Amorphization of single-crystalline silicon by thermal-energy atomic hydrogen

J. H. Kang and S. K. Jo
Department of Chemistry, Kyung Won University, Sung-Nam, Kyung-Ki 461-701, South Korea

Science and Technology Center, University of Texas, Austin, Texas 78712

(Received 25 February 1999; accepted for publication 10 May 1999)

Si(100)-(2×1) was exposed to gas-phase atomic hydrogen, H(g), at various substrate temperatures T_s between 115 and 300 K. No low-energy electron diffraction patterns could be obtained from such hydrogenated surfaces. In temperature-programmed desorption measurements, SiH_x (x=1–3) radical species as well as SiH_4 desorbed at T_s between 600 and 1000 K, in addition to β_1- and β_2–H_2 desorption peaks. Combined together, the results indicate that amorphous hydrogenated silicon (a-Si:H) films are formed. While surface etching competes, a-Si:H formation dominates. Once formed, a-Si:H further suppresses etching. © 1999 American Institute of Physics.

Hydrogen interaction with amorphous silicon (a-Si) and crystalline (c-Si) surfaces has been intensively studied.1–3 Amorphous silicon hydride (a-Si:H) films find use in large-area applications such as thin-film transistors, solar cells, and image scanners.2 Hydrogen passivates dangling bonds in a-Si:H films, improving their stability and electronic performance. Gas-phase H atoms preferentially attack, and thereby remove, strained Si–Si bonds in a-Si:H films, from which microcrystalline Si (μc-Si) films are obtained.4 Atomic H reactions with c-Si surfaces, including surface hydrogenation,3 etching,3,5 and bulk penetration,6–8 have been reported. Here, we explore how substrate temperature T_s determines different H atom reaction pathways at c-Si surfaces.

A standard ultrahigh vacuum chamber was equipped with a quadrupole mass spectrometer for temperature-programmed desorption (TPD), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED) optics.5 n-type (P-doped; C_p=2×10^{14} cm^{-3}) Si(100) samples, 0.5×12×20 mm in size, were used. The backside was coated with 2000 Å of tungsten sandwiched between 200 Å tantalum films (as a tungsten diffusion barrier and capping layer) to facilitate resistive heating up to 1300 K. The substrate temperature was monitored by a chromel–alumel (type K) thermocouple.8 After 5 K/s heating to 1300 K and subsequent 1 K/s cooling to room temperature, a clean Si(100)-2×1 surface was obtained.

Atomic H(g) was generated by a hot (∼1900 K) spiral tungsten filament positioned in front of 0.63-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 (<0.3 eV) atomic hydrogen is produced with an unknown low efficiency.7 Because the H atom flux can only be estimated,8 H_2 exposures in Langmuirs (1 L=1×10^{-6} Torr s) are reported and used as a measure of relative H atom fluences.

The (2×1) reconstructed structure and cleanliness of Si(100) were confirmed by LEED and AES prior to H atom exposures. With increasing H exposures, the initially sharp (2×1) LEED pattern transformed first to (1×1), and then gradually disappeared. As can be seen in Fig. 1, no diffraction pattern could be obtained from the surface exposed to atomic H(g) from 28,000 L H_2 at 115 K (T_s), indicating that several layers of the ordered substrate structure are destroyed. Also shown in Fig. 1 are the LEED pictures taken after sequential isochronal annealing of the H-exposed substrate to the indicated temperatures. The characteristic dif-

Image 343x98 to 533x326

FIG. 1. LEED pattern evolution, following successive 1 min isochronal annealing to the indicated temperatures, of the Si(100) surface exposed to atomic H(g) of 28 000 L H_2 at T_s = 115 K. Also shown are the H_2^+, Si^+, SiH^+, SiH_2^+, and SiH_4^+ (m/z=2 and 28–32) TPD spectra from Si(100) pretreated with H(g) of the same exposure at T_s = 115 K.
fraction spots for a (2×1)-reconstructed Si(100) surface reappeared only after a 1000 K anneal, becoming sharper with a further anneal to 1200 K. No LEED pattern is recovered with a 1 min 750 K anneal, a temperature at which almost all surface-adsorbed monohydride and dihydride ($\beta_1$ and $\beta_2$, respectively) have desorbed.

In Fig. 1 we also show the H$_2$ and SiH$_4$ TPD spectra for the surface preexposed to atomic H($g$) from 28 000 L H$_2$ at 115 K. In addition to broad H$_2$ desorption at 670 K ($\beta_2$) and 780 K ($\beta_1$), three SiH$_4$ desorption peaks are observed at 600, 720, and 1030 K. The desorption of SiH$_4$($x$=0–4) at 600 K has been attributed to a surface reaction of SiH$_3$($g$) and H($g$).$^5$,$^10$ The two high $T_s$ SiH$_4$ desorption peaks have not been reported from H-treated Si(100) surfaces. We cannot determine the exact x value of the desorbing SiH$_x$ species at 720 and 1030 K as the electron impact ionization cracking patterns for SiH, SiH$_2$, and SiH$_3$ species are unknown. Nonetheless, we assign the 720 and 1030 K peaks to desorption of SiH$_x$($x$≤3) and SiH$_x$($x$≤2) radicals, respectively.

From Fig. 1, we conclude that an amorphous surface, a-Si:H, is formed. The desorption of SiH$_x$ radicals in TPD is attributed to the thermal decomposition of the H-deficient a-Si:H film formed. Significant amounts of SiH$_2$ and H$_2$ desorb between 800 and 1000 K, demonstrating that a-Si:H requires high $T_s$ to be recrystallized, as does the partial desorption as SiH$_x$($g$) radicals and H$_2$($g$).$^11$ This a-Si:H matrix inhibits any ordered LEED structures until the surface is annealed to ~1000 K. Desorption of SiH$_x$ radicals species occurs at $T_s$ as high as 1030 K in TPD. We speculate the SiH$_4$ radical desorption peaks at 720 and 1030 K result from destruction and recrystallization of the relatively H-rich upper and H-deficient lower parts of the porous a-Si:H matrix, respectively.

Similar TPD and LEED results were obtained for Si(100) exposed to H($g$) at $T_s$=180 and 300 K, but the higher $T_s$ required higher H exposures for comparable results. Figure 2 presents TPD intensity variations as a function of H exposure for $T_s$=180 K. The 300 L spectra indicate the formation of monohydride ($\beta_1$H$_2$); a (2×1) LEED pattern remains. As the H exposure increases, the $\beta_2$–H$_2$ (650 K) and SiH$_4$ desorptions (600 K) increase maximizing at 3600 L. SiH$_4$ was identified by its fragmentation pattern determined in situ.

SiH$_x$($a$) is formed and abstracted by H($g$) to form gas-phase SiH$_x$($g$) as an etching product during the H($g$) exposure. The 600 K SiH$_4$ desorption in TPD probes the surface coverage of residual SiH$_x$($a$). The intensity of this peak drops as H($g$) exposure increases and is a monitor of the rate of surface etching at the point where the H($g$) flux is terminated. A reference H$_2$ spectrum from a well-ordered Si(100)–(3×1):H ($\theta_{H_2}$=1.33) formed at $T_s$=415 K is overlaid on the 3600 L spectrum.$^8$ Comparing the 300 and 3600 L spectra, it is clear the some di- and trihydride ($\beta_2$H$_2$650 K and SiH$_3$ at 600 K, respectively) form well before monohydride ($\beta_1$H$_2$) saturates. In fact, saturation monohydride coverage ($\theta_{H_2}$=1) is never achieved. The 600 K SiH$_4$ desorption, together with the intense $\beta_2$–H$_2$ desorption signal, suggests that the surface is etched and that the atomically roughened surface is consequently covered with significant amounts of SiH$_x$($a$) and SiH$_x$($a$). The corresponding LEED pattern for 3600 L H$_2$ exposure was nearly (1×1) with barely visible half-order spots.

Beyond 3600 L H$_2$ exposure, striking new features emerge in both TPD and LEED: (1) H$_2$ desorption peaks at about 720 and 1030 K grow in, while $\beta_1$ and $\beta_2$H$_2$ decrease; (2) the 600 K SiH$_4$ desorption peak decays, while new SiH$_x$($x$≤3) desorption peaks at 720 and 1030 K emerge; and (3) the initially faint (1×1) LEED pattern completely disappears (not shown). The suppressed 600 K SiH$_4$ peak and the strong SiH$_4$ radical peaks indicate that the substrate has been hydrogenated well past the topmost layer. Since a surface-limited disordering would still give a (1×1) LEED pattern, it is evident that a fairly thick amorphous hydrogenated silicon (a-Si:H) forms. This experimental evidence for the amorphization of crystalline Si by thermal-energy atomic hydrogen.

In TPD, H$_2$ desorption starts at $T_s$ as low as 200 K and SiH$_4$ signals are also observed, indicating partial decomposition of the H-rich upper layers of a-Si:H. We expect upper-lying a-Si:H layers to anneal out first, resulting in the 720 K SiH$_4$ radical desorption x as high as 3.

Our results contrast with literature reports for H plasma-induced etching and crystallization of a-Si:H. a-Si:H films, typically grown by plasma-enhanced chemical vapor deposition of SiH$_4$ at $T_s$, between 400 and 600 K, can be readily crystallized by H plasmas.$^4$ Our results show that for $T_s$
$\approx 300$ K, $a$-Si:H formation is competitive with etching.

The broad $H_2$ desorption signals at 720 and 1030 K that track the SiH$_x$ signals are mainly fragments of desorbing SiH$_x$ radicals. The apparent total integrated $H_2$ desorption amount from the fully hydrogenated surface (45 000 L) corresponds to only $\sim 2.8$ ML (1 ML=6.78×10$^{14}$ cm$^{-2}$), because the majority of the H content in $a$-Si:H desorbs as SiH$_x$($x$$\leq$3) radicals. In a similar experiment, Lu et al. reported a total deuterium coverage of $\sim 3$ ML for a Si(100) surface extensively treated with atomic D($g$) near room temperature, attributing their high $\theta$ values to an increased surface area due to surface etching. Our results rather suggest that their 3 ML D uptake, determined by nuclear reaction and Rutherford backscattering analyses, can be also ascribed to a multilayer $a$-Si:D film.

We now discuss the dominance of $a$-Si:H formation over surface etching at $T_s \approx 300$ K on extensively hydrogenated Si(100) surfaces. Once formed, the $a$-Si:H passivates further surface etching, as indicated by suppressed SiH$_x$ and H$_2$ desorption in the 45 000 L TPD in Fig. 2. In earlier work, we showed that slow but continuous etching occurs, without $a$-Si:H formation, at $T_s > 400$ K, consistent with the H plasma-induced etching and crystallization of $a$-Si:H reported in the literature. We also showed that $H(g)$ abstracts SiH$_x(a)$ on Si(100) more efficiently at higher $T_s$. While the formation of precursor species, SiH$_x$($x\leq3$), is favored by low $T_s$, the final step for etching, SiH$_x(a)$+H($g$) $\rightarrow$ SiH$_d$($g$), is enhanced at high $T_s$. The enhanced stability of SiH$_x(a)$ and consequently slower etching of SiH$_x(a)$ by H($g$) at $T_s \approx 300$ K allow reaction of H($g$) at subsurface Si–Si backbones to compete successfully with the abstraction of SiH$_x$($a$).

We also speculate that the atomic-scale surface roughening induced by etching exposes more subsurface Si–Si backbones to incoming atomic H($g$) and thereby facilitates hydrogenation of the subsurface. As a result, a thick $a$-Si:H film forms. A steady-state $a$-Si:H thickness is established when the amorphization rate equals the surface etching rate. We confirmed this by noting that H$_2$ and SiH$_x$, TPD spectral features did not change appreciably beyond the 45 000 L exposure. The $a$-Si:H film thickness was estimated to be at least 4–5 ML, judging from complete loss of the LEED pattern and the desorption intensities for the SiH$_x$($x\leq3$) radicals in TPD. The porous nature of the newly formed $a$-Si:H film and the accompanying lower SiH$_x$($a$) surface concentration are manifested in the diminished 600 K SiH$_4$ TPD peak.

Although further structural studies are needed for a more complete explanation, our data clearly show that the amorphized surface contains fewer SiH$_x(a)$ species. Thus, a much lower steady-state etching rate is realized for such hydroge-

nated surfaces. It has been widely suggested that lower substrate temperatures enhance the H-induced silicon etching.$^{3,14-16}$ Our results, however, suggest that lowering $T_s$ below room temperature lowers the etching rate due to $a$-Si:H formation. In related work, Glass et al. also reported that the direct etching reaction, SiH$_3(a)$+H($g$) $\rightarrow$ SiH$_d$($g$), did not occur on a porous Si surface at $T_s = 133$ K.$^{17}$

In summary, we have shown that crystalline silicon substrates are readily hydrogenated to a significant depth at $T_s \approx 300$ K by thermally generated ($<0.3$ eV), gas-phase atomic H($g$) despite the fact that the surface is etched at the same time. Resulting amorphous silicon hydride ($a$-Si:H) films show a very small surface concentration of SiH$_3(a)$, suggesting that surface etching is greatly suppressed. Large amounts of SiH$_x$ radical species desorbed upon thermal decomposition of such $a$-Si:H films.

S.K.J. acknowledges the Korea Science and Engineering Foundation for funding this work (Grant No. KOSEF 97-05-01-01-01-3). J.H.K. is grateful to KOSEF for intern research fellowship (1998). This work was supported in part by the Science and Technology Centers Program of the US National Science Foundation, Grant No. CHE8920120 and the AFOSR/DARPA MURI Grant No. F49620-95-1-0475.

13 The SiH$_4$ 600 K TPD area somewhat understimates the surface concentration of SiH$_3(a)$ since there is shallow but broad SiH$_4$ desorption over a wide $T_s$ range below 500 K (see Fig. 2).