VI-F Synchrotron Radiation Stimulated Surface Reaction and Nanoscience

Synchrotron radiation (SR) stimulated process (etching, CVD) has excellent characteristics of unique material selectivity, low damage, low contamination, high spatial resolution, and high precision *etc*. In this project, nanolevel controlled structures are created by using synchrotron radiation stimulated process, and the reaction mechanisms are investigated by using STM and AFM. Concerning the SR etching, we are considering to apply this technique to the microfabrication of integrated protein transistor circuits.

VI-F-1 Patterning SiO_2 Thin Films Using Synchrotron Radiation Stimulated Etching with a Co Contact Mask

WANG, Changshun[1]; WANG, Zhihong; MORÉ, Sam D. ; YAMAMURA, Shusaku; NONOGAKI, Youichi; URISU, Tsuneo
([1]Henan Univ.)

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Patterning SiO_2 thin films on Si(100) surface was successfully demonstrated using the synchrotron radiation (SR) stimulated etching with the $SF_6 + O_2$ as the reaction gas and a Co contact mask, as shown in Figure 1. The etching completely stopped at the SiO_2/Si(100) interface. The morphology of the Si surface after the etching, evaluated by the atomic force microscopy (AFM), was almost atomically flat (R_a ~ 0.33 nm), and an well-ordered self-assembled monolayer (SAM) of dodecene was deposited on the SR etched region area-selectively, as shown in Figure 2. Co was found to show sufficient resistivity against the SR etching as a mask material and to be easily removed by a dilute acid, without damaging the SAM. The SR etching of the SiO_2 thin films on the Si surface with the Co contact mask is a suitable patterning technique for the area-selective deposition of alkyl SAMs.

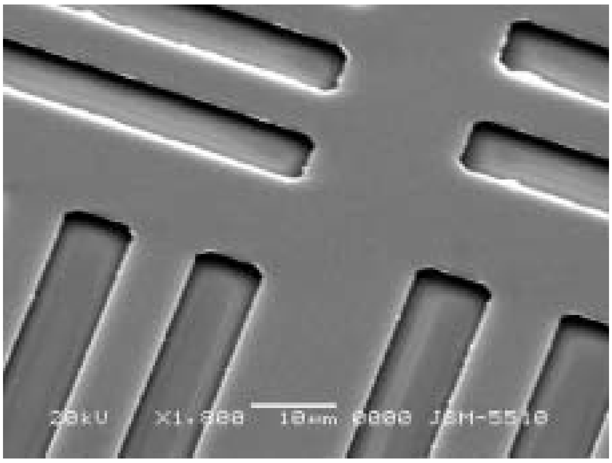

Figure 1. The SEM image of the pattern obtained by the SR etching SiO_2.

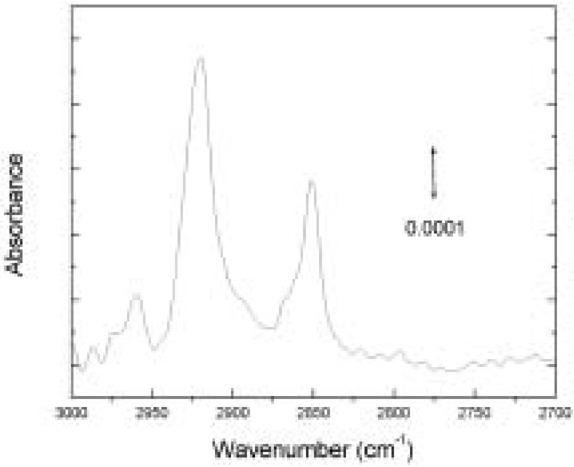

Figure 2. An IRTS of the dodecene SAM deposited on the SR etched surface.

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), which have unique characteristics of high resolution and high sensitivity at finger print regions. Several Si surface chemical reactions are investigated using this BML-IRRAS. As a new fabrication technique of BML substrate, we have almost succeeded in developing the wafer bonding technique. It is considered that BML-IRRAS is also extremely useful in the research of bio-material integration on Si substrates.

VI-G-1 Infrared Reflection Absorption Spectroscopy Using $CoSi_2$ Buried Metal Layer Substrate Made by Wafer-Bonding

YAMAMURA, Shusaku; YAMAUCHI, Shouichi[1]; WATANABE, Satoru[2]; TABE, Michiharu[3]; KASAI, Toshio[4]; NONOGAKI, Youichi; URISU, Tsuneo
([1]DENSO Res. Lab.; [2]Fujitsu Lab.; [3]Shizuoka Univ. ; [4]Saitama Univ.)

[*Jpn. J. Appl. Phys.* submitted]

The conventional infrared reflection absorption spectroscopy (IRRAS) covers wide energy regions including so-called finger print region with sub-monolayer sensitivity. However, it is applicable only for the metal. Therefore we have developed the IRRAS using buried metal layer (BML) substrate. BML wafers have been made so far by ion implantation method. This methods, however, has several problems. A large ion current required for the ion implantation often cause the breakdown of the ion implanter. It is difficult to remove the surface roughness due to the ion implantation damage even after epitaxial growth. Wafer-bonding technique have a possibility to solve these. We have fabricated BML substrates with atom-level flat surfaces by a wafer-bonding technique with a Co deposited Si (100) wafer and SIMOX or SOI wafer (Figure 1). Using the BML substrate fabricated by this method, we successfully observed the stretching and bending vibration bands of self-assembled alkyl monolayers of octadecyltrichlorosilane (OTS) and octenyltrichlorosilane (OTTS) on the Si (100) surface.

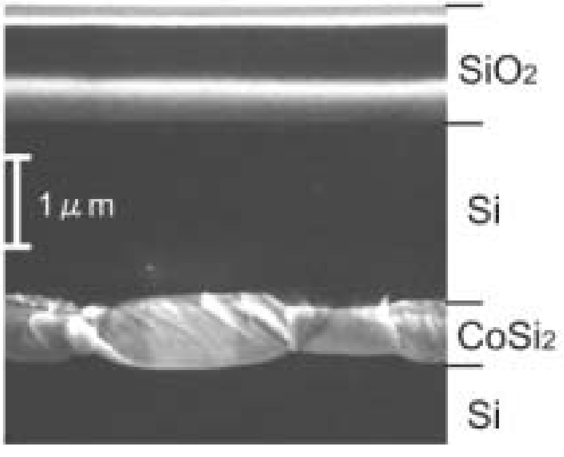

Figure 1. Cross-sectional SEM image of $Si(100)/CoSi_2/Si(100)$ BML substrate made from the SOI wafer.

VI-G-2 Hydrogen Diffusion and Chemical Reactivity with Water on Nearly Ideally H-Terminated Si(100) Surface

WANG, Zhihong; NODA, Hideyuki[1]; NONOGAKI, Youichi; YABUMOTO, Norikuni[2]; URISU, Tsuneo
([1]Hitachi Ltd.,; [2]NTT Adv. Tech. Corp.)

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A nearly ideally H-terminated condition for a Si(100) 2×1 surface is determined from the dependence of the peak intensity and the linewidth of the coupled monohydride symmetric stretching vibration on the hydrogen exposure and exposure temperature, which has been investigated with infrared reflection absorption spectroscopy (IRRAS) using $CoSi_2$ buried metal layer substrate. Even for nearly ideally H-terminated surfaces, the linewidth significantly changes depending on the hydrogen exposure and the exposure temperature. The concentration of deuterium atoms incorporated in the Si bulk is measured by temperature programmed desorption, and it is concluded that hydrogen diffusion into the subsurface of Si has a significant influence on the linewidth broadening. The chemical reactivity with water on the H-terminated Si surface is also investigated.

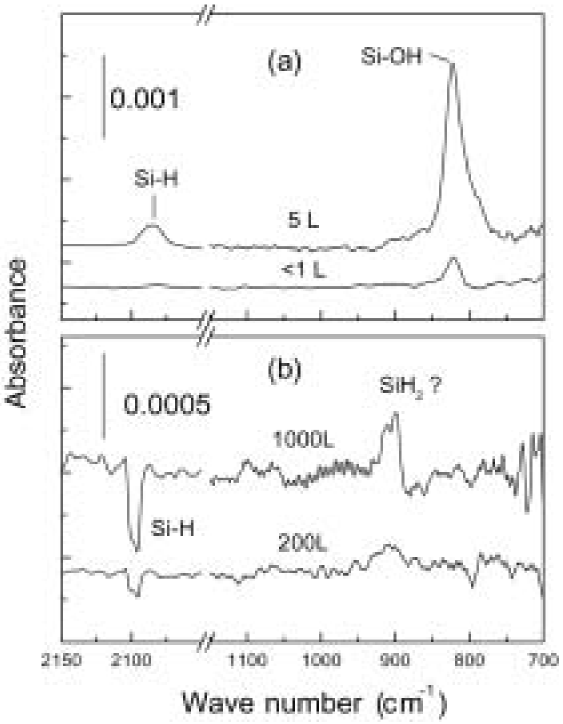

Figure 1. Observed BML-IRRAS spectra (circles) of atomic H-exposed H_2O: Si(100)-(2×1) surfaces at T_m = 373 K for D = 1000 L (top) and D = 50 L (bottom). The results of curve-resolutions assuming a Lorenzian form are compared (solid and dotted lines).

VI-G-3 Atomic Hydrogen-Induced Oxidation on Water-Adsorbed Si(100)-(2×1) Surfaces

WANG, Zhihong; URISU, Tsuneo; NANBU, Shinkoh; MAKI, Jun; AOYAGI, Mutsumi; WATANABE, Hidekazu[1]; OOI, Kenta[1]
([1]Natl. Inst. Adv. Ind. Sci. Tech.)

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Infrared reflection absorption spectroscopy using buried metal layer substrates (BML-IRRAS) and density functional cluster calculations are used to analyze the atomic hydrogen-induced oxidation on water-adsorbed Si(100)-(2x1) surfaces. In addition to the oxygen inserted coupled monohydrides previously reported, zero, one and two oxygen inserted dihydride species have been clearly observed for the first time due to the high sensitivity of BML-IRRAS for the perpendicular dynamic dipole moment in the finger print region. It is also found that double oxygen insertion is clearly favored over single oxygen insertions. A new oxidation mechanism, H–Si–Si–OH + 2H → SiH_2 + $Si(O)H_2$ is proposed. In high exposure regions, H–Si–O–Si–H + 2H → SiH_2 + $Si(O)H_2$ reaction is also observed.

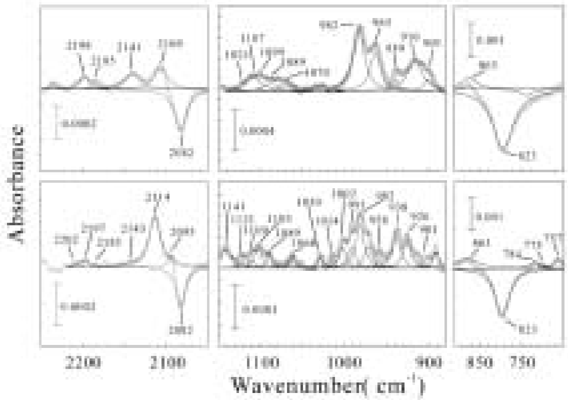

Figure 1. Change of the BML-IRRAS spectra by exposing to water at 373 K, (a) in the case of clean Si(100)(2×1) surface, and (b) nearly ideally H-terminated Si(100)(2×1) surface.

VI-H Integration of Bio-Functional Materials on Silicon

Integration of bio-functional materials such as lipids and proteins are expected to find important applications in biosensors, development 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 integration of lipid bilayers supporting channel proteins keeping their bio-activities. Our special interests are developing “protein transistors” and co-integrating them together with the Si MOS FETs on the same Si chip.

VI-H-1 Hydrophobic/Hydrophilic Interactions of Cytochrome *c* with Functionalized Self-Assembled Monolayers on Silicon

MORÉ, Sam D. ; HUDECECK, Jiri[1]; URISU, Tsuneo
([1]Charles Univ.)

[*Surf. Sci.* in press]

Cytochrome *c* (horse heart) has been adsorbed onto self-assembled monolayers (SAM) on silicon single crystal substrates. Layer thickness was determined using ellipsometry and atomic force microscopy (AFM) in the DFM tapping mode in air. Both hydrophilic (COOH containing SAM) and hydrophobic self-assembled monolayers were used. The protein layers were found to consist of adsorbed 2-dimensional islands.

Concentration, exposure time and the defect-density of the self-assembled monolayer substrates determined the wetting properties of the resulting layer, indicating that the surface orientation of the protein is driven by the interaction with the substrate. On well ordered self-assembled monolayers, the protein layer thicknesses were 1.76 nm for charged surfaces and 2.3 nm for hydrophobic surfaces. Self-assembled monolayers of a lower density resulted in a prevalence of cytochrome *c* islands of 3.2 nm thickness for both cases.

Defects in the SAM facilitate protein adsorption, a denser monolayer of a third orientation type, which leads to the largest adsorbed protein density. At the protein-film air interface 2-dimensional protein islands form, which can be manipulated with an AFM tip in the case of CH_3-terminated SAMs, but not in the case of COO– containing layers.

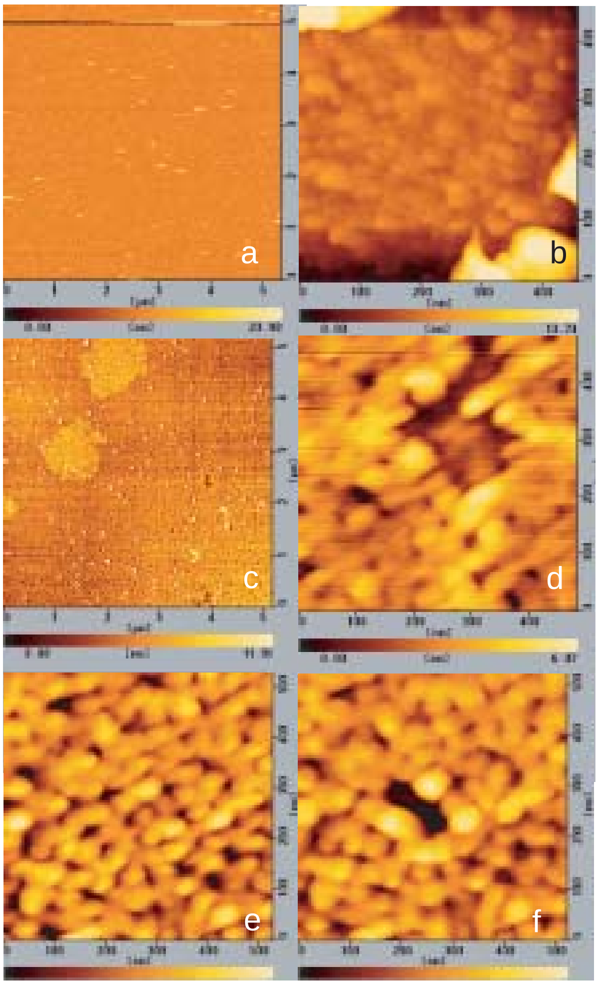

Figure 1. (a) and (b) eicocene terminated SAM prior protein adsorption, (c) and (d) after protein adsorption on a SAM with large defect density. (e) and (f) after selective movement of protein islands into the second layer.

VI-H-2 Influence of Substrate Roughness on the Formation of Self-Assembled Monolayers (SAM) on Silicon(100)

MORÉ, Sam D. ; GRAAF, Harald; BAUNE, Micheal[1]; WANG, Changshun; URISU, Tsuneo
([1]Bremen Univ.)

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The peak shifts of the CH_2-vibration are an indicator of the amount of gauche-conformational disorder present in aliphatic self-assembled monolayers (SAM). The property of the SAM layer was characterized by measuring the $–CH_3$ and $–CH_2$ stretching vibration modes using FTIR transmission spectroscopy, investigating the relationship between the surface roughness and the peak position as a function of temperature and alkyl chain-length. With increasing substrate surface roughness both the symmetric CH_2-peak as well as the asymmetric CH_2-peak shift to higher wave numbers. The magnitude of the shift is about 6 cm^{-1} at 150 °C and is due to a change from a condensed, almost *all-trans* conformational phase to liquid like layers.

For polished substrates although increased temperatures lead to a slightly more ordered SAM, the layers were in almost an "*all-trans*"-conformational phase independent on the coverage. From these results an "island growth and annealing effect"-model is proposed, which explains relation between the disorder increase and the surface roughness.

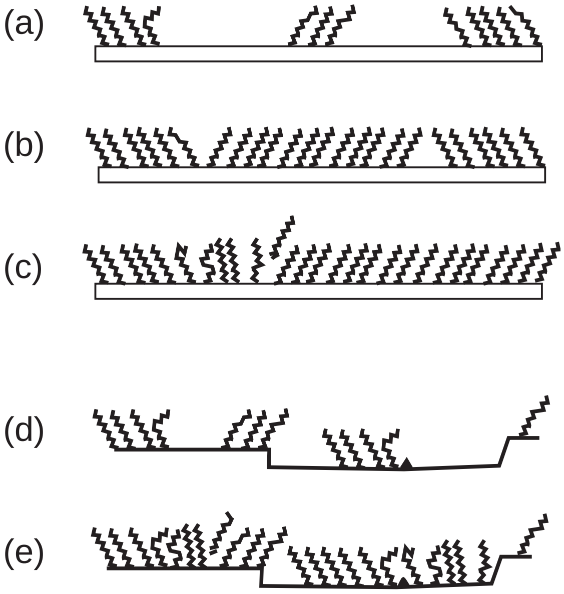

Figure 1. Model for SAM layer growth on flat and rough surfaces explaining the increase of disorder on rough surfaces. (a) Self assembled monolayer starts to form at several sites on the flat Si-surface (b) Domain formation due to different nucleation sites. Monolayer orders itsself due to van der Waals forces (c) Domains anneal and gaps are filled with additional molecules, if the temperature is high enough and the reaction time is sufficient. (d) Self-assembled monolayer starts to form at many sites on the rough surface (e) Self-assembled monolayer starts to anneal, but steps and defects inhibit the annealing process, as the overlap between the chains at the steps is too small. The relative but not the absolute surface coverage is smaller and the disorder, due to gauche defects, larger.