VI-C 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, nano-level 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-C-1 Design and Performance of Undulator Beamline (BL7U) for In-Situ Observation of Synchrotron Radiation Stimulated Etching by STM

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An undulator beamline of BL7U equipped with an ultra-high vacuum STM system is constructed at the UVSOR facility to investigate excitation energy dependence in synchrotron radiation stimulated etching. A schematic drawing of BL7U is shown in Figure 1. The SR beam is focused using two cylindrical mirrors on a sample surface just under the STM tip. The photon flux density is calculated to be 10^{19} photons (cm^2 sec 100mA)$^{-1}$ within the spot of 0.67 mm (H) × 0.17 mm (V) on the sample surface at the first harmonic tuned to 100 eV. The hydrogen adsorbed Si(111) surfaces were investigated using the STM apparatus before the undulator irradiation experiments were performed. We successfully observed the etching reaction from rest-atom monohydride surface by hydrogen exposure at room temperature.

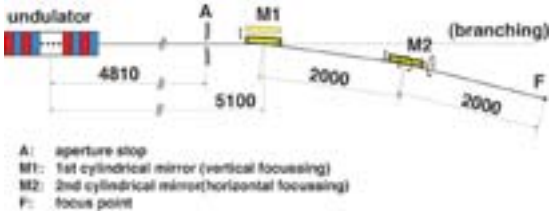

Figure 1. Schematic drawing of BL7U.

VI-C-2 Three-Dimensional Fine Structure on SOG/Si Surface Fabricated by Focused Ion Beam Mask Patterning and Synchrotron Radiation Etching

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Synchrotron radiation (SR) etching of SiO_2 is a unique device process technique.[1)] The advantages of SR etching are unique material-selectivity, anisotropicity (vertical side wall) and low contaminations.[1),2)] When SiO_2 surfaces are patterned by SR etching using a contact mask,[2)] spatial resolution is limited by the available size of the photomask. Focused ion beam (FIB) is one of promising techniques which can make nano-scale patterning on metal, insulator and semiconductor materials.[3)] Therefore, nano-processing utilizing the advantages of SR etching will become practicable by applying FIB technique to patterning of etching mask. We have tried for the first time a new three dimensional fine process applying FIB and SR etching methods on spin-on glass (SOG), which is a widely used material in semiconductor processes because planar film with low dielectric constant is easily obtained.

SOG films with thickness of 450–500 nm were obtained after spin-coating on 14 mm square Si wafers followed by curing under flowing N_2 at 698 K for 30 min. SR etching was performed in UHV chamber in BL4A2, under mixture of 2.66×10^{-3} Pa of O_2 and 6.65×10^{-2} Pa of SF_6. Ion beam milling was carried out using 31 keV Ga FIB with a beam spot size of ~ 0.1 μm.

Experiments were performed as followed. First, the SOG film was covered by a Co layer with thickness of ~ 200 nm. Then, the Co photomask was patterned with FIB and the sample was exposed to SR. At last, the Co layer was removed by 0.01 M HNO_3 *aq*. Figure 1 shows an AFM image of the SOG surface after SR etching (2.0×10^4 mA min) followed by removal of the Co layer. Three-dimensional double-step well was successfully obtained in single irradiation process. The Co mask (~ 200 nm thick) was excavated by FIB before irradiation process in the region A and B; Co mask was penetrated to SOG therefore SOG was directly exposed to SR in A; Co mask in B was dug by only 95 nm, which meant FIB milling was stopped in the middle of the Co layer. The AFM profile in Figure 1 clearly shows that the SOG film has been removed and the Si substrate has appeared in the region A. In the region B, the SOG shrank maybe due to a curing effect by penetrating light through the thin Co layer.

Nanometer scale patterning by this combination method is aimed in the future. Effect of diffusion rate of etching gas and interference of light would also be investigated because these factors possibly become important in nano-scale processing.

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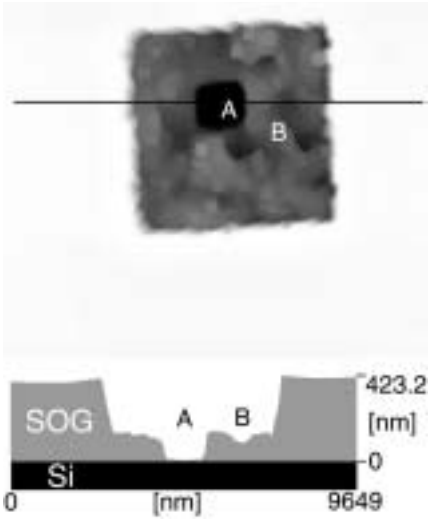

Figure 1. AFM image (10 × 10 μm^2) and a line profile of the SOG/Si surface after SR etching.

VI-C-3 Shrinking of Spin-on-Glass Films Induced by Synchrotron Radiation and Its Application to the 3-D Microfabrications

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Spin-on-glass (SOG) is an important material in the semiconductor integrated circuit fabrication and widely used for flattening of the inter level dielectrics. Typical thicknesses of SOG films are hundreds of nanometers. It is usually cured with reducing the thickness by heating to high temperatures (for examples at 400 °C–500 °C) in the last stage of the processes. In the present work, we have found that the thickness is also reduced by the irradiation of the synchrotron radiation (SR) beam with covering the surface by Co mask. We are considering that this phenomenon is applied to three-dimensional microfabrications, since the degree of the shrinking depends on the thickness of the mask.

A commercial siloxane type SOG (Honeywell, Accuglass 312B) was used in this study. SOG was spun on 14 mm^2 silicon wafer at a spin speed of 3000 rpm for 10 sec. Immediately after spin coating, the film were subjected to three stages of soft baking on hot plates at 80 °C, 150 °C and 250 °C for 1 min at each temperature. The final curing was performed at 425 °C with a nitrogen gas flow of approximately 1.0 liters/min. After these curing process, thickness of SOG film was approximately 550 nm on Si wafer.

The SR etching of SOG was performed under mixture gas of SF_6 (0.05 Torr) and O_2 (0.002 Torr) at room temperature using a Co mask. The Co contact mask on SOG surface was fabricated by deposition of Co thin film (230 nm) on a resist pattern which was made by the photolithography and lift off technique. The thicker Co mask pattern area was formed by additional deposition of 330 nm Co film. After 20000 mA min dose of SR etching the Co mask was removed by 0.1 N HNO_3 for 3 min. The surface structure was measured by step profilometer (Dektak).

The open region of SOG film was completely etched and the etching was neatly stopped on the Si surface as reported by Urisu and Kyuragi. At the region covered by the thinner Co mask (230 nm), the thickness of SOG film reduced by 152 nm. At the region covered by thicker Co mask, no shrinkage was observed.

The SR etching rate of SOG was investigated. Etched depth of SOG gradually increased with the SR dose. In the present experiment we found that SOG thickness was reduced by the SR etching with thin Co mask and the SR shrinkage of SOG can be controlled with the Co mask thickness. Using this phenomenon we can make three-dimensional structures by one time of SR exposure.

VI-D 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-D-1 Three Pairs of Doublet Bands Assigned to SiH_2 Scissoring Modes Observed in H_2O-Induced Oxidation of Si(100) Surfaces

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[*Phys. Rev. B* accepted]

Oxidation of Si(100) surfaces by H_2O has been investigated on 2H + H_2O/Si(100)-(2×1), H_2O + Si(100)-(2×1) as well as H_2O + H/Si(100)-(2×1) systems by infrared reflection absorption spectroscopy using $CoSi_2$ buried metal layer substrates (BML-

IRRAS). Three pairs of new doublet bands assigned to the scissoring modes of adjacent and isolated SiH_2 with zero, one and two inserted back bond oxygen atoms, respectively, have been reported for the first time. This is also the first report that has clearly shown the unique high sensitivity of BML-IRRAS for the perpendicular components in the finger print region compared to the multiple internal reflection and the external transmission arrangements. New oxidation mechanisms have been proposed. In the 2H + H_2O/Si(100)-(2×1) system, oxygen insertion into the back bond occurs easily. In the H_2O + H/Si(100) system, however, the tunneling effect is important to reach the oxygen inserted state.

VI-D-2 Assignment of Surface IR Absorption Spectra Measured in the Oxidation Reactions: 2H + H_2O/Si(100) and H_2O + H/Si(100)

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[*Phys. Rev. B* to be submitted]

Infrared reflection absorption spectroscopy using buried metal layer substrates (BML-IRRAS) and density functional cluster calculations have been employed to study the water related oxidation reactions of 2H + H_2O/Si(100)-(2×1), 2D + H_2O/Si(100)-(2×1) and H_2O + H/Si(100)-(2×1). In addition to the oxygen inserted coupled monohydrides reported earlier in the former reaction system, we report several other oxidized Si hydride species in our BML-IRRAS experiments. Three pairs of new vibrational bands are identified between 900 and 1000 cm^{-1} region. These vibrational frequencies have been calculated using Si9 and Si10 cluster models which include all possible structures from zero to five oxygen insertions into the top layer silicon atoms using B3LYP gradient corrected density functional method with polarized 6-31G** basic set to all atoms. The three pairs of vibrational modes are assigned to the scissoring modes of adjacent and isolated SiH_2 with zero, one and two oxygen atoms inserted into the Si back bonds. All the other observed vibrational peaks related to Si oxidation have also been assigned in this study.

VI-D-3 A Comparative Infrared Study of H_2O Reactivity on Si(100)-(2x1), (2x1)-H, (1x1)-H and (3x1)-H Surfaces

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[*Surf. Sci.* submitted]

Water adsorption on bare and H-terminated Si(100) surfaces has been studied by BML-IRRAS technique. It is found that H-terminated surfaces are much less reactive compared to 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, water reaction with coupled monohydride species provides an effective channel for oxygen insertion into the back bonds of dihydride species.

VI-D-4 Theoretical Analysis of the Oxygen Insertion Process in the Oxidation Reactions of H_2O + H/Si(100) and 2H + H_2O/Si(100); Calculation of an Ab Initio Molecular Orbital Method and an Analysis of the Tunneling Reaction

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[*Chem. Phys. Lett.* submitted]

The reaction paths were analyzed, by an ab initio molecular orbital method, for the surface reaction systems, 2H + H_2O/Si(100)-(2×1) and H_2O + H/Si-(100)-(2×1), in which SiH_2 species with one or two oxygen atom-inserted back bonds have been observed as new stable reaction products. It was found that common metastable states exist in both systems, and the initial energy is sufficiently higher than all transition state energies in the former system, while in the latter system, the energy of the highest transition state is much higher than the initial energy, and thus a tunneling effect plays an important role.

VI-D-5 Structure-Optimized $CoSi_2$-Buried-Metal-Layer Substrates for IRRAS Fabricated by Wafer-Bonding

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The conventional infrared reflection absorption spectroscopy (IRRAS) is applicable only on the metal substrates. We are developing the IRRAS of semiconductor surfaces using buried metal layer (BML) substrates fabricated by wafer-bonding technique. To obtain high sensitivity in BML-IRRAS, it is essentially important to control the top Si layer thickness less than 200 nm. In this work, we have successfully fabricated BML substrates with 200 nm top Si layer by wafer-bonding technique for the first time using SOI wafers of which Si layer thickness is controlled definitely. Comparing with the ion implantation method, the wafer-bonding method has advantages of (1) atomically flat and (2) low-damaged top Si surfaces without epitaxial growth, which is essentially required in the ion implantation method to remove the ion implantation damage. The preliminary formation of thin (100 nm) SiO_2 layer on the SOI surface was effective to reduce the interface roughness between the top Si and the $CoSi_2$ layers. The self-assembled alkyl monolayer was deposited on the BML substrate, and its IRRAS was measured in the wide frequency range from stretching to bending regions.

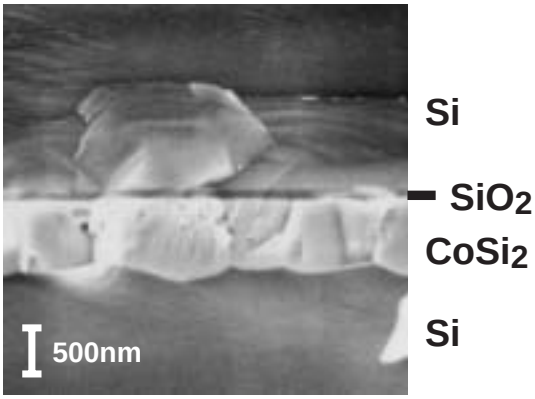

Figure 1. Cross-sectional SEM image of fabricated BML substrate by using preliminary formation of thin SiO_2 layer on the SOI surface.

VI-E 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-E-1 Deposition of Lipid DPPC Monolayer on SiO_2 Surface Using OTS Self-Assembled Monolayer Islands as Anchor Molecules

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Bilayer lipid membranes (BLMs) supported on the solid surface are attractive research target from the viewpoint of application to the biosensors. The stability of the membrane can be increased significantly by using the *anchor molecules*. We have investigated the deposition of dipalmitoylphoshatidylcholine (DPPC) monolayer on SiO_2 surface using *n*-octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) islands as anchor molecules. After deposition of OTS SAM islands on SiO_2 surface, the DPPC monolayer was transferred to the surfaces by Langmuir-Blodgett method. The surface morphology observed by AFM shows that the flat DPPC monolayer is area-selectively deposited almost completely on the hydrophilic SiO_2 surface. On the hydrophobic OTS SAM surface, DPPC molecules were not observed as a form of monolayer. Bright protrusions were observed on and at the edges of the OTS islands, suggesting excess DPPC molecules accumulate and form three-dimensional islands. These results indicate that the OTS SAM islands have a potential of effective anchor molecules in DPPC BLM depositions on SiO_2 surfaces.

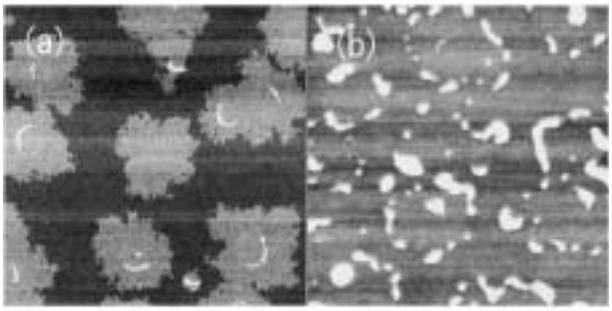

Figure 1. 5 μm × 5 μm AFM images of (a) OTS SAM islands and (b) DPPC monolayer deposition on OTS SAM/SiO_2 surface.

VI-E-2 Self-Assembled Monolayers on H-Si (111) Surfaces Studied by AFM Deposition of Undecenoic Acid

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A large number of studies have been conducted on the self-assembled monolayers (SAMs) from the view points of structure, formation process, and physical properties, for it is one of the promising candidates in applications such as adhesion promotion, surface modifications, surface protective films and the fabrication of devices such as field effect transistors.[1)–3)] The alkyl SAMs on Si substrates are relatively new topis and, among them, deposition of SAMs with a reactive group such as –COOH is especially interesting,[3)] since easiness of successive chemical treatments has potential applications to area selective immobilization of many kinds of bio-functional materials which is a key technology in the bioelectronics device fabrications. In

the present work, the undecenoic acid (CH_2=CH-C_8H_{16}-COOH) SAMs were deposited on the hydrogen-terminated Si (111) surface, and the surface morphology was successfully observed for the first time by AFM.

The B-doped *p*-type Si(111) wafers with a resistivity in the rang of 8.4–8.9 Ω cm were cleaned, thermally oxidized and after removal of the oxide layer, the undecenoic acid SAM layer was deposited and AFM observation was performed. The wafer cleaning process was wet method as follows; (1) H_2O_2:H_2SO_4 = 1:4 → NH_4OH:H_2O_2:H_2O = 1:4:20 → diluted HF treatments, (2) HCl:H_2O_2:H_2O = 1:1:6 → diluted HF treatments. In each step, copious rinsing with ultrapure water, (3) oxidation of the Si sample at 1000 °C for one hour, (4) removal of the thermal oxide layer by HF (2%) solution, and (5) the etching of the Si sample by the solution of NH_4F:NH_4OH (pH = 8) for 5 min. Then the H-terminated Si sample was immediately placed in the distilled the undecenoic acid solution. The deposition process was as follows: (1) bubbling of the undecenoic acid solution by N_2 gas for 30 min at RT. (2) dipping of the Si sample into the solution with continuous N_2 bubbling for 30 min at RT. (3) heating of the solution at 200 °C for requesting time with continuous N_2 bubbling, (4) cooling down to RT, and (5) rinsing of the sample by methanol and propanol. After these processes, the sample surface morphology was investigated by AFM in the tapping mode.

Figure 1(a) shows the AFM image of the Si sample surface just after the cleaning process. The step edges are clearly observed. Figures 1(b) and (c) show the AFM images after the undecenoic acid deposition for 20 min. The island growth was confirmed on the Si(111) terraces, and the islands show unique hexagonal shapes, which is considered to be the reflection of the deposition mechanisms. We will make a detailed analysis about the AFM data in the succeeding research.

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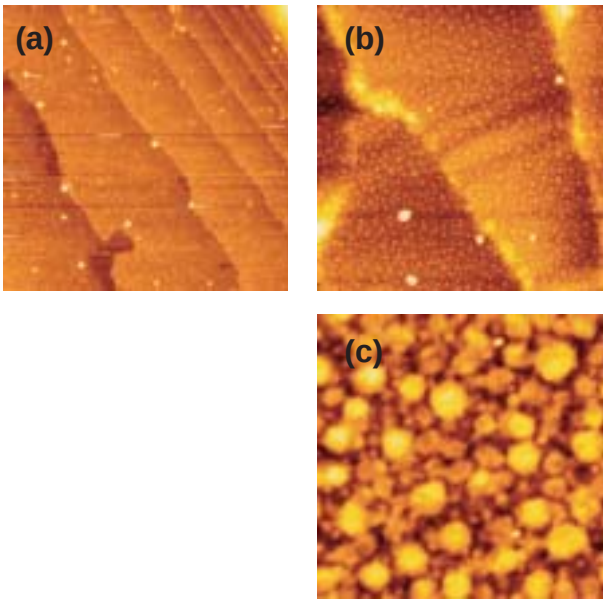

Figure 1. AFM images of the Si(111) sample surface, (a) just after the cleaning (800 μm × 800 μm) (b) after the undecenoic acid deposition (4 μm × 4 μm) and (c) in high magnification of (b) (800 nm × 800 nm).

VI-E-3 Characterization of Dipalmitoylphosphatidylcholine (DPPC)/Cholesterol Langmuir-Blodgett Monolayers by AFM and FT-IR

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In advent of bio-nano technology, many experimental approaches have been performed to fabricate biosensors mimicking the ion channel system of cell membranes. In such system, intensity and lifetime of the ion channel current largely depend on membrane properties. Cholesterol is one of the major constituents in membranes and diminishes the gel to liquid crystalline phase transition. the chemical and physical properties and formation of the liquid-ordered phase (L_O), occurring at a certain cholesterol concentration, have been of considerable interest because the studies of this phase can provide important information related to the numerous biological functions in cell membranes, including signal transductions to immune systems and the activity of membrane proteins

It is the aim of this study to examine interactions of cholesterols with L_α phase of DPPC monolayer prepared by the Langmuir-Blodgett method. We have focused on effects of cholesterols, causing the formation of L_O phase, in relation to the conformational order of acyl chains of mixed (DPPC/cholesterol) monlayers and the behavior of phase separations in combination with FT-IR and AFM, respectively.