VI-D 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-D-1 Construction of Undulator Beamline for STM Observations of Surface Reaction Stimulated by Synchrotron Irradiation

NONOGAKI, Youichi; URISU, Tsuneo

[*J. Electron Spectrosc. Relat. Phenom.* submitted]

To investigate excitation energy dependence of SR-stimulated reactions, we have designed and constructed an undulator beamline equipped with an UHV-STM system at the UVSOR facility. Since 1st harmonic emission from the undulator is changed from 50 eV to 120 eV, it is possible that the emission is tuned to Si 2p (~100 eV) core-level. The undulator emission is focused by two cylindrical mirrors. The spot size is 1.0 mm × 0.4 mm and photon flux density is estimated to 10^{18} $cm^{-2}sec^{-1}$ on a sample surface in the UHV-STM chamber set at the end station.

Although ESD of H-Si(111) surfaces have been studied extensively, there is no report of photon-stimulated reaction on the H-Si(111) surfaces observed by STM. We have successfully observed morphological changes of H-Si(111) after undulator irradiation by STM. Figure 1(a) shows an STM image of a H-Si(111) prepared by 1000L H-exposure to a clean Si(111)-7×7 surface at 400 °C. A 7×7 rest-atom monohydride surface appeared with adatom islands (A) and small protrusions (B). This surface was exposed to undulator irradiation (~ 100 eV) at an irradiation dose of 4900 mAsec. Figure 1(b) shows an STM image of the surface after irradiation. It is found that density of the small protrusions drastically increased on the 7×7 rest-atom monohydride surface. Creation of the small protrusions would be related to H-desorption stimulated by undulator irradiation.

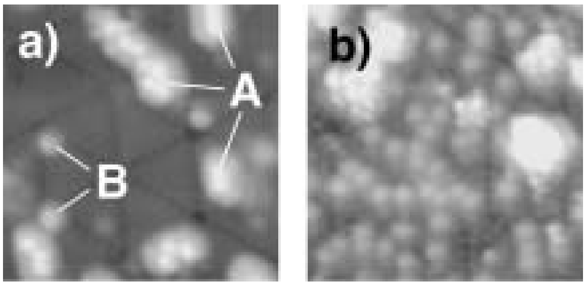

Figure 1. 11 nm × 11 nm STM images of a) H-Si(111) surface and b) surface after undulator irradiation.

VI-D-2 Shrinking of Spin-On-Glass Films Induced by Synchrotron Radiation and Its Application to Three-Dimensional Microfabrications

RAHMAN, Md. Mashiur; TERO, Ryugo; URISU, Tsuneo

[*Jpn. J. Appl. Phys.* **43**, 4591–4594 (2004)]

Photoinduced etching of siloxane-type spin-on-glass (SOG) by synchrotron radiation (SR) using a SF_6/O_2 etching gas and a Co contact mask has been investigated. The SOG film was etched by direct SR irradiation similarly to the case of thermally oxidized SiO_2. We found that the indirect exposure to SR caused shrinkage of SOG under the Co mask. The shrinkage depth of SOG was attenuated by the thickness of the Co mask, but not eliminated even by a Co mask 350 nm thick, due to the highenergy photons (230 eV) being transmitted through the mask. The shrinkage phenomenon was successfully applied in the fabrication of a three-dimensional structure of the SOG thin film on Si(100). Atomic force microscopy observations showed that the surfaces were very smooth both on the completely etched Si area and on the shrunken SOG area. We investigated the mechanism of the shrinkage of SOG by Fourier-transform infrared spectroscopy.

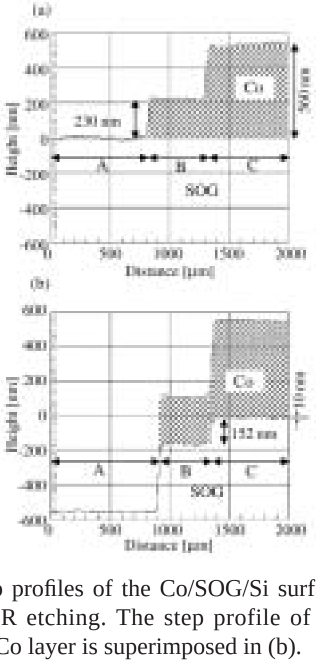

Figure 1. Step profiles of the Co/SOG/Si surface (a) before and (b) after SR etching. The step profile of SOG/Si after removal of the Co layer is superimposed in (b).

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

WANG, Zhi-Hong; URISU, Tsuneo; NANBU, Shinkoh; MAKI, Jun; GANGAVARAPU, Ranga Rao; AOYAGI, Mutsumi[1]; WATANABE, Hidekazu[1]; OOI, Kenta[2]
([1]Kyushu Univ.; [2]AIST Shikoku)

[*Phys. Rev. B* **69**, 045309 (5 pages) (2004)]

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 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. This report also has clearly shown the unique high sensitivity of BML-IRRAS for the perpendicular components in the fingerprint region, compared to the multiple internal reflection and the external transmission arrangements. 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.

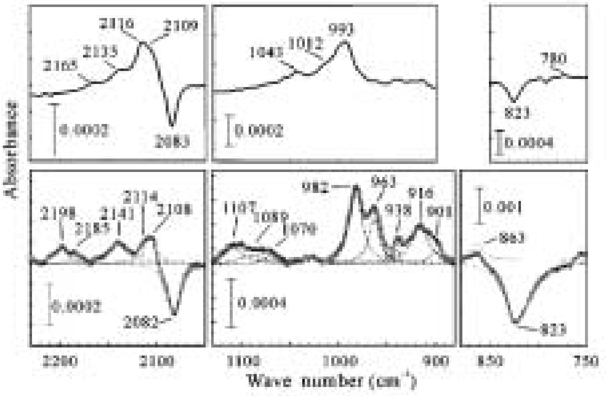

Figure 1. Observed BML-IRRAS spectrum (circles, in the lower panel) of the reaction system $2H+H_2O(5\times l)$/Si(100)-(2×1) at T_m = 373 K for D = 1000 l. The curve resolutions assuming a Lorenzian form (solid and dotted lines) are also shown. Compared in the upper part is the reported IR spectrum by ET for the similar reaction system. The three pairs of doublet bands are observed at 982, 963, 938, 926, 916, and 901 cm^{-1}, respectively. The 926-cm^{-1} band, which is not clear in this spectrum, is observed clearly at the lower H doses.

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

GANGAVARAPU, Ranga Rao; WANG, Zhi-Hong; WATANABE, Hidekazu[1]; AOYAGI, Mutsumi[1]; URISU, Tsuneo
([1]Kyushu Univ.)

[*Surf. Sci.* in press]

The water adsorption on the bare and H-terminated Si(100) surfaces has been studied by the BML-IRRAS technique. It is found that H-terminated surfaces are much less reactive compared to the 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, the water reaction with coupled monohydride species provides an effective channel for oxygen insertion into the back bonds of dihydride species. It is not attributed to the H–Si–Si–H + H_2O → H–Si–Si–OH + H_2, which could give rise to the characteristic Si–H and Si–OH modes, respectively at 2081 and 921 cm^{-1}. A more suitable reaction mechanism involving a metastable species, H–Si–Si–H + H_2O → $H_2Si\cdots HO$–Si–H (metastable) explains well the bending modes of oxygen inserted silicon dihydride species which are observed relatively strongly in the reaction of water with H-terminated Si(100) surfaces.

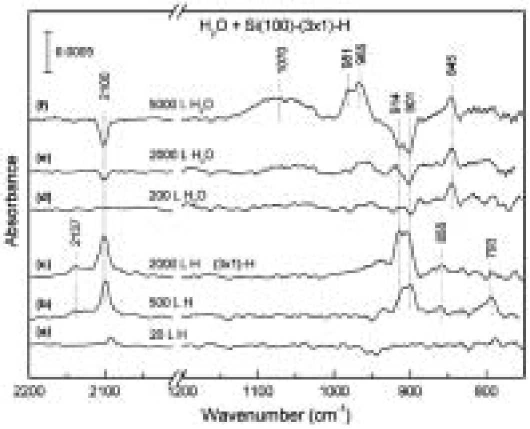

Figure 1. BML-IRRAS spectra of the Si(100)-(3×1)-H surface exposed to (a) 20 L atomic H, (b) 500 L atomic H, (c) 2000 L atomic H, (d) 200 L H_2O, (e) 2000 L H_2O, (f) 5000 L H_2O at 400 K. The spectra (a)–(c) are the ratios of absorption spectra of the H exposed Si(100)-(2×1)-D surfaces to the Si (100)-(2×1)-D surface, and the spectra (d)–(f) are the ratios of the absorption spectra of the water exposed Si(100)-(3×1)-H surfaces to the Si(100)-(3×1)-H surface, recorded at 400 K.

VI-E-3 Theoretical Analysis of the Oxygen Insertion Process in the Oxidation Reactions of H_2O+H/Si(100) and 2H+H_2O/Si(100): a Molecular Orbital Calculation and an Analysis of Tunneling Reaction

WATANABE, Hidekazu[1]; NANBU, Shinkoh; WANG, Zhi-Hong; MAKI, Jun; URISU, Tsuneo; AOYAGI, Mutsumi[1]; OOI, Kenta[2]
([1]Kyushu Univ.; [2]AIST Shikoku)

[*Chem. Phys. Lett.* **383**, 523–527 (2004)]

The reaction paths are 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 stable reaction products. The following results are obtained: The initial energy for the former system is 87.97 kJ/mol higher than the highest transition state energies with the HF/6-31+G* level. In the latter system, the highest transition state is located 175.66 kJ/ mol higher than the initial energy, and tunneling effect plays an important role.

VI-E-4 Fabrication of $CoSi_2$-Buried-Metal-Layer Si Substrates for Infrared Reflection Absorption Spectroscopy by Wafer-Bonding

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([1]DENSO Res. Laboratories; [2]FUJITSU Laboratories Ltd.; [3]Shizuoka Univ.; [4]Saitama Univ.)

[*Jpn. J. Appl. Phys.* **42**, 3942–3945 (2003)]

Infrared reflection absorption spectroscopy (IRRAS) using buried metal layer substrates (BML) is one of the high resolution and high sensitive surface vibration spectroscopy techniques. A unique characteristic is the wide frequency range including the so-called finger print region. The $CoSi_2$ Si(100) BML substrates fabricated by Co ion implantation have been used to date. However, the technique has several problems such as the resultant surface roughness due to the ion implantation damage. To solve these problems, in this work, we have examined the fabrication of BML substrates with atomic-level flat surfaces by the wafer-bonding between a Co deposited Si(100) wafer and a Si on insulator (SOI) wafer. Self-assembled alkyl monolayers (SAMs) of octadecyltrichlorosilane and octenyltrichlorosilane were deposited on the fabricated BML substrate surface. Good BML-IRRAS spectra were observed in the wide frequency range from stretching to bending regions. It was also found that well-ordered SAMs were deposited.

VI-E-5 Design of the Sample Holder System for BML-IRRAS in-Liquid

UNO, Hidetaka; URISU, Tsuneo

We have performed BML-IRRAS in a ultra-high vacuum condition, and investigated hydrogen adsorption on Si clean surfaces. In this report, we present a new project in which the BML-IRRAS is adopted to the bio-material spectroscopy in liquid conditions.

Figure 1 shows a schematic drawing of the sample holder for BML-IRRAS in liquid. The liquid is filled between the BML substrate and the BaF_2 prism. In order to estimate the influence of H_2O to the IR spectrum, we performed calculations with a model in which H_2O was used as a buffer solution. In this model, proteins were substituted by SiC to illustrate the influence of H_2O clearly in the region of Amide I and Amide II bands, because SiC has no spectral features in this region.

The reflectance of the model system was calculated by using the complex refractive indexes of each layer. Figure 2 shows the observed spectrum of the sample with proteins on the BML substrate in a dry condition and the calculated spectrum of the model system described above. Absorption peaks of Amide I and II are clearly seen in the experimental spectrum. In the calculated spectrum, on the other hand, the absorption peak is also seen at 1640 cm^{-1} which is assigned to the absorption peak of H_2O. It will be very difficult to find Amide I and II peaks from the background of H_2O absorption. This problem should be avoided by using D_2O instead of H_2O. The influence of D_2O should be estimated in the near future.

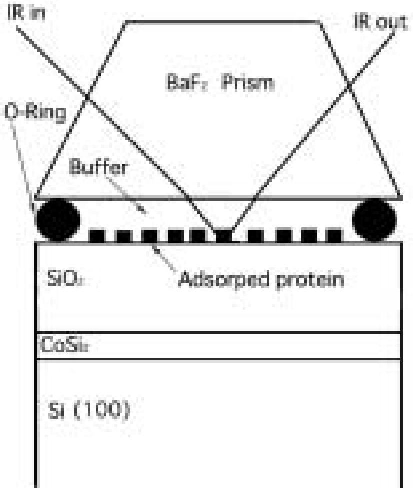

Figure 1. Schematic drawing of the sample holder for BML-IRRAS in liquid.

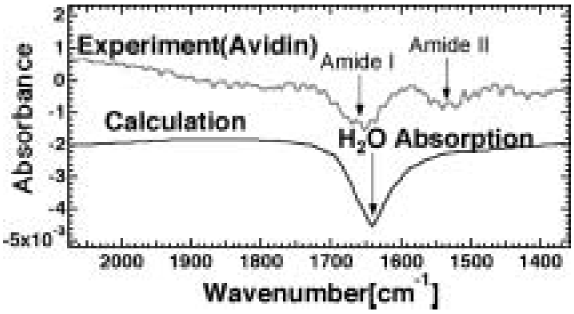

Figure 2. Experimental spectrum of the sample with proteins on the BML substrate in the dry condition and the calculated spectrum of the $BaF_2/H_2O/SiC/SiO_2/Co$ model.

VI-F 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 specialinterests are developing "protein transistors" and co-integrating them together with the Si MOS FETs on the same Si chip.

VI-F-1 Deposition of Phospholipid Layers on SiO_2 Surface Modified by Alkyl-SAM Islands

TERO, Ryugo; LI, Yanjun; YAMAZAKI, Masahito[1]; URISU, Tsuneo
([1]Shizuoka Univ.)

[*Appl. Surf. Sci.* in press]

Formation of the supported planar bilayer of dipalmitoylphosphatidylcholine (DPPC) on SiO_2 surfaces modified with the selfassembled monolayer (SAM) of octadecyltrichlorosilane (OTS) has been investigated by atomic force microscopy (AFM). DPPC was deposited by the fusion of vesicles on SiO_2 surfaces with OTS-SAM islands of different sizes and densities. The DPPC bilayer membrane formed self-organizingly on the SiO_2 surface with small and sparse OTS islands, while did not when the OTS islands were larger and denser. The relative size between the vesicles and the SiO_2 regions is the critical factor for the formation of the DPPC bilayer membrane.

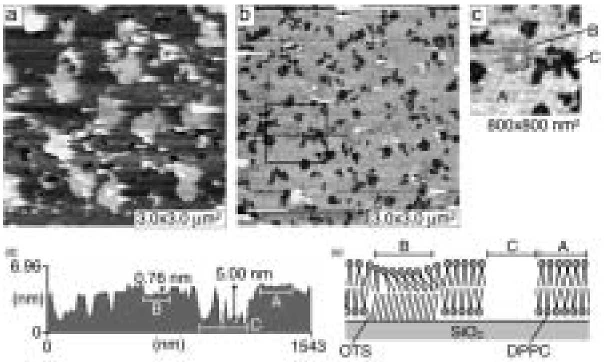

Figure 1. AFM images ($3.0 \times 3.0\ \mu m^2$) of the OTS-modified SiO_2 surface ($\theta_{OTS} = 0.21$) obtained in the buffer solution (a) before and (b) after the deposition of DPPC. (c) The magnified image of the square area in (b) ($800 \times 800\ nm^2$). (d) The profile of the line drawn in (b). (e) Schematic illustration for the line profile in (d).

VI-F-2 Deposition of 10-Undecenoic Acid Self-Assembled Layers on H-Si(111) Surfaces Studied with AFM and FT-IR

LI, Yanjun; TERO, Ryugo; NAGASAWA, Takayuki; NAGATA, Toshi; URISU, Tsuneo

[*Appl. Surf. Sci.* in press]

Self-assembling layers of 10-undecenoic acid (UA) were deposited on H-terminated Si(111) surfaces and characterized with atomic force microscopy (AFM) and Fourier-transform infrared (FT-IR) spectroscopy measurements for the first time. The unique island structures are deposited by layer-by-layer growth mechanism. The IR spectra suggest that the multilayers grown over the first monolayer are deposited by weak intermolecular interactions such as Van der Waals force and hydrogen bonding.

VI-F-3 Structure and Deposition Mechanism of 10-Undecenoic Acid Self-Assembled Layers on H-Si(111) Surfaces Studied by Atomic Force Microscopy and Fourier-Transform Infrared Spectroscopy

LI, Yanjun; TERO, Ryugo; NAGASAWA, Takayuki; NAGATA, Toshi; HARUYAMA, Yuichi[1]; URISU, Tsuneo
([1]Univ. Hyogo)

[*Jpn. J. Appl. Phys.* **43**, 4591–4594 (2004)]

Ten-undecenoic acid self-assembled multilayers were deposited on H-Si(111) surfaces and the surface morphology was investigated by atomic force microscopy (AFM). Namely, we studied the H-Si(111) surface modification of –COOH terminal functional groups. Characteristic islands of almost the same height are observed. From AFM images and transmission IR spectra, it was confirmed that multilayer deposition easily occurs through weak intermolecular interactions such as the Van der Waals force and hydrogen bond interactions. The growth mechanism and film structure were discussed.

VI-F-4 Deposition of DPPC Monolayers by the Langmuir-Blodgett Method on SiO_2 Surfaces Covered by Octadecyltrichlorosilane Self-Assembled Monolayer Islands

TAKIZAWA, Morio; KIM, Yong-Hoon; URISU, Tsuneo

[*Chem. Phys. Lett.* **385**, 220–224 (2004)]

The morphology of self-assembled monolayer (SAM) islands of *n*-octadecyltrichlorosilane (OTS) deposited on chemically and thermally oxidized SiO_2 surfaces was studied by dynamic force microscopy (DFM). The shape and size of the islands were found to depend significantly on the hydrophilicity of the SiO_2 surface. Langmuir-Blodgett (LB) monolayers of a lipid, dipalmitoylphosphatidylcholine (DPPC), deposited on these SiO_2 surfaces covered by OTS-SAM islands have shown that the DPPC monolayer is supported firmly on the SiO_2 surface by the hydrophobic islands acting as anchor molecules.

VI-F-5 Characterization of Dipalmitoylphosphatidylcholine/Cholesterol Langmuir-Blodgett Monolayers Investigated by Atomic Force Microscopy and Fourier Transform Infrared Spectroscopy

KIM, Yong-Hoon; TERO, Ryugo; TAKIZAWA, Morio; URISU, Tsuneo

[*Jpn. J. Appl. Phys.* **43**, 3860–3864 (2004)]

The addition effects of cholesterol on the dipalmitoylphosphatidylcholine (DPPC) Langmuir-Blodgett (LB) monolayer have been investigated by atomic force microscopy (AFM) and infrared reflection absorption spectroscopy (IRRAS). The phase transformation from pure DPPC to the DPPC/cholesterol phase proceeds through two stages: initial drastic changes in the surface morphology and the conformation of the DPPC acyl chains below 10% cholesterol, and the gradual homogenization of the morphology towards the liquid-order phase up to 35% cholesterol. The IRRAS peak position indicates that the conformational disorder of the acyl chain becomes almost that of the liquid level at 10% cholesterol addition. In the homogeneous liquid-order phase at 35% cholesterol, the terminal methyl groups of the DPPC are aligned in good order similarly to the solidlike gel phase, whereas the acyl chains have a liquid-level disordered conformation.

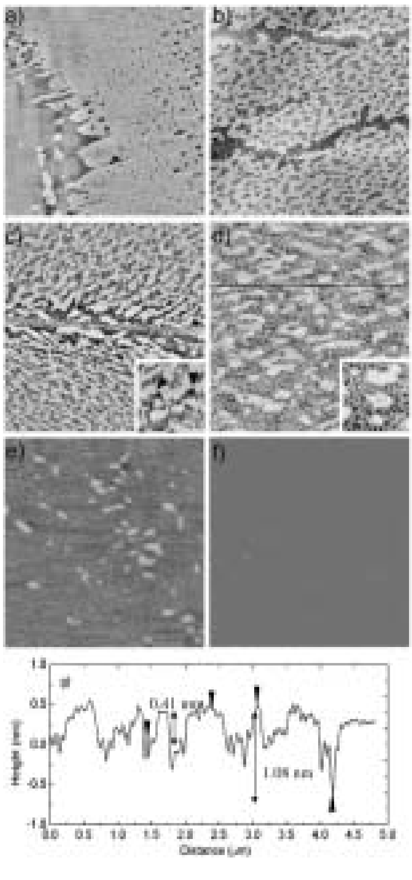

Figure 1. AFM images (5.0 × 5.0 μm^2) of DPPC/cholesterol LB monolayers transferred onto the mica surface at the surface pressure of 10 mNm^{-1}. The concentrations of cholesterol are a) 0% (pure DPPC), b) 5%, c) 10%, d) 20%, e) 30% and f) 35% in molar ratio. g) The profile of the line drawn in d). The scale of the insets in (c) and (d) is 1.34 × 1.34 μm^2.

VI-F-6 An AFM Characterization of Gramicidin A in Tethered Lipid Membrane on Silicon Surface

LEI, Shenbin; TERO, Ryugo; MISAWA, Nobuo; WAN, Lijun; URISU, Tsuneo

Recently there has been growing interest in supported bilayer lipid membranes (sBLMs). The supported lipid membrane is much more stable in comparison with the unsupported lipid membrane, extending their life from hours to a period of days withstanding mechanical distortion and repeated washes. This stability of sBLMs enables its research applications such as use in developing biosensors and surface coatings.1)

Here we use the avidin-biotin interaction, which is known to be one of the strongest bindings between a protein and a ligand and is a key example of the biological specificity and the biological adaptation,2) to form a tethered phospholipid membrane on oxidized Si(100) surfaces. The procedure for our strategy is schematically shown in Scheme 1. AFM characterizations show avidin molecules are well dispersed and the surface density is estimated to be about 40 molecule/μm^2. When sonicated unilamellae vesicles (SUVs) (0.3 mM DPPC in 0.1 M HEPES buffer) containing 2% mol gramicidin A was deposited on this surface, single lipid bilayers formed in the large area, but with high density of defects as compared with that on the mica surface. The thickness of this bilayer is measured to be 5.8 to 6.1 nm, in consistent with previous reports. In the tethered membrane, gramicidin A appear as depressions, which is the same as reported for gramicidin in supported membrane on mica. However, the topography is significantly different. On mica surface, gramicidin A aggregates into linear structures. However, in the tethered membrane on the silicon surface, both linear and spot like gramicidin aggregations appear. The width and height of these depressions are also different in the tethered membrane as compared with that in the supported membrane on mica. Also, in the tethered membrane, gramicidin appears with higher density than expected. These results seem to indicate that gramicidin A aggregates into larger aggregations in the supported membrane than in the tethered membrane. Certainly the current conclusion needs further characterizations to make it more solid.

References

1) U. Rädler, J. Mack, N. Persike, G. Jung and R. Tampé, *Biophys. J.* **79**, 3144 (2000).
2) A. Torreggiani, G. Bottura and G. Fini, J. Raman *Spectrosc.* **31**, 445 (2000).

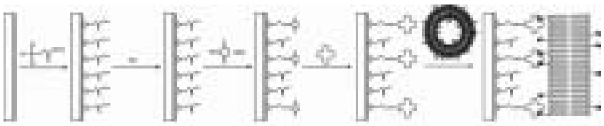

Figure 1. Scheme 1.

VI-F-7 Immobilization of Avidin on COOH-Modified SiO_2/Si(100) Surface and Characterization by AFM and BML-IRRAS

MISAWA, Nobuo; YAMAMURA, Shusaku; URISU, Tsuneo

Nowadays bio-mimetic sensing techniques, using immobilization of intact biomolecules on solid surfaces, attract significant attentions. For solid substrates, silicon is a suitable material since precise micro-fabrication has been established. New biosensors can be combined with electronics devices on the same chip. Characterizations by IR spectroscopy and AFM observation are useful tools to investigate biomolecules immobilized on silicon surface. It is known that BML-IRRAS (Infrared Reflection Absorption Spectroscopy using Buried Metal Layer substrate$^{1)}$) is a high-resolution surface vibration spectroscopy on the semiconductor or insulator materials, which has sub-monolayer sensitivity for the wide frequency range including fingerprint regions. In this study we have immobilized avidin, which has high versatility for conjugation of biomolecules with solid surfaces, on the SiO_2/Si(100) surface modified with carboxyl groups, and characterized the surface by AFM and BML-IRRAS for the first time. The –COOH modification was produced by the deposition of 2-(carbomethoxy)ethyltrichlorosilane and sequential hydrolysis by HCl. Immobilization of avidin was performed after condensation reaction by N-hydroxysucciniimide and EDC, which enhanced the reactivity of carboxyl group with amino group of avidin.

AFM images (Figure 1) showed that the roughness of the –COOH modified surface was less than 0.5 nm, and protrusions with about 15 nm diameter and 2 nm height appeared after the avidin immobilization. The BML-IRRAS measurements showed clear peaks at 1650 cm^{-1} and 1550 cm^{-1}, which were assigned to Amide I and Amide II bands of avidin. These bands also consisted of several fine structures which might be assigned to secondary structures such as α-helix and β-sheet *etc.* The detailed shape analysis of these bands could give the information with orientations of these immobilized proteins.

Reference

1) S. Yamamura. *et al., Jpn. J. Appl. Phys.* **42**, 3942 (2003).

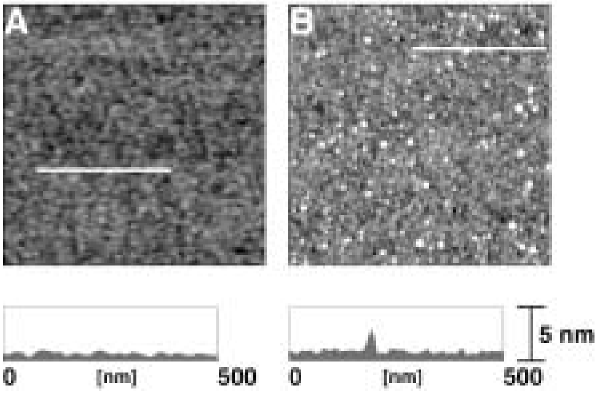

Figure 1. AFM images (1.0 μm × 1.0 μm) and line profiles of COOH-modified surfaces (A) before and (B) after immobilization of avidin.