# 6 Surface science, photochemistry and Others

#### BL4A

## Development of Differential Pump System for Studies the Effects of XeF<sup>2</sup> Etching of Si and SiO<sub>2</sub> Induced by Synchrotron Radiation

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An etching system was constructed to clarify the difference between synchrotron radiation (SR) -induced reaction and dark reaction in XeF<sub>2</sub> etching of Si experiment at the beam-line BL4A1 in the UVSOR last year, and an etching rate of 0.9  $\mu$ m/min on Si surface was achieved. A XeF<sub>2</sub>-flow chamber isolated and evacuated independently with a LiF window is installed in the end-station beam chamber, in order to avoid the damage of vacuum pressure and evacuation instruments in the beam-line. However, the LiF window is damaged easily owing to the violent collision of photon. So an apparent result can not be observed at long-time performances that escape the balance of selective and non-selective reactions of XeF<sub>2</sub> Etching on Si.

In order to eliminate the constraint imposed by the damage on the entrance window of the reaction cell, a differential pump apparatus system has been developed. The entrance window is replaced by an aperture and a sequence of pressure stages which reduce a pressure of 0.5 Torr in the reaction cell to  $10^{-9}$  Torr in the pre-mirror chamber as shown in Fig.1 and Fig. 2. By means of this technology a higher energy resolution and a beam size of 1 mm in the energy direction can be obtained.

The non-condensed beam spot of incident beam after pre-mirror chamber is about  $10 \times 10 \text{ mm}^2$ . In order to focus the beam trajectory to pass through the aperture, a paraboloid mirror is designed to condense the divergent incident beam. As illustrated in Fig. 3, the horizontal beam profile far from pre-mirror is expected to be condensed at sample position.

A part of the beam condensed apparatus was fabricated and an extremely high etching rate and spacial resolution was obtained from a performance test of Teflon etching. After the setting up of new etching chamber, we are planning to study the SR irradiation effects on the material selectivity of etching between Si and SiO<sub>2</sub>, to find whether there exist an anisotropic character in desorption reaction

of XeF<sub>2</sub> etching induced by synchrotron radiation.



Fig. 2 Characteristic of the pressure variation in differential pump system after etcher gas injected by simulation - The system restrains the variation of pressure from etcher injection, and obtains achievement of experiment pressure.



Fig. 3 Schematic optical layout of beam condenser system



Fig. 1 Schematic section view of the etching chamber, beam converged on the sample surface by moving the position of the condenser mirror.

**BL8B2** 

# Electronic Structure of Pentacene Thin Film Converted from IBM Type Precursor and Vacuum Deposit

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#### Introduction

Pentacene has high hole mobility, and many studies have been performed on it. Pentacene film can be fabricated only by vacuum deposition due to its poor solubility to solvent. But recent study reported highly soluble pentacene precursor shown in Fig.1 (IBN type precursor), which can be spin-cast to form a film [1]. A retro Diels-Ader reaction caused by heating converts this precursor to a pentacene. In this study, we performed a UPS study of the change of the pentacene precursor film to pentacene, showing that the same electronic structure are that for a vacuum deposited film was actually observed.



Fig. 1 IBM type pentacene precursor

#### **Experimental**

The pentacene vacuum deposition film was deposited on a Au/Si substrate. The pentacene precursor film was prepared by the spin coating of the precursor solution of chloroform. Spin coated film was heated at 150°C under nitrogen atmosphere about 10 minutes. UPS measurements were performed for these films at BL-8B2 of UVSOR facility.

#### **Results and discussion**

Figure 2 shows the UPS spectra of pentacene precursor film before and after heating. The binding energy in this figure is given with respect to the Au Fermi level. We see a clear change between pentacene precursor and heated film can see at the region of the HOMO peak. Heated precursor film show the HOMO peak at 1.5-1.6eV while the precursor film does not show such peak at this energy. The simulated spectra by molecular orbital calculations for these spectra also show good agreement with the observed spectra.

Figure 3 shows the UPS spectra of vacuum deposited pentacene film and the heated pentacene precursor film. These spectra are very similar, except that the peak intensity is a little different at around 0-4eV. This structure is ascribed to the combined

contribution from  $\sigma$  and  $\pi$  orbitals. Supplemental penning ionization electron spectroscopy (PIES) study indicated that this difference of intensity around 3eV comes from the film structure. Similar structure difference between spin-coat and evaporated film are reported for other compound [2].

Moreover, XPS study at the  $S_{2p}$  region also showed that the adduct part is completely removed from the film by heating. These results indicate that the IBM type pentacene precursor can give high quality pentacene film from the view point of electronic structure.



Fig. 2 UPS spectra of pentacene precursor film before (bottom) and after (top) heating compared with the theoretically simulated results.



Fig. 3 UPS spectra of vacuum deposited pentacene film and heated pentacene precursor film.

- A. Afzali, C. D. Dimitrakopoulos, T. L. Breen, J. Am. Chem. Soc. **124** (2002) 8812
- [2] H. Ozaki, J. Chem. Phys. 113 (2000) 6361

BL4B

# X-ray Magnetic Circular Dichroism of Co Nanorods Grown on Cu(110)-(2×3)N surface

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Magnetic properties of nanorods are hot subjects in recent years. York *et al.* [1] discovered self-assembled Co nanorods on Cu(110)-(2×3)N that are  $\sim$ 1 nm thick and well separated with each other up to as much as  $\sim$ 2 ML (monolayer). In the present work, we have investigated the magnetic properties of the Co nanorods by combining x-ray magnetic circular dichroism (XMCD) with the magneto-optical Kerr effect (MOKE) measurements.

The experiments were performed at soft X-ray varied line monochromator station Beamline 4B. The Co nanorods on Cu(110)-(2×3)N were grown along the [1-10] direction. The Co  $L_{III,II}$ -edge XMCD were taken with the polarization factor of 0.70 at ~90 K.

Figure 1 shows the Auger electron spectra (AES) and the LEED patterns. The N-KLL AES intensity is found to be kept constant on Co deposition, implying that the N atoms are located always at the surface even after deposition of Co. On the contrary, the Cu-MNN AES is reduced quickly with the Co deposition, suggesting that Cu does not migrate on/in the Co rods so significantly. On the other hand, the LEED patterns show (1×6) superstructure as in Figs. 1(d) and 1(e), consistent with the previous STM observation. This implies successful preparation of the Co nanrods.

Figure 2(a) depicts the anisotropic magnetization curves taken by MOKE. The hysteresis accompanied by remanent magnetization can be seen only along the [001] direction, implying that the magnetic easy axis is [001] that is perpendicular to the rod axis. The shape anisotropy does not determine the magnetic easy axis. Figure 2(b) shows the anisotropic XMCD. The inset of Fig. 2(b) gives the XMCD normalized with the edge jump. The [001] spectrum yields the most intense XMCD among the three directions of [001], [1-10] and [110], confirming that the present magnetic anisotropy is derived from the anisotropic spin-orbit interaction. Moreover, one can note that the orbital magnetic moment is rapidly enhanced on the formation of nanorods (<2 ML), as shown in Fig. 2(c).

[1] S.M York et al., Phy. Rev. B 64 (2001) 033411.



(a) N-KLL and (b) Co, Cu-MNN AES and

LEED (c-e) of the Co nanorods on  $Cu(110)-(2\times 3)N$ .



Fig. 1

Fig. 2 (a) Magnetic curves taken by MOKE. (b) Co L-edge XMCD normalized with the  $L_{II}$  peak, together with those normalized with the edge jumps in the inset. (c) Ratio of the orbital/spin magnetic moment as a function of the Co thickness, together with the thermally averaged spin magnetic moment in the inset.

### **Terahertz Spectroscopy of Protein Powder**

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Biological polymers are expected to exhibit broad vibrational spectral features in terahertz regime corresponding to functionally relevant, global and subglobal collective modes on the picosecond timescale. This is supported by theoretical molecular dynamics studies and normal mode calculations [1,2]. Due to the strong frequency-dependent terahertz attenuation of water, these studies should have dry, or partially hydrated samples. Here we report the terahertz spectra of representative proteins having various secondary structures, myoglobin, lysozyme,  $\alpha$ -synuclein,  $\beta$ -lactoglobulin and src-SH3 domain.

All experiments were done at terahertz beam line BL6B at UVSOR-II. The thickness of the samples was around 0.1 mm. The wavenumber range we monitored was 10-250 cm<sup>-1</sup>. Each spectrum was accumulated 100 times. The final spectra were divided by cell spectrum in order to subtract influence of the cell. All measurements were accumulated five times to get good S/N ratio.

Myoglobin is rich in  $\alpha$ -helices. Figure 1 shows its terahertz spectrum.  $\beta$ -Lactoglobulin is rich in  $\beta$ -sheets (Figure 2). Lysozyme is one of  $\alpha/\beta$  proteins (Figure 3).  $\alpha$ -synuclein does not form any secondary structures and takes only random coil (Figure 4). Src-SH3 forms  $\beta$ -sheets mostly (Figure 5).

Results show significant difference between  $\alpha$ -synuclein and other proteins at around 20 – 130 cm<sup>-1</sup>.

[1] Brooks, B. and Karplus, M. (1983) Proc. Natl. Acad. Sci. 80: 6571-6575

[2] Tama, F., Gadea, F.X., Marquues, O., and Sanejouand, Y.H. (2000) Proteins 41: 1-7



Fig.1 Terahertz spectroscopy of myoglobin



Fig.2 Terahertz spectroscopy of β-lactoglobulin



Fig.3 Terahertz spectroscopy of lysozyme



Fig.4 Terahertz spectroscppy of α-synuclein



Fig.5 Terahertz spectroscopy of src-SH3 domain