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 SiO₂ Thin Films Using Synchrotron Radiation Stimulated Etching with a Co Contact Mask

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Patterning SiO₂ thin films on Si(100) surface was successfully demonstrated using the synchrotron radiation (SR) stimulated etching with the SF₆ + O₂ as the reaction gas and a Co contact mask, as shown in Figure 1. The etching completely stopped at the SiO₂/Si(100) interface. The morphology of the Si surface after the etching, evaluated by the atomic force microscopy (AFM), was almost atomically flat ($R_a \sim 0.33$ 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 SiO₂ thin films on the Si surface with the Co contact mask is a suitable patterning technique for the area-selective deposition of alkyl SAMs.

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.

Figure 1. The SEM image of the pattern obtained by the SR etching SiO₂.

Figure 2. An IRTS of the dodecene SAM deposited on the SR etched surface.
VI-G-1 Infrared Reflection Absorption Spectroscopy Using CoSi2 Buried Metal Layer Substrate Made by Wafer-Bonding

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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.

![Cross-sectional SEM image of Si(100)/CoSi2/ Si(100) BML substrate made from the SOI wafer.](image1)

Figure 1. Cross-sectional SEM image of Si(100)/CoSi2/ 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

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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 monohydrde previously reported, zero, one and two oxygen inserted dihydride species have been

![Observed BML-IRRAS spectra (circles) of atomic H-exposed H2O: Si(100)-(2x1) surfaces at Tm = 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).](image2)

Figure 1. Observed BML-IRRAS spectra (circles) of atomic H-exposed H2O: Si(100)-(2x1) surfaces at Tm = 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)-(2x1) Surfaces

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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 monohydrde 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 fingerprint region. It is also found that double oxygen insertion is clearly favored over single oxygen insertions. A new oxidation mechanism, $\text{H-Si-Si-OH} + 2\text{H} \rightarrow \text{SiH}_2 + \text{Si(O)H}_2$ is proposed. In high exposure regions, $\text{H-Si-O-Si-H} + 2\text{H} \rightarrow \text{SiH}_2 + \text{Si(O)H}_2$ 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

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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.
The peak shifts of the CH\textsubscript{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\textsubscript{3} and –CH\textsubscript{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\textsubscript{2}-peak as well as the asymmetric CH\textsubscript{2}-peak shift to higher wave numbers. The magnitude of the shift is about 6 cm\textsuperscript{-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.