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Shrinking of Spin-on-Glass Films Induced by Synchrotron Radiation and Its Application to Three-Dimensional Microfabrications

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In this work, we have performed experiments on the SR etching of SOG using a Co thin film as an etching mask and a mixture of SF_6 and O_2 as an etching gas. It was found that the thickness of SOG under the Co mask was also reduced by irradiation with the SR beam. The shrinkage phenomenon is a photoinduced process caused by SR permeating through the Co mask due to the high-energy photons rather than a thermal process, because the SOG is pre-annealed at 425˚C before irradiation with SR. The shrinkage of SOG was attenuated by increasing the Co thickness. An application of this phenomenon to a three-dimensional (3-D) microfabrication process using Co masks of varying thickness has also been demonstrated. Atomic force microscopy (AFM) observations showed that the surface of the shrunken SOG was as flat as a mirror-polished level. We have also investigated the mechanism and the characteristics of the shrinkage process by Fourier-transform infrared spectroscopy (FT-IR).

The Co contact mask was deposited in two steps as shown in Fig. 1a. First a line-and-space pattern was formed by photolithography and the lift-off technique (mask A). Then a rectangular Co layer was deposited using a stainless mask (mask B). The thickness of the former and the latter masks were 315 nm and 245 nm, respectively. Thus the SOG surface was covered with Co masks 560, 315 and 245 nm thick which are represented by areas 1-3 in Fig. 1a, respectively. The area without the Co mask is represented by area 4 in Fig. 1a. Figure 1b shows the SEM image of the SOG/Si surface after exposure to 2.00×10^4 mA min of SR using the Co mask shown in Fig. 1a, followed by removal of the Co mask with aqueous HNO_3 (0.1 N). The 3D structure of SOG is successfully obtained with only one SR irradiation, because the thinner the Co mask is, the deeper the SOG shrinks.

We have found that the thickness of the SOG film on the Si(100) surface is reduced by SR irradiation under a Co mask. This shrinkage phenomenon is a photoinduced process occurring due to the transmission of SR through the Co mask. A 550 nm thick SOG film shrinks by 152 nm under the Co mask that is 230 nm thick after exposure to 2.0×10^4 mA min of SR. Without the Co mask, the etching depth of SOG increased with the SR dose and the SOG film was completely removed by the exposure of 1.8×10^4 mA min. The shrinkage of SOG decreased with an increase in the Co mask thickness.

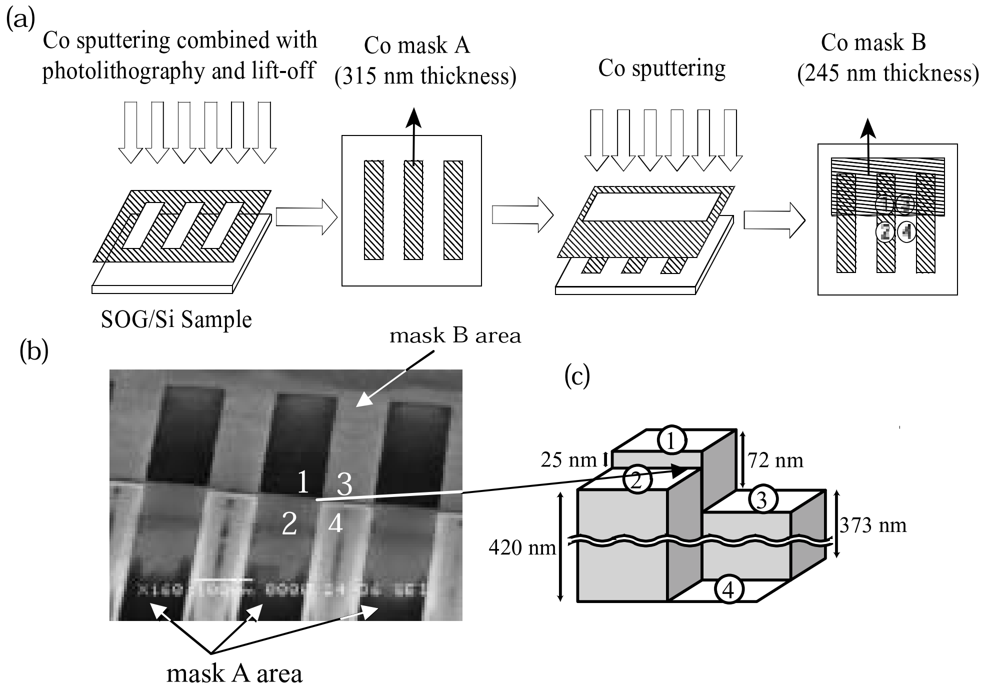

Fig. 1. Fabrication process of the Co contact mask. Mask A (315 nm thick) and mask B (245 nm thick) were overlapped. (b) SEM image of the 3D structure of SOG on Si fabricated by exposure to 2.00×104 mA min of SR using the Co contact mask in (a). (c) The schematic drawing of the 3-D structure.

BL4B

X-ray Magnetic Circular Dichroism Study on Cu Capping on Ni/Cu(001)

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Ultrathin Ni/Cu(001) films are well known to show unique magnetic properties. The spin reorientation transition occurs twice by varying the Ni thickness; at <8 ML (monolayer) the easy axis is in plane, at 8-40 ML it is perpendicular, and at >40 ML it is again in plane. O'Brien *et al.* [1] reported previously that the Cu capping stabilizes perpendicular magnetic anisotropy. They showed that the critical thickness for the first transition (~8 ML) is reduced by ~2 ML using Ni *L*-edge x-ray magnetic circular dichroism (XMCD). Although these results seem established, a recent work by Zhao *et al.* [2] shows essentially contradictory findings by means of magneto-optical Kerr effect (MOKE); the critical thickness increases upon the Cu capping. In this work, we tried to confirm the effect of Cu capping on Ni/Cu(001) by using both XMCD and MOKE.

Experiments

Ni was deposited on clean and ordered Cu(001) at room temperature in ultrahigh vacuum chambers. The thickness was monitored with the RHEED oscillations. Cu was subsequently deposited on Ni/Cu(001). Ni *L*-edge XMCD was taken at BL4B [3]. For XMCD films with an uniform thickness were prepared, while those for MOKE were wedge shaped.

Results

Figure 1 shows the polar MOKE intensity (only perpendicular magnetization was detected) as a function of the Ni thickness. These data were taken at room temperature. It is apparent that the critical thickness decreases with the Cu capping, being consistent with the results by O'Brien *et al* [1].

Figure 2 gives the Ni *L*-edge XMCD of 5.5 ML (in-plane magnetization) and 11 ML (perpendicular) Ni/Cu(001) before and after Cu deposition, taken at a temperature of 100 K and a magnetic field of 1000 G. It is easily found that the 11ML Ni does not show any significant change with the Cu deposition, while the 5.5ML film gives gradual reduction of the L_{III} XMCD intensity leaving the L_{II} intensity rather constant. These findings imply that the in-plane orbital magnetic moment (5.5 ML) is suppressed, while the perpendicular one is kept unchanged (11 ML). Figure 3 shows the results of the orbital magnetic moments given by the sum-rule analysis. It can be concluded that the in-plane magnetic anisotropy is unstabilized compared to the perpendicular magnetic anisotropy upon the Cu capping.

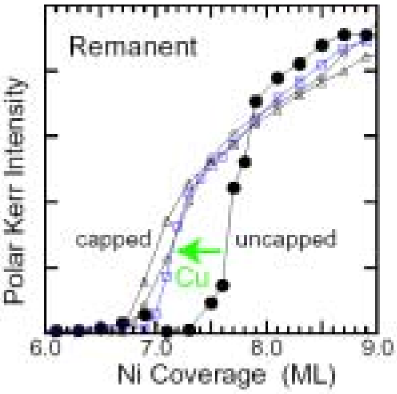

Fig. 1 Polar MOKE intensity (remanence) as a function of Ni thickness. The thickness of the Cu capping layer increases as a sequence of filled circle (clean), square, diamond, and triangle.

[1] W. L. O'Brien *et al. Phys. Rev.* **B54** (1996) 9297.
[2] H. W. Zhao *et al. Phys. Rev.* **B66** (2002) 104402.
[3] T. Nakagawa *et al.* this volume.

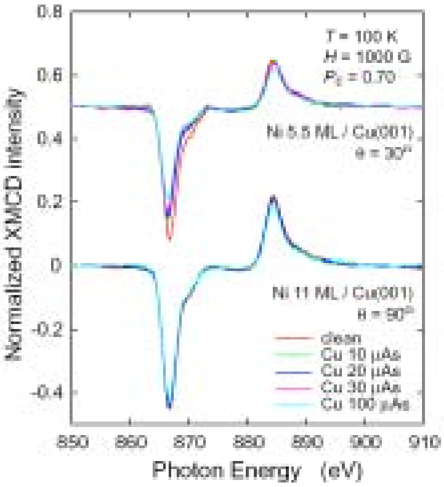

Fig. 2 Ni *L*-edge XMCD of 5.5 ML (in-plane magnetization, grazing x-ray incidence) and 11 ML (perpendicular, normal incidence). The amount of Cu deposition approximately corresponds to 1 ML to 100 μAs.

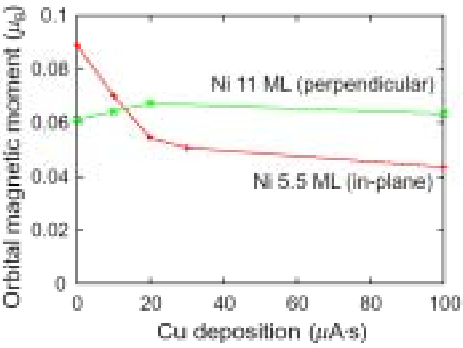

Fig. 3 Orbital magnetic moments of the Cu-capped Ni/Cu(001) as a function of Cu coverage (100 μAs is approximately 1 ML).

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X-ray Magnetic Circular Dichroism Study on NO Adsorbed Co and Ni Ultrathin Films on Cu(001)

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NO is well known as an effective magnetic killer since NO interacts with magnetic metal surfaces very strongly and the unpaired electron couples with the metal spins antiferromagnetically. In this work, we have investigated the effect of NO adsorption on ultrathin Co and Ni/Cu(001) films from the view point of magnetic anisotropy.

Experiments

Co and Ni were deposited on clean and ordered Cu(001) at room temperature in an ultrahigh vacuum chamber. The thickness was monitored with the RHEED oscillations. The obtained metal films were subsequently dosed with 0.5-1.0 L NO (1 L = 1×10^{-6} Torr·s) at 200 K. Co and Ni *L*-edge XMCD was taken at BL4B [1] at a temperature of 200 K.

Results

Figure 1 shows the Co *L*-edge XMCD of 3 ML (monolayer) in-plane magnetized Co/Cu(001) at the x-ray incidence angles θ of 30° (grazing incidence, close to the easy axis) and 90° (normal incidence, along the hard axis) before and after NO adsorption. It is apparently found that in the 30° spectra the magnetization is reduced drastically upon NO adsorption. On the contrary, the magnetization along surface normal (hard axis) is not so much reduced on NO adsorption, although the magnetization is not saturated under a magnetic field of 2000 G,.

Figure 2 depicts the Ni *L*-edge XMCD of 5.5 and 9 ML Ni/Cu(001). In the case of in-plane magnetized 5.5 ML Ni/Cu(001), both θ=30° and θ=90° spectra were taken at a magnetic field of 1000 G. The θ=30° spectra show noticeable reduction of the magnetization on NO adsorption, while less prominent suppression is found in the θ=90° spectra. This finding is similar to the NO/Co/Cu(001) case. The 9 ML spectra show much less change between clean and NO-adsorbed Ni along the easy axis, being different from the 5.5 ML case.

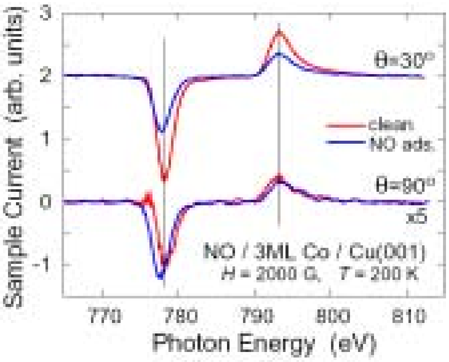

Fig. 1 Co *L*-edge XMCD of 3 ML Co/Cu(001) before and after NO adsorption. The x-ray incidence angles were θ=30° and 90°.

The results of the sum rule analysis are summarized in Table 1. In the in-plane magnetized films of 3 ML Co and 5.5 ML Ni, the in-plane orbital moments m_l (see 30° data) are significantly suppressed on NO adsorption, while perpendicular m_l (see 90° data) show much less change. The Ni 9 ML films give again almost no change in perpendicular m_l. These results imply that NO suppress the in-plane orbital moment drastically, while the perpendicular orbital moment is much less influenced. Namely, NO relatively stabilizes perpendicular magnetization effectively.

[1] T. Nakagawa *et al*. this volume.

Table 1 Results of the sum rule analysis.

Sample	State	θ(°)	m_l (μ_B)	m_s (μ_B)
Co 3 ML (in-plane)	Clean	30	0.164	1.65
	NO	30	0.095	0.82
	Clean	90	0.0169	0.18
	NO	90	0.039	0.18
Ni 5.5 ML (in-plane)	Clean	30	0.125	0.63
	NO	30	0.057	0.33
	Clean	90	0.024	0.30
	NO	90	0.020	0.17
Ni 9 ML (perpen.)	Clean	90	0.055	0.56
	NO	90	0.052	0.50

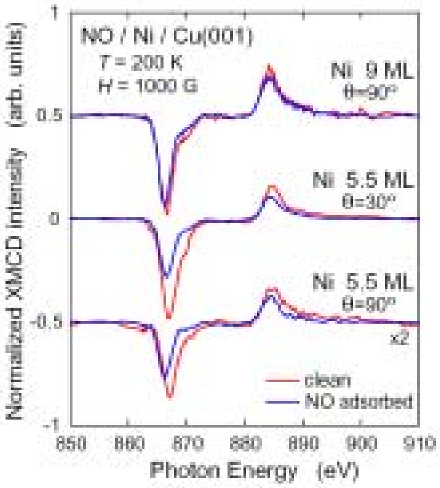

Fig. 2 Ni *L*-edge XMCD of 5.5 and 9 ML Ni/Cu(001) before and after NO adsorption. The x-ray incidence angles were θ=30° and 90° for 5.5 ML Ni and θ=90° for 9 ML Ni.

BL5U

Surface Photo-voltage Effect on *n*-GaAs(100) Surface Studied by Combination of SR and Laser

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Electronic non-equilibrium in the surface layer of photo-excited semiconductors has been attracting much interest from the basic scientific point of view and also from the practical applications for photo-electronic devices. In order to elucidate the electronic non-equilibrium in the surface layer of photo-excited semiconductors, it is indispensable to understand the transient state of photo-excited semiconductor surface. In this work, we have performed time-resolved photoemission spectroscopy in nano-second region with the combinational use of synchrotron radiation and laser.

Experimental

Experiments were performed at BL5U. An As-capped *n*-type GaAs(100) (Si-doped, 3.0x10^{16} cm^{-3}) was used for the measurements. An As capping layer was removed by heating the sample in the ultra-high vacuum. We used the mode-locked Ti:Sapphire laser (COHERENT Mira 900-F) which is synchronized with the synchrotron radiation in the multi-bunch operation. The time-resolved photoemission measurements in nano-second region were performed by the so-called pump-probe technique with the synchrotron radiation and laser. The laser light was transported to the viewport of the main experimental chamber using an optical fiber. The laser light was then focused onto the sample surface with a 3 mm radius spot. The spatial overlap of the laser with the synchrotron radiation was adjusted by eyes.

Results and Discussions

Figure 1 shows the Ga *3d* photoemission spectra with and without laser illumination measured at room temperature. The delay time between laser and SR is 0 ns. As shown in Fig. 1, it is clearly seen that the peak position of the Ga *3d* spectrum is shifted to lower kinetic energy under the laser excitation. From the conjunction with our previous studies, we have concluded that the present core-level shift is originated from the surface photo-voltage (SPV) effect. The SPV effect is closely related to the concept of the band bending in semiconductor surfaces. The intrinsic or extrinsic charges in the surface states are compensated by the underlying bulk charges, thus resulting in the band bending. When electrons and holes are produced in n-type semiconductors by laser excitation, the photo-excited holes move toward the surface and the electrons go into the bulk according to the potential curves due to the band bending. This charge separation in space produces another electric field in the space-charge region, and changes the magnitude of the band bending.

In addition to the peak shift caused by the SPV effect, it should be noted that the spectral shape changes under laser excitation. As shown in Fig. 1, it is clearly seen that the dip between two spin-orbit splitting components become shallow under laser illumination. The change of the spectral shape has been clearly observed for the first time by the high energy resolution measurements. We have confirmed that the change of the spectral shape is reproducible phenomena. Therefore, the decomposition of the surface stoichiometry due to the laser illumination can be excluded as the origin of the measured change of the spectral shape. It has been reported that the decapped GaAs(100) surface produces a Ga-rich composition which shows the (4x2)-c(8x2) low-energy electron diffraction pattern. In this case, two surface components on ether side of the bulk component are necessary to reproduce the observed spectral shape of the Ga *3d* core-level. These surface components correspond to the inequivalent surface Ga sites in the (4x2) unit cell. It is considered that the change of the spectral shape observed in this work can be explained by different SPV shift for each Ga site. In order to clarify the site dependent SPV effect and its time dependence, the detailed analysis including the line-shape analysis using a least-squares-fitting is in progress.

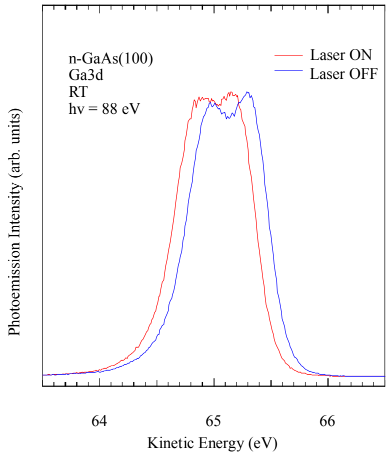

Fig. 1. Ga *3d* photoemission spectra with and without laser illumination.

BL5U

Photoelectron Spectroscopy of ErAs/GaAs(100)

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Introduction

In recent years much attention has been focused on the quantum size effect in thin films on semiconductor. The electron confinement induced by the quantization of its states was found in thin ErAs films epitaxially grown on the GaAs(100) surface [1]. A semimetal to semiconductor transition has been also predicted as the ErAs film thickness is decreased [2]. In this report, we will present results of angle-resolved photoelectron spectroscopic study on the electronic structure of ultrathin ErAs films on GaAs(100).

Experiments

Photoelectron measurements were carried out in the normal emission angle-resolved mode with the angle acceptance of ±1° at BL5A of UVSOR. Thin ErAs films were grown on GaAs(100) substrates with a 200 nm thick GaAs buffer layer by molecular beam epitaxy, and then capped with a thick As overlayer to prevent oxidation. This overlayer was removed by annealing in an ultrahigh vacuum just before the photoelectron measurement, as shown below. A clean GaAs(100) surface was also prepared by an Ar$^+$ ion sputtering and annealing procedure.

Results and Discussion

Figure 1 shows typical spectra recorded with the excitation photon energy $h\nu$ = 120 eV for 9 ML thick ErAs films on GaAs(100) at different stages of successive annealings, each of which was made at the temperature indicated in the figure for 10 min. The spectrum of the clean GaAs(100) is also presented for comparison. Features around the binding energy E_B of 20, 41 and 45 eV are ascribed to the Ga 3*d* and As 3*d* states of ErAs/GaAs and the As 3*d* one of the As oxides in the overlayer, respectively. No lines due to Ga oxides are observed. After annealing, the As 3*d* line at ~41 eV increased, while the As oxide line at ~45 eV decreased. The Er 5*p* line at E_B ~ 32 eV and the Er 4*f* multiplets around 4~11 eV also appear after annealing. These results show that the As overlayer can be removed by the longer annealing at 740 K.

In Fig.2, we compare the valence band spectra of 2 ML and 9 ML thick ErAs/GaAs (100) after the 740 K annealing with that of a thick ErAs layer reported by Komesu *et al.* [3]. Here, the 2 ML-ErAs/GaAs spectrum was recorded with a He I light source. It shows the less noticeable Er 4*f* features because of its small ionization cross section at $h\nu$ = 21.2 eV and of the low Er concentration. As for the electronic structure near the Fermi level (E_B = 0 eV), the thick ErAs reveals the definite intensity at the Fermi level, representing a semimetallic electronic structure, while the ultrathin 2 ML-ErAs/GaAs indicates an energy gap. This implies that the semimetal-semiconductor transition may occur at some thickness, though the detailed thickness dependence of the electronic states of ErAs/GaAs has not been clarified at present.

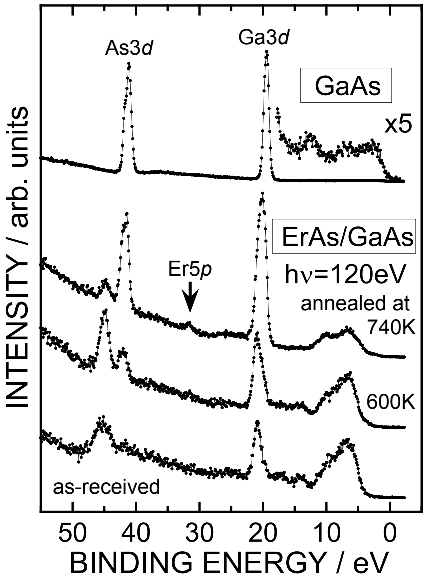

Fig. 1 Photoelectron spectra of ErAs/GaAs(100) at different annealing stages. A spectrum for a clean GaAs(100) is presented for comparison.

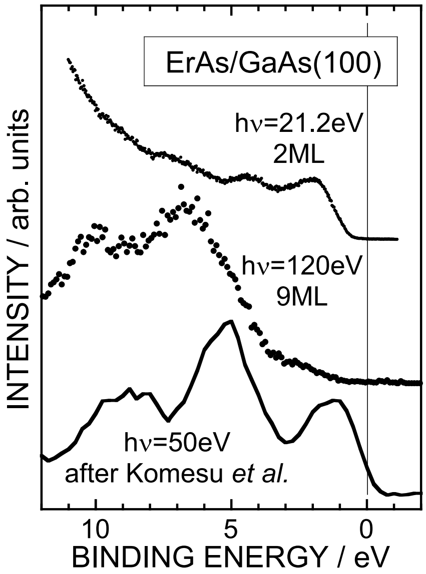

Fig.2 Valence band spectra of ErAs/GaAs(100).

[1] L. Ilver *et al.* Phys. Rev. Lett. **77,** 4946 (1996).
[2] S. J. Allen *et al.* Surf. Sci. **228,** 13 (1990).
[3] T. Komesu *et al.* Phys. Rev. B **67**, 035104 (2003).

BL5U

Atomic Arrangement of Si(111) 2√7×3-(Pb,Sn) Surface

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Binary metal adsorbing system on a semiconductor surface possesses a possibility of showing unique atomic arrangement and electronic properties, which are different from those for a single adsorbate system. Recently, we have found a new superstructure, a Si(111) 2√7×3-(Pb,Sn) surface, on the coadsorption of Pb and Sn at their coverages, θ_{Pb} and θ_{Sn}, of 0.25 and 0.5 ML, respectively [1]. Here, 1 ML is defined as 7.8×10^{14} atoms·cm^{-2}. However, its detailed atomic arrangement has not been clarified yet. In this study, we have measured the Pb 5*d* and Sn 4*d* photoelectron spectra of the Si(111) 2√7×3-(Pb,Sn) surface and proposed its atomic arrangement model.

Experimental

An n-type Si(111) wafer of 5 Ωcm and 5×10×0.5 mm^3 in size was used for a substrate of the Si(111) 2√7×3-(Pb,Sn) surface. This surface was prepared by annealing at 620 K after deposition of ~ 1 ML Pb onto a Si(111) √3×√3 + faint 2√3×2√3-Sn surface at θ_{Sn} = 0.5 ML, which was made by deposition of 1 ML Sn onto a clean Si(111) 7×7 surface and subsequent annealing at 970 K. The completion of the surface was confirmed by low energy electron diffraction. Photoelectron spectra were recorded at the normal emission at 100 K with the excitation photon energy of 52 eV, the angle acceptance of ±1° of an electron analyzer, and total energy resolution of ~80 meV.

Results and Discussion

Figure 1 shows typical Pb 5*d* and Sn 4*d* core-level spectra for the Si(111) 2√7×3-(Pb,Sn) surface. The Pb 5*d* spectrum consists of single component, while the Sn 4*d* one exhibits two components C1 and C2, the ratio of which is C1:C2 = 100:31. This suggests that the Pb atoms are located at single adsorption site and the Sn atoms are adsorbed on two inequivalent sites at their ratio of 100:31. Taking account of results of scanning tunneling microscopy (STM) as well, we propose a model for the atomic arrangement of the Si(111) 2√7×3-(Pb,Sn) surface in Fig.2. Here, typical STM image for the surface is also presented for a filled state of -0.8 V sample bias in a scanned area of 50×50 Å^2. In this model, all dangling bonds of the first Si layer are terminated by metal adsorbates and the number of Pb and Sn atoms per unit cell are 4 and 8, corresponding to the coverages θ_{Pb} = 0.22 and θ_{Sn} = 0.44 ML respectively.

[1] J. Yuhara *et al.*, Nucl. Instrum. Methods B **199** (2003) 422.

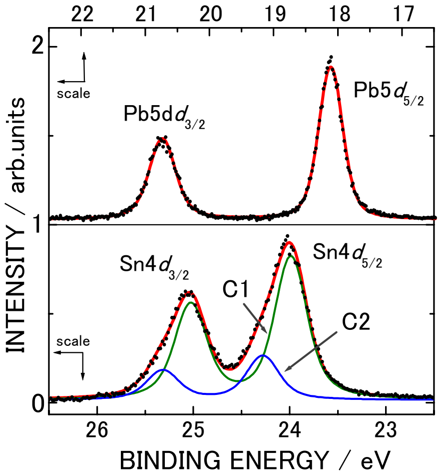

Fig.1. Pb 5*d* and Sn 4*d* photoelectron spectra of the Si(111) 2√7×3-(Pb,Sn) surface.

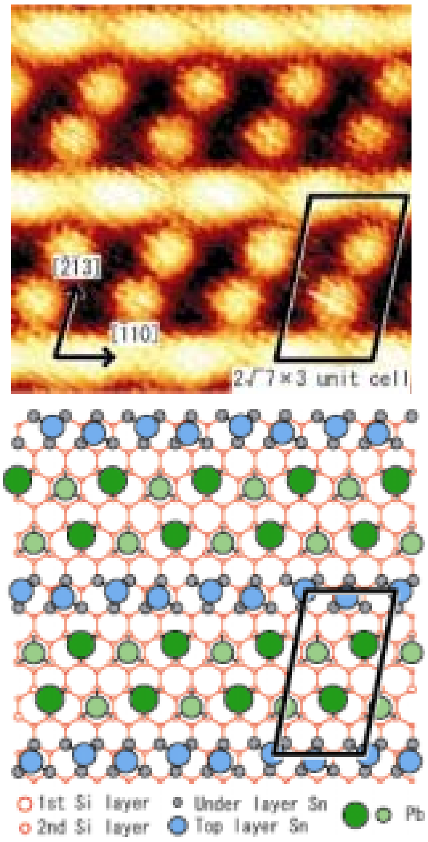

Fig.2. STM image and atomic arrangement model for the Si(111) 2√7×3-(Pb,Sn) surface.

BL5B Photodesorption of Ionized Clusters from Water Physisorbed on Rare Gas Solids: Measurements of the Desorption Yield

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A variety of studies have been made on electron- and photon-stimulated desorption (ESD/PSD) of water adsorbed on various substrates, and the mechanisms of desrobed species have been discussed. Recently, Souda has examined D_2O adsorbed on rare gas solids by means of ESD and found $(D_2O)_nD^+$ [n=1-10]. The result is interpreted that the desorption of the cluster are due to Coulombic expulsion between valence holes in the water cluster[1].

We have studied PSD of $(H_2O)_nH^+$ from water physisorbed on rare gas solids Ar through Xe by using synchrotron radiation and by a laser-plasma ultraviolet light source (LPLS). Previous PSD experiment of the threshold for the desorption of $(H_2O)_nH^+$ from the substrate Ar was found to 240 eV, and the desorption yield dependence on the incident energy after the threshold is clearly corresponds to the absorption spectrum of solid Ar near the onset of 2p transitions. In the present study, the desorption yields of $(H_2O)_nH^+$ from water adsorbed on solid Xe and on solid Kr were measured as a function of the incident photon energy. The same as a result of H_2O / Ar, the results indicated that the core excitation of rare gas atoms leads the desorption of clusters.

Experimental

The PSD-experiments have been carried out in two independent ultra-high vacuum systems; One at the Gakushuin University and the other at the beam line 5B at UVSOR in Institute for Molecular Science, Okazaki. The mass spectrum of PSD ions was measured by a time-of-flight (TOF) technique. The desorption yield was normalized by the light intensity, which was continuously monitored by the photoelectronic current from a gold-plated mesh, inserted in the beam lines.

In Gakushuin, the experiments were performed with the ultrahigh-vacuum instrument attached to LPLS, which was developed for purpose of using it as an excitation light source in exprimental studies of DIET. Radiation is produced by plasma on a Ta surface which is induced by YAG-laser irradiation focused on the surface. The photon energy was monochromatized using troidal grating monochromators and a exist slit in the range of 11.5 to 310 eV. The pulse width of the order of 10 ns makes it possible to obtain higher time resolution in a TOF measurement of desorbed particles. Water was physisorbed on the rare gas solids which was condensed on a Copper substrate attached to the He gas flow cryostat. The samples were held at ~17 K.

In UVSOR, The sample film was prepared on a Pt(111). This was fixed to a liquid He cryostat and cooled down to 6 K. the cryostat surrounded by a liquid N_2 cooled heat shield. Monochromatized synchrotron radiation in the range of 6 to 1000 eV was focused on the sample. The incident angle of the photon beam was 20 deg from the normal direction of the sample surface. A voltage pulse was applied to the sample, and the desorbed cations extracted into the drift tube were detected by a channeltron electron multiplier, which was placed at off-axis with respect to the surface normal.

Results

The results of the $(H_2O)_nH^+$ desorption yield from a surface of (a)Kr and (b)Xe were shown fig. 1. The desorption yield is quite similar to the absorption spectrum near the onset of 4d (3d) transitions of solid Xe (Kr)[2]. However, there was no increasing of the desorption yield 20-40 eV incident photon energy, which was reported as the desorption threshold of the H^+ for bulk water[3]. We can conclude that the inner-shell ionization of the rare gas atom plays a important role as a primary excitation which leads to the desorption of the $(H_2O)_nH^+$ at the rare gas solids.

[1] R. Souda, Surf. Sci. 511, 147 (2002)
[2] Hansel at el., J. Phys. **32**, 236 (1971)
[3] Noell et al., Surf. Sci. **157**, 99 (1985)

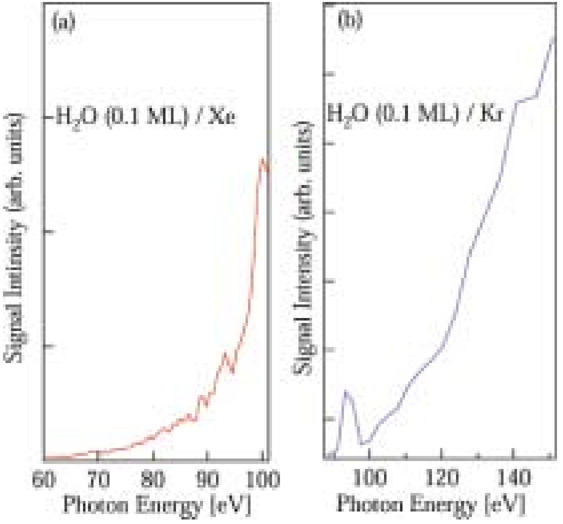

Fig. 1. Excitation energy dependence of the PSD cluster ion yield from adsorbed on (a)solid Xe and (b)solid Kr.

BL7U

Construction of BL7U and STM Observations of H-Si (111)

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SR stimulated etching and deposition have been attractive for fabrications of semiconductor devices with nanometer-scale fine structures due to their high spatial resolution and low damage properties. From the viewpoint of photochemistry, they are also very important because there are a few reports of STM observation of surface reactions stimulated by SR irradiation[1]. Particularly, STM observations of their excitation energy dependence are much interesting.

BL7U was designed that the 1st order harmonic of the undulator radiation was changed from 70 eV to 140 eV with high photon flux achieving to 10^{20} phot. cm^{-2} on the sample surfaces. Two Pt-coated cylindrical mirrors were used for vertical and horizontal focusing. These two mirrors also suppress the higher harmonics of the undulator radiation into ~10% with respect to the first harmonic. The spectral resolution of this beamline is determined by the light source characteristics of the undulator radiation and an aperture stop set at the point 4810 mm downstream from the middle of the undulator. The calculated FWHMs at K parameter of 0.985 (1st harmonic at ~100 eV) are 9.3 eV and 4.5 eV for the radiation divergences of 500 µrad and 250 µrad respectively.

The UHV-STM system (UNISOKU Sci. Instrument) was installed at the end station and the atomic images of the clean Si (111) and H-adsorbed Si (111) surfaces were observed as a preliminary experiment. For a simplicity of the H/Si system, observation of SR irradiation effects and its excitation energy dependence by STM are interesting research targets.

The STM observations of H-Si (111) surfaces before undulator irradiation were carried out in the UHV chamber with a base pressure below 1×10^{-10} Torr. Although there are a lot of reports about the studies of H-Si (111) surfaces[2-4], interaction between rest-atom monohydride and H-atoms is still unclear. To observe the interaction of rest-atom monohydride and H-atoms, we used monohydride surfaces that were prepared by H-atom exposure on the Si 7x7 surface at a sample temperature of ~400°C.

Figure 1 shows 11 nm x 11 nm STM images that were recorded with a sample voltage of -2.00 V at a constant current of 0.25 – 0.30 nA. A sufficiently clear image of Si (111)-7x7 was obtained as shown in Fig. 1 (a). Figure 1 (b) shows a monohydride surface with several adatom islands prepared by 1000 L H-exposure at a sample temperature of ~400°C. It is observed that the area of the faulted regions is reduced. Further exposure of H atom of 1000 L at RT, shown in Fig. 1(c). The vacancies of the rest-atom are observed near the boundary of the faulted and unfaulted domains, which indicates that rest-atom etching occurred by H-exposure at RT.

At ~400°C, the H-exposure on clean Si 7x7 surface terminates the dangling bonds on the Si surface. The adatom hydrides move around on the rest-layer monohydride surface, fill the defects and enlarge the unfaulted domain, or form adatom islands. Excess H-atoms would partly contribute to the enlargement of the unfaulted domains and partly desorb by forming H_2 since the sample temperature is above the H_2 desorption threshold of 325°C [10]. However, at RT where H_2 desorption rate is low, excess H-atoms would break Si-Si bonds in the rest-atom layer and in adatom islands. Subsequential Si-Si bond breaking can lead the formation of SiH_4, which is then removed from the surface.

We are planning to investigate photon-stimulated desorption of a H-Si (111) surface, and the etching reaction by inner-shell excitation of the H-Si (111) surface and its excitation-energy dependence in the next experiments at BL7U.

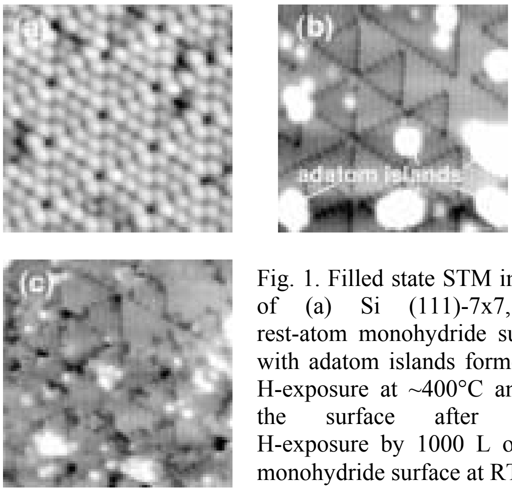

Fig. 1. Filled state STM images of (a) Si (111)-7x7, (b) rest-atom monohydride surface with adatom islands formed by H-exposure at ~400°C and (c) the surface after more H-exposure by 1000 L on the monohydride surface at RT.

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Investigation of Synchrotron Radiation Induced Etching of Polytetrafluoroethylene

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Polytetrafluoroethylene (PTFE) has many unique properties such as high thermal and chemical stability, low coefficient of friction, high electrical resistively, hydrophobicity (contact angle ~108°), and so on. By taking advantage of these characteristics, this material is expected for applications in various fields such in chemical, mechanical, electronics and so on. Recently, some reports about high aspect ratio fabrication for PTFE by synchrotron radiation (SR) are reported.[1,2) However the etching mechanism of PTFE by SR beam irradiation is not well understood yet. Adding to this, properties of the SR beam irradiated surface should be characterized for further application. In this study, etching of the PTFE by SR and surface characteristics after the processing was investigated.

In this study, etching of PTFE was made using SR of UVSOR facility with various holder temperatures (150~250°C) and photon fluxes ($1.5 \times 10^{17} \sim 3.1 \times 10^{17}$ /s/cm^2). SR beam induced etching was done in the vacuum chamber having turbo molecular pump. For the PTFE target, Naflon by Nichias was used. Chemical composition of the etched surface was analyzed by XPS system in author's group laboratory

Figure 1 shows the etching rate dependence on the photon flux for various holder temperatures. Higher etching rate was obtained with higher photon flux. Higher etching rate was also observed in higher holder temperature, however, after the SR beam irradiation at 150°C , the etching rate was noticeably low and surface color change into brown was observed.

To clarify this point, XPS spectrum of PTFE surface before and after the SR beam irradiation was investigated. As shown in Fig. 2, C_{1s} spectrum of bulk PTFE before the irradiation showed two major peaks marked as A and C. Here, the peak A and the peak C correspond to CF_2 and C-C component, respectively. After the irradiation at holder temperature of 150°C, the peak A became ambiguous, and the peak C became major. Additional signal was also found at around the binding energy of 295 eV. After the irradiation at holder temperature of 250°C, the peak A suggesting CF_2 component became major again, and the peak C was not seen. Around 295 eV, peak B was seen and was thought to be –C-CF_3 component.

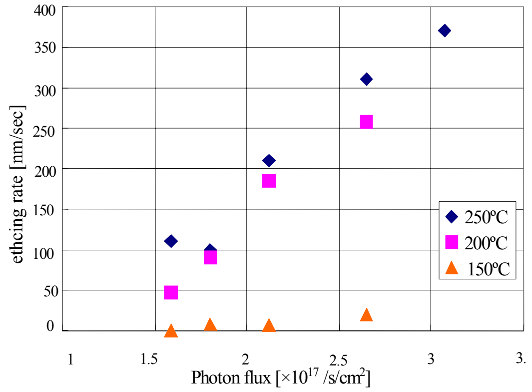

Fig.1 Etching rate vs. photon flux for various holder temperatures

From XPS, surface after the SR beam irradiation at higher temperatures is close to the bulk PTFE. On the other hand, SR beam irradiation at 150°C, marked composition change suggests that removal of fluorine from the surface. SR beam irradiation at lower temperatures causes carbon-rich surface which prevents further PTFE etching by SR beam irradiation. In the case of the irradiation in 200-250°C, some dissociation mechanism by heat may assist the etching process. Thus, the holder temperature is a key parameter for SR beam induced etching of PTFE by means of surface composition control because which affects chemical properties and hydrophobicity of the surface.

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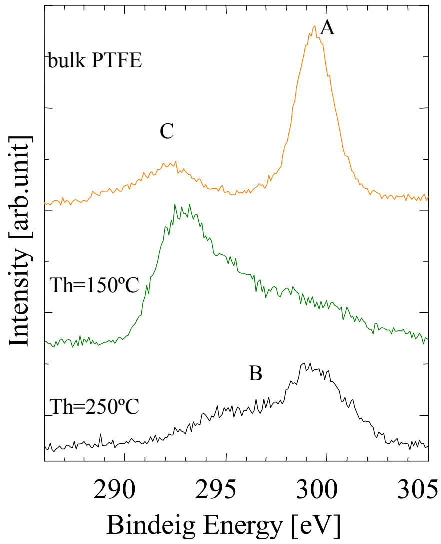

Fig.2 XPS spectrum of PTFE before and after the beam irradiation

BL8A

Synchrotron Radiation-excited Etching of ZnTe Using Ar Gas

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Synchrotron radiation (SR) is an ideal light source for the photo-excited process. Many studies on the technological utilization of SR-stimulated reactions, such as chemical vapor deposition [1,2], etching [3,4], and epitaxy [5,6] have been carried out so far. Concerning the SR-excited etching, the materials for integrated circuit such as Si, SiO_2, SiC, *etc*, have been studied actively using SF_6 as a reaction gas together with Ar gas [3]. SF_6 seems to be useful for SR-excited etching. On the other hand, few papers concerning the etching of compound materials such as III-V and II-VI semiconductors have been published to date in spite of their importance in optoelectronic application [7]. As II-VI semiconductors, *e.g.* ZnTe, with good quality can be grown by SR-excited growth [6], the study on the SR etching of them is the important next step to make the electronic devices by SR. In this study, we have described the SR-excited etching of ZnTe using SF_6 and Ar gas.

Experiments

The irradiation experiments were performed at beam line, BL-8A, in UVSOR. The focused SR from the bending magnet field of the 750 MeV electron storage ring was shone upon ZnTe (100) in Ar gas atmosphere. The spot size of SR on the sample was about 2×4 mm. A Ni mesh of 100 lines/in. and 80% transmittance, which is used as a mask, was placed on the sample surface. The synchrotron light is irradiated perpendicularly to the surface at room temperature (RT). The electric current for the SR emission in the storage ring was varied up to 300 mA. After the reaction chamber was evacuated to less than 10^{-7} Torr, the etching gas was fed into the chamber. The pressure in a reaction chamber was changed between 10^{-2} and 10^{-1} Torr. The substrate was negatively biased against the reaction chamber. A large pressure difference was sustained between the storage ring and the reaction chamber using multiple differential vacuum pumping system.

Results

ZnTe was etched by the irradiation of the SR beam under the negative bias to the sample. The surface step profile of this sample is shown in Figure 1. The shadow area due to 50 μm wide Ni wires is not etched but the irradiated area is etched. The pattern of metal mask was found to be transferred exactly. In this experiment, we used focused SR beam as mentioned above, and the center area of the beam was etched deeply, indicating that the etching rate depends on the photon flux. The maximum etching rate was estimated to be around 4.5×10^{-2} Å/mA·min. The etching is supposed to be proceeded by the excitation of Ar gas by high-energy SR beam, followed by the bombardment of Ar ion to the surface of ZnTe due to the negative bias. Since the etched area was relatively large compared with the beam spot size (2×4 mm), the physical etching process is considered to be dominant rather than chemical process with surface excitation. Further investigation will be required to clarify the mechanism and improve the etching rate.

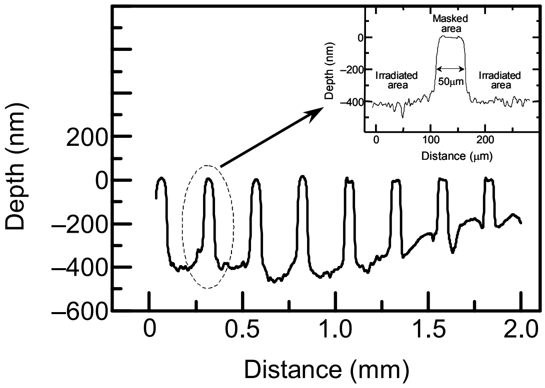

Fig. 1. Surface step profile of ZnTe etched in Ar atmosphere under negative bias to the sample.

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BL8A

Surface Properties of Synchrotron Radiation Irradiated PTFE

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High hydrophobicity of polytetrafluoroethylene (PTFE) is a one of the standing feature of this material. With this unique feature together with its high chemical stability, PTFE is quite useful for the application to bio-sensors, tissue engineering and so on. SR beam induced etching of PTFE have a high potential for micro fabrication of this material1). In this study, we have studied surface properties of PTFE after the synchrotron radiation (SR) beam irradiation.

In this study, commercially available PTFE bulk was used for the experiments. SR beam irradiation onto the PTFE was made in vacuum chamber which was connected to the UVSOR beam line, as mentioned in previous report.2,3) PTFE samples were placed on the sample holder having a heater. In this study, holder temperature was changed in the range of 150°C to 250°C. Characterization of SR beam irradiated PTFE was made by SEM observation, and XPS measurement. To evaluate the surface hydrophobicity, measurement of the contact angle of the PTFE surface was done following JIS R3257.

Figure 1 shows SEM image of SR beam irradiated PTFE surface at 250°C. As reported in our previous report, SR beam induced etching of PTFE was clearly found. From the SEM observation of the etched surface, some microstructures were found. Roughness of the structure became large with increasing an irradiation time, photon flux and holder temperature.

Contact angle of the irradiated surface became as high as 156°, which is clearly exceeded that of bare PTFE surface. According to Wenzel's model, an introduction of fine structures on the surface enhances the hydrophobicity of the surface. Although the mechanism of the fine structures on SR beam irradiated surface of PTFE, observed enhancement of hydrophobicity is thought to be come from the introduction of surface structures as shown in Fig. 1.

Irradiation time dependence on the contact angle was characterized. Contact angle became larger with irradiation time. Here, increase of the contact angle was observed up to 156°. As compared with the case of holder temperature of 200°C, result of holder temperature of 250°C showed rapid enhance of hydrophobicity with short irradiation time. This suggests that the surface decomposition process of PTFE by SR beam irradiation affects the hydrophobicity of PTFE.

Then, to investigate a relation between the hydrophobicity and the compositional change by the SR beam irradiation, XPS measurements of the PTFE surfaces were made. As shown in Fig. 2, chemical composition of the PTFE surface clearly depend on the holder temperature. Namely, SR beam irradiated samples at lower temperature showed F-poor (C-rich) surfaces as compared with bare surfaces. However, as area ratio of XPS peak of fluorine and carbon (F/C ratio) increased in higher temperatures, contact angle becomes higher. This suggests that the hydrophobicity enhancement by SR beam irradiation is not only from the introduction of the fine structures on the surface, but also the control of the chemical composition of PTFE surfaces.

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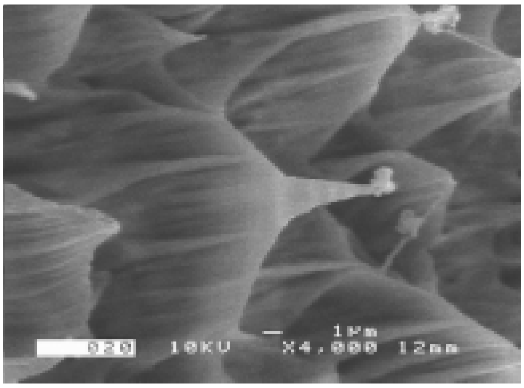

Fig.1 SEM image (tilted) of UVSOR irradiated surface.

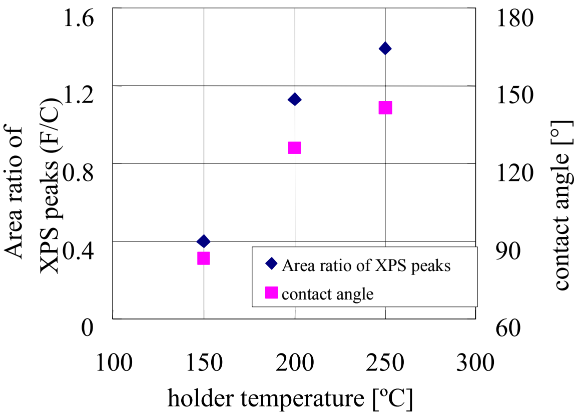

Fig.2 Holder temperature dependence on the area ratio of XPS peaks (F/C) and contact angle.

BL8B2

Chalcogen-Au Bonding State of Self-assembled Monolayers on Au(111)

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Self-assembled monolayers (SAMs) on metal surfaces present many interesting aspects in resent years from the viewpoints of both basic science and practical applications. Although a variety of substrates and functional groups are known to form SAMs, the thiol/disulfide monolayer on Au has received considerable attention due to its simplicity and ease of preparation. In contrast to the many reports of monolayers derived from organosulfur reagents containing functional groups in the ω-position, there has been relatively little work done to build organic monolayers on metals without using sulfur as the anchor group. Moreover, there is little attention for the electronic states which originate from anchored part of adsorbed SAM molecules adsorbed on metal surfaces. In this report, we have studied the molecular conformation and the electronic structural study of dialkyl telluride adsorption on Au(111) with ultraviolet photoelectron spectroscopy (UPS).

Experiments

The Au(111) substrates were prepared by thermally evaporated on mica. The substrate was immersed into a try toluene diluted Oc_2S_2 or Oc_2Te_2 solution at a concentration of about 1 mM for 24 h in dry nitrogen atmosphere. After removal from the solution, the samples were rinsed and stored in dried ethanol until measurements under dark condition. ARUPS measurements were carried out at the beamline 8B2 of the UVSOR facility.

Results and Discussion

Figure 1 shows the UPS spectra of Oc_2S_2 and Oc_2Te_2 monolayers adsorbed on Au(111) at the incident photon energy $h\nu = 40$ eV on a binding energy scale relative to the Fermi level. Bands A and B are ascribed to pseudo-π and C2s orbital distributed on the alkyl chain, respectively. ARUPS spectra of Oc_2S_2 on Au(111) exhibit polarization dependence suggestive of formation of a well-oriented film. In contrast, the bands A and B of Oc_2Te_2 on Au does not show polarization dependence, indicating that the conformation of the alkyl chain is more randomly oriented than that of Oc_2S_2. In Fig, 2, we show the UPS spectra of clean Au(111), and Oc_2S_2 and Oc_2Te_2 monolayers near the Fermi level. In the case of the clean Au(111), the Shockley surface state is clearly observed just below the Fermi level. The quenching of the surface state and the emergence of additional bands attributed to the MOs of the dialkyl dichalcogenide-derived adsorbates. In the case of the Oc_2S_2, a low intensity feature is observed at approximately 1.5 eV below Fermi level and prior to the Au 5d band onset. We measured with the different photon energies thus changing the relative cross section between Au 6s and the binding orbital (largely S 2p), and the band has a small contribution of Au 6s. Similar low intensity bands are also observed at around 1.5 eV for the Oc_2Te_2 on Au. These band observed at around 1.5 eV for dioctyl dichalcogenide adsorbed on Au(111) can thus be taken as evidence of Au-chalcogen bonding.

In our previous report for the Oc_2Te_2 monolayer, the ditelluride derived adsorbed layer is easily oxidized in air atmosphere than the disulfide and diselenide adsorbed monolayers [1]. By exposing to air for Oc_2Te_2 monolayer, this band is completely disappeared, indicating that the Au-Te bonding cleavage proceeds by the oxidation in the atmosphere.

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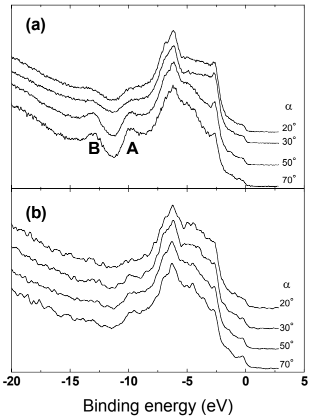

Fig. 1. Normal emission UPS spectra of Oc_2S_2 and Oc_2Te_2 on Au(111) as a function of photon angle of incidence α.

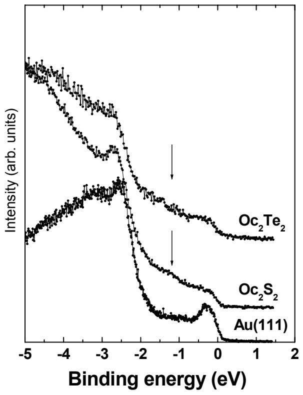

Fig. 2. Expanded normal emission UPS spectra of Oc_2S_2 and Oc_2Te_2 on Au(111) and clean Au(111) surface.