

Available online at www.sciencedirect.com



Surface Science 570 (2004) 178-188



www.elsevier.com/locate/susc

A comparative infrared study of H₂O reactivity on Si(100)-(2 × 1), (2 × 1)-H, (1 × 1)-H and (3 × 1)-H surfaces

G. Ranga Rao^{a,1}, Zhi-Hong Wang^a, Hidekazu Watanabe^b, Mutsumi Aoyagi^b, Tsuneo Urisu^{a,*}

^a Department of Vacuum UV Photoscience, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan ^b Kyushu University, Hakozaki 6-10-1, Higashi, Fukuoka 812-8581, Japan

> Received 14 November 2003; accepted for publication 20 July 2004 Available online 12 August 2004

Abstract

The water adsorption on the bare and H-terminated Si(100) surfaces has been studied by the BML-IRRAS technique. It is found that H-terminated surfaces are much less reactive compared to the bare silicon surfaces. The (1 × 1)-H and (3 × 1)-H surfaces show similar and less reactivity pattern compared to the (2 × 1)-H surface. At higher exposures, the water reaction with coupled monohydride species provides an effective channel for oxygen insertion into the back bonds of dihydride species. It is not attributed to the H–Si–Si–H + H₂O → H–S–Si–OH + H₂, which could give rise to the characteristic Si–H and Si–OH modes, respectively at 2081 and 921 cm⁻¹. A more suitable reaction mechanism involving a metastable species, H–Si–Si–H + H₂O → H₂Si ··· HO–Si–H (metastable) explains well the bending modes of oxygen inserted silicon dihydride species which are observed relatively strongly in the reaction of water with H-terminated Si(100) surfaces.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Silicon; Infrared absorption spectroscopy; Surface chemical reaction; Density functional calculations; Hydrogen atom; Water

* Corresponding author. Tel.: +81 564 55 7444; fax: +81 564 53 7327.

E-mail address: urisu@ims.ac.jp (T. Urisu).

¹ Present address: Department of Chemistry, Indian Institute of Technology, Madras, Chennai 600 036, India.

1. Introduction

Water adsorption on Si(100) surface continues to be a subject of investigation to unravel the fundamental and chemical aspects occurring at the Si/ SiO₂ interface [1–13]. The silicon oxidation process with gas phase water has been widely used in the

fabrication of Si-based devices and it is crucial to study the interaction of water molecules with variety of Si surfaces to understand and monitor the oxidation process. High resolution electron energy loss spectroscopy (HREELS) [1-6,10,13], infrared (IR) absorption spectroscopy methods such as multiple internal reflection (MIR) geometry [8, 14], external transmission (ET) geometry [11,15] and buried metal layer-infrared reflection and absorption spectroscopy (BML-IRRAS) techniques [9,12,16–21] have been employed to study the nature of surface Si-H, Si-O and Si-OH species and the complex oxidation process of Si surface followed by dissociative adsorption of H₂O. However, only few studies on the reactivity of water with hydrogen passivated Si(100) surfaces have been reported [12] and there is considerable scope to investigate this aspect using sensitive BML-IRRAS method. It is well known that the Si(100) surface used in many Si-based electronic devises undergoes the (2×1) reconstruction in which adjacent Si atoms pair together by combining two dangling bonds into Si dimers. These dimers are reactive towards variety of adsorbate molecules. When the clean Si(100) surface is exposed to H atoms under varying experimental conditions, three main types of surface hydride phases can be obtained [11,22–24]. These phases comprise of the (2×1) structure with coupled monohydride (CM) (H–Si–Si–H) [22], the (3×1) structure with alternating isolated dihydride SiH₂ (ID) and CM pairs [23,25], and the (1×1) structure consisting of a mixture of monohydride, dihydride and trihydride species on the Si(100) surface [24]. The various Si-hydride phases, namely Si(100)- (1×1) -H, Si(100)-(2 \times 1)-H and Si(100)-(3 \times 1)-H have been characterized by HREELS [10] and IR techniques [11,12,18,24,26]. CM of the (2×1) -H surface exhibits characteristic symmetric and asymmetric stretching modes at 2099 and 2088 cm⁻¹, respectively [10-12,18,26]. The SiH₂ dihydride species of (3×1) -H and/or (1×1) -H surface shows several characteristic vibrational bands in the Si-H bending region (902 and 913 cm⁻¹ assigned respectively to the ID and adjacent dihydride (AD)) and in the Si–H stretching region (2090 (ID) and 2107 cm⁻¹ (AD)) of the BML-IRRAS spectra [18]. All these H-terminated Si(100) surfaces can be prepared at

appropriate temperature and atomic hydrogen exposures [27]. The formation of Si–H bonds as a result of the reaction with the dangling bonds leads to high degree of passivation of Si surfaces due to substantial reduction in the surface free energy [13,23,24,28].

The reactivity of water with the bare Si(100)surface and H-terminated Si(100) surfaces has evoked considerable interest in order to find the nature and extent of reactivity of clean and H-terminated surfaces. The aim of this investigation is to elucidate the influence of surface hydrogen termination on the oxidation process with water and to identify some of the complex surface reaction products at various stages of the Si surface reaction. Oxidation process of clean [3,8,9,29] and H-terminated Si(100) surfaces have been carried out mainly by molecular oxygen [4,6,30] and to some extent by water adsorption [11,12]. Water exposure to Si(100) leads to the passivation of dangling bonds by H and OH groups. Further, thermal annealing leads to the progressive insertion of oxygen atoms into the Si back-bonds and the oxidation of Si surface with hydrogen desorption above 650 K [27]. In the present work we have made a comparative study of the reactivity of water with three different H-terminated Si(100) surfaces, namely, the Si(100)-(1 \times 1)-H, Si(100)- (2×1) -H and Si(100)- (3×1) -H surfaces and also with the Si(100)-(2 \times 1) bare surface using the BML-IRRAS technique. The results indicate that the H-terminated surfaces are much less reactive compared to bare silicon surfaces. Further, the (1×1) -H and (3×1) -H surfaces show similar and slightly less reactivity pattern compared to the (2×1) -H surfaces.

2. Experimental

The infrared reflection absorption spectroscopy (IRRAS) experiments were carried out using an ultrahigh-vacuum (UHV) reaction chamber equipped with IRRAS optical system and reflective high-energy electron diffraction (RHEED) facility [12]. The base pressure of the experimental chamber is maintained at $\leq 2 \times 10^{-10}$ Torr by pumping with a turbo-molecular pump (500)

 $1s^{-1}$). The optical path of the IRRAS system was continuously purged by pure N₂ gas. A p-polarized IR beam from a Fourier transform spectrometer (JEOL JIR 7000) was selected by a wire grid polarizer using KRS-5 substrate and directed into the reaction chamber through a ZnSe view port at an incident angle of 85° with respect to the sample surface normal. The reflected IR beam is detected by using liquid nitrogen cooled HgCdTe (MCT) detector outside the UHV chamber.

The Si(100)-CoSi₂ BML wafer prepared by Co⁺-ion implantation (200 keV, 3×10^{17} ions cm⁻² and annealing at 1170 K, Toray Research Center) have been employed in this study. The wafer contains the 100 nm thick CoSi2 layer buried under the 50 nm thick Si layer. A piece of 14×14 mm² size is cut and cleaned by wet chemical methods. The samples are first degreased in acetone and methanol solutions. Then the samples are treated with HF solution and then with $HCl + H_2O_2 +$ H₂O solution before transferring into the experimental chamber. The BML-Si(100) sample is then degassed by heating slowly up to 600 K with pressure not exceeding 5×10^{-9} Torr, followed by a flash up to 1200 K to remove the surface oxide. A silicon epitaxial layer of about 50 nm thick has been grown over the BML-Si(100) surface using Si₂H₆ gas at 975 K. After epitaxy, the total thickness of the Si overlayer above the CoSi₂ reflector is about 100 nm. Annealing of the sample at 870 K produces clear Si(100)-(2 \times 1) RHEED pattern [16]. In this study, the (2×1) surface periodicity of Si(100) is the starting point in preparing the other H-terminated Si surfaces. The IR external reflection optical geometry described above, using the sample containing the CoSi₂ BML reflector beneath the ~ 100 nm thick Si layer, is sensitive to the vibrational components that are perpendicular to the surface [12,20,31,32]. The IRRAS measurements have been performed by 300 scan accumulations at 2 cm^{-1} resolution and the spectra are reported as the ratio of the signal spectrum to the background spectrum recorded at the same temperature. The sample is heated by using ceramic heater (pyrolytic graphite/pyrolytic boron nitride). The sample temperature is controlled by a PID (proportion-integral-differential) controller with a W-Re thermocouple attached to the rear side of the Si substrate. The thermocouple is calibrated by an optical pyrometer (Emissivity = 0.8 for Si) and the sample temperature is kept constant during the IR measurements to avoid spectral distortions.

Atomic hydrogen and deuterium have been produced at appropriate gas exposures by using incandescent tungsten filament (0.15 mm diameter, 2.25 A current) and the typical dosing time is 20 s. The exposures have been measured in Langmuir units $(1 L = 1 \times 10^{-6} \text{ Torrs})$ from ion gauge readings. The common procedures followed for IR measurements in this study include thermal cleaning of the Si(100) BML sample up to about 1200 K, and 2000 L saturation exposure of atomic hydrogen or deuterium at 648 K, maintaining the (2×1) periodicity [33]. Since the bare Si surface is extremely reactive, the Si(100) surface is significantly contaminated by the background water even at the base pressure of 1×10^{-10} Torr. So the deuterium saturated (2×1) surface has been used occasionally to measure the background spectra with no residual water contamination [18]. The stable hydrogen covered (2×1) -H, (3×1) -H and (1×1) -H surfaces are prepared by exposing clean or D-terminated Si(100)-(2×1) surface to atomic hydrogen respectively at 648, 400 and 300 K. The measurement temperatures are selected by considering the thermal background noise and the time lapse before the measurement. The sample is exposed to controlled amount of water at a desired temperature as mentioned in the text.

3. Results and discussion

The spectra observed in the present experiments are presented in Figs. 1–4 for H₂O + Si(100)- (2×1) , (2×1) -H, (3×1) -H and (1×1) -H, respectively. The vibrational frequencies of almost all possible modes, which should be observed by BML-IRRAS (that means the transition perpendicular to the surface) in the frequency range 750–2300 cm⁻¹, have been calculated by ab initio molecular orbital calculations employing two types of cluster model systems containing 9 and 10 silicon atoms. The details of the theoretical analysis, and the vibrational frequencies of all pos-



Fig. 1. BML-IRRAS spectra of the bare Si(100)-(2 × 1) surface exposed to (a) 1 L H₂O, (b) 200 L H₂O, (c) 2000 L H₂O at 373 K. The spectra are presented as the ratios of the absorption spectra of water exposed Si(100)-(2 × 1) surfaces to the Si(100)-(2 × 1)-D surface, recorded at the same temperature.



Fig. 2. BML-IRRAS spectra of the Si(100)-(2×1)-H surface exposed to (a) 100 L H₂O, (b) 500 L H₂O, (c) 2000 L H₂O at 373 K and (c') 2000 L H₂O at 300 K. The spectra are presented as the ratios of the absorption spectra of the water exposed Si(100)-(2×1)-H surface to the Si(100)-(2×1)-H surface, recorded at the same temperature.

sible modes are presented in Ref. [31]. In the model systems, the dangling bonds of Si atoms other than the top silicon atoms have been terminated by tritium atoms to avoid artifacts due to excess spin or



Fig. 3. BML-IRRAS spectra of the Si(100)-(3×1)-H surface exposed to (a) 20 L atomic H, (b) 500 L atomic H, (c) 2000 L atomic H, (d) 200 L H₂O, (e) 2000 L H₂O, (f) 5000 L H₂O at 400 K. The spectra (a)–(c) are the ratios of absorption spectra of the H exposed Si(100)-(2×1)-D surfaces to the Si(100)-(2×1)-D surface, and the spectra (d)–(f) are the ratios of the absorption spectra of the water exposed Si(100)-(3×1)-H surfaces to the Si(100)-(3×1)-H surface, recorded at 400 K.



Fig. 4. BML-IRRAS spectra of the Si(100)-(1×1)-H surface exposed to (a) 20 L atomic H, (b) 500 L atomic H, (c) 2000 L atomic H, (d) 2000 L H₂O, (e) 5000 L H₂O at 300 K. The spectra (a)–(c) are the ratios of the absorption spectra of the H exposed Si(100)-(2×1)-D surfaces to the Si(100)-(2×1)-D surface, and the spectra (d)–(e) are the ratios of absorption spectra of the water exposed Si(100)-(1×1)-H surfaces to the Si(100)-(1×1)-H surface, recorded at 300 K.

charge. Unlike the reported theoretical methods in which the third and forth layer silicon atoms are fixed at the ideal bulk crystalline positions [8,9,11,34], all atoms of the clusters in this study are allowed to fully relax with no constraints. The minimized total energy geometry is then obtained for each cluster via gradient corrected density functional calculations using the B3LYP method [35]. We have used the polarized 6-31G** basis set for all the atoms and the calculations are performed with Gaussian-98 [36]. In our calculations, the variation of Si-Si bond length was 2.35-2.38 Å which is close to the reported experimental value 2.35 Å. The observed bands have been assigned referring the calculated results presented in Ref. [31] and several other reported data for H-Si-D [17] and SiH₃ [37], and summarized in Tables 1 and 2.

3.1. Water adsorption on the Si(100)- (2×1) bare surface

The BML-IRRAS spectra of water adsorbed on bare Si(100)-(2 \times 1) surface for different exposures at 373 K are presented in Fig. 1. The vibrational peaks at 821 and 2081 cm⁻¹ are assigned, respectively, to the stretching modes of Si-OH and Si-H species typically formed from the dissociated fragments of water molecule and bonded to the two Si atoms of the same (2×1) dimmer unit giving rise to H–Si–Si–OH surface species [3,8,11,26,34,38]. At higher exposures, however, the Si-OH stretching peak at 821 cm⁻¹ losses intensity and extends towards the lower frequency range, $750-850 \text{ cm}^{-1}$ as seen in the spectra 1(b) and 1(c). Significant changes have also occurred in the regions of 870-1150 and 2050-2180 cm⁻¹ as a function of water exposure at 373 K. This indicates that the stable Si-H and Si-OH groups are undergoing substantial structural changes due to the large scale decomposition of water and adsorbed O-H groups at higher exposures. The Si surface is at the primary stage of oxidation where the Si-OH modes gradually decrease giving rise to a number of oxygen inserted species containing Si-O-Si units, and H-terminated Si surface dimers exhibiting a range of Si-O and Si-H stretching and bending modes in these frequency regions. Weldon et al. [8] reported similar IR features using multiple internal reflection geometry for H_2O -saturated Si(100) surface annealed at 300 and 675 K.

The region $850-1200 \text{ cm}^{-1}$ where discrete vibrational modes related to Si-O stretching and Si-H bending modes of various oxygenated Si species occur at higher exposures, while the Si-H feature at 2081 cm⁻¹ has changed into a continuum of variety of oxygen inserted Si-H stretching vibrations between 2050 and 2180 cm^{-1} . In the earlier studies, the broad vibrational structure between 2045 and 2150 cm^{-1} has been attributed to pure SiH, SiH₂ and SiH₃ species including the coupled monohydride at 2090 and 2099 cm^{-1} . The relatively weak stretching modes at 2113 and 2162 cm^{-1} are accounted in the earlier studies for the formation of intermediate Si oxidation species such as H-Si-O-Si-H and H-Si-O-Si(O)-H groups in which the O-atoms are inserted into the Si-Si dimer and Si-back bonds [8].

At higher water exposures (Table 2) [31,32], the oxygen atom from Si-OH groups is further transferred effectively to the Si-Si dimer and back bonds leading to the formation of highly oxidized species such as H-Si-O-Si(O)x-H, H-Si(O)x-Si-H, H-Si(O)x-H, H₂Si(O)x···SiH₂ and $H_2Si(O) \cdots Si(O)xH_2$ with x = 0-2. Here "-" means the existence of the chemical bond, and "..." means the adjacent species. The Si-O stretching and SiH₂ scissoring modes typically occur in the region between 850 and 1200 cm^{-1} (Table 1) [31,32]. The spectra 1(b) and 1(c) in this region show new discrete vibrational bands emerging at 901, 932, 963, 982 cm^{-1} and a broad feature above 1000 cm^{-1} as a function of water exposure. The origin of the first four vibrational bands has been proposed to be due to the SiH₂ scissoring modes of isolated and adjacent dihydride species of the type $H_2Si(O)x$ with x = 0-2 oxygen atoms inserted into the Si back bonds [17,31,32].

The absorption peaks observed in the lower frequency region are at 784, 805 and 854 cm⁻¹. These absorption peaks come partly from the unaffected OH groups on the Si surface as well as the Si–H bending modes of H–Si(O)*x*–O–Si–H with x = 0– 2, H–Si(O)*x*–Si–H with x = 1 and 2, H–Si(O)₂– O–Si–(O)–H and SiH₃ species as given in Table

Table 1 Vibrational frequencies for various silicon hydride species in the low frequency region

Structure/species	Vibrational mode	Frequency (cm ⁻¹)	
		Expt.	Calc.
H–Si(O)–Si–H	$\delta(Si-H)_{CM(\Omega)}$	784	777
H-Si(O) ₂ -Si-H	$\delta(\text{Si-H})^{1}_{\text{CM(OO)}}$	784	784
H-Si-O-Si-H	$\delta(Si-H)_{CM(M)}$	784	791
H–Si–D	δ(H–Si–D)	$793-795^{\rm a}$	
H-Si(O)-O-Si-H	$\delta(Si-H)^1_{CM(O,M)}$	805	796
H-Si(O) ₂ -Si(O)-H	$\delta(\text{Si}-\text{H})_{\text{CM}(\Omega\Omega,\Omega)}$	805	796
H-Si(O) ₂ -O-Si(O)-H	$\delta(\text{Si-H})^{1}_{\text{CM}(OO,M,O)}$	805	808
H-Si(O) ₂ -Si-H	$\delta(Si-H)^2_{CM(OO)}$	821	817
H-Si(O)2-Si(O)2-H	$\delta(Si-H)_{CM(OO,OO)}$	821	819
H-Si(O)2-O-Si-H	$\delta(\text{Si-H})^2_{\text{CM}(\Omega,M)}$	821	821
H-Si-Si-OH	v(Si–OH)	821	826
H-Si(O)2-O-Si-H	(Si-H) _{CM(OO,M)}	845	848
H-Si(O) ₂ -O-Si(O)-H	$\delta(\text{Si-H})^2_{\text{CM}(\Omega\Omega,M,\Omega)}$	850	856
H-Si(O) ₂ -O-Si(O) ₂ -H	$\delta(\text{Si-H})_{CM(OO,M,OO)}$	850	868
SiH ₃	δ(Si–H) _{IT}	855–863 ^b	
H–Si–H	δ(Si–H) _{ID}	900-901	901
$H_2Si \cdots SiH_2$	δ(Si–H) _{AD}	913–914	917
H–Si(O)–H	$\delta(Si-H)_{ID(O)}$	929	928
$H_2Si(O) \cdots SiH_2$	$\delta(\text{Si-H})^2_{AD(0)}$	932	942
$H_2Si(O)_2 \cdots Si(O)H_2$	$\delta(\text{Si}-\text{H})^{1}_{\text{AD}(\text{OO} \text{O})}$	932	944
$H_2Si(O) \cdots Si(O)H_2(cis)$	$\delta(Si-H)_{AD}(OO)$	932	946
$H_2Si(O) \cdots Si(O)H_2(trans)$	$\delta(Si-H)_{AD(0,0')}$	932	946
H-Si(O) ₂ -H	$\delta(Si-H)_{ID(OO)}$	965	962
$H_2Si(O)_2 \cdots Si(O)H_2$	$\delta(\text{Si-H})^2_{\text{AD}(\Omega\Omega\Omega)}$	978–983	973
$H_2Si(O)_2 \cdots SiH_2$	$\delta(Si-H)^2$	978–983	976
$H_2Si(O)_2 \cdots Si(O)_2H_2$	$\delta(Si-H)_{AD}(OO,OO)$	978–983	978
H–Si(O) ₂ –Si–H	v(Si–O) _{CM(OO)}	1020-1130	1029
H-Si(O) ₂ -O-Si-H	$v(Si-O)^{1}_{CM(OOM)}$	1020-1130	1029
H-Si(O)-Si(O)-H(cis)	$v(Si-O)_{CM(O,O)}$	1020-1130	1039
H-Si(O)-O-Si(O)-H(trans)	$v(Si-O)_{CM(O,M,O')}$	1020-1130	1040
H–Si(O)–O–Si–H	$v(Si-O)^2_{CM(O,M)}$	1020-1130	1043
H–Si(O)–H	$v(Si-O)_{ID(O)}$	1020-1130	1057
H-Si(O) ₂ -Si(O)-H	$v(Si-O)_{CM(OO,O)}$	1020-1130	1064
H-Si(O)-O-Si(O)-H(cis)	$v(Si-O)_{CM(O,M,O)}$	1020-1130	1071
$H_2Si(O) \cdots Si(O)H_2(trans)$	v(Si–O) _{AD(O,O')}	1020-1130	1087
H-Si(O)2-O-Si-H	$v(Si-O)^2_{CM(OOM)}$	1020-1130	1088
$H_2Si(O) \cdots SiH_2$	$v(Si-O)_{AD(O)}$	1020-1130	1092
H-Si(O) ₂ -Si(O) ₂ -H	v(Si–O) _{CM(OO,OO)}	1020-1130	1092
$H_2Si(O) \cdots SiH_2$	v(Si–O) _{AD(O)}	1020-1130	1092
H-Si(O)2-H	v(Si–O) _{ID(OO)}	1020–1130	1097
H-Si(O)2-O-Si(O)-H	$v(Si-O)^2_{CM(OO,M,O)}$	1020–1130	1100
$H_2Si(O) \cdots Si(O)H_2(cis)$	$v(Si-O)_{AD(O,O)}$	1020–1130	1102
H-Si(O)2-O-Si(O)2-H	v(Si-O) _{CM(OO,M,OO)}	1020–1130	1107
$H_2Si(O)_2 \cdots Si(O)H_2$	v(Si-O) _{AD(OO,O)}	1020–1130	1110
$H_2Si(O)_2 \cdots Si(O)_2H_2$	v(Si-O) _{AD(OO,OO)}	1020–1130	1115
$H_2Si(O)_2\cdots SiH_2$	v(Si-O) _{AD(OO)}	1020–1130	1125

Superscripts 1 and 2 indicate the existence of different frequencies for similar vibrational excitations of the same cluster structure. $\delta(Si-H)_{IT}$ is the symmetric bending mode of isolated trihydride. Symbols identifying the symmetric and asymmetric vibrations are not used, since only the modes having the perpendicular components are listed in this table.

^a see Ref. [35]. ^b see Ref. [17].

Structure/species	Vibrational mode	Frequency (cm ⁻¹)	
		Expt.	Calc.
H–Si–Si–OH	v(Si–H)	2081	2087
H-Si(O) ₂ -Si-H	$v(Si-H)^{1}_{CM(OO)}$	2090	2085
H-Si(O)-Si-H	$v(Si-H)^{1}_{CM(Q)}$	2090	2088
H–Si–H	v(Si–H) _{ID}	2090	2090
H–Si–Si–H	v(Si-H) _{CM}	2100	2100
$H_2Si(O) \cdots SiH_2$	$v(Si-H)^{1}_{AD(O)}$	2113	2104
H-Si(O)-Si(O)-H(cis)	$v(Si-H)_{CM(O,O)}$	2113	2106
$H_2Si(O)_2 \cdots SiH_2$	$v(Si-H)^{1}_{AD(OO)}$	2113	2106
H-Si(O)-H	v(Si-H) _{ID(O)}	2113	2107
$H_2Si\cdots SiH_2$	v(Si-H) _{AD}	2113	2107
H-Si(O)-Si(O)-H(trans)	v(Si-H) _{CM(O,O')}	2113	2108
H–Si(O)–Si–H	$v(Si-H)^2_{CM(O)}$	2113	2112
$H_2Si(O) \cdots SiH_2$	ν (Si–H) ¹ _{AD(O)}	2113	2113
$H_2Si(O) \cdots SiH_2$	$v(Si-H)^2_{AD(O)}$	2113	2113
$H_2Si(O) \cdots SiH_2$	$v(Si-H)^3_{AD(O)}$	2113	2114
H-Si(O)2-O-Si-H	ν (Si–H) ¹ _{CM(OO,M)}	2113	2115
$H_2Si(O)_2 \cdots Si(O)H_2$	$v(Si-H)^{1}_{AD(OO,O)}$	2113	2115
$H_2Si(O) \cdots Si(O)H_2(cis)$	$v(Si-H)_{AD(O,O)}$	2113	2116
$H_2Si(O) \cdots Si(O)H_2(trans)$	v(Si-H) _{AD(O,O')}	2113	2116
H–Si–O–Si–H	v(Si-H) _{CM(M)}	2113	2118
H–Si(O)–O–Si–H	ν (Si–H) ¹ _{CM(O,M)}	2113	2120
SiH ₃	v(Si–H) _{IT}	2137–2140 ^a	
H-Si(O) ₂ -Si(O)-H	$v(Si-H)^2_{CM(OO,O)}$	2143	2147
H-Si(O)2-Si(O)2-H	v(Si-H) _{CM(OO,OO)}	2143	2148
$H_2Si(O)_2 \cdots Si(O)H_2$	ν (Si–H) ² _{AD(OO,O)}	2143	2149
H-Si(O) ₂ -Si-H	$v(Si-H)^2_{CM(OO)}$	2143	2154
$H_2Si(O)_2 \cdots Si(O)_2H_2$	$v(Si-H)^{1}_{AD(OO,OO)}$	2143	2155
H-Si(O) ₂ -H	v(Si–H) _{ID(OO)}	2162	2160
H-Si(O)2-O-Si(O)-H	ν (Si–H) ¹ _{CM(OO,M,O)}	2162	2162
H-Si(O)-O-Si(O)-H(cis)	$v(Si-H)_{CM(O,M,O)}$	2162	2163
H-Si(O)-O-Si-H	$v(Si-H)^2_{CM(O,M)}$	2162	2164
H-Si(O)-O-Si(O)-H(trans)	v(Si-H) _{CM(O,M,O')}	2162	2164
H-Si(O) ₂ -SiH ₂	$\nu(Si-H)^2_{AD(OO)}$	2162	2169

 Table 2

 Vibrational frequencies for various silicon hydride species in the high frequency region

Superscripts 1 and 2 indicate the existence of different frequencies for similar vibrational excitations of the same cluster structure. $v(Si-H)_{IT}$ is the symmetric stretching mode of isolated trihydride. Symbols identifying the symmetric and asymmetric vibrations are not used, since only the modes having the perpendicular components are listed in this table.

^a see Ref. [17].

1. The broad feature between 1000 and 1150 cm^{-1} is essentially due to the Si–O stretching vibrational modes attributed to a lot of oxygen inserted monohydrides, isolated and adjacent dihydrides. This is a characteristic feature indicating the formation of surface silicon oxides such as Si–O–Si [11,31]. In a recent study using IR external transmission geometry, the formation of silicon epoxides containing Si–O–Si rings has been reported in this frequency region after annealing the water dosed Si surface at 875 K under UHV conditions [34].

The high frequency region of water exposed Si(100) surface shows three major absorption peaks at 2090, 2113 and 2162 cm⁻¹. The 2090 cm⁻¹ peak is stronger in intensity and at higher exposures, the 2113 and 2162 cm⁻¹ peaks appear to grow at the expense of the former (Fig. 1(b) and (c)). The absorption peak at 2090 cm⁻¹ is as-

signed to the Si-H stretching mode of unoxidized isolated dihydride while the the 2113 cm^{-1} is attributed to a large number of oxygen inserted coupled monohydrides and adjacent dihydride species as given in Table 2. The growth of the absorption peak at 2113 cm⁻¹ seems to indicate that the unoxidized isolated dihydrides at 2090 cm⁻¹ are transforming to oxygenated adjacent dihydrides due to the oxygen migration into the back bonds. In addition, direct interaction of H₂O molecules with surface Si atoms at 373 K can also produce H-Si-O-Si(O)x-H as well as $H_2Si(O) \cdots Si(O)xH_2$ species with x = 0-2 which can contribute to the intensity of the broad vibrational band in this high frequency region. The oxygen agglomeration is further confirmed by the observation of the 2162 cm^{-1} peak attributed to highly oxidized surface Si hydride species given in Table 2. We have further examined the reactivity pattern of water with H-covered Si(100) surfaces.

3.2. Water adsorption on the $Si(100)-(2 \times 1)-H$ surface

The Si(100)-(2 \times 1)-H surface is prepared by exposing the bare Si(100)-(2 \times 1) surface to 2000 L atomic hydrogen at 648 K. Fig. 2 shows the IR spectra of the water exposed Si(100)-(2 \times 1)-H surface at 373 and 300 K. The negative absorption peak at 2100 cm^{-1} is due to the coupled monohydride present on the H-terminated (2×1) surface [11,12,18]. The reactivity of the (2×1) -H surface with water is strikingly different compared to that of the Si(100)-(2 \times 1) bare surface discussed earlier from Fig. 2. When the (2×1) -H surface is exposed to water at 373 K the surface hydride phase is found to be gradually eliminated. This is evident from Fig. 2 in which the intensity of the negative absorption peak at 2100 cm^{-1} and the intensity of the positive absorption peaks in the range of $880-1000 \text{ cm}^{-1}$ increase simultaneously with water exposures. However, the reaction occurring on the (2×1) -H surface can not be attributed to the H-Si-Si-H + $H_2O \rightarrow H$ -Si-Si- $OH + H_2$ which could give rise to the characteristic Si-H and Si-OH modes, respectively, at 2081 and 821 cm^{-1} . A more suitable reaction mechanism

involving a metastable species, HO-Si-H, has been proposed as, $H-Si-Si-H + H_2O \rightarrow H_2Si \cdots HO-$ Si-H (metastable) \rightarrow H₂Si · · · Si(O)H₂ [39]. This provides an efficient route for the aggregation of oxygen atoms in the silicon back bonds due to effective inter-back-bond oxygen migration [11,32]. This mechanism explains well the positive absorption peaks at 900, 913, 929, 961 and 978 cm^{-1} in Fig. 2 which appear to have grown out of the coupled monohydride species due to the water exposures. The intense absorption peaks at 900 and 913 cm^{-1} are assigned to the scissoring modes of isolated and adjacent SiH₂ species [11,18]. Based on the calculated frequency values given in Table 1, the smaller absorption peaks at 929, 961 and 978 cm^{-1} in Fig. 2 are identified as H-Si(O)-H, H-Si(O)₂-H and H₂Si(O)₂... $Si(O)xH_2$ species with x = 0-2, respectively [31,32]. The later species and $H-Si(O)_2-Si(O)x-H$ with x = 1 and 2 also show the Si–H stretching signature at 2143 cm^{-1} (Table 2). The vibrational features emerging in the region $880-1000 \text{ cm}^{-1}$ at higher exposures of water, however, reveal that the (2×1) -H surface is less reactive compare to the (2×1) bare surface. Under the experimental conditions employed in this study, the Si-O vibrational structure above 1000 cm^{-1} is elusive indicating that water dissociation does not occur readily on the (2×1) -H surface as it does in the case of (2×1) bare surface. The IR spectrum of the water (2000 L) exposed Si(100)- (2×1) -H surface at 300 K is inserted as Fig. 2(c'). The overall feature relating to the oxide peaks is not so different from the corresponding spectrum at 373 K. The bands of oxidized isolated dihydride H-Si(O)2-H (961 cm⁻¹) and adjacent SiH₂ scissoring modes (913 m^{-1}) and isolated SiH₃ (isolated trihydride, IT) (865 cm⁻¹) bending mode are observed to be relatively intense. This is explained by the lowering of the mobility of the inter-back-bond oxygen migration and the surface hydrogen migration.

3.3. Water adsorption on the $Si(100)-(3 \times 1)-H$ surface

The Si(100)-(3 \times 1)-H surface is prepared by saturating clean Si(2 \times 1) surface with atomic deuterium at 648 K and replacing it by atomic hydro-

gen at 400 K to obtain the (3×1) -H surface structure. The water exposures are given at 400 K and IR spectra recorded at the same temperature are presented in Fig. 3. The spectra 3(a)-(c) show the replacement process of D-atom by H atom on $Si(100)-(2 \times 1)$ -D surface, simultaneously changing the (2×1) surface structure to the (3×1) surface structure. The completion of this process has been ensured from the elimination of Si-D symmetric stretching mode at 1525 cm⁻¹ as well as the scissoring mode at \sim 793 cm⁻¹ related to the intermediate H-Si-D species shown in spectrum 3(b) [22,36]. The H-Si-D species has been completely eliminated at saturation coverage of atomic hydrogen as shown in spectrum 3(c). The intense vibrational modes at 901 and 914 cm⁻¹ due to ID and AD as well as the 2100 cm^{-1} from CM species confirm the formation of (3×1) -H surface at 400 K [11,18]. The weak Si-H stretching modes expected at 2090 cm⁻¹ for ID and 2107 cm⁻¹ for AD can also be observed in the remnants on either side of the 2100 cm^{-1} absorption peak as reported [18]. A small amount of IT species is also presented as indicated by the absorption peaks at 2137 and 855 cm^{-1} . This (3 × 1)-H surface is further exposed to water at 400 K. All the (3×1) -H related vibrational modes turn out to be negative features when the IR spectrum of Si(100)-(3×1)-H surface is selected as background as shown in spectra 3(d)–(f). The water exposure leads to the growth of the narrow vibrational bands primarily at 845, 965 and 981 cm⁻¹ and a broad vibrational structure between 1000 and 1150 cm^{-1} . The new positive absorption peaks at 845, 965 and 981 cm^{-1} are identified in our calculations as H-Si(O)2-O-Si-H, H–Si(O)₂–H and H₂Si(O)₂··· Si(O)xH₂ with x = 0-2, as discussed before. The unresolved broad feature above 1000 cm^{-1} is essentially related to stretching vibrations of Si-O type species which are also formed in the case of the (1×1) -H surface discussed in the following section.

3.4. Water adsorption on the $Si(100)-(1 \times 1)-H$ surface

Firstly, the Si(100)-(2 × 1)-D surface is prepared by saturation exposure of atomic deuterium to Si(100)-(2 × 1) at 648 K. The surface deuterium atoms are then replaced by atomic hydrogen at room temperature to obtain the (1×1) -H surface structure. The IR spectra recorded during the preparation of the (1×1) -H surface are shown in Fig. 4(a)–(c). They clearly exhibit the bending/scissoring modes at 863, 902 and 914 cm⁻¹ for δ (Si– H)_{IT}, $\delta(Si-H)_{ID}$ and $\delta(Si-H)_{AD}$, respectively and the Si-H stretching modes at 2100 cm^{-1} for v(Si-H)_{CM} and 2140 cm⁻¹ for v(Si–H)_{IT} species, characteristic of the (1×1) -H surface structure [18,22] (Tables 1 and 2). The vibrational feature around 795 cm⁻¹ is again due to the H-Si-D species formed in the process of D-atom replacement by H-atom as discussed earlier. In this case we have selected the IR spectrum of Si(100)-(1 \times 1)-H surface as background and all the (1×1) -H vibrational features have turned out to be negative during the process of water adsorption. The spectra 4(d)-(e) show the IR features of the water exposed (1×1) -H surfaces at 300 K. There are several IR absorption peaks centered at 844, 965, 983 cm⁻¹ and a broad feature between 1000 and 1160 cm^{-1} . These spectra are similar to those observed on the Si(100)-(3×1)-H surface shown in Fig. 3 and the absorption peaks at 844, 965, 983 cm^{-1} are assigned accordingly to the same silicon surface species (Table 1). However, at large water exposure as in spectrum 4(e), the intensity of the 983 cm⁻¹ absorption peak increases along with the accumulation of the intense broad structure above 1000 cm^{-1} which splits further into two peaks around 1096 and 1115 cm⁻¹. The model calculations predict that the species such as H₂Si-(O) \cdots Si(O)xH₂ with x = 0-1, H₂Si(O)₂ \cdots $Si(O)xH_2$ with x = 0-2, $H-Si(O)_2-O-Si(O)x-H$ with x = 0-2 and H-Si(O)₂-Si(O)₂-H can contribute significantly to the IR absorption in this region (Table 1).

In the above sections we have discussed the water reactivity pattern on (2×1) , (2×1) -H, (3×1) -H and (1×1) -H surfaces of Si(100). The reaction temperatures are different among these systems; 373 K for (2×1) and (2×1) -H, and 400 and 300 K (the temperature of the air-conditioned experimental room) at which the (3×1) -H and (1×1) -H structures are stable, respectively. However, concerning the reaction H₂O + (2×1) -H, significant difference relating to the oxide peaks was

not observed between 373 and 300 K as already mentioned above. So we think that the reasonable discussion is possible for the difference of the reactivity among these different reaction systems by using the results shown in Figs. 1-4. The results reveal that the bare Si(100) surface is unequivocally more reactive than H-terminated Si surfaces. The barrier-less water dissociation giving rise to Si-H and Si-OH groups on Si dimers is suppressed to a large extent on the hydride phases of Si(100) due to the nonavailability of the dangling bonds for the reaction. The 2000 L water exposed Si(100)-(2 \times 1) surface produces several oxygen inserted silicon hydrides while the same exposure on Si(100)-(2 \times 1)-H generates mainly ID and AD. At the same dose, however, the (3×1) -H and (1×1) -H surfaces do not show significant reactivity. ID and AD species on the silicon surfaces appear to hinder the direct oxidation process, under the conditions employed in this study. However, there is a possibility that these species acquire back bond oxygen atoms on (3×1) -H and (1×1) -H surfaces through oxygen migration forming the oxidized SiH₂ species at higher exposures of water. This is clearly observed in the case of water exposures greater than 2000 L on (3×1) -H and (1×1) -H surfaces generating $H_2Si(O)x$ species with vibrational modes around 965 and 980 cm^{-1} . These species are in fact formed to a certain extent on all four Si(100) surfaces at various water exposures. However, the deeper surface oxidation seems to occur on (3×1) -H and (1×1) -H surfaces only at higher water exposures showing the 985 and 981 cm⁻¹ peaks and the broad Si–O absorption band between 1000 and 1180 cm^{-1} .

These results can be explained by that H_2O reacts with H–Si–Si–H, and not with SiH₂ and SiH₃. This, however, is not inconsistent with the results of Takagi et al. [13] in which no reaction was observed at the H₂O exposure less than 10 L at 300 K, since in our experiments the clear change was observed only at higher exposures than 100 L. It has recently been found by the reaction pass analysis in the reaction system 2H + H–Si–Si–OH and H₂O + Si(100)-(2 × 1)-H that the reaction proceeds through the metastable states H₂Si ··· H–Si–OH or H₂Si ··· HO–Si–H and results in the final product H₂Si ··· Si(O)H₂ [39]. Therefore

as a common reaction pass in the present reaction systems, the reaction pass $H_2O + H_Si_Si_ H \rightarrow H_2Si \cdots H_-Si_-OH$ or $H_2Si \cdots HO_-Si_-H \rightarrow$ $H_2Si \cdots Si(O)H_2$ is considered. It is also known that oxygen atom aggregates through the interback-bond migration of oxygen atom [11,32]. These reaction model well explains the results that the scissoring modes of ID and AD of SiH₂ (at 900 and 913 cm⁻¹, respectively) and $H_2Si(O)_2$ (at 961 and 978 cm⁻¹, respectively) become clearly observable at the higher amount of H₂O exposure commonly in all present reaction systems. Takagi et al. also reported that any reaction was not observed at 90 K with the H₂O + Si(100)-(2×1)-H system [13]. These results are well explained by considering the potential barrier between the reactant $H_2O + Si(100) - (2 \times 1) - H, (3 \times 1) - H$ and (1×1) -H and the metastable states. It is also concluded that the difference among the reactivity of H-Si-Si-H, SiH₂ and SiH₃ is due to a relatively high reactivity of Si-Si bond of H-Si-Si-H, and not due to the stress of the Si back-bonds, since the back-bond stress is considered to increase in the order (2×1) -H, (3×1) -H and (1×1) -H surface.

4. Conclusions

This study clearly demonstrates that the H-terminated Si(100)surfaces are less reactive compared to the bare Si(100)-(2 × 1) surface and tend to form primarily the oxidized ID and AD species possibly via the reaction mechanism involving the metastable species, H–Si–Si– H + H₂O \rightarrow H₂Si \cdots HO–Si–H (metastable). The Si(100)-(2 × 1) surface, however, produces large number of oxygenated silicon hydrides. This shows the passivation effects of the surface hydride phases on the water reactivity with the Si(100) surfaces.

Acknowledgments

This work is supported by the Collaboration Program of the Graduate University for Advanced Studies and the Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, (12440202) and (2001–2006, 13GS0016).

References

- H. Ibach, H. Wagner, D. Bruchmann, Solid State Commun. 42 (1982) 457.
- [2] J.A. Schaefer, F. Stucki, D.J. Frankel, W. Göpel, G.J. Lapeyre, J. Vac. Sci. Technol. B 2 (1984) 359.
- [3] P.A. Thiel, T.E. Madey, Surf. Sci. Rep. 7 (1987) 211.
- [4] D. Gräf, M. Grundner, R. Schulz, L. Mühlho, Appl. Phys. 68 (1990) 5155.
- [5] H. Ikeda, K. Hotta, T. Yamada, S. Zaima, Y. Yasuda, Jpn. J. Appl. Phys. 34 (1995) 2191.
- [6] H. Ikeda, K. Hotta, S. Furuta, S. Zaima, Y. Yasuda, Appl. Surf. Sci. 104–105 (1996) 354.
- [7] K. Raghavachari, Y.J. Chabal, L.M. Struck, Chem. Phys. Lett. 252 (1996) 230.
- [8] M.K. Weldon, B.B. Stefanov, K. Raghavachari, Y.J. Chabal, Phys. Rev. Lett. 79 (1997) 2851.
- [9] L.M. Struck, et al., Surf. Sci. 380 (1997) 444.
- [10] F.S. Tautz, J.A. Schaefer, J. Appl. Phys. 84 (1998) 6636.
- [11] M.K. Weldon, K.T. Queeney, A.B. Gurevich, B.B. Stefanov, Y.J. Chabal, K. Raghavachari, J. Chem. Phys. 113 (2000) 2440.
- [12] Z.-H. Wang, H. Noda, Y. Nonogaki, N. Yabumoto, T. Urisu, Jpn. J. Appl. Phys. 41 (2002) 4275.
- [13] N. Takagi, N. Minami, T. Furukawa, M. Nishijima, Surf. Sci. Lett. 297 (1993) L43.
- [14] M. Niwano, M. Terashi, M. Shinohara, D. Shoji, N. Miyamoto, Surf. Sci. 401 (1998) 364.
- [15] S. Watanabe, J. Chem. Phys. 108 (1998) 5965.
- [16] Y. Kobayashi, K. Sumitomo, K. Prabhakaran, T. Ogino, J. Vac. Sci. Technol. A 14 (1996) 2263.
- [17] W. Ehrley, R. Butz, S. Mantl, Surf. Sci. 248 (1991) 193.
- [18] H. Noda, T. Urisu, Chem. Phys. Lett. 326 (2000) 163.

- [19] A. Yoshigoe, K. Mase, Y. Tsusaka, T. Urisu, Y. Kobayashi, T. Ogino, Appl. Phys. Lett. 67 (1995) 2364.
- [20] V.M. Bermudez, S.M. Prokes, Surf. Sci. 248 (1991) 201.
- [21] Y. Zhang, S. Sato, H. Ohshima, T. Hattori, T. Urisu, Appl. Surf. Sci. 79/80 (1994) 422.
- [22] Y.J. Chabal, K. Raghavachari, Phys. Rev. Lett. 54 (1985) 1055.
- [23] C.C. Cheng, J.T. Yates Jr., Phys. Rev. B 43 (1991) 4041.
- [24] Y.J. Chabal, Physica B 170 (1991) 447.
- [25] D.T. Jiang, G.W. Anderson, K. Griffiths, T.K. Sham, P.R. Nroton, Phys. Rev. B 48 (1993) 4952.
- [26] Y.J. Chabal, K. Raghavachari, Phys. Rev. Lett. 53 (1984) 282.
- [27] H.N. Waltenburg, J.T. Yates Jr., Chem. Rev. 95 (1995) 1589.
- [28] J.J. Boland, Surf. Sci. 261 (1992) 17.
- [29] Y.J. Chabal, K. Raghavachari, Surf. Sci. 502–503 (2002) 41.
- [30] Y.J. Chabal, K. Raghavachari, X. Zhang, E. Garfunkel, Phys. Rev. B 66 (2002) 161315(R).
- [31] Z.-H. Wang, T. Urisu, G. Ranga Rao, S. Nanbu, J. Maki, M. Aoyagi, H. Watanabe, K. Ooi, Surf. Sci., submitted for publication.
- [32] Z.-H. Wang, T. Urisu, S. Nanbu, J. Maki, G. Ranga Rao, M. Aoyagi, H. Watanabe, K. Ooi, Phys. Rev. B 69 (2004) 045309.
- [33] Z.-H. Wang, H. Noda, Y. Nonogaki, N. Yabumoto, T. Urisu, Surf. Sci. 502–503 (2002) 86.
- [34] B.B. Stefanov, A.B. Gurevich, M.K. Weldon, K. Raghavachari, Y.J. Chabal, Phys. Rev. Lett. 81 (1998) 3908.
- [35] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [36] M.J. Frisch et al., GAUSSIAN 98, Gaussian Inc., Pittsburgh, PA, 1998.
- [37] H. Wagner, R. Butz, U. Backes, D. Bruchmann, Solid State Commun. 38 (1981) 1155.
- [38] A.B. Gurevich, B.B. Stefanov, M.K. Weldon, Y.J. Chabal, K. Raghavachari, Phys. Rev. B 58 (1998) R13434.
- [39] H. Watanabe, K. Ooi, S. Nanbu, J. Maki, M. Aoyagi, Z.-H. Wang, T. Urisu, Chem. Phys. Lett. 383 (2004) 523.