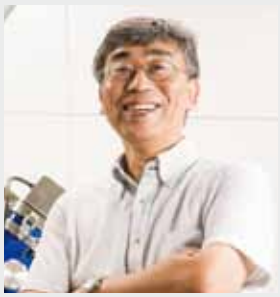
Exploitations of Novel Spectroscopic Methods Using Synchrotron Radiations and Lasers for Materials Science

Department of Materials Molecular Science
Division of Electronic Structure



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To develop novel functional materials, it is also essentially important to exploit new characterization methods that improve spatial and time resolving powers substantially and allow one to investigate the materials in operand conditions. In our group, we are interested in the developments of new spectroscopic methods for materials science using synchrotron radiation and lasers. Especially, we have been investigated surface and thin-film magnetism and related magnetic materials for the last decade. Recently, to investigate surface reaction process in working condition, we began to exploit hard x-ray photoelectron spectroscopy at ambient pressure.

1. Novel Magnetic Nanoscope: Ultraviolet Magnetic Circular Dichrosim Photoelectron Emission Microscope (UVMCD PEEM)[1)]

Since we discovered dramatic enhancement of visible and ultraviolet photoemission magnetic circular dichroism of 3d transition metal ultrathin films in the vicinity of the work function threshold,[1)] we have been exploiting UVMCD PEEM to visualize magnetic domains with a spatial resolution of ~30 nm and a time resolution of ~100 fs. Compared to X-ray MCD PEEM that has now become a widely established technique, this technique is advantageous in that the measurements can be performed in laboratory and the time resolution of ~100 fs can easily be achieved by using ultrashort pulsed lasers that are commercially available.

The light source is a wavelength-tunable high-power mode-locked Ti:Sapphire laser, and by using the second-, third- and fourth-order harmonics available photon energies are 3.0–6.0 eV with sufficient intensity. Two-photon processes are also available for the requirement of higher photon energies. The pulse width is ~200 fs and the ultrafast pump-and-probe experiment can be performed. Figure 1 is the demonstrative magnetic domain images of ~15 monolayer Ni films grown epitaxially on Cu(001) during hydrogen adsorption with almost real-time observation interval. Bright and dark contrasts stand for upward and downward magnetic domains. As H_2 adsorbs on the Ni surface, it is clearly found that the shape of the magnetic domains becomes simpler so that the length of domain wall may be reduced. This originates from stabilization of the perpendicular magnetic anisotropy of the Ni films upon hydrogen adsorption. To reduce unstability at the domain walls with a large perpendicular magnetic anisotropy, the domain wall length is shorter with H_2 adsorption.

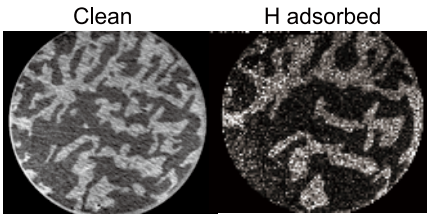

Figure 1. Magnetic domain images of ~15 ML Ni on Cu(001) at 300 K before and after hydrogen adsorption. The field of view is 100 μm.

2. Ambient Pressure Hard X-Ray Photo-Electron Spectroscopy

In order to investigate Pt-based catalysts in polymer electrolyte fuel cells under working conditions, we are exploiting hard x-ray photoelectron spectroscopy in an ambient pressure. Ambient pressure soft x-ray photoelectron spectroscopy is now available in several third-generation synchrotron facilities

in the world and allows one to characterize the surface of the specimen at ~100 Pa. However, the maximum pressure is still too small to study wet materials. Because of substantially longer mean free paths of electrons with much higher electron kinetic energies, the usage of hard x-rays can extend the pressure range up to ~3000 Pa that corresponds to the vapor pressure of water at room temperature. Up to now, no reports concerning this technique are seen in the literatures.

We have joined NEDO (New Energy and Industrial Technology Development Organization) fuel cell project and installed an ambient pressure hard x-ray photoelectron spectrometer in Beamline 36XU of SPring-8, as shown in Figures 2(a) and 2(b). The hard x-rays from the undulator source with photon energies of 6–8 keV, are monochromatized by four Si crystals, and the total energy resolution including the electron energy analyzer is ~0.35 eV for practical use. Figure 2(c) shows the Au 4f spectra of Au foil by varying the environmental pressure. Up to 3000 Pa N_2, we have successfully obtained good Au 4f spectra of Au foil without any discharging problem concerning high voltages applied to the electron lenses. We have tried to measure Pt 3d spectra [Figure 2(d)] of the Pt-C electrode in sulfuric acid solution with Nafion membrane by applying the voltage to conduct water electrolysis. With increasing the applied voltage, Pt is gradually oxidized to provide larger Pt–OH and Pt–O signals. At 1.8 V, the electrolysis of water takes place and again the Pt–O signal is reduced. Since the performance of the spectrometer is found to be excellent, an application to real fuel cell systems is desired as soon as possible.

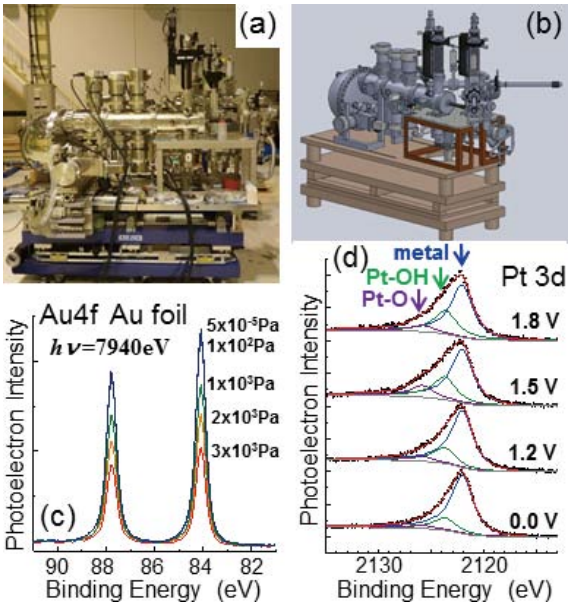

Figure 2. Photo (a) and schematic drawing (b) of the ambient pressure hard x-ray electron spectrometer. (c) Au 4f photoelectron spectra of Au foil under N_2. (d) Pt 3d photoelectron spectra of the Pt-C/Nafion/H_2SO_4(aq)/Pt system under 2000 Pa O_2 atmosphere by varying the voltage applied to the Pt-C electrode.

3. Anisotropic Thermal Expansion and Invar/Anti-Invar Effects in MnNi[3)]

An Invar alloy $Fe_{66}Ni_{34}$ that shows anomalously small thermal expansion over a wide temperature range was discovered in 1897. Basically, the coexistence of the different electronic states in Fe compensates for thermal expansion. The detailed origin of the Invar effect is however a famous long-standing problem. Previously we have studied local thermal expansion and its quantum effect.[2)] In this work, anisotropic thermal expansion in fct $Mn_{88}Ni_{12}$ alloy, which has a martensitic shape memory effect, was investigated by EXAFS and the path-integral simulations.[3)]

In the lattice constants, the *a* axis shows somewhat larger thermal expansion than usual, while the *c* axis exhibits almost no thermal expansion. The environment around Mn is found to be really tetragonally distorted, while the Ni environment is regarded as cubic. It should be noted here that in spite of the fact that the average x-ray structure is fct, the local structures of Mn and Ni are essentially different. It is also clearly found that the theoretical simulations based on the low-spin/high-spin two-state model successfully reproduce all the experimental lattice constants and bond distances. This confirms that the two inequivalent bonds around Mn are regarded as the bonds within the *bc*/*ca* and *ab* planes. Consequently, the present anisotropic thermal expansion is explained by the cooperative Invar/anti-Invar effects in the Mn atom, where the tetragonally distorted more stable low-spin Mn state gives a smaller atomic radius within the *ab* plane and a larger radius along the *c* axis than the spherical one of the HS state, as depicted in Figure 3(c).

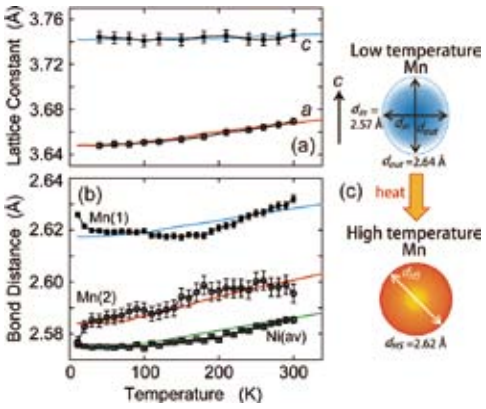

Figure 3. Experimental and simulated (a) lattice constants and (b) bond distances. (c) Schematic model of electronic structure change in Mn at low and high temperatures.

References

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2) T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
3) T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).

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