, 14–20 Ω cm), Czochralski-grown Si(100) samples (0.5 mm×12 mm×20 mm) were used. The backside was coated with 2000 Å of tungsten sandwiched between 200 Å tantalum films to facilitate linear direct-current resistive heating up to 1400 K. The substrate temperature was monitored by a chromel-alumel thermocoupled glued into a small hole near the sample edge with a high-temperature ceramic glue. After a 5 K/s heating to 1300 K and subsequent 1 K/s cooling, a well-ordered clean Si(100)-2×1 surface was obtained, as confirmed by Auger electron spectroscopy (AES) and LEED.

Atomic H was generated by a hot (~1900 K) spiral tungsten filament positioned in front of a 0.64-cm-diam, tubular stainless-steel H_2 gas doser facing the sample surface from a distance of 3 cm. When the W filament is heated to 1900 K, thermal-energy ($\sim kT$) atomic hydrogen is produced with a H_2 cracking probability of a few percent.[25,26] Because the H_2

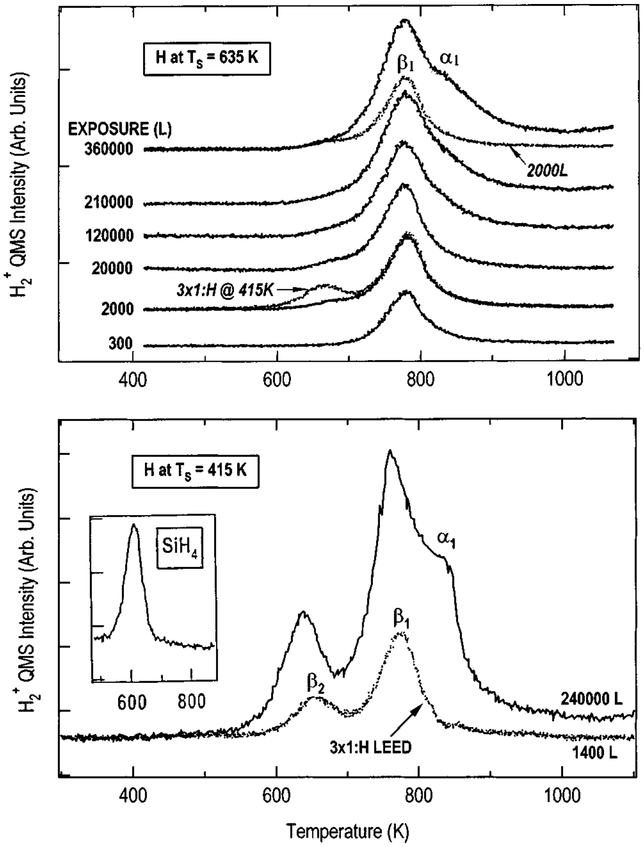

FIG. 1. Top panel: H_2 TPD spectra after dosing Si(100) held at 635 K (T_s) with atomic hydrogen formed on a hot tungsten filament from 1×10^{-4} torr H_2. The H atom dose is proportional to the measured H_2 exposure (1 L$=10^{-6}$ torr sec). Also shown for H coverage ($\theta_H=1.33$ ML) calibration is the H_2 TPD spectrum obtained for a 1.4×10^3-L H_2 exposure at $T_s=415$ K (see text). The 2×10^3-L H_2 TPD spectrum after dosing at 635 K thus corresponds to $\theta_H=1$ML. Bottom panel: TPD spectra of H_2 for 1.4×10^3-L and 2.4×10^5-L H_2 exposed at $T_s=415$ K.

cracking efficiency and H atom flux to the substrate surface can only be estimated (see below), H_2 exposures in Langmuirs (1 L$=1\times10^{-6}$ torr sec) are reported and used as a measure of H atom fluences. TPD measurements (5 K/sec) were made with a shielded, differentially pumped quadrupole mass spectrometer (QMS) through a 3-mm-diam conical aperture positioned 1 mm in front of the sample. The ultrahigh-vacuum system with a base pressure of 1×10^{-10} torr was pumped by a combination of turbomolecular, Ti sublimation and ion pumps. Turbomolecular pumps for the QMS and main chambers were separately backed by diffusion and rotary pumps in series in order to maintain the background H_2 pressure low.

RESULTS AND DISCUSSION

Si(100) surfaces saturated with H atoms at ~400 K exhibit a (3×1) LEED pattern with 1.33 H atoms per surface Si, i.e., $\theta_H=1.33$ ML.[1,27,28] The bottom panel of Fig. 1 shows H_2 TPD after a dose of 1.4×10^3 L H_2 for which a well-developed (3×1) LEED pattern is observed. A lower limit for the H atom flux is 0.23 H atom per second per surface Si atom at a H_2 partial pressure of 1×10^{-4} torr. This estimate assumes a unity sticking coefficient up to $\theta_H=0.7$ ML (1 ML$=6.78\times10^{14}$ atoms/cm^2).[29,30] TPD gives the β_1 (780 K) and β_2 (670 K) H_2 TPD peaks arising from monohydride and dihydride surface species.[1] Similar saturation for doses near 600 K gives 1 ML coverage and (2×1) LEED pattern,[1,27,28] observations reproduced in our work (2×10^3 L curve in upper panel).

For much larger doses, two striking features appear in Fig. 1: (i) the β_1 and β_2H_2 desorption peaks grow more slowly; and (ii) a shoulder peak (α_1) at higher temperatures emerges as exposures in the 10^5 L regime are employed. The intensities in the β_1 peak grow by a factor of 1.9 (1.9 ML) at 635 K and 2.8 (3.7 ML, β_1 plus β_2) at 415 K as the dose increases from 10^3 to 10^5 L (of H_2). When the intensity of α_1 is added, the coverages are 3.2 ML at 635 K and 4.2 ML at 415 K for the highest doses in Fig. 1.

For surface Si atoms on Si(100), the maximum uptake is two H atoms per Si (2 ML) but steric repulsion between neighboring dihydride units make it difficult to achieve.[31,32] While most published maximum θ_H values lie in the range of 1.5 to 1.9 ML for $T_s\leqslant300$ K,[1,27,28,33,34] we find coverages ~2.8 ML (Ref. 35) while others find $\theta_H=3.2$ ML,[36] the latter based on nuclear reaction and Rutherford backscattering channeling measurements. Increased surface areas caused by etching[36] and *a*-Si H film formation[35] have been proposed to account for these large H uptakes for $T_s\leqslant300$ K. For the conditions of Fig. 1, there was no evidence for *a*-Si:H formation, and while etching contributes and accounts for the increased β_1 and β_2H_2 intensities, to account for the α_1 intensity we propose H_2 evolution from interstitial sites in bulk *c*-Si. Etching was confirmed by noting SiH_4 desorption at ~600 K in TPD for surfaces exposed to atomic H at $T_s=415$ K (inset of Fig. 1). T_s-dependent efficiency and mechanisms of surface etching and *a*-Si:H formation will be reported elsewhere.[35]

LEED patterns for exposures corresponding to the TPD spectra show that the initially sharp (2×1) LEED pattern did not change appreciably until the surface was exposed to very large amounts of atomic H at $T_s=635$ K. It became diffuse with a strong background at the 3.6×10^5 L H_2 exposure (top left picture in Fig. 2). The spot broadening and strong background of the LEED pattern suggest high step and point defect densities. On the other hand, the LEED pattern changed from (2×1) to (3×1) to (1×1) with increasing H exposures at $T_s=415$ K. A diffuse (1×1) LEED pattern was obtained for the surface exposed to atomic H of 2.4×10^5 L H_2 at $T_s=415$ K. From these LEED pattern changes, we conclude, consistent with TPD, that the surface was extensively etched.

A series of LEED pictures were taken after successive isochronal annealing to the indicated temperatures (635–1200 K) for a surface exposed to the atomic H associated with 3.6×10^5 L H_2 at $T_s=635$ K. It is interesting that the diffuse (2×1) pattern of the as-exposed surface transforms to a (1×1) pattern, followed by increasingly sharper (1×1) patterns up to 900 K. The (2×1) pattern of a clean reconstructed Si(100) surface is not recovered until the surface is annealed to 1200 K. In the 700–900 K regime, where the (2×1) to (1×1) transition occurs, all the β_1 and α_1H_2 desorb leaving a clean surface.

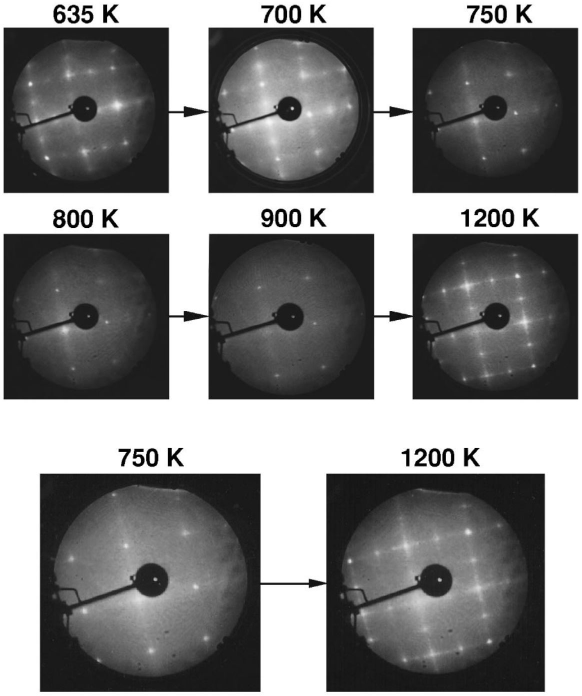

FIG. 2. Top panel: LEED patterns taken for H-exposed Si(100) successively annealed to the indicated temperatures for 1 min. The clean Si(100)-2×1 surface was exposed to atomic H of 3.6×10^5-L H_2 at T_s=635 K prior to annealing. Bottom panel: LEED patterns taken for a Si(100) surface exposed to atomic hydrogen of 3.6×10^5-L H_2 at T_s=750 K and after a 1200-K annealing. All LEED pictures are taken near room temperature following each annealing with a primary electron energy of 55–65 eV and a camera exposure of 20 sec at an *f* number of 5.6.

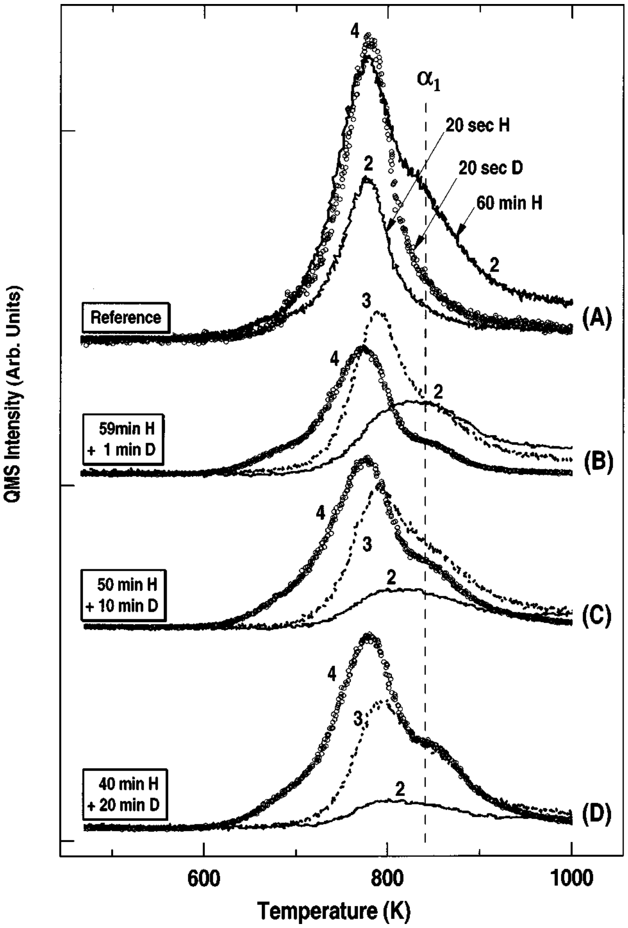

FIG. 3. TPD spectra of H_2, HD, and D_2, labeled 2, 3, and 4 for Si(100) successively exposed to H and D for the indicated times—(b)–(d) dosed at T_s=635 K and 1×10^{-4} torr H_2 (D_2) pressure. Also shown in (a) are TPD spectra of 20-sec H, 20-sec D, and 60-min H exposure times at T_s=635 K and H_2 (D_2) pressure of 1×10^{-4} torr.

From the diffuse (2×1):H LEED with a strong background (top left picture in Fig. 2), we conclude that (2×1)-ordered terrace domain widths barely exceed the LEED coherence length (~100 Å). Surface Si diffusion is known to be greatly inhibited by the presence of adsorbed H.[37] Thus, dimer vacancies and roughness would not begin to anneal out until the surface H desorbs.[38] This would keep ordered (2×1) domains from forming and the surface would exhibit a (1×1) LEED pattern until the surface is smoothed and reconstructed by defect clustering and step bunching for even higher T_s annealing. For an exposure of 3.6×10^5 L H_2 at T_s= 750 K, a (1×1) LEED pattern is recorded (lower part of Fig. 2) like that found with annealing at 750 K (upper part of Fig. 2) and it converts to a (2×1) pattern after a 1200 K anneal. We believe that the (1×1) pattern is not indicative of an ordered unreconstructed (100) surface caused by subsurface hydrogen (α_1 state) because the (1×1) pattern persists even after a 900 K anneal, a temperature at which the majority of the hydrogen has desorbed.

Since (111) facets are often formed on Si(100) as a result of an extensive surface etching,[22,28,39,40] we consider whether the α_1H_2 desorption could arise from (111) domains. To account for the large α_1H uptake (~1 ML) such facets must comprise a relatively large fraction of the total surface area while, at the same time, there can be no decrease in the (100) domain area since the β-H_2 intensity increased. In LEED, we did not observe trajectory crossing of LEED spots as the primary electron beam energy is varied,[41] ruling out Si(111) facets with widths of order 100 Å or larger. Moreover, large concentrations of much smaller facets cannot be reconciled with the assumed desorption of α_1 from (111) facets since they would form at the expense of the (100) domains,[28] contrary to the evidence.

One other possibility for the α_1 state involves carbon contamination; a high-temperature shoulder following β_1H_2 has been reported for carbon-contaminated Si(100).[42] After large H exposures, we found no evidence for accumulation of carbon, based on AES. Although AES is relatively insensitive to C, to account for the nearly 1 ML α_1H_2 desorption, carbon contamination would have to be well above the AES detection limit. Since the α_1H_2 peak is observed only for these large exposures, we rule out carbon contamination as its source.

Taken together, these TPD, LEED, and AES results are consistent with the proposed model that attributes the large H_2 uptakes to a combination of surface etching and H_2 formation at interstitial sites in *c*-Si. To further elucidate the origin of the α_1H_2 peak, D-for-H isotope exchange experiments, Fig. 3, were performed. Reference spectra for $\theta_{H(D)}$ =1 ML [the 20 s H and 20 s D exposures in Fig. 3(a)] formed at T_s=635 K and 1×10^{-4} torr H_2 or D_2 show that the mass spectrometer sensitivity for D_2 is 1.9 times that for H_2. The reference 60 min H spectrum exhibits the expected β_1 and α_1 peaks. Three other experiments are shown—(B) through (D)—in which 60 min doses are comprised of various H doses followed by D doses. The curves labeled 2, 3, and 4 depict desorption profiles for H_2, HD, and D_2, respectively. For a long dose of H (59 min) and a short dose of D (1 min), it is immediately clear that, compared to 60 min of H, $\beta_1 H_2$ is largely replaced by $\beta_1 D_2$ while most of the $\alpha_1 H_2$ remains. Thus, once formed, $\alpha_1 H_2$ is much more difficult than β_1 monohydride to replace with D. This conclusion persists for the shorter H and longer D exposure results; $\beta_1 D_2$ emerges much more rapidly than $\alpha_1 D_2$. The increasing relative intensity ratio of α_1-D_2/β_1-D_2 with longer D doses further illustrates that D continues to penetrate into the *c*-Si while surface H atoms become depleted. The increasing $\beta_1 D_2$ and decreasing β_1HD are consistent with the etching- and abstraction-induced increases of surface area and θ_D, respectively.

Adsorbed hydrogen atoms, $\beta_1$state, are abstracted by gas-phase H (or D) with a probability of 0.3–0.4.[29] Were the α_1 state hydrogen at the surface, its activity would have to be more than 100-fold less than the β_1 state to account for the above results. The isotope exchange, the high dose requirement, and the LEED data all point to hydrogen beneath the surface as the source of α_1.

As a further test, we also performed the following series of experiments: (i) the surface was first exposed to 3.6×10^5 L H_2 at 635 K; (ii) after TPD to 870 K, the sample was cooled to 635 K; (iii) the surface was exposed to atomic D (6×10^3 L D_2 at $T_s = 635$ K); and (iv) finally, TPD to 1270 K. After TPD to 870 K in step (ii), the surface showed a (1×1) LEED pattern, in agreement with the annealing LEED series in Fig. 2, indicating that the roughened surface is not smoothed by the 870 K anneal. The D_2 TPD spectra from step (iv) was very similar to that of the 2×10^3 L D_2 at $T_s = 635$ K on a smooth (2×1) surface [see Fig. 3(a)]. No $\alpha_1 D_2$ desorption was detected. If the α_1 state were a surface state, we would have observed $\alpha_1 D_2$ desorption as well as $\beta_1 D_2$ desorption. This result further confirms that the α_1 state is a bulk state, accessible only by a prolonged H(D) exposure.

According to the proposed model, during lengthy H exposures at $T_s = 415$ and 635 K, a measurable fraction of H atoms diffuses with low activation barriers[2,43] into the bulk where recombination and trapping occurs leaving stable H_2 at tetrahedral (T_d) interstitial sites.[13–15,17–21] This molecular H_2 would move very slowly at $T_s = 415$ and 635 K since the H_2 diffusion barrier would be high (1.2–2.7 eV).[2,8,13,14] H_2 trapped in platelets, which are often formed by H plasma treatment, has been reported to be stable up to 523 K (Ref. 22) or 673 K,[21] but the low energies (~0.16 eV) of the thermal H atoms employed in this work are incapable of creating platelet defects in *c*-Si bulk. The amount of H trapped at defect and dopant sites in *c*-Si would be too small to contribute significantly to the H_2 desorption because the doping level of our sample is low (2×10^{14} cm^{-3}). Moreover, these internal H atoms are expected to evolve out at a T_s significantly lower than the $\beta_1 H_2$ peak temperature, considering their shallow trap depths and high mobility in *c*-Si.[2,44] In our early work,[45] we showed that adsorbed H on internal surfaces of Ar^+-created voids in silicon evolved out as H_2 in TPD at the same temperatures as the surface-adsorbed H. The P in samples doped with phosphorus can be hydrogenated but this hydrogen is liberated during a 423-K anneal.[2] Further, contrary to our observations, highly P-doped ($C_P = 4\times10^{19}$ cm^{-3} or $\theta_P \approx 0.02$ ML) Si(100) surfaces exhibit significantly less H_2 (β_1 and β_2) desorption and up to 40 K higher TPD peaks.[46,47] Not surprisingly, the effects of P doping are undetectable in our experiments.

In Czochralsky (CZ)-grown Si crystals, bond-centered interstitial oxygen atoms (O_i) are incorporated in the range of 10^{17}–10^{18} cm^{-3}.[48,49] Hydrogen introduced into these crystals by annealing at ~1200 °C in atmospheric H_2 gas ambient has been suggested to occupy T_d interstitial sites in its molecular form. These H_2 molecules exhibit infrared-active O_i-H stretches at 3789 (ν_1), 3731 (ν_2), and 3618 cm^{-1} (ν_3).[48] The ν_1 and ν_2 intensities first increased upon annealing at 340–380 K, and then decreased with 380–590 K annealing, while the ν_3 intensity first increased with the low-T_s annealing, remaining constant with annealing at $T_s \geqslant 420$ K. Pitchard *et al.*[48] attributed the ν_1 and ν_2 modes to two types of O_i-H_2 complexes formed by association with H_2 that had migrated from T_d sites, and the ν_3 stretch mode to H_2 trapped at defect sites. This assignment was based on the fact that the ν_3 stretch was observed only in float zone-grown silicon crystals with a very low $[O_i]$ of 2×10^{15} cm^{-3}. The ν_3 mode has also been detected by Raman spectroscopy and is attributed to the vibration of H_2 molecules trapped at T_d sites.[15,21]

Thus, all the evidence indicates that $\alpha_1 H_2$ peaks arise from the desorption of molecular H_2 trapped in *c*-Si, likely at T_d interstitial sites. The $\alpha_1 H_2$ peak breadth [see Fig. 3(b)] suggests that the thermal evolution of bulk H_2 is limited by bulk diffusion through the interstitial space, not by surface desorption. H_2 TPD following large H exposures at $T_s = 750$ K showed only one shallow and broad peak at 930 K. This H_2 peak is attributed to H_2 evolution (α_1) from deeper interstitial sites in *c*-Si, consistent with a diffusion-limited H_2 evolution model. Assuming first-order kinetics and a preexponential factor of 10^{13} sec^{-1}, a diffusion activation energy of 3.5 eV is estimated from Fig. 3(b). Markevich *et al.*[49] obtained a much lower value of ~0.8 eV, which was estimated by the increased infrared absorption for the O-H complex stretching mode with annealing in the 300–420 K range. We speculate that their small activation energy reflects the diffusion of $T_d H_2$ within the close proximity of interstitial oxygen (O_i), which might be an accelerated process rather than diffusion through the *c*-Si lattice. Further investigation of these different energy estimates is needed.

The β_1 HD desorption peak is about 20 K higher than $\beta_1 D_2$ in spectra (b)–(d) in Fig. 3. We ascribe this to the effects of surface etching which produces, for example, (111) nanofacets where Si-H bonds are slightly stronger,[40] and require somewhat higher temperature for efficient abstraction by D(*g*).[50] We also speculate that H indiffusion, in addition to H abstraction, by subsequent D atoms occurred. It is likely that atomic H arriving from the gas phase both penetrates into the bulk directly and induces preadsorbed H to diffuse into the bulk. We suppose, that, as on metallic surfaces, e.g., Cu, Ni, and Pd, atomic H first saturates the surface sites before diffusing into subsurface or bulk sites.[51,52]

SUMMARY

In summary, after dosing Si(100) at 415 and 635 K large amounts of hydrogen desorb, up to 3.2 and 4.2 ML, respectively. Extensive surface etching was evidenced by LEED and, in addition, by surface H bound in the commonly observed β_1 and β_2 sites. There is a new high-temperature H_2 desorption feature, denoted α_1, near 850 K. This peak is ascribed to H_2 evolving by diffusion from the bulk of crystalline Si, having been formed there during exposure to atomic H by the slow migration of H atoms from a H-saturated surface, either directly from the gas phase or from atoms first bound at the surface. Based on other work, the most likely bulk binding sites in void-free crystalline silicon are the tetrahedral interstices between Si atoms.

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