Si(001) surface variation with annealing in ambient H$_2$

T. Komeda* and Y. Kumagai

Texas Instruments, Tsukuba Research and Development Center, Miyukigaoka 17, Tsukuba 305, Japan

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Monohydride termination and surface variation of Si(001)-2×1 by annealing in H$_2$ ambient has been investigated with scanning-tunneling-microscopy (STM). A clean Si(001)-2×1 surface was annealed and cooled to room temperature in H$_2$ ambient with various partial pressure of $P(H_2)$. Hydrogen termination of the surface is observed when $P(H_2)$ exceeds 10^{-3} torr, and complete monohydride termination is obtained with $P(H_2) \sim 0.1$ torr. The results are reproduced well by the calculation using the temperature-dependent sticking coefficient of molecular H$_2$ on Si(001). [Kolasinski *et al.*, J. Chem. Phys. **101**, 7082 (1994)]. The surface obtained by H$_2$ annealing shows characteristic S_B-step shape, which has a long kink-free portion connected by a long kink. It is shown that the etching of Si surface by H$_2$ is not responsible for the determination of the shape of S_B steps. Instead, the presence of passivating hydrogen at the temperature above the frozen temperature of step motion on Si(001) is the origin of the characteristic step shape. [S0163-1829(98)03127-0]

I. INTRODUCTION

There is a great demand for an atomically flat and hydrogen-terminated Si(001) substrate; one of its important applications is pretreatment of Si wafer for gate oxide formation in metal-oxide semiconductor (MOS) devices, which has been shrinking in the recent ultra-large-scale integration technologies. Though wet-chemical treatment is the most convenient method, there are few reports that realized these conditions by wet treatment.[1] Instead, a method of annealing Si wafers in molecular H$_2$ ambient has attracted attention as a technique to obtain an atomically flat and hydrogen-terminated Si surface. Scanning probe microscopy observation has shown that this method can form a flat Si(001) surface with step-and-terrace structures.[2–5] Also infrared-spectroscopy experiments have shown that this process forms monohydride-terminated surface.[5,6] The surface obtained by annealing the Si(001) surface in H$_2$ ambient is apparently similar to the one formed by exposing well-defined Si(001)-2×1 surface to atomic hydrogen flux.[7–9]

However, in the scientific viewpoint, many issues are still in debate. In this paper, we investigated the variation of Si(001) surface by UHV-type scanning-tunneling-microscopy (STM) when a well-ordered Si(001)-2×1 surface is heated and cooled in H$_2$ ambient to reveal the following issues. First we measure the H coverage as a function of H$_2$ partial pressure after the sample is cooled to room temperature (RT). The results are compared with the calculation of the H coverage as functions of H$_2$ partial pressure and substrate temperature, taking into account the recent report on the temperature-dependent sticking coefficient of molecular hydrogen on Si(001). Second, we observe the surface morphology variation at an atomic-scale resolution in order to understand the interaction of the Si(001) surface with H$_2$ molecules such as etching. Also we discuss the origin of the characteristic shape of surface steps; finger-shaped steps are reported on a H$_2$-annealed Si(001) surface.[2] We want to determine whether they are thermodynamically or kinetically stabilized, in conjunction with the limited Si atom diffusion length on H-passivated surface.

II. EXPERIMENTS

Si(001) (*p*-type, 1 Ω cm) wafer was cut to be the size of 1×7 mm^2. The sample was cleaned chemically before loaded into UHV chamber. The clean surface of Si(001)-2×1 is prepared by annealing the sample at 1350 K for 1 min with the pressure below 1×10^{-9} torr during the flashing. After the well-defined Si(001)-2×1 surface is confirmed by STM, the sample was transferred to a preparation chamber. Next, the preparation chamber was filled with H$_2$. The partial pressure of H$_2$ above 1×10^{-3} torr was measured with Pirani gauge, and the pressure below that was measured by ion gauge, which was turned off after the pressure was stabilized. Then the sample was heated by running current through a wafer for 60 sec. After that, the sample was cooled by turning off the current. Finally the H$_2$ was evacuated by a turbo pump to recover the UHV condition.

The elimination of contaminants in H$_2$ gas is a crucial process to get an atomically smooth surface. This might be due to the reaction of oxygen with Si at elevated temperature, which has been shown to etch the surface and make voids on the Si surface.[10] To remove contamination, a cold trap of liquid nitrogen was installed in the gas line, which can trap water vapor and oxygen residual gas effectively.

III. RESULTS AND DISCUSSION

First we show the image of a clean Si(001)-2×1 surface obtained by annealing the surface at 1350 K for 1 min and cooled to RT. The image in Fig. 1(a) is for a large area, which contains straight S_A and zigzag S_B steps. The x-ray diffraction obtained for the sample showed that the normal direction of this wafer is tilted from ideal [001] direction by 0.1°; the terrace width expected from this vicinality agrees well with ones observed in STM images. The high-resolution image obtained in the occupied state is shown in Fig. 1(b). The majority of the surface is covered by symmetric dimers, but the regions near the defects contain $c(2\times4)$ structures. It has been explained that the appearance of $c(2\times4)$ structure is due to the freezing of flipping of buckled dimers near the defects.[11]
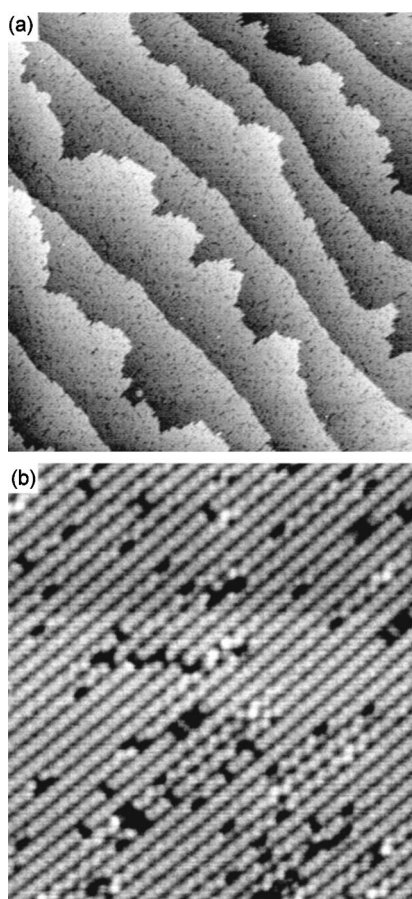
FIG. 1. (a) Occupied state images of a clean Si(001)-2×1 surface taken with sample bias of -1.3 V (area 1060×1150 Å^2). (b) Magnified image of (a) for the area of 185×200 Å^2.

Next we want to describe the variation of the surface after being annealed at 1300 K and cooled to RT in H_2 ambient whose partial pressure is $P(H_2)$. In the condition of $P(H_2) < 10^{-3}$ torr, the surface shows almost no change from the clean surface and it shows well-defined 2×1 structure. When $P(H_2)$ exceeds 10^{-3} torr, changes on the surface can be observed, as shown in Fig. 2(a). The surface is composed of high-density protrusions with 2×1 underneath.

With the increase of $P(H_2)$, the number of protrusions decreases. The surface obtained with $P(H_2)=0.1$ torr shows a very small number of protrusions, whose image taken in the occupied state is shown in Fig. 2(b). At this stage, it can be speculated that the protrusions that are observed on the surface annealed in $P(H_2)=10^{-3}$ torr correspond to the Si dangling bonds (DB's), which are not terminated by H atoms, and the surface after H_2 annealing with $P(H_2) \sim 0.1$ torr is terminated by H almost completely.

High-resolution images of the surface can give useful information of surface termination by hydrogen. Figure 3 shows occupied-state and unoccupied-state images for the surface of Fig. 2(b). Several characteristic features can be observed that cannot be seen on the clean surface. One is the absence of $c(2 \times 4)$ structures in the vicinity of the defects or step edges that are seen on the clean surface image. If we assume the surface is terminated by monohydride, this can be well explained, since the monohydride-terminated Si dimer is symmetric.[7] The other is the existence of protru-
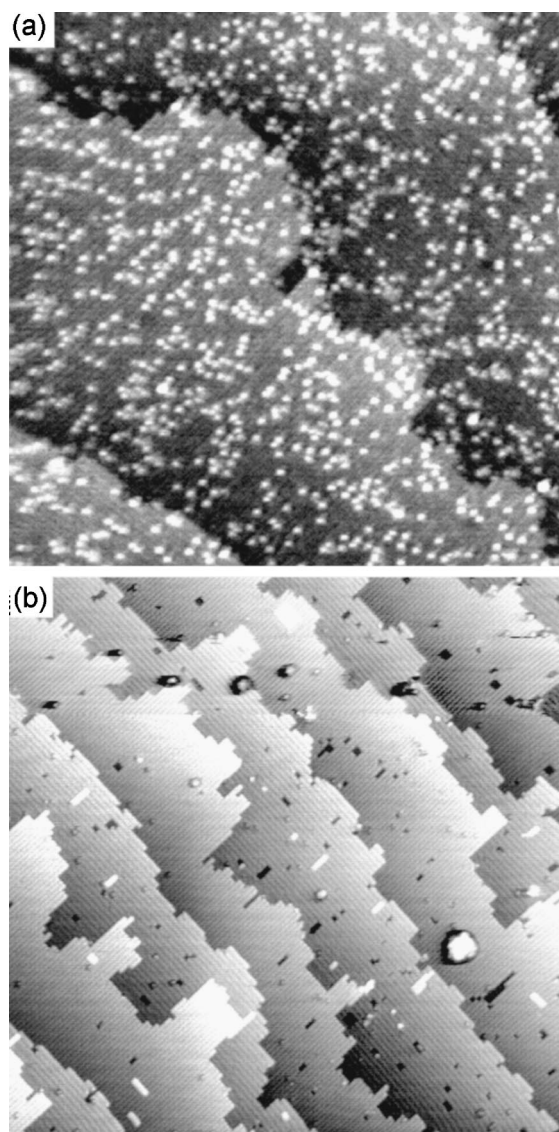

FIG. 2. (a) An occupied state image of the surface after clean Si(001)-2×1 surface is annealed at 1300 K and quenched to RT in H_2 whose pressure $P(H_2)$ is 10^{-3} torr taken with sample bias of -1.3 V (area 815×815 Å^2). (b) Same as (a) except $P(H_2)$ is 0.1 torr (area 1060×1060 Å^2).

sions in the unoccupied-state image that has a gap in the middle, whose node is above the center of the dimer rows. They are marked by arrows in Fig. 3(b). Similar features were reported by Boland for the Si(001)-2×1:H surface obtained by exposing the Si(001)-2×1 surface to atomic hydrogen, which are assigned to DB's of Si, which have π_a^* character and contains a node in the middle.[7,8] This is strong evidence that the surface after H_2 annealing is terminated with monohydride and can be described as a Si(001):2×1-H surface.

More direct evidence of the surface termination by hydrogen can be obtained by the tip-induced H desorption technique, which has been demonstrated by Shen et al.[12] In this experiment, the STM tip is scanned randomly with applying a positive bias of $+3.5$ V to the sample. In Fig. 4, the surface before and after the tip-induced H desorption is shown in (a) and (b), respectively. The image of Fig. 4(b) clearly indicates that the tip-scanned area becomes brighter in the image,
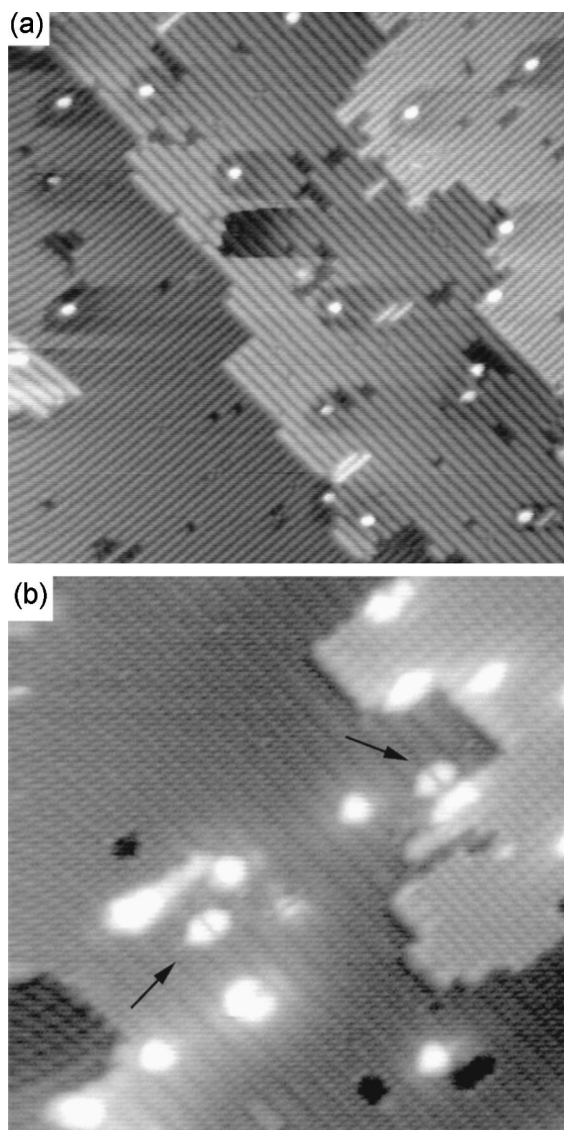
FIG. 3. (a) Magnified image of occupied state images of Fig. 2(b) taken with sample bias of -2.5 V (area 510×510 Å^2). (b) Unoccupied state image of the surface Fig. 2(b) taken with sample bias of 1.9 V for the area of 250×250 Å^2. Characteristic split of protrusions are marked by arrows.

which is ~ 1.4 Å protruded. Also 2×1 structure can be observed in the bright area. This can be explained by the model that Si DB's are recovered and 2×1 structure of bare Si surface is exposed.

So we conclude that the surface after annealing at 1300 K with $P(\mathrm{H}_2) = 0.1$ torr is terminated by monohydride with quite a small density of DB's of Si. Let us point out several intriguing morphological features on this surface.

First, there are linear chains on the terrace with the height of ~ 1.4 Å, which cannot be observed on the clean Si(001) surface. The long perimeters of these chains are perpendicular to the dimer rows, as the chains that can be seen in the initial stage of Si growth of molecular-beam epitaxy (MBE) or chemical-vapor deposition (CVD) at the substrate temperature 600–700 K.[13–15] Also similar chains can be seen when Si is etched by halogens.[16]

They might be assigned as the Si atoms that are etched from the surface and rebonded on the terrace. We reported
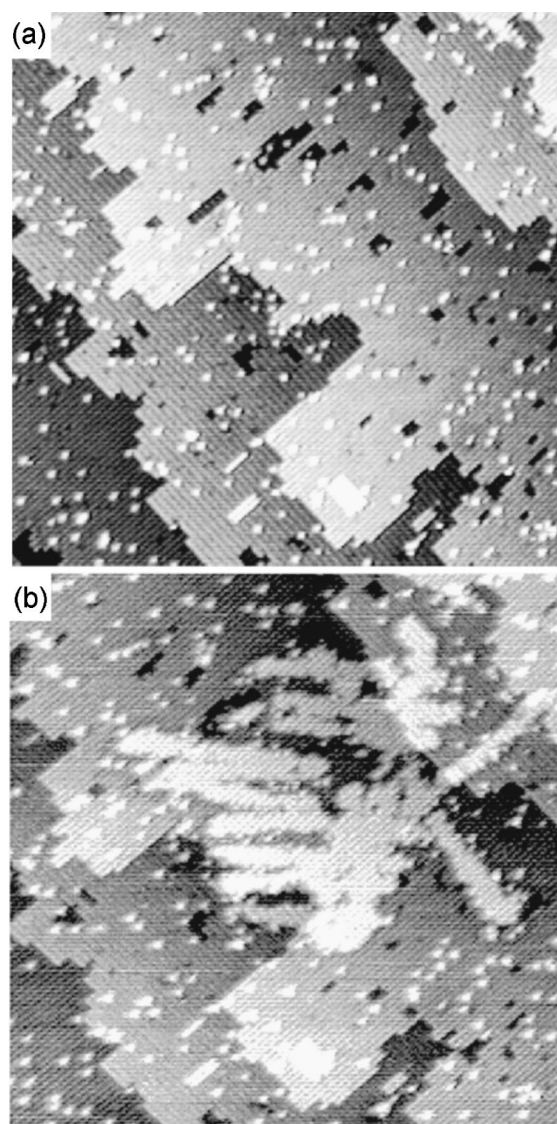
FIG. 4. The variation of the surface of Fig. 2(b) by tip-induced hydrogen desorption. The surface before (a) and after (b) highly biased tip (sample bias of $+3.5$ V) is scanned in the center region of the image are shown for the same area. (area 700×700 Å^2) The white region in the middle of (b) correspond to the area where hydrogen are desorbed and 2×1 structure of bare Si surface recovered which can be observed by dimer rows in this area. Hydrogen is desorbed by tip desorption biased with higher tip voltage of $+3.5$ V.

the etching rate of Si(001) surface by H_2 as a function of substrate temperature previously.[5] The results show, however, the etching rate is pretty small, which is 0.3 Å/min with the $P(\mathrm{H}_2) \sim 23$ torr at 1300 K, and its temperature dependence is proportional to $\exp(-E_{\mathrm{etch}}/kT)$ where $E_{\mathrm{etch}} \sim 1.3$ eV. Expected etched Si is 0.001 ML in case the surface is annealed at 1300 K with $P(\mathrm{H}_2) = 0.1$ torr for 1 min. The etching in the cooling process is negligible. Since the substrate temperature is ~ 1300 K, the migration of Si adatoms is expected to be rapid. So even if the etched Si atoms are rebonded on the Si surface, it is doubtful they form linear chains like the one obtained in MBE growth at the substrate temperature of 600–700 K. Instead, we consider that they are Si atoms that are detached from step edges and migrated on

the terrace in the cooling process.

Second, we note the shape of S_B steps, which shows a significant difference from the one on the clean Si(001). Compared to the clean surface, there can be seen long kinks on the H_2 annealed surface. At the same time, there is a long kink-free portion in S_B steps.

Such behaviors of steps can be understood with the help of statistical analysis. It has been demonstrated by Swartzen-truber *et al.* that the kink energy of steps can be estimated by examining the distribution of kink lengths on a Si(001) surface.[17] They measured the number of kinks of length n dimers [$N(n)$], and $N(n)$ is plotted as a function of n. Under the assumption of independent kinks, $N(n)$ is expected to be proportional to $\exp[-E(n)/kT]$, where $E(n)$ is the energy of a kink of length n dimers. The energy fits the form $E(n) = n\varepsilon + C$, where the ε is a step energy per unit length and C is a constant and effective corner energy.

We apply this analysis for the H_2-annealed surface, comparing with the case of clean Si(001) surface. Figure 5(a) corresponds to the plot of the probability of kinks of length n dimers. As stated above as an increase of kink-free portion of S_B steps, we can observe a higher probability for $N(0)$ that corresponds to the sites without kinks. As a result, the average kink length decreases to 0.76 dimers on the H_2-annealed surface from 1.20 dimers on the clean surface.

In Fig. 5(b), $-\ln[N(n)/2N(0)]$ is plotted for both clean and H_2-annealed surfaces. The data can be fitted by the functional form $E(n) = n\varepsilon + C$. The best-fit parameters for the clean surface and the H_2-annealed surface are as follows: $\varepsilon/kT = 0.90$ (dimer)$^{-1}$ and $C/kT = 0.30$ for the clean surface, $\varepsilon/kT = 0.83$ (dimer)$^{-1}$ and $C/kT = 0.97$ for the H_2-annealed surface with $P(H_2) = 0.1$ torr. Note that C increases significantly for the H_2-annealed surface compared to the one for the clean surface. This might indicate that the corner energy of kinks on the H-passivated surface is higher than the one on the clean surface.

The expected total amount of etched Si, ~ 0.001 ML, is apparently too small to account for the difference of the shape of step edges for the H_2-annealed surface. At this stage, we speculate that it corresponds to the energetically favored shape of steps instead of the trace of the etching by H_2.

To further examine the etching effect on the step shape, we anneal the surface for an elongated time at lower temperature. The surface shown in Fig. 6 corresponds to the one annealed in $P(H_2) = 0.1$ torr at 900 K for 10 min. We can see higher density of linear chains grown in the direction perpendicular to the dimer row. However, at this temperature region, the etching of the Si surface can be neglected.

So it is highly possible that Si chains are originated from the Si atoms detached from step edges and trapped in the middle of the terrace while they are migrating on the terrace. Since such chains are not detectable on the clean surface, there should be some mechanism in the H_2 annealing that enhances the formation of chains. One possibility is the enhancement of the detaching rate of Si atoms from the step edges due to the weakening of backbonds of Si in the presence of passivating H atoms.[18,19] Due to the enhanced detaching rate, the migrating Si atoms can form stable chains in the middle of terraces. The other possibility is the reduced diffusion length in the presence of passivating H atoms on
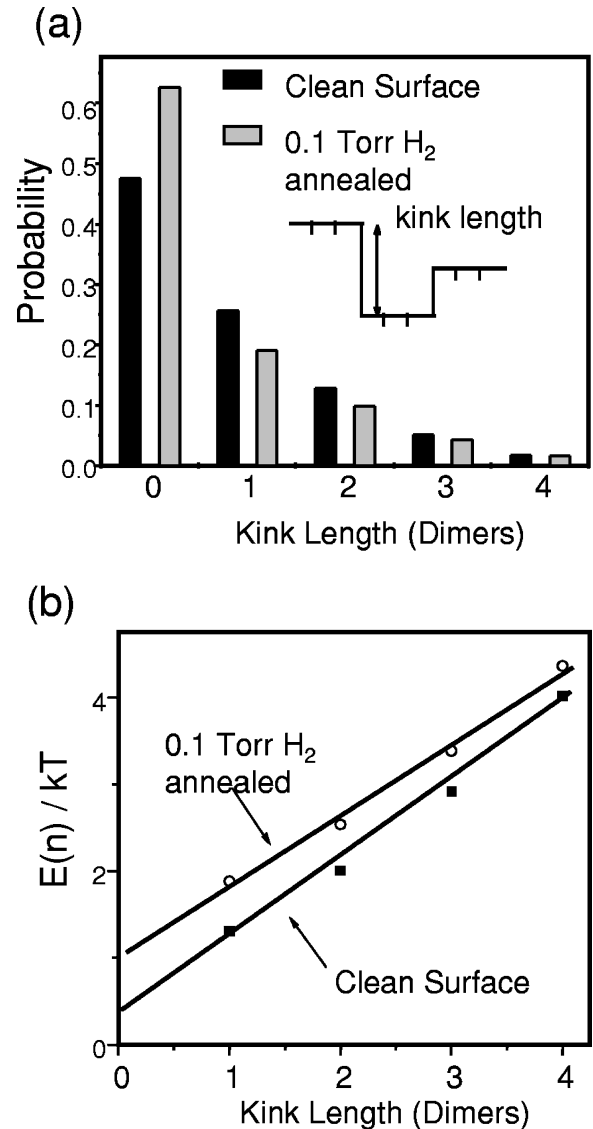

FIG. 5. (a) Measured probability of appearance of kinks of length n dimers vs n, comparing the cases of clean surface and H_2 annealed surface with $P(H_2) = 0.1$ torr. The value at $n = 0$ is the number of sites at which there is no kink. Inset: Schematic picture of a typical step showing direction of kink length, which is perpendicular to the nominal step direction. (b) The measured energy of a kink of length n dimers analyzed from the data of (a) for clean and H_2 annealed surfaces. The line is a fit by the form $E(n) = n\varepsilon + C$.

the surface. The decrease of the diffusion length might prohibit the migrating Si atoms reach step edges. Actually the limited diffusion length of Si atoms on the H-passivated Si(001) has been proposed to explain why long Si chains are not formed in CVD growth.[16,17] We will discuss later the possibility of the H passivation at the temperatures where step edges are mobile.

The surface that is exposed to higher partial pressure of H_2 during the annealing is shown in Fig. 7, where the surface is annealed for 1 min with $P(H_2) = 10$ torr. The surface shows many protrusions on the terrace, together with high density defects. It is unlikely that these protrusions are originated from Si DB's that are not terminated by H, because the partial pressure of H_2 is ~ 100 times higher than the one of Fig. 2. Instead, these are rebonded Si or SiH$_x$ species that do
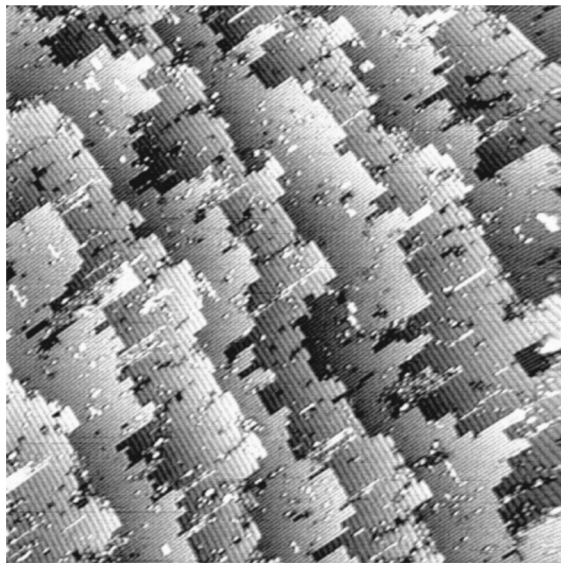
FIG. 6. Occupied state image of the surface which is annealed in $P(H_2)=0.1$ torr for 10 min at the substrate temperature of 900 K. The image is taken with the sample bias of -1.5 V (area 1060 $\times 1060$ Å^2).

not form ordered structures like linear chains. The latter idea is confirmed by a tip-induced H-desorption method, which is described in the previous section; if the protrusions are rebonded SiH$_x$ species, then these sites remain protruded even after hydrogen is desorbed from the neighbors.

The defect density on the terrace is much higher than the one obtained with $P(H_2)=0.1$ torr. The defects are most probably formed by the etching of the terrace by H$_2$. Though the actual defect density is much smaller than the expected amount of etched Si, ~ 0.14 ML, it can be explained by the rapid migration of defects at high temperature to heal the defects.

In spite of the trace of large etching on the terrace, the averaged kink length is identical with that of Fig. 2(b), 0.79
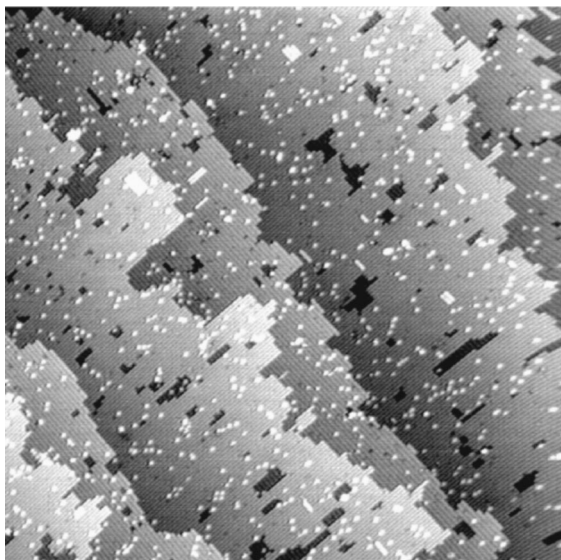

FIG. 7. Occupied state images of the surface after Si(001)-2 $\times 1$ surface is exposed to $P(H_2)=10$ torr taken with sample bias of -1.5 V (area 1250$\times$1250 Å^2).

dimers. This shows a clear contrast to etching of the Si(001) surface by halogens of Cl and Br, where the averaged kink length of the S_B step increases as a function of the halogen exposure time. This supports the idea that the shape of steps edges obtained in this experiment is not determined by the etching of Si atoms, but is a stable configuration for a monohydride-terminated Si(001)-2$\times$1 surface.

Now we want to estimate the H coverage as functions of $P(H_2)$ and substrate temperature in the process of cooling the Si surface from 1300 K in H$_2$ ambient. This is intended to evaluate the effect of H passivation on the Si atom diffusion.

The hydrogen coverage on the Si surface is the balance between the rate of adsorption and desorption of the hydrogen on Si surfaces. So we need the parameters both for desorption and adsorption of hydrogen on the Si(001) surface. For the desorption parameters, we can find many reports on the kinetics of the desorption of the hydrogen-terminated Si(001) surface. For the adsorption parameters, on the other hand, we found only a couple of reports that measured the sticking coefficient of molecular hydrogen on Si(001) surface as a function of the substrate temperature. Kolasinski et al. reported in detail on the sticking coefficient of the molecular hydrogen as functions of the substrate and the gas-nozzle temperature for the substrate temperature range between 300 and 1500 K.[20]

We want to note that the increase of the sticking coefficient is observed with the increase of the substrate temperature.[20] This is a unique phenomenon on the Si surface, which cannot be seen on metal surfaces. The role of surface vibrations for the dissociation of molecular hydrogen has been discussed. This might be a very important mechanism for H passivation by annealing the Si(001) surface in H$_2$ ambient. Hereafter, we estimate the H coverage based on the sticking coefficient reported in the paper.

The time derivative of hydrogen coverage (θ) can be described as follows:

$$\frac{d\theta}{dt} = R_{\text{ads}} - R_{\text{des}},$$

where R_{ads} and R_{des} indicate the rate of adsorption and desorption, respectively.

The rate of adsorption can be expressed with the following formula:

$$R_{\text{ads}} = S_0(T_s, T_g) f[\theta(t)] F.$$

$S_0(T_s)$ indicates the temperature-dependent sticking coefficient where T_s and T_g are the substrate and gas temperature, respectively. The $f[\theta(t)]$ term corresponds to coverage dependence of the adsorption rate, which can be expressed as $1-\theta$ with the most simple form. F corresponds to the flux of impinging H$_2$ molecules.

Kolasiniski reported a temperature-dependent sticking coefficient with the use of the error function, which is given in the following formula:[20]

$$S_0(T_s) = S_1 + \frac{S_2(T_s)}{2}\left[1 + \text{erf}\left(\frac{E_{\text{tot}} - E_{\text{barrier}}}{W_{\text{barrier}}}\right)\right],$$

$$S_2(T_s) = \frac{A}{2}\left[1 + \text{erf}\left(\frac{kT - E_a}{W_a}\right)\right],$$
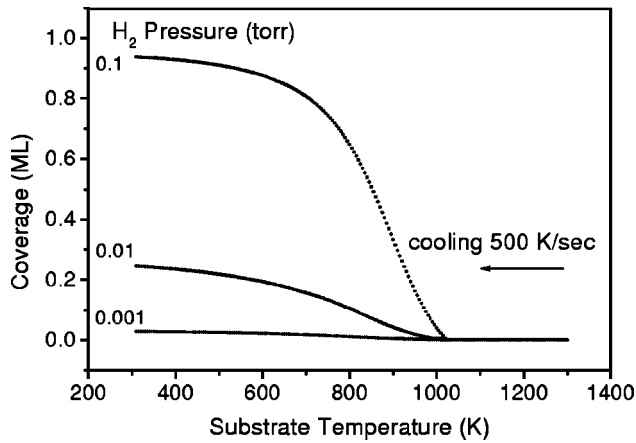
FIG. 8. Calculated hydrogen coverage as a function of a substrate temperature with various H_2 partial pressures. The sample is assumed to be cooled from 1300 K to RT within 2 sec (temperature drop of 500 K/sec). The sticking coefficient of molecular H_2 as a function of Si(001) substrate temperature is after Kolasinski (Ref. 20).

where s_1 corresponds to the background; the parameters are assigned as follows: $s_1 = 5 \times 10^{-7}$, $A = 1$, $E_a = 0.32$ eV, $W_a = 0.12$ eV, $E_{tot} = 0.09$ eV, $E_{barrier} = 1.0$ eV, $W_{barrier} = 0.06$ eV.[20]

The desorption rate can be expressed by the following formula:

$$R_{des} = \theta(t)^n A_d \exp\left(-\frac{E_d}{k_B T}\right),$$

where n is the reaction order, and A_d is the Arrhenius prefactor, E_d is the desorption activation energy, and k_B is Boltzmann's constant.

The desorption rate, on the other hand, has been studied in detail. Sinniah reported the analysis of first-order desorption ($n=1$) with the Arrhenius prefactor and the desorption activation energy of 5.5×10^{11} and 1.98 eV, respectively.[21]

Based on the equations and parameters stated above, the hydrogen coverage is calculated assuming the Si wafer at 1300 K is cooled to RT with the rate of 500 K/s in the H_2 ambient with the partial pressure of $P(H_2)$. The results calculated for the partial pressure of $P(H_2) = 10^{-3}$, 10^{-2}, and 0.1 torr are shown in Fig. 8. The coverage is practically zero for the substrate temperature above 1000 K for all H_2 partial pressure. When the substrate is cooled below ~ 1000 K, increase of the coverage can be seen. The coverage gradually increases with the lowering of the substrate temperature, and it reaches ~ 1 for the case of $P(H_2) = 0.1$ torr.

The hydrogen coverage as a function of the H_2 partial pressure can be compared with the STM observation stated above. The surface obtained with $P(H_2) = 0.1$ torr shows monohydrite-terminated surface with very small Si DB's. This is consistent with the expected coverage of ~ 1 in Fig. 8. In addition, the hydrogen termination is observed for $P(H_2)$ above 10^{-3} torr by STM, while the results in Fig. 8 show $\theta \sim 0.03$ for $P(H_2) \sim 10^{-3}$ torr, which increases rapidly to $\theta \sim 0.25$ with $P(H_2) \sim 0.01$ torr. We believe this estimation reproduces the variation of the hydrogen coverage quite well.

Using the temperature-dependent coverage curve in Fig. 8, we can discuss the effect of the surface termination by

hydrogen on the Si atom diffusion and step motion. The surface is free from hydrogen above 1000 K, and the increase of the H coverage can be seen below this temperature.

The majority of etching should occur at the high substrate temperature, ~ 1300 K, since the etching decreases rapidly with lowering the substrate temperature. In this temperature range, the surface is free from hydrogen passivation. The migration of defects on the terrace is as active as the one on the clean surface.

On the other hand, step motion is not frozen until the surface is cooled to 600–700 K with the cooling rate of this experiment.[22] The onset temperature of the hydrogen passivation, ~ 1000 K, is much higher than the frozen temperature of the step motion. This implies that the characteristic structures of the S_B step are formed in the presence of H passivation, which is a stable configuration for monohydride-terminated Si(001).

In addition to the step motion, the detachment of Si atoms from step edges and migration on the terrace can be expected. On the clean surface, it is considered they reach to the neighboring step edges and attach to them. However, the diffusion length of Si atoms decreases when the surface is terminated by H compared to the case of clean Si surface. The decreased diffusion rate can assist the nucleation of Si in the middle of the terrace. The high density of chains obtained by elongated annealing at the temperature ~ 1000 K may be formed by such mechanism.

IV. SUMMARY

As a summary, we have investigated the variation of the Si(001) surface when exposed to molecular H_2 at elevated temperature. The Si(001) surface is annealed at 1300 K and cooled to RT in H_2 ambient with partial pressure of $P(H_2)$. When $P(H_2)$ exceeds 10^{-3} torr, hydrogen termination of the surface starts. The surface obtained with $P(H_2) = 0.1$ torr shows monohydride terminated surface with very small density of DB's of Si atoms, whose atomic structures are equivalent with the one obtained by exposing the Si(001) surface to atomic hydrogen. Characteristic step structure can be seen in S_B steps, which has a long kink-free portion compared with the one for a clean Si(001) surface. The statistical analysis of S_B steps revealed large averaged kink separation and small average kink length, which corresponds to a high corner energy of kinks. The variation of hydrogen coverage in the process of cooling from 1300 K to RT is simulated based on the sticking coefficient of molecular hydrogen on the Si(001) surface at elevated temperature reported by Kolasiniski et al. The results show that the hydrogen coverage (θ) is ~ 0.03 for $P(H_2) \sim 10^{-3}$ torr and $\theta \sim 0.93$ for $P(H_2) \sim 0.1$ torr, after the sample is cooled to RT. We believe this estimation reproduces the variation of the hydrogen coverage well. In addition, the increase of the θ starts when the sample is cooled below 1000 K. We note that this temperature is above the reported freezing temperature of step motion of Si(001) and the shape of step edges should be formed in the presence of H termination. Since the shape of S_B step edge does not show significant change with the increase of the etching rate of Si by H_2, the step-edge shape is considered to be thermodynamically stable step configuration for monohydride terminated Si(001) surface.

*Electronic address: komeda@trdc.ti.com

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