

VI-F Synchrotron Radiation Stimulated Surface Reaction and Nanoscience

Synchrotron radiation stimulated process (etching, CVD) has characteristics of low damage, low contamination, high spatial resolution, and high precision etc. In this project, nanostructures are created by using synchrotron radiation stimulated process, and the reaction mechanisms are investigated by using STM.

VI-F-1 Nanostructure Formation on Si (111) Surface Assisted by Synchrotron Radiation Illumination—Characterization by Scanning Tunneling Microscopy—

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[*J. Electron Spectrosc. Relat. Phenom.* **119**, 241 (2001)]

The surface structures after the synchrotron radiation (SR) stimulated removal of native oxide on Si (111) exactly oriented and 4° misoriented surfaces were investigated by scanning tunneling microscopy. The exactly oriented surface showed large regions of atomically flat Si(111)-7×7 structure, and was characterized by the formation of single bilayer steps nicely registered to the underlying crystal structure, clearly different from the disordered step edge obtained by the usual high temperature thermal cleaning. The 4° misoriented sample showed nearly uniformly spaced steps bunched and terraces terminated by 7×7 unit cells in both SR assisted and thermal cleanings, indicating that both cleanings give almost thermal equilibrium surfaces.

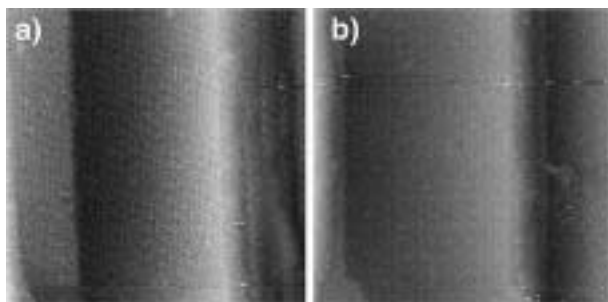


Figure 1. 50 nm × 50 nm STM images of the Si(111) 4° misoriented surfaces after 880 °C 1 min thermal (a), and the 700 °C 2 h SR stimulated cleaning (b), respectively.

VI-F-2 Construction of UHV Variable Temperature STM for *in situ* Observation of SR Stimulated Surface Reaction

NONOGAKI, Youichi; URISU, Tsuneo

We have investigated SR assisted desorption of SiO₂

on Si substrates under the various conditions and have found the significant difference between the thermal and SR-assisted desorption by STM observations. However, these STM images were not taken just after the SiO₂ desorption, since sample setting positions are different between the SR irradiation and STM observation. It is also unclear how the Si surfaces degrade during transferring the samples. To observe the time variation of the surface images more accurately, we have made a new STM system with STM and LEED as shown in Figure 1. By this system, the STM observation and SR irradiation can be conducted at the same sample position.

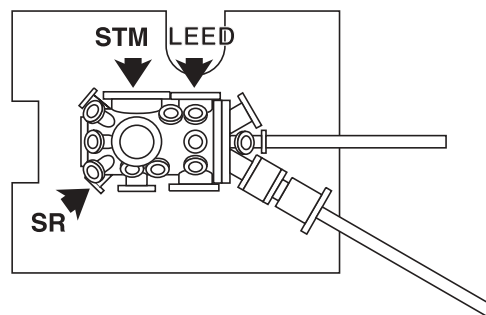


Figure 1. Schematic drawing of new STM system.

VI-F-3 Construction of Low Temperature UHV STM for Observation of Organic- or Bio-Molecules Assembled Silicon Surface

TAKIZAWA, Morio; URISU, Tsuneo

The study on organic- or bio- molecules assembled silicon surfaces is one of the important fields in nanoscience. We are now preparing low temperature STM for this purpose. The STM is equipped with VTI unit for temperature control from 2.5 K to R. T. The bio-molecules which are solid, liquid and gas phase materials can be adsorbed by using a small crucible, liquid- and gas- doser, respectively. These evaporators can control a very small amount of exposure to the surfaces. Now, the chamber vacuums are reaching to less than 5.0×10^{-11} Torr (that is detection limit of our ion gauge). Although the condition is not optimized, we have got current-constant images of silicon(111) surface. In the next step, we will observe organic- or bio- molecules assembled on Si(100) surface in UHV.

VI-G Noble Semiconductor Surface Vibration Spectroscopy

As a new high sensitive and high resolution surface vibration spectroscopy technique, we are developing an infrared reflection absorption spectroscopy using buried metal layer substrate (BML-IRRAS). We are now developing a fabrication technique of BML substrate by wafer bonding. We are also investigating several surface chemical reactions on Si surfaces using this BML-IRRAS.

VI-G-1 Initial Stage of Hydrogen Etching of Si Surfaces Investigated by Infrared Reflection Absorption Spectroscopy

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[*Jpn. J. Appl. Phys.* **39**, 6985 (2000)]

The initial stage of etching reactions (breaking the Si-Si back bonds) of Si(100) and Si(111) surfaces exposed to hydrogen at room temperature was investigated by buried metal layer-infrared reflection absorption spectroscopy. The peaks of SiH₂ scissors and SiH₃ deformation modes (< 1000 cm⁻¹) were successfully observed as clear indicators of the initial stage of hydrogen etching reactions. On the Si(100) surface, the hydrogen exposure dependence of these peaks indicated that the etching reaction starts in the relatively low-exposure region of ≥ 300 L (1 L = 1×10^{-6} Torr s). We found that the adjacent dihydride is a precursor to breaking the Si back bonds. On the Si(111) surface, it was found that the adatom's two back bonds are easily broken, and that adatom trihydride is generated at a low H-exposure of 70–500 L. Adding to this dominant reaction, the etching of the rest-atom layer was observed at H-exposures higher than 10000 L.

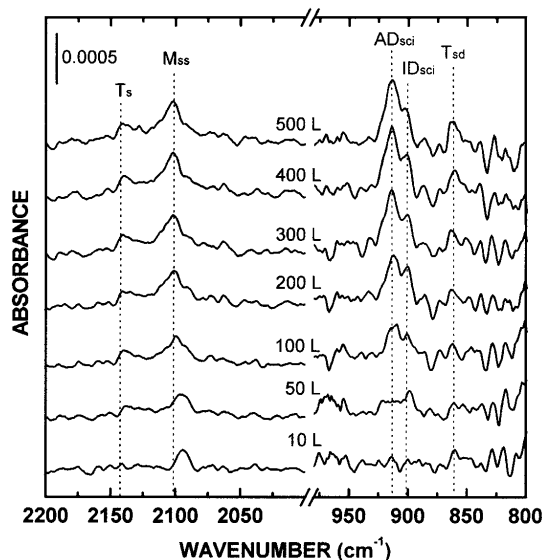


Figure 1. BML-IRRAS spectra of p-polarization for H/Si(100) formed by H-exposure at RT. The resolution is 2 cm⁻¹. H-exposure in units of Langmuir (L) is attached to each spectrum. Peak positions of SiH_n vibration modes are indicated by dotted lines. (M_{ss}: SiH symmetric stretching, T_s: SiH₃ stretching, T_{sd}: SiH₃ symmetric deformation, I_{Dsci}: isolated SiH₂ scissors, A_{Dsci}: adjacent SiH₂ scissors)

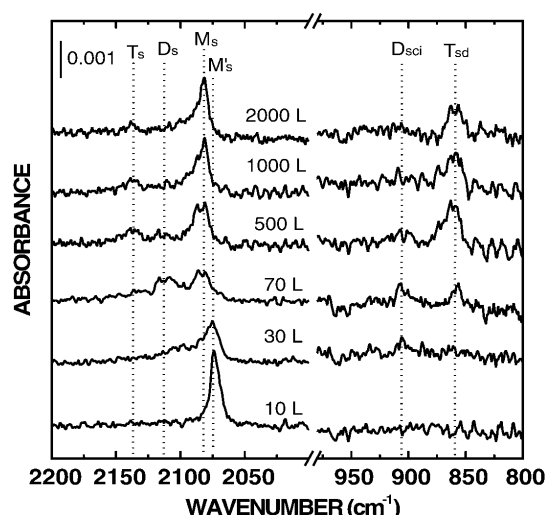


Figure 2. BML-IRRAS spectra of p-polarization for H/Si(111) formed by H-exposure at RT. The resolution is 2 cm⁻¹. H-exposure in units of L is attached to each spectrum. Peak positions of SiH_n vibration modes are indicated by dotted lines. (M_{s'}: SiH stretching of adatom site, M_s: SiH stretching of rest-atom site, D_s: SiH₂ stretching, T_s: SiH₃ stretching, T_{sd}: SiH₃ symmetric deformation, D_{sci}: SiH₂ scissors)

VI-G-2 Nearly Ideally H-Terminated Si(100) Surfaces and IR-Line Width Broadening due to Hydrogen Diffusion into the Subsurface

WANG, Zhihong; NODA, Hideyuki; NONOGAKI, Youichi; URISU, Tsuneo

[*Surf. Sci.* submitted]

Infrared reflection absorption spectroscopy using the buried metal layer substrate (BML-IRRAS) is known to be an unique vibration spectroscopy having a high sensitivity and a high resolution in the wide energy range covering the finger print regions on the semiconductor surfaces. In the present work, dependence of the line width with the coupled monohydride symmetric stretching vibration of the H-terminated Si(100) surface on the adsorption temperature and the hydrogen exposure are investigated by BML-IRRAS method. (Figure 1) The line width significantly changes depending on the adsorption temperature and hydrogen exposure. The reason of the line width broadening is discussed, and it is strongly suggested that the hydrogen diffusion into the subsurface of Si has a significant influence on the line width broadening. The evidence of hydrogen (deuterium) diffusion into the subsurface is investigated for the first time by using IRRAS measurement.

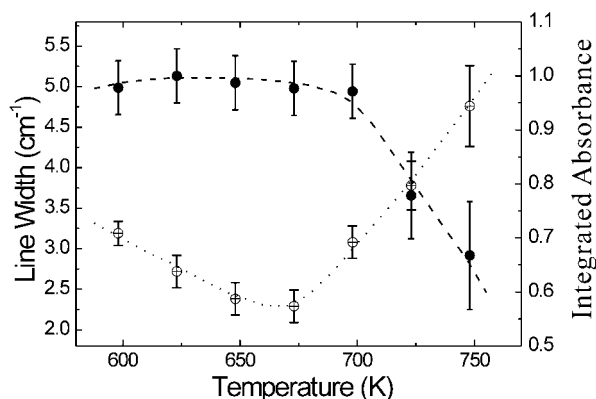


Figure 1. Dependence of line-width (○) and integrated absorbance (●) of the Si-H symmetric stretching peak on the hydrogen atom adsorption temperature.

VI-G-3 Hydrogen Diffusion and Water Reaction on the H-Terminated Si(100) Surface

WANG, Zhihong; NONOGAKI, Youichi; URISU, Tsuneo

[*Jpn. J. Appl. Phys.* submitted (2001)]

Hydrogen terminated Silicon surfaces are interesting not only from the physical studies but also from the application to semiconductor device fabrication. It is known that ideally hydrogen terminated Si(111) surface can be obtained both by wet and dry process and its passivation effects are well investigated. It is also known that the atomically flat hydrogen terminated Si(100) surface is not obtained by wet processes and the chemical reactivity of the hydrogen terminated Si(100) surfaces is also not well understood. The diffusion of hydrogen into silicon bulk is important but not well

understood yet due to the difficulties of observation on bulk hydrogen. The reaction with water on H-terminated Si(100) surface is interesting from the viewpoint of understanding the first oxidation step of Si(100) surface. The authors studied these phenomena in detail by measuring the surface vibration spectra of H-terminated Si(100) surfaces using the Infrared reflection absorption spectroscopy using the buried metal layer substrate (BML-IRRAS). It has been observed that the IR line-width changes significantly depending on the hydrogen exposure and adsorption temperature. The line-width broadening was explained by diffusion of hydrogen into Si(100) bulk. The ideally H-terminated Si(100) surfaces were made and the reaction with water was also studied. It has been found that the ideally H-terminated Si(100) surface is easily attacked by water as shown in Figure 1. IR spectrum after 1000L water exposure shows that the original SiH vibration peak decrease (2100 cm^{-1}), SiH₂ peaks generate ($\sim 900\text{ cm}^{-1}$) and the surface is oxidized ($\sim 1000\text{ cm}^{-1}$ band).

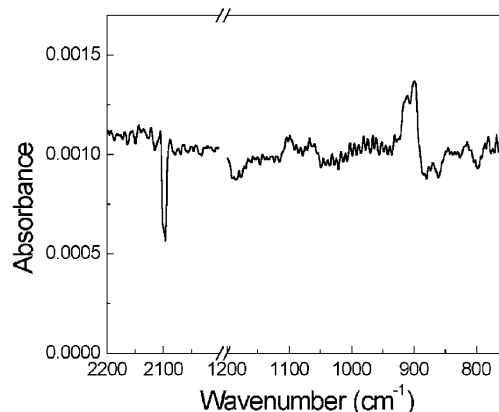


Figure 1. BML-IRRAS spectrum of water reaction with H-terminated Si (100) surface.

VI-H Integration of Bio-Functional Materials on Silicon

Integration of biofunctional materials such as lipids and proteins are expected to find an important applications in biosensors, developments of new medicines, and diagnosis of intractable diseases *etc.* In this project, we are investigating the area selective modification of Si surfaces by depositing the self assembled alkyl monolayers and the characterization by AFM and IRRAS, to integrate biomaterials such as lipids and membrane proteins on Si surfaces with controlled arrangement and orientations.

VI-H-1 Influence of Substrate Roughness on the Formation of Self-Assembled Monolayers (SAM) on Silicon(100)

MORÉ, Sam Dylan; GRAAF, Harald; BAUNE, Michael¹; WANG, Changshun¹; NONOGAKI, Youichi; URISU, Tsuneo
(¹Bremen Univ.)

The peak shifts of the CH₂-vibration are an indicator of the amount of gauche-conformational disorder. We have investigated the relationship between surface roughness and morphology and the peak position.

With increasing substrate surface roughness both the symmetric CH₂-peak as well as the asymmetric CH₂-peak shift to higher wave numbers. The magnitude of the shift is about 6 cm^{-1} . The CH₂-peak position correlates with the trans/gauche conformational order in the aliphatic chain.

Scanning electron micrographs showed that the samples which yielded the highest signal intensity exhibited a the highest degree of roughness. This could be confirmed with laser light scattering and qualitatively with profilometer scans.

As trans/gauche order/disorder and surface density are in close correlation, the insulating properties of

SAM-layers will depend on the microscopic order of the substrate at least for medium length C-chains. Controlling these properties would therefore mandate control of the surface roughness.

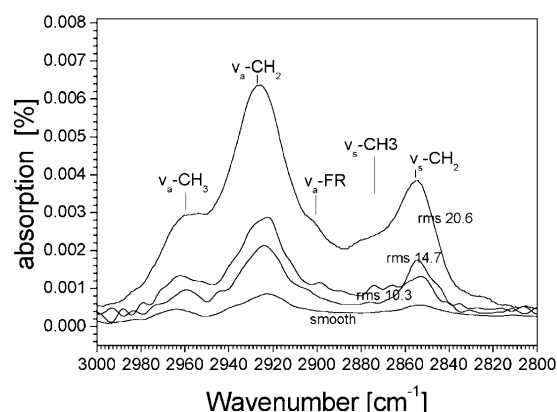


Figure 1. Symmetric (ν_s) and asymmetric (ν_a) CH_2 and ν_a - CH_3 vibrational peaks for the smooth Si(100) and three different roughened Si(100) surfaces (a, b, c), which are covered with an aliphatic self-assembled monolayer. ν_a -FR marks a Fermi-resonance and ν_a - CH_3 the CH_3 asymmetric peak.

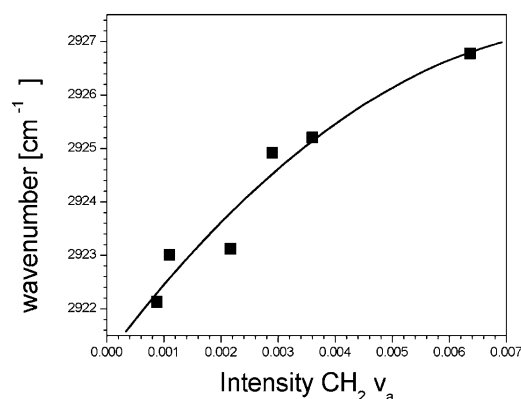


Figure 2. Peak position of the CH_2 -asymmetric vibration as a function of peak intensity for an aliphatic SAM (dodecan) on roughened Si(100).

VI-H-2 Characterization of Oligo-Ethylene Glycol Ethers Bound to Self-Assembled Monolayers (SAM) on Silicon with FTIR Spectroscopy and Ellipsometry

MORÉ, Sam Dylan; WANG, Changshun¹; URISU, Tsuneo

Amphiphilic molecules bound to self assembled monolayers (SAM) can serve as anchor molecules for supported lipid membranes. The resulting anchor entities, bound covalently to the Si-substrate, increase the non-covalently interaction of the lipid with its SAM sublayer, thus enhancing the mechanical stability of the system. Oligo-ethylene glycol molecules, which have been bound to an aliphatic chain are of special interest as the polar chain can further provide hydrophilic pockets to accommodate membrane proteins.

Two different approaches were investigated: Firstly, binding Poly-oxyethylene stearyl ethers to preexisting

functionalized self-assembled monolayers on Si(100) via an ester bond and secondly to graft undecenyl acid Brij-esters via the double bond directly to a H terminated Si(100) surface.

Only Poly-oxyethylene stearyl ethers with oxyethylene chainlengths of n ($\text{O}-\text{CH}_2-\text{CH}_2$) = 2 and 10. Longer chainlengths (n = 20, 23, 100) could however be attached via the direct grafting method.

Both methods lead to a significant amount of highly ordered Poly-oxyethylene stearyl domains.

VI-H-3 Deposition of Self-Assembled Alkyl Monolayers on Si and SiO_2

WANG, Changshun¹; MORÉ, Sam Dylan; URISU, Tsuneo
(¹IMS and Henan Univ.)

Preparations of alkyl monolayers on Si and SiO_2 are technologically important for their potential utility. We have deposited octadecyltrichlorosilane (OTS) self-assembled-monolayers (SAM) on silicon substrates with a native oxide (nominally SiO_2) layer. Structural features of the films were characterized using Fourier transform infrared spectroscopy (FTIR) and ellipsometry. The adsorption temperature dependency of FTIR frequencies and intensities of CH_2 stretching vibration bands indicate the existence of a characteristic temperature T_c . The hydrocarbon chains observe an ordered and closely packed state when the monolayers are prepared below T_c , whilst disordered monolayers with low molecular density are formed above T_c . Moreover, dense, well-ordered alkyl SAMs are prepared on the silicon surface by the reactions of neat and dilute 1-alkenes (dodecene, octadecene, *etc.*) with the hydrogen-terminated silicon surface. The hydrosilylation reaction results in the formation of very stable silicon-carbon bonds, which yield dense monolayers as evidenced from infrared spectroscopy and ellipsometry. And the reaction is more efficient at higher temperatures than that at lower temperatures, as shown in Figure 1.

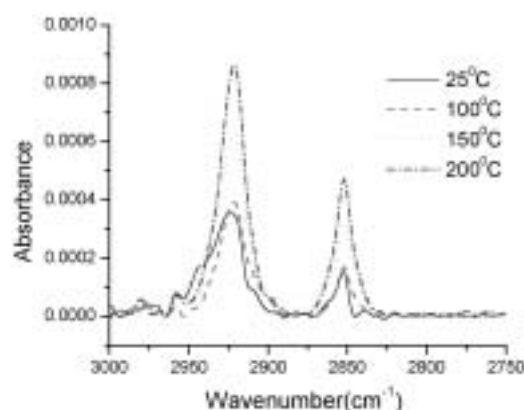


Figure 1. FTIR spectra of SAM obtained from the reaction of pure dodecene with the hydrogen-terminated Si(100) surface at different solution temperatures.