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| Description | |

Sum frequency generation spectroscopy study of hydrogenated stepped Si(111) surfaces made by molecular hydrogen exposure

K.T.T. Hien¹, M.A Sattar¹, Y. Miyauchi², G. Mizutani¹, H.N. Rutt³

¹ School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

² Department of Physics, National Academy of Japan, Hashirimizu 1-10-20, Yokosuka, Kanagawa 239-8686, Japan

³ School of Electronics and Computer Science, University of Southampton, Southampton SO17 1BJ, U.K.

Contact email: ktt-hien@jaist.ac.jp

ABSTRACT

Hydrogen adsorption on stepped Si(111) surfaces 9.5° miscut in the $[\bar{1}\bar{1}2]$ direction has been investigated *in situ* in a UHV chamber with a base pressure of $\sim 10^{-8}$ Pa. The H-Si(111)1x1 surface was prepared by exposing the wafer to ultra-pure hydrogen gas at a pressure of ~ 470 Pa. Termination of hydrogen on terraces and steps was observed by sum frequency generation (SFG) with several polarization combinations such as *ppp*, *ssp*, *pps*, *spp*, *psp*, *sps*, *pss* and *sss*. Here the 1st, 2nd and 3rd symbols indicate SFG, visible and IR polarizations, respectively. *ppp* and *ssp*-SFG clearly showed only two modes: the Si-H stretching vibration terrace mode at 2082 cm⁻¹ (A) and the vertical step dihydride vibration mode at 2094 cm⁻¹ (C₁). Interesting points are the appearance of the C₁ mode in contrast to the previous SFG spectrum of the H-Si(111)1x1 surface with the same miscut surface angle prepared by wet chemical etching. We suggest that the **formation of step dihydride and its orientation on the Si(111)** stepped surfaces depend strongly on the preparation method.

Keywords: Sum frequency generation, vibration, hydrogen dosing, wet chemical etching.

1. INTRODUCTION

Increasingly flat H-Si(111) surfaces have been used as effective substrates for modern devices and sensors technology [1,2]. Before fabricating ultrathin films, hydrogen is used to terminate the silicon surfaces. Therefore, how the hydrogen adsorbs and how uniform the adsorption is are very important in order to secure the quality of the ultrathin films. In general, Si surfaces are terminated with hydrogen by either wet chemical etching [3-5] or hydrogen exposure [6-9]. Because of the different termination mechanisms, each of them has advantages and disadvantages. Although wet chemical etching was believed to be a good method to make atomically flat Si surfaces with one monolayer (1ML) of hydrogen, the surface structure still shows species other than monohydride ($\equiv\text{SiH}$), such as dihydride ($=\text{SiH}_2$) and trihydride ($-\text{SiH}_3$) [10]. Wet chemical etching becomes much more complicated on stepped Si surfaces [4]. Namely, the pH of the etching solution and the effect of oxygen are critical in order to control the hydrogen adsorption at defects and kinks. Therefore, the problem of etching becomes complicated on the step Si surfaces and how the hydride is terminated on the step becomes very important.

The vicinal Si(111) surfaces with some miscut angles are the ideal case to study the nature of defects and steps. In this research, step structures and dihydride orientation on vicinal Si(111) surfaces with 9.5° miscut angle toward $[\bar{1}\bar{1}2]$ direction are studied with hydrogen molecular

adsorption in a UHV chamber with negligible influence from water. Here we note that stepped Si(111) are promising substrates for quantum dots and nanowires growth due to their active sites, and they are worth characterizing [11,12].

The detailed structure of Si(111) surfaces with a miscut angle of 9.5° toward $[\bar{1}\bar{1}2]$ direction was described by other groups [5, 13]. Jakob and Chabal suggested that single steps exist with an atomic step height of 3.4 \AA and a terrace width of 18.86 \AA . If hydrogen was terminated on this surface, the dihydride $=\text{SiH}_2$ could lie in a plane parallel or perpendicular to the step edge, but it prefers to lie in a perpendicular plane as shown as red dotted lines in Fig. 1 because of the lowest surface energy [5]. Figure 1a and 1b show two suggested possible in-plane rotations of clockwise and anticlockwise directions compared to the original position of red dotted dihydride set. The rotation angle α or β equals 0 degree when the Si-H_C lies in the $[557]$ direction. The relaxation of the dihydride-terminated step can cause a number of possible distortions. Raghavachari *et al.* suggested that the dihydride was distorted in the plane or out-of-plane of H_C and H_B [14]. Several researchers reported different twisted and titled angles of this dihydride by different investigation methods [15]. This difference may depend on the preparation methods. IR spectra of the vicinal H-Si(111) surface [5], etched by wet chemical solutions, with multi reflection geometry showed clearly the step modes, but surface Raman showed rather weak step mode peaks [16], especially for the vertical dihydride mode. The SFG spectrum by Morin could not even detect the vertical dihydride mode, and the other step modes were weak [13]. Until now, nobody reported step hydrogen termination by hydrogen exposure in a UHV chamber, and thus the corresponding hydrogen adsorption on the step area has not yet been well understood.

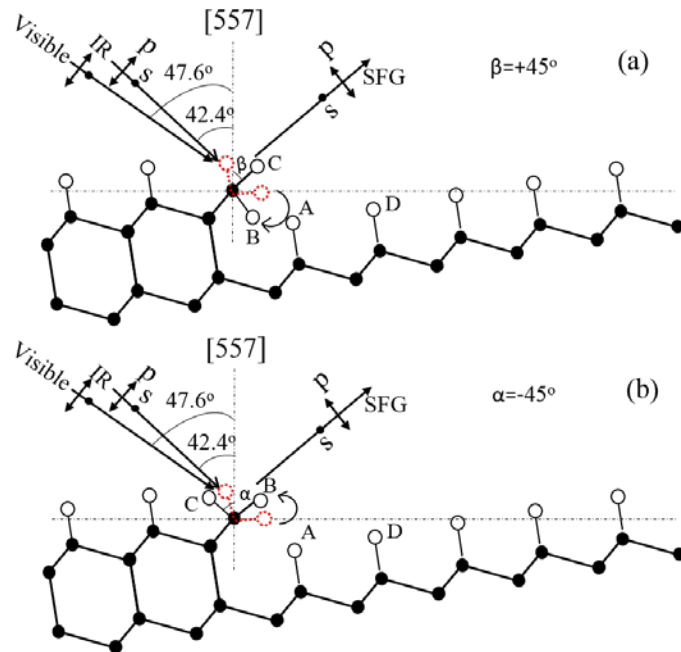


Fig.1: Side view of the hydrogenated single step of the Si(111) surface with 9.5° miscut angle toward $[\bar{1}\bar{1}2]$ direction. Configuration of incident lights and SFG observation direction: (a) the dihydride rotated in-plane from the red dotted line position in the clockwise direction, (b) the dihydride rotated in-plane from the red dotted line position in the anticlockwise direction.

Recently, the structure of this vicinal Si(111) surface (or Si(557) surface) has been clearly observed by STM and LEED [17-19]. They proved that there are mixture of single and triple steps on the surface. The number of triple steps increases when the miscut angle increases. Jian *et al.* [20] indicated that the proportion of triple steps was 71% for a 6.4 ± 0.6 degree miscut angle. Therefore, triple steps are considered to dominate on the 9.5° miscut angle surface. The atomic surface structure of this Si(557) surface was suggested by Prevot *et al.* [21] and clearly seen by STM images by Teys [22] with the periodic terrace width of 53.3 Å and step high of $3d_{111}$ corresponding to triple steps.

In order to clarify the surface atomic structure and formation of dihydride on steps, in this research, vicinal Si(111) surfaces with 9.5° miscut angle in the $[\bar{1}\bar{1}2]$ direction are terminated by molecular hydrogen exposure in a UHV chamber. The step hydrogen termination is investigated by observing SFG spectra with several polarization combinations. Second order nonlinear spectroscopy has the advantage that it is only sensitive to one monolayer depth of the adsorbates. Therefore, the observed SFG signal contains information on adsorbed Si-H molecules only. The polarization dependence of the SFG spectra can clarify the Si-H bond orientation on the surface.

2. EXPERIMENTAL

The vicinal Si(111) substrate (n-doped by phosphorus manufactured by CrysTec) of dimensions $20 \times 2 \times 0.1 \text{ mm}^3$ with a resistivity of $\sim 10 \text{ } \Omega \cdot \text{cm}$ was used as the sample. First of all, it was cleaned with acetone for 10 min in an ultrasonic bath, then was introduced in a special holder in a UHV chamber. This sample in the holder was first connected to high voltage source to reduce the resistivity and then was switched to the possibly high current source in order to heat at high temperature. The chamber was baked at 150°C for a week and the best pressure reached $\sim 1.0 \times 10^{-8} \text{ Pa}$. After baking the chamber, the amount of nitrogen gas, water and some other gases were obtained by quadrupole mass analyzer. The existence of these gases were too small so that they can be neglected. The pump valve of a UHV chamber was closed in 10 min and the released contamination's pressure was measured as $\sim 1.3 \times 10^{-6} \text{ Pa}$. Before hydrogen exposure, it was necessary to make the Si(111) 7×7 reconstruction by flashing the substrate at 1100°C several times and the total flashing time was 60 s. Then it was kept at $\sim 600^\circ \text{C}$. During this heating, hydrogen molecules (99.99995 % produced by Takachiho Chemical Industrial Co. Ltd) were passed through a 20 m length of a steel tube coil cooled down in liquid nitrogen to filter out contamination, especially water, filling a UHV chamber to a pressure of $\sim 470 \text{ Pa}$ ($\sim 3.5 \text{ Torr}$). This was kept for 10 min during which the amount of released gas pressure of $\sim 10^{-6} \text{ Pa}$ was $\sim 10^8$ times smaller than that of the hydrogen gas and was negligible. This surface temperature of 600°C was higher than the hydrogen desorption temperature of $\sim 500^\circ \text{C}$. The hydrogen adsorption still happened because of high pressure of hydrogen molecules. In this condition, the adsorption is much more efficient than the desorption. After that, the residual hydrogen molecules were removed from the UHV chamber and the surface was cooled down to room temperature. 1×1 surface structure was constructed after hydrogen exposure. The 7×7 and 1×1 structures were observed clearly in the LEED patterns before and after the hydrogen exposure as shown in Fig. 2 to 4. The detailed description of LEED patterns will be discussed on the next section. The strong point of this experiment is that there was no effect of contamination and water molecules on the adsorption process of hydrogen on the Si surface.

The optical setup was shown in our previous report [23]. As the incident visible light, we used a second harmonic light of 2.33 eV (0.532 μm , second harmonic) of the fundamental light of 1.17 eV (1.064 μm) from a mode-locked Nd^{3+} :YAG laser with a pulse width of 30 ps and repetition rate of 10 Hz. As the incident energy-tunable IR light, the output from an optical parametric generator and amplifier system (OPG/OPA) with photon energy of ~ 0.26 eV was used. The incident angles of the visible and IR light were 47.6° and 42.4° , respectively. With changing the polarizations of the SFG, visible, and IR light beams either *s* or *p*, the SFG spectra with different polarization combinations were obtained with the IR light wave number from 2060 cm^{-1} to 2140 cm^{-1} with a scanning step of 1 cm^{-1} . For each SFG data point, the measurement took $\sim 30\text{ s}$. Therefore, the acquisition time for one SFG spectrum was $\sim 40\text{ min}$. The typical photon count rate at the SFG peak was ~ 10 photons per second.

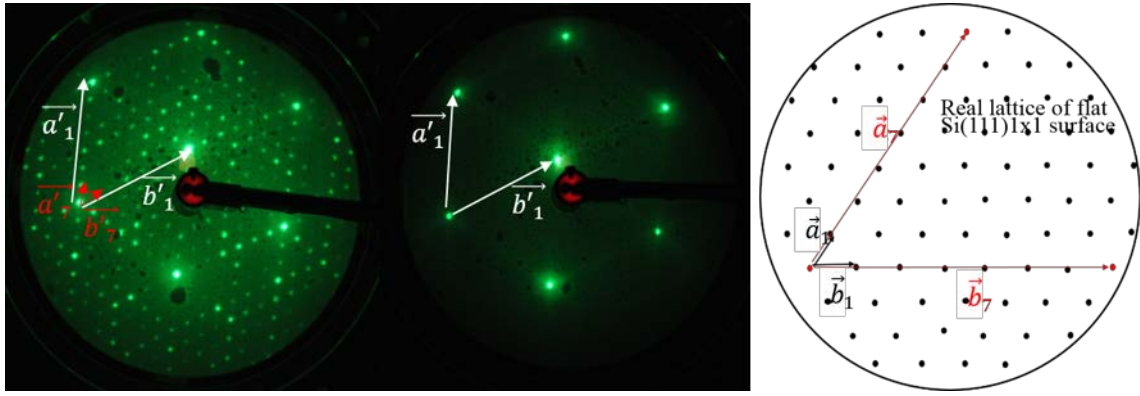


Fig. 2: LEED patterns of the flat Si(111) surface; 7×7 and 1×1 surface structures are seen before and after hydrogen exposure in the left and right figure with the same electron beam energy of 45eV, respectively; the top view of the real lattice of the flat Si(111) 1×1 surface with the unit cell size (a_1, b_1), the 7×7 structure is identified with unit cell size ($a_7=7a_1, b_7=7b_1$).

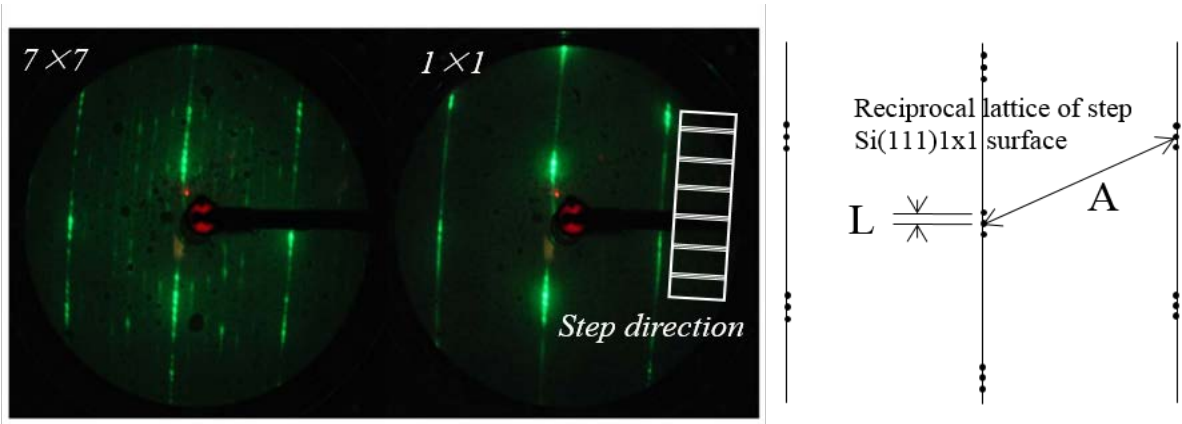


Fig. 3: LEED patterns of the **5-steps bunched** Si(111) surface with 9.45° miscut toward $[\bar{1}\bar{1}2]$ direction corresponding to the step direction as shown in the inset figure; 7×7 and 1×1 surface structures are seen before and after hydrogen exposure in the left and right figure with the same electron beam energy of 45eV, respectively. On the right, the reciprocal lattice of step Si surface is shown.

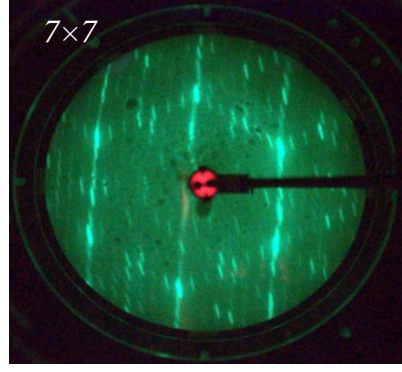


Fig. 4: LEED pattern of the 7×7 surface structure of the *large bunched step* Si(111) surface with 9.45° miscut toward $[\bar{1}\bar{1}2]$ direction. The terrace width is $\sim 6\text{-}8\ \mu\text{m}$.

3. RESULTS AND DISCUSSION

Before discussion of the main results on the vicinal step H-Si(111) surface, we review the LEED patterns and SFG spectrum of the flat H-Si(111) surface. Note that in our experiment, all the hydrogenation was done by hydrogen exposure in a UHV chamber. Figure 2 shows the LEED patterns of 7×7 and 1×1 structures of the flat Si surface taken at the same electron beam energy of 45 eV. Each bright spot represents one lattice point in the reciprocal lattice. In the real lattice as shown on the right hand side, the 7×7 unit cell is seven time larger than the 1×1 unit cell ($a_7=7a_1$, $b_7=7b_1$). In the reciprocal lattice, the sizes of the two unit cells are inverse as seen as the bright spots in the 7×7 LEED pattern ($a'_7=1/7a_1$, $b'_7=1/7b_1$).

Corresponding to the 1×1 structure in Fig. 2, the *ssp*-SFG spectrum of a flat H-Si(111) 1×1 surface previously observed by our group is shown in Fig. 5 [23]. The black dots are experimental results and the solid curve is a Gaussian fitting curve. Only one peak is observed at 2084.4 cm^{-1} attributed to the stretching vibration of monohydride Si-H. This result matches the literature [24-25].

The LEED patterns of the vicinal step Si(111) surface (main sample in this research) before and after the hydrogen exposure as described in the experimental section are shown in Fig. 3 dominated by 7×7 and 1×1 structures, respectively. In contrast with the LEED patterns of the flat surface in the Fig. 2, extra bright spots around the main six brightest ones appear in line due to the step. The distance between the spots corresponds to the terrace length in the real lattice. The right hand side shows the description of the 1×1 LEED pattern. From the measured L and A, the real terrace length is calculated as $\sim 135.68 \pm 35\text{ \AA}$. This value is 5~7 times larger than the regular terrace length $\sim 18.86\text{ \AA}$ of the (111) surface with 9.5° miscut angle as mentioned in previous section, or 2.5 times larger than the terrace width of triple steps of 53.3 \AA . Therefore, after the flash heating at 1100°C , the surface has 5 to 7 bunched steps, so we call it 5-steps bunched H-Si(111) surface. This result is consistent with the report of Hibino *et al.* [26]. They said that the step bunches could happen even for 20 s of flashing at over 1000°C .

After confirmation of 1×1 structures meaning that hydrogen adsorbed by one monolayer on the surface, the SFG spectra were obtained with different polarization combinations of *ppp*, *ssp*, *pps*, *spp*, *psp*, *sps*, *pss* and *sss* as shown in Fig. 6. Here the 1st, 2nd and 3rd symbols indicate SFG, visible and IR polarizations, respectively. Most of the spectra do not show any vibrational mode except *ppp*, *ssp*, *psp* and *spp* polarizations. The *ppp*-SFG and *ssp*-SFG spectra show two clear peaks at 2082 cm^{-1} (A) and 2094 cm^{-1} (C₁). The SFG with *psp* polarization also shows these two peaks but the intensities are weak compared to *ssp* polarization. The peaks of SFG spectra for *pps*, *pss*, *sps*, and *sss* polarization combinations are weak because the infrared polarization

(s-polarization) is perpendicular to the Si-H bond. The peaks for *psp* and *spp* are weak because the combinations of the SFG and visible polarizations correspond to the off-diagonal Raman tensor elements. The A and C_1 peaks may be stronger for *psp* (Fig. 6(c)) than for *spp* (Fig. 6(f)) because the emission efficiency of the SFG light with p-polarization is bigger due to the Brewster effect. The black dots are the experimental SFG data. Two solid curves in Fig. 6(a) and (e) are fitted curves. The A peak at 2082 cm^{-1} is attributed to the terrace vibrational stretching monohydride as it is consistent with that in IR [4,5,27], Raman [16], other SFG spectra [13,28,29] of the vicinal Si surface, and also the flat Si surface shown in Fig. 5 [23]. The C_1 peak at 2094 cm^{-1} is attributed to isolated SiH_C of step dihydride and has never been reported in SFG spectra. This could be formed on the 5-steps bunched Si surface only, not on the large bunched step Si surface (Fig. 7). The 5-steps bunched Si surface was formed after flash heating at high temperature of 1100°C in 60 s as described in the experimental section. The large bunched step surface was formed after heating at the same temperature of 1100°C for a longer time of 18 hours in a UHV chamber. The wide terrace length of $6\text{--}8\text{ }\mu\text{m}$ ($3181 \sim 4241$ steps) was measured by AFM.

Figs. 4 and 7 show the LEED patterns and *spp*-SFG spectrum of the large bunched step H-Si(111) 1×1 surface with 9.5° miscut toward $[\bar{1}\bar{1}2]$ direction, respectively. Because of a large number of step bunches, each extra bright spot is streaky in Fig. 4 and not in a round shape of the 5-steps bunched surface in Fig. 3. The uniquely fitted SFG peak is at 2083.5 cm^{-1} and no other step mode is detected (Fig.7). Although we have not yet made the final interpretation of the unobservable C_1 mode in the large bunched step surface, we would like to suggest that it might be due to the difference of the number density of dihydrides between the large bunched step and 5-steps bunched surfaces. If we assume that the dihydrides exist only at the top edge of each bunch of steps, the number density of dihydrides of the large bunched step surface is around 60 times smaller than that of the 5-steps bunched surface. In that case, the intensity of dihydride is much weaker for the large bunched step surface than for the 5-steps bunched one. However, there has been no evidence about our above assumption. In this paper, we will only focus our attention on the 5-steps bunched surface. These experimental results are very highly reproducible so that we believe that the C_1 mode is really observed.

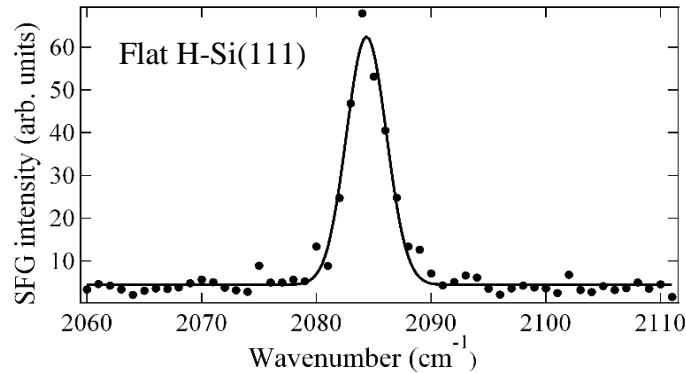


Fig. 5: SFG spectra of the flat H-Si(111) surface with the polarization combinations of *spp* (corresponding to 1×1 LEED pattern in the Fig. 2). The dots are the experimental SFG, and the solid curve is the Gaussian fitting. The fitted peak is at 2084.4 cm^{-1} .

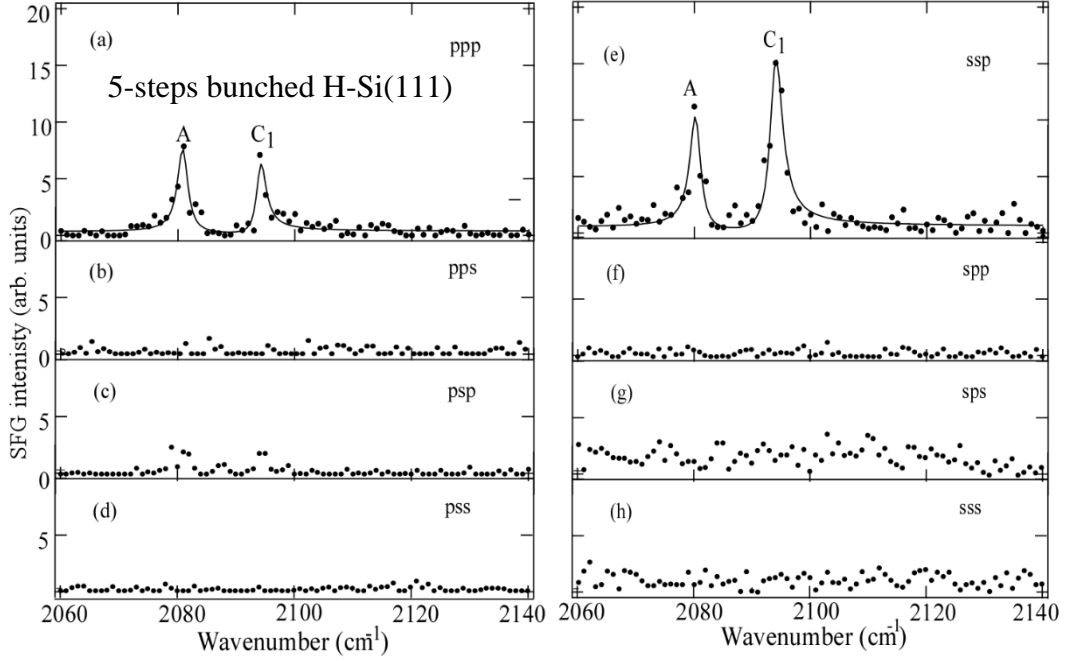


Fig. 6: SFG spectra of the 5-steps bunched H-Si(111) surface with 9.5° miscut toward $[\bar{1}\bar{1}2]$ direction with the polarization combinations of ppp, ssp, pps, spp, psp, sps, pss and sss. The dots are the experimental SFG, and the two solid curves are the Gaussian fitting. The fitted peaks are 2082 cm^{-1} and 2094 cm^{-1} .

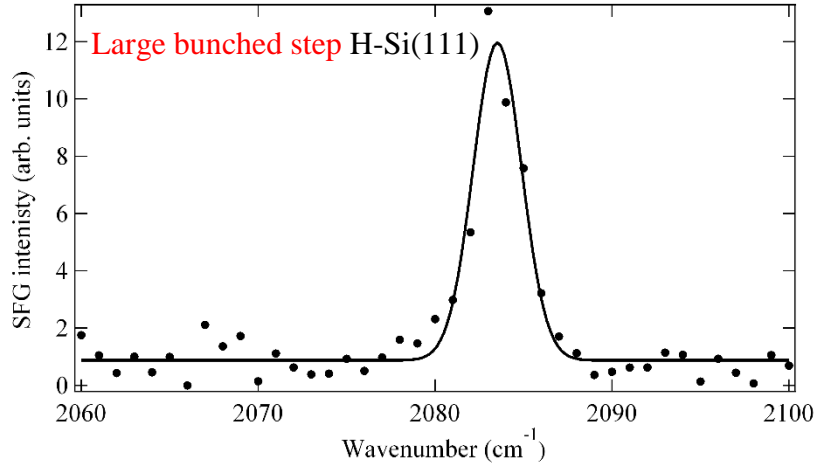


Fig. 7: SFG spectra of the **large bunched step** H-Si(111) surface with 9.5° miscut toward $[\bar{1}\bar{1}2]$ direction with the polarization combinations of ssp. The heating temperature was 1100°C during 18 hours. The terrace length was $6\text{--}8\text{ }\mu\text{m}$. The dots are the experimental SFG, and the solid curve is the Gaussian fitting. The fitted peak is at 2083.5 cm^{-1} .

We will compare our SFG spectra with the literature using a different sample preparation method, i.e wet chemical etching. Morin and his coworkers fabricated a vicinal

H-Si(111) surface with 9° miscut angle toward $[\bar{1}\bar{1}2]$ direction by etching in buffered HF and Shiraki solution, and finally it was rinsed by deionized water [13]. They took the SFG spectrum of this surface and found three vibrational modes. One was the terrace mode A, and the other two step modes were C_2 at 2101.3 cm^{-1} and C_3 at 2134.7 cm^{-1} . Until now, the maximum number of observable peaks on this vicinal surface is four: A, C_1 , C_2 and C_3 . They were usually observed simultaneously in IR spectroscopy [5,13]. C_2 and C_3 are the frequencies of the in-phase and out-of-phase vibrations of step SiH_B and SiH_A on the lower terrace (see Fig. 1) [5]. These two peaks' intensities were lower for the lower step density surfaces. The intensity reduced for the SFG spectrum of 9° and disappeared on that of 5° miscut angles [13]. In our spectra, these two C_2 and C_3 peaks could not be observed and it might be due to step bunches. An interesting point here is that C_1 peak corresponding to the step mode was not observed by Morin, while it was clearly seen in our *ppp* and *ssp* SFG spectra in Fig. 6. Although Morin said that this C_1 mode could not be observed due to its small Raman cross section, another explanation should be suggested. Considering the whole experimental process, the sample preparation methods were different and the samples were different, too. Our sample was 5-steps bunches after flashing and Morin's one was triple steps regular H-Si(111) surface. There are two significant aspects to discuss. The first point is whether dissolved oxygen or water molecules in chemical solution could prevent the formation of dihydride or not. The second point is what is the orientation of the dihydride if it is formed on the step.

Concerning the first point, there are several reports on Si(111) surfaces after hydrogen termination showing strong dependence of the resultant structures on the *pH* levels of wet etching solutions. Higashi *et al.* found that there were several species such as monohydride, dihydrides and trihydrides on the flat Si surfaces with the etching in dilute HF at *pH*~2 [4, 30]. When the *pH* increases, formation of the ideal monohydride is dominant. This proved that high *pH* solutions can efficiently remove isolated defect adatoms on the (111) terraces. The problem becomes more complicated with the stepped Si surfaces with a high concentration of one-dimensional defects, such as step edges, kinks, adatoms and so on. Hines *et al.* [15] predicted that etching happened preferentially at the adatoms, then at kink sites, then at step edges and finally at the terrace. Therefore, the *pH* is critically important to make terminated monohydride on the terrace and dihydride at the steps. Otherwise, oxygen may block the attack of etching species on the reactive sites on the Si surface in solution [31,32]. Reports proved that if $(\text{NH}_4)_2\text{SO}_3$ was added to the solution, the dissolved atmospheric oxygen reduced and the surface became morphologically smooth and high quality hydrogen termination was attained [33]. P. Jakob and Y. Chabal [5] have found the critical *pH* ~ 6.6 etching in 3 min, suitable for hydrogenation of the whole Si surface. In that way, the C_1 mode of vertical dihydride mode appeared in the internal reflection IR spectrum observed by Chabal. Morin followed the same method of hydrogen termination, and then observed the SFG spectrum. However, as we mentioned before, they could not detect the C_1 mode. We must point out the possibility that in Morin's case, oxygen in the solution might have prohibited the formation of SiH_C .

Concerning the second point, let us mention two contradictory theoretical calculations of the step dihydride and compare them to the experimental results. The structure of dihydride SiH_2 at the step is dominated by steric interaction between H_B and H_A . Considering one unit cell in the bulk, the distance between them is 1.4 \AA which is less than the hydrogen Van Der Waals radius of

2.4 Å. Therefore, they need to be relaxed in some possible ways. According to the cluster calculation [14], it was predicted to rotate away in-plane from the optical plane by 31° . As the result, steric effects lead to rotation of H_B and H_A far from their original position (red dotted lines in Fig. 1) producing an out-of-phase (C_2) and in-phase (C_3) pair of vibrations (Fig.1). Besides that, H_C is not constrained sterically and decoupled from H_B . Thus its frequency of 2094 cm^{-1} is largely independent of H_B . However, in this calculation, the cluster size was not enough compared to the real system. In order to overcome this limitation, Li *et al.* [34] used first principles pseudopotentials, and performed a slab calculation. Unexpectedly, in the fully relaxed structure, they predicted 11° rotation of the dihydride away from the optical axis [557] drawn in Fig. 1. On the other hand, experimentally, with the same preparation method of wet chemical etching with ammonium fluoride, the tilt angles of the dihydride were determined as -35° according to the Raman spectra and $\pm 45^\circ$ from the IR spectra. [14]. If we adopt $+45^\circ$ as seen in Fig. 1a, the orientation of the adsorbed step dihydride $H_C\text{-Si-}H_B$ with respect to the surface plane may be suitable for SFG excitation, since the electric field of the IR is parallel to the SiH_C bond. If we adopted -45° , we should not predict a finite SFG intensity because the IR light polarization is perpendicular to the SiH_C bond (Fig.1b). In these two calculation methods, they considered the single step only, but not triple-step regular surface. That explains why the results were inconsistent with the experimental results. Still roughly speaking, we suggest that the step dihydride was tilted some degrees from the surface normal of the (557) plane.

4. CONCLUSION

The step edges of the vicinal Si(111) surface were terminated by exposure to hydrogen molecules in a UHV chamber for the first time. In this experiment, the effect of oxygen and water molecules was negligible. On the other hand, from the observed LEED patterns, the 5-7 step bunches were defined to occur when the surface was flashed at high temperature of 1100°C even for a short time of one minute. SFG spectra of this stepped H-Si(111) surface with *ppp* and *ssp* polarization combinations showed clearly step vibrational mode at 2094 cm^{-1} (C_1). From these results, we conclude that the hydrogen termination method has affected the formation and orientation of step dihydride. Further experiment and explanation will be reported in the future.

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References

- [1] Hochberg, L.R., Serruya, Mijail D., Friehs, Gerhard M., Mukand, Jon A., Saleh, Maryam, Caplan, Abraham H., Branner, Almut, Chen, David, Penn, Richard D., Donoghue, John P., Nature, 2006/07/13/print. **442**(7099): p. 164.
- [2] Vilan, A., Omer Yaffe, Ariel Biller, Adi Salomon, Antoine Kahn and David Cahen, Advanced Materials, 2010. **22**(2): p. 140-159.
- [3] Fenner, D.B., D.K. Biegelsen, and R.D. Bringans, Journal of Applied Physics, 1989. **66**(1): p. 419-424.
- [4] Higashi, G. S.; Y. J. Chabal ; G. W. Trucks ; Krishnan Raghavachari, Applied Physics Letters, 1990. **56**(7): p. 656-658.
- [5] Jakob, P. and Y.J. Chabal, The Journal of Chemical Physics, 1991. **95**(4): p. 2897-2909.

- [6] Schulze, G. and M. Henzler, Surface Science, 1983. **124**(2–3): p. 336-350.
- [7] Owman, F. and P. Mårtensson, Surface Science, 1995. **324**(2–3): p. 211-225.
- [8] Bratu, P. and U. Höfer, Physical Review Letters, 1995. **74**(9): p. 1625-1628.
- [9] Bratu, P., K.L. Kompa, and U. Höfer, Chemical Physics Letters, 1996. **251**(1–2): p. 1-7.
- [10] Kawasuno, A., M. Yoshikawa, K. Kojima, S. Okada, and A. Ichimiya, Physical Review B, 2000. **61**(3): p. 2102-2106.
- [11] Haick, H., T., Hurley P. T., Hochbaum, A. I., Yang, P., Lewis, N. S., Journal of the American Chemical Society, 2006. **128**(28): p. 8990-8991.
- [12] Masood, M. N., Chen, S., Carlen, E. T., Van den Berg, A., ACS Appl. Materials & Interfaces, 2010. **2**(12): p. 3422-3428.
- [13] Morin, M., Jakob, P., Levinos, N. J., Chabal, Y. J., Harris, A. L., The Journal of Chemical Physics, 1992. **96**(8): p. 6203-6212.
- [14] Raghavachari, K., P. Jakob, and Y.J. Chabal, Chemical Physics Letters, 1993. **206**(1–4): p. 156-160.
- [15] Melissa A. Hines, Yves J. Chabal, Timothy D. Harris and Alexander L. Harris, The Journal of Chemical Physics, 1994. **101**(9): p. 8055-8072.
- [16] Melissa A. Hines ; Yves J. Chabal ; Timothy D. Harris ; Alexander L. Harris, Physical Review Letters, 1993. **71**(14): p. 2280-2283.
- [17] S.A. Teys, K.N. Romanyuk, R.A. Zhachuk, B.Z. Olshanetsky, Surf. Sci., 2006, **600**: p. 4878.
- [18] A. Kirakosian, R. Bennewitz, J.N. Crain, Th. Fauster, J.L. Lin, D.Y. Petrovykh, and F. J. Himpsel, Appl. Phys. Lett., 2001, **79** (11): p.1608.
- [19] M. Henzler, R. Zhachuk, Thin Solid Film, 2003, **428**: p.129.
- [20] Jian Wei, X.S. Wang, J. L. Goldberg, N.C. Bartelt, and Ellen D. Williams, Phys. Rev. Lett., 1992, **68**(26): p. 3885.
- [21] G. Prevot, F. Leroy, B. Croset, Y. Garreau, A. Coati, and P. Muller, Surf. Sci., 2012, **606**: p. 209.
- [22] S.A. Teys, K.N. Romanyuk, R.A. Zhachuk, B.Z. Olshanetsky, Surf. Sci., 2006, **600**: p.4878.
- [23] K. T. T. Hien, Y. Miyauchi, M. Kikuchi and G. Mizutani, Surface and Interface Analysis, 2012, **44**: p. 662-665.
- [24] M. Y. Mao, P. B. Miranda, D. S. Kim, Y. R. Shen, Phys. Rev. B, 2001, **64**: p. 035415.
- [25] G. S. Higashi, Y. J. chabal, G. W. Trucks, K. Raghavachari, Appl. Surf. Lett., 1990, **56**: p.656.
- [26] Y. Hamma, R.J. McClelland and H. Hibino, **Jpn. J. Appl. Phys.**, 1990, **29**(12): L2254.
- [27] Dumas, P., Y.J. Chabal, and G.S. Higashi, Physical Review Letters, 1990, **65**(9): p. 1124-1127.
- [28] Guyot-Sionnest, P.; P. Dumas; Y. J. Chabal; G. S. Higashi, Physical Review Letters, 1990, **64**(18): p. 2156-2159.
- [29] Guyot-Sionnest, P., P. Dumas, and Y.J. Chabal, Journal of Electron Spectroscopy and Related Phenomena, 1990, **54–55**(0): p. 27-38.
- [30] G. S. Higashi, R. S. Becker, Y. J. Chabal, and A. J. Becker, Applied Physics Letter, 1991, **58**: p.1656-1658.
- [31] H. Fukidome and M. Matsumura, Applied Surface Science, 1997, **130-132**: p. 146-150.
- [32] S. P. Garcia, H. Bao and M. A. Hines, Surface Science, 2003, **541**: p. 252-261.
- [33] H. Kato, T. Taoka, S. Nishikata, et al., **Jpn. J. Appl. Phys.**, 2007, **46**, 5701
- [34] Li, X.P., D. Vanderbilt, and R.D. King-Smith, Physical Review B, 1994, **50**(7): p. 4637-4641.