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Infrared reflection absorption study of water interaction with H-terminated Si(100) surfaces

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Abstract. **Water adsorption on clean and hydrogenated Si(100) surfaces was studied under ultra high vacuum conditions using surface infrared spectroscopy. The study shows that H–Si–Si–OH and SiH_2 species are formed on Si(100)–(2 × 1) and Si(100)–(2 × 1)–H surfaces, respectively. The reactivity behaviour of Si(100)–(3 × 1)–H and Si(100)–(1 × 1)–H is similar, both stabilizing oxygen inserted silicon dihydrides.**

Keywords. **IR; Si(100); water adsorption.**

1. Introduction

Chemistry of silicon surfaces and interfaces is widely explored due to the importance of silicon in semiconductor industry. Interaction of variety of small and large adsorbate molecules with silicon surfaces has been the subject of recent interest aimed at tuning the surface molecular properties and the development of silicon-based biosensors and membrane chips (Waltenburg and Yates 1995; Hamers *et al* 2000; Reddy *et al* 2001; Ashkenasy *et al* 2002; Buriak 2002). The adsorption of water on silicon single-crystal surfaces is another area of interest in silicon surface chemistry to reveal the atomic details of the surface oxidation mechanisms for controlling the SiO_2 gate oxide thickness to ~ 2 nm in microelectronics (Gurevich *et al* 1998; Chabal and Raghavachari 2002). The creation and selective removal of thin SiO_2 layers are thus important processes in semiconductor device fabrication. The stable ultra thin surface SiO_2 layers are usually formed using water as an oxidant and etched off by weak acid, HF, which can remove SiO_2 layers at the rate of 100 nm per min (Liu *et al* 1992; Jones *et al* 1995). In order to understand the chemical oxidation process by water adsorption, the Si(100) surfaces have been investigated under ultra high vacuum conditions by high resolution electron energy loss spectroscopy (Ibach *et al* 1982; Ikeda *et al* 1995; Bitzera *et al* 1997) and surface infrared spectroscopy (Struck *et al* 1997; Weldon *et al* 1997, 2000; Chabal and Raghavachari 2002; Wang *et al* 2002, 2004; Ranga Rao *et al* 2004).

Silicon crystal has diamond lattice structure with sp^3 hybridization. The surfaces of silicon crystals contain dangling bonds due to the cleavage of covalent bonds. The dangling bonds at the surface are responsible for the reconstruction of Si(100) leading to the formation of Si(100)–(2 × 1) structure consisting of surface Si = Si dimers with a σ and a π bond. Adsorption of atomic hydrogen on Si(100) surfaces at different temperatures under ultra high vacuum conditions gives rise to H-terminated (2 × 1) coupled monohydride (CM) (H–Si–Si–H), (1 × 1) isolated dihydride (ID) (H–Si–H), and (3 × 1) coupled monohydride and dihydride structures. The Si(100)–(2 × 1)–H structure which forms after saturation exposure of atomic H at the surface temperature of about 600–650 K exhibits characteristic ν(Si–H) modes at 2099 (A_1 symmetry) and 2088 cm^{-1} (B_1 symmetry) (Tautz and Schaefer 1998). The Si(100)–(3 × 1)–H structure consisting of coupled monohydride and dihydride species can be produced by exposing Si(100)–(2 × 1) surface to saturation atomic H at 400 K (Weldon *et al* 2000; Noda and Urisu 2000). The Si(100)–(1 × 1)–H structure is prepared by saturation exposure of atomic H to Si(100)–(2 × 1) at 300 K. The (1 × 1)–H phase is reported to be a disordered mixture of coupled monohydride, di- and tri-hydrides (SiH_3) (Waltenburg and Yates 1995). Both (3 × 1)–H and (1 × 1)–H structures show 902 and 913 cm^{-1} peaks in the Si–H bending region due to the isolated (ID) and adjacent (AD) SiH_2, respectively. In the Si–H stretching region, the isolated and adjacent SiH_2 species are identified with 2090 cm^{-1} and 2107 cm^{-1}, respectively (Noda and Urisu 2000).

The vibrational spectroscopic investigations of water adsorption on Si(100)–(2 × 1) surfaces have shown the formation of H–Si–Si–OH species on each Si = Si dimer (Ibach *et al* 1982; Struck *et al* 1997; Weldon *et al* 2000; Wang *et al* 2002). Upon thermal annealing the decomposition of surface hydroxyl groups and the incorporation of oxygen atoms into the Si dimer-bonds as well as Si back-bonds occur in the top layers of Si until the hydrogen desorption temperatures above 650 K. The surface IR spectroscopy has provided impetus to study the mechanistic aspects of oxygen atom insertion into surface Si layers (Mawhinney *et al* 1997; Ogata *et al* 1995; Gurevich *et al* 1998; Chabal and Raghavachari 2002; Ranga Rao *et al* 2004; Wang *et al* 2004). This article reports the

interaction of water with H-terminated Si(100) surfaces under UHV conditions employing surface sensitive infrared reflection method. The study indicates that H-terminated Si(100) surfaces are less reactive due to the non-availability of dangling bonds compared to the bare Si(100) surfaces and tend to form oxygen inserted surface silicon dihydrides.

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 (Wang *et al* 2002; Ranga Rao *et al* 2004). The base pressure of the experimental chamber was maintained at $< 2 \times 10^{-10}$ Torr by pumping with a turbomolecular pump (500 L s^{-1}). The optical path of the IRRAS system was continuously purged with pure N_2 gas. A *p*-polarized IR beam from a Fourier transform spectrometer (JEOL JIR 7000) was selected by a wire grid polarizer using KRS-5 infrared transmissive lens and directed into the reaction chamber through a ZnSe view port at an incident angle of 85° with respect to the silicon surface normal. The reflected IR beam was detected by liquid nitrogen cooled HgCdTe (MCT) detector outside the UHV chamber.

The $CoSi_2$ burried metal layer (BML) Si(100) wafer was employed in this study. The 100 nm thick $CoSi_2$ layer acts as an IR reflector and the vibrational components perpendicular to the sample surface can be detected by the IR external reflection optical geometry without the interference of Si phonons (Ehrley *et al* 1991; Struck *et al* 1997). A piece of silicon wafer was cut and cleaned by wet chemical methods (Liu *et al* 1992). The sample cleaning procedure involved degreasing in acetone and methanol solutions, treatment with HF solution and finally with $HCl + H_2O_2 + H_2O$ solution before transferring into the experimental chamber. The BML–Si(100) sample was then degassed slowly up to 600 K keeping the chamber pressure $< 5 \times 10^{-9}$ Torr followed by a flash to 1200 K to remove the surface oxide. A silicon epitaxial layer of about 50 nm thick was grown over the rough BML–Si(100) surface using Si_2H_6 gas at 975 K. The deposition of 50 nm thick silicon epitaxial film required Si_2H_6 gas exposure at 10^{-3} Torr for 30 s. After epitaxy, the total thickness of the Si overlayer above the $CoSi_2$ reflector was about 100 nm which was sufficient to obtain good surface IR reflection signal. The sample showed clear Si(100)–(2 × 1) RHEED pattern after brief annealing (Kobayashi *et al* 1996). The Si(100)–(2 × 1) surface was further used to prepare H-terminated silicon surfaces.

The IRRAS measurements were carried out by accumulating 300 scans at 2 cm^{-1} resolution and the reported spectra are the ratio of absorption spectra for water covered Si surfaces to the D- or H-terminated Si surfaces recorded at the same temperature. The sample was heated by using ceramic heater (pyrolytic graphite/pyrolytic boron nitride). The sample temperature was controlled by a proportion-integral-differential (PID) controller with a W–Re thermocouple attached to the rear side of the Si(100) substrate. The thermocouple was calibrated by an optical pyrometer (emissivity = 0·8 for Si) and the sample temperature was kept constant during the IR measurements to avoid spectral distortions.

Atomic H and D were produced at appropriate gas pressures by using incandescent tungsten filament and the typical dosing time is 20 s. The exposures were measured in Langmuir units (1 L = 10^{-6} Torr-s) from uncalibrated ion gauge readings. In this study, the procedures followed for IR measurements include thermal cleaning of the Si(100) BML sample up to 1200 K, 2000 L saturation exposure of atomic H or D at 673 K and allowing the samples to reach the measurement temperatures. The samples were exposed to controlled amount of water at a desired temperature. All the samples were checked for appropriate surface periodicity after hydrogen or deuterium exposures. The hydrogen covered (2 × 1)–H, (3 × 1)–H and (1 × 1)–H surfaces were prepared by exposing clean or deuteriated Si(100)–(2 × 1) surface to atomic H at 648 K, 400 K and 300 K, respectively, under UHV conditions.

3. Results and discussion

The clean Si(100)–(2 × 1) surface is prepared as described in the experimental section and exposed to 2000 L atomic deuterium at 648 K before cooling to 373 K to collect background surface infrared signal. The deuterium atoms are subsequently flashed out at 1050 K. The clean Si(100)–(2 × 1) surface is exposed to 2000 L atomic hydrogen at 648 K to obtain Si(100)–(2 × 1)–H. These surfaces are further used for water adsorption experiments. The infrared reflection spectra of water adsorbed on bare Si(100)–(2 × 1) and Si(100)–(2 × 1)–H surfaces at 373 K are shown in figure 1. The spectra are presented as the ratios of absorption spectra of the water exposed Si(100)–(2 × 1) surface to the Si(100)–(2 × 1)–D surface (figure 1a) and the water exposed Si(100)–(2 × 1)–H surface to the Si(100)–(2 × 1)–H surface (figure 1b) recorded at 373 K. The vibrational peaks at 822, 1526 and 2081 cm^{-1} are assigned, respectively, to the stretching modes of Si–OH, Si–D and Si–H species present on Si(100)–(2 × 1) surface. The negative infrared absorption peak at 1526 cm^{-1} is from the deuteriated Si(100)–(2 × 1) surface which was taken as infrared background. The Si–OH and Si–H species are formed from the dissociative adsorption of water molecule and bonded to the two Si atoms of the same (2 × 1) dimer unit giving rise to H–Si–Si–OH surface species (Ibach *et al* 1982; Weldon *et al* 2000). At higher exposures of water the stable Si–H and Si–OH groups undergo considerable structural changes due to large scale decomposition of water and

adsorbed O–H groups generating several oxygenated surface hydride species. The initial stage of oxidation of silicon surface involves oxygen insertion into the silicon back bonds. The low intense peak around 979 cm^{-1} is due to the scissoring mode of oxygen inserted $Si–H_2$ species and indicates the presence of $H_2Si(O)_x$ type species with $x = 0 \sim 2$ oxygen atoms inserted into Si back bonds (Ranga Rao *et al* 2004; Wang *et al* 2004).

The reactivity pattern of water with H-covered Si(100)–(2 × 1) surface is shown in figure 1b. Even at high exposure of water, the surface does not show the presence of H–Si–Si–OH species indicating a change in the reactivity of hydrogen covered silicon surface with water. The infrared peaks are seen at 900, 913, 961, 2100 and 2142 cm^{-1}. The negative infrared absorption peak at 2100 cm^{-1} is due to the Si–H stretch of the surface hydride phase (coupled monohydride species) of Si(100)–(2 × 1)–H, the surface infrared signal of which was taken as a background. The infrared peaks at 900 and 913 cm^{-1} are attributed to the scissoring modes of isolated and adjacent SiH_2 species. The formation of dihydrides and oxygen inserted dihydride species from coupled monohydride in the presence of water seem to occur by oxygen insertion and migration through silicon back bonds (Weldon *et al* 2000). The smaller intensity peak at 961 cm^{-1} indicates the nucleation of highly oxidized species of the type $H_2Si(O)_x$ which has the Si–H stretching signature around 2142 cm^{-1}. This type of species are also present to a lesser extent on water exposed Si(100)–(2 × 1) surface in spectrum 1(a). It is clear that water adsorption at low exposures on clean Si(100)–(2 × 1) surface produces dissociated fragments H and OH attached to silicon atoms while hydrogenated silicon (2 × 1) surface seems to favour the formation of dihydride species.

Water adsorption is further studied on hydrogen terminated Si(100)–(3 × 1) and Si(100)–(1 × 1) surfaces. The Si(100)–(3 × 1)–H and Si(100)–(1 × 1)–H surfaces are obtained by saturating clean Si(100)–(2 × 1) surface with atomic deuterium at 648 K and replacing it by atomic hydrogen, respectively, at 400 K and 300 K. The infrared spectra of 5000 L water dosed silicon surfaces are shown in figure 2. The infrared spectra are presented as the ratios of the absorption spectra of water exposed Si(100)–(3 × 1)–H surface to the Si(100)–(3 × 1)–H surface (spectrum 2(a)), and the water exposed Si(100)–(1 × 1)–H surface to the Si(100)–(1 × 1)–H surface (spectrum 2(b)). The spectrum 2(a) shows a number of infrared absorption peaks at 845, 902, 914, 966, 981, 2100 and an intense broad band at 1000–1150 cm^{-1}. These infrared peaks also appear in spectrum 2(b) along with new peaks at 863 and 2140 cm^{-1}. The negative absorption peaks in spectrum 2(a) at 902 and 914 cm^{-1} are due to isolated and adjacent SiH_2 species and the 2100 cm^{-1} is from coupled monohydride species present on the Si(100)–(3 × 1)–H surface which is taken as a background. The remaining vibrational peaks at 845, 966, 981 are assigned to oxygen inserted coupled monohydride, isolated and adjacent dihydride species, respectively (table 1). The unresolved broad vibrational feature at 1000–1150 cm^{-1} is related to collective Si–O–Si stretching vibrations observed on silicon surfaces containing variety of oxygen inserted silicon dimers and bulk oxides (Mawhinney *et al* 1997; Weldon *et al* 2000; Ranga Rao *et al* 2004).

The Si(100)–(1 × 1)–H surface shows similar reactivity pattern as that of Si(100)–(3 × 1)–H surface with water. The spectrum 2(b) shows infrared absorption peaks at 845, 863, 902, 914, 966, 981, 2100, 2140 and the broad vibrational feature at 1000–1150 cm^{-1}. The negative peaks

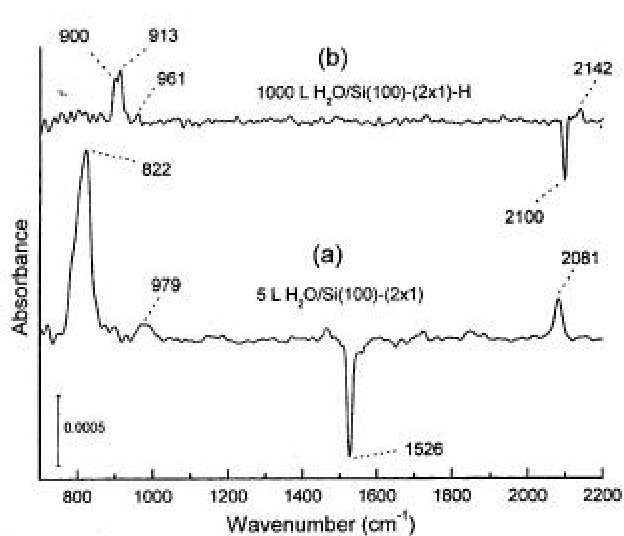

Figure 1. Infrared reflection absorption spectra of water exposed (**a**) Si(100)–(2 × 1) and (**b**) Si(100)–(2 × 1)–H surfaces at 373 K.

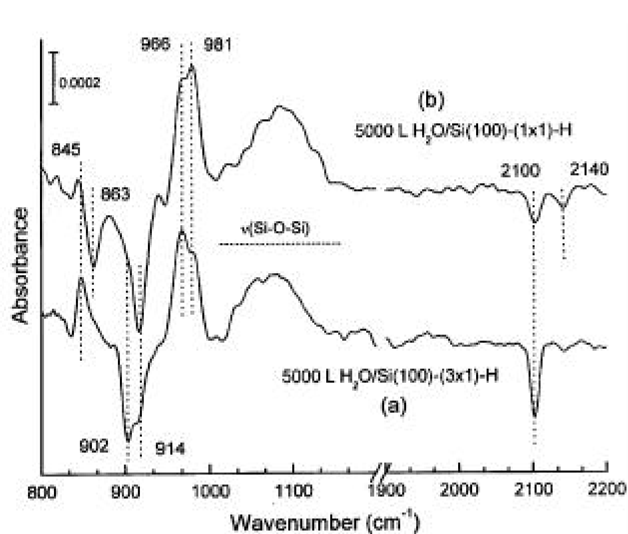

Figure 2. Infrared reflection absorption spectra of water exposed (**a**) Si(100)–(3 × 1)–H surface at 400 K and (**b**) Si(100)–(1 × 1)–H surface at 300 K.

Table 1. The surface species and their vibrational frequencies measured on different Si(100) surfaces by infrared reflection absorption method.

Species	Vibrational mode	Frequency (cm^{-1})
H–Si–Si–OH	***n***(Si–OH)	822
	n(Si–H)	2081
	n(Si–D)	1526
H–Si–H	***d***(Si–H)$_{ID}$	900–902
H–Si(O)$_2$–H	***d***(Si–H)$_{ID}$	961–966
H$_2$Si…SiH$_2$	***d***(Si–H)$_{AD}$	913–914
H$_2$Si(O)$_2$…Si(O)$_x$H$_2$, x = 0–2	***d***(Si–H)$_{AD}$	979–981
H–Si–Si–H	***n***(Si–H)$_{CM}$	2100
H–Si(O)$_2$–Si(O)$_x$–H, x = 1,2	***n***(Si–H)$_{CM}$	2142
H–Si(O)$_2$–O–Si–H	***d***(Si–H)$_{CM}$	845
SiH$_3$	***d***(Si–H)	863
SiH$_3$	***n***(Si–H)	2140

observed in the bending/scissoring region at 863, 902 and 914 cm^{-1} show the presence of SiH_3, isolated and adjacent SiH_2 species, respectively. In the Si–H stretching region, the peaks at 2100 and 2140 cm^{-1} are the signatures of the couple monohydride and SiH_3 species, respectively (Noda and Urisu 2000). These characteristic Si–H bending and stretching modes confirm the (1×1)–H surface as a starting point. Water adsorption on this surface gives positive peaks at 845, 966 and 981 cm^{-1} and the broad vibrational structure at 1000–1150 cm^{-1} which are similar to those observed on Si(100)–(3×1)–H surface (table 1). These results show that clean Si(100) surface is more sensitive to water chemisorption than H-terminated Si surfaces. At low exposures bare Si(100)–(2×1) surface dissociates water molecule. The hydrogen reconstructed silicon surfaces tend to produce surface oxygenated dihydrides which show blue shifts in the ***d***(Si–H) vibrational frequencies.

4. Conclusions

Water adsorption is dissociative on Si(100)–(2×1) surface giving rise to H–Si–Si–OH species. The hydrogenated Si(100) surfaces tend to produce dihydride and oxygenated dihydride species at larger water exposures.

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