Observation of Energy-Filtered Image for X-Ray Photoemission Electron Microscopy (EXPEEM) Using a Retarding Wien-Filter Energy Analyzer

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We observed surface images of the Au islands periodically deposited on a Ta sheet by means of an energy-filtered XPEEM using a retarding Wien-filter energy analyzer and a high energy X-ray. By changing the passing photoelectron kinetic energy (E_{kin}), we had a brighter Au island image at the $E_{kin} = 0$ eV and 60 eV while we had a brighter Ta substrate image at $E_{kin} = 102$ eV, corresponding to a Ta $3p_{3/2}$ photoelectron peak.

Surface imaging is an important tool to investigate surface chemical processes, such as migration, reaction, adsorption and desorption. Photoemission electron microscopy (PEEM) can be a promising technique for the real-time investigation of nanoscale surface chemical processes. Ertl and Rotermund showed real-time spatio-temporal concentration patterns of adsorbates during the CO oxidation reactions.[1,2] However, the conventional PEEM image reflects the distribution of surface local work functions and it is difficult to identify chemical species at surface directly. If the core-level electrons are excited by X-ray and their kinetic energies are analyzed by an electron energy analyzer, one may have a PEEM image according to the element and chemical state distributions because the core-level photoelectrons have kinetic energies specific to elements and their chemical states as is known as X-ray photoelectron spectroscopy (XPS). The PEEM combined with XPS can be called as ''energy-filtered X-ray PEEM (EXPEEM)''. There are several imaging energy analyzers proposed for EXPEEM such as a hemispherical energy analyzer and an omega type energy analyzer.[3–5] In this work we report the first energy-filtered XPEEM image using ''a retarding Wien-filter type energy analyzer''. This energy analyzer has an advantage of collinear arrangement of electron lenses and an energy analyzer which simplifies the adjustment processes to attain energy filtered image. Nanoscale surface imaging has already been done and reported in literatures using a retarding Wien-filter spectro-microscopy with electron or metastable atoms as an excitation source.[6–9] But no energy-filtered images excited by X-ray has been obtained using the Wien-filter energy analyzer. This may be due to a lower transmittance of electrons for the Wien-filter than that for the hemispherical type energy analyzer in the same size. Many people, hence, believe that it is inappropriate to attain the EXPEEM image by using the Wien-filter energy analyzer. In this work we tried to measure EXPEEM image using the Wien-filter in order to evaluate its real ability and performance. We also check the possibility to gain EXPEEM images using a higher energy X-ray (2300 eV). Previous energy-filtered XPEEM image was obtained using an X-ray energy about 50–200 eV.[3,4] In this region, the cross section of X-ray absorption is large and the background coming from the secondary electron is small, which benefit good contrast imaging. However, many photoelectron peaks may overlap with each other at this small energy region. On the other hand, the core-level photoelectron excited by a higher energy X-ray will simplify the photoelectron spectrum because core level photoelectron peaks are well separated.

Figure 1 shows the diagram of the EXPEEM system which has been developed,[10,11] based on a previous LEEM-MEEM instrument.[6–9] The sample bias is varied by -10.03–-8.0 kV to the first electrode of the objective lens that is grounded. The electrons pass through the objective lenses, apertures and intermediate lenses and then travel through the Wien-filter type energy analyzer. In the Wien-filter the electric and magnetic fields ($\vec{E}$, $\vec{B}$) are perpendicularly applied to the electrons which are deflected according to their velocity ($\vec{v}$). The electrons with an energy of $\vec{E} = \vec{v} \times \vec{B}$ can go straight without deflection[8,12] and go through the energy separation slit to give the energy-filtered XPEEM images. The EXPEEM system was installed at BL11B of Photon Factory, a bending magnet beam line equipped with a Ge(111) double crystal monochromator. In order to excite core-level electrons, we chose the soft X-ray beam line with its photon energy variable between 1800–3900 eV. The beam was focused to 7 mm × 2 mm using a Ni coated bent cylindrical mirror. The higher harmonics were rejected by a total reflection mirror after the double crystal monochromator. Photon flux was 10^{11} photons/s at maximum.[13,14] The X-ray beam hit the sample at an angle of 70 degree from its normal. In order to reduce the background electron emission due to the irradiation of a sample holder or parts of the instrument, an incident X-ray slit was closed and the sample

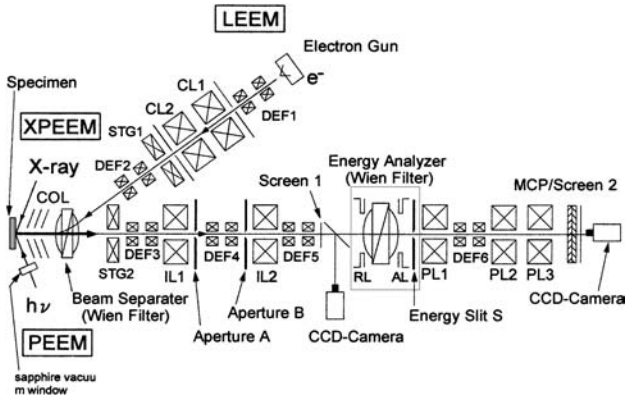

Figure 1. Sketch of the EXPEEM system with a retarding Wien-filter.

was illuminated by 1 mm × 1 mm beam. Thus the effective photon flux at the sample was about 10^{10} photons/s. We have prepared Au square islands on a Ta sheet. The samples were prepared by a vacuum evaporation of Au on a Ni mesh-covered substrate. The mesh was 10 μm square opening with a periodicity of 25 μm. Thickness of the Au islands was 1 μm. The sample was loaded in a UHV chamber and sputtered with Ar^+. The photon energy was fixed at 2300 eV just above the Au M_4 edge (2291 eV, $3d_{3/2}$).

Figure 2 shows the energy-filtered XPEEM images with various kinetic energies. The pass energy of the Wien-filter was 880 eV and the energy selecting slit was 0.3 mm in its width, which provided enough intensity. The selected electron energy width was estimated to be 15 eV. The measuring times for getting each image in Figure 2(a)–(d) were 30 s, 1 min, 10 min and 10 min, respectively. When electrons with $E_{kin} = 0$ eV was selected, we had a brighter image of the Au islands (Figure 2a) because the photon energy was just above the Au M_4 edge. Then the retarding voltage was adjusted and the kinetic energy of electrons going through the Wien-filter increased. When the pass energy of the Wien filter was set at 60 eV which was larger than the kinetic energy of Au$3d_{3/2}$ but smaller than that of Au $3d_{5/2}$ photoelectron (binding energy = 2205 eV), the image brightness became much smaller than before. But Au islands appeared still brighter than the Ta region (Figure 2b). More electrons were ejected from Au islands because the inelastic photoelectrons, secondary electrons and Auger electrons arising from Au $3d_{5/2}$ photoemission were present at this energy region. Figure 2c shows the EXPEEM image with $E_{kin} = 102$ eV, which corresponds to Ta $3p_{3/2}$ photoelectron peak. The Ta substrate became brighter in this case. The spatial resolution was estimated to be 2 μm from the edge slope of the Au island. In principle this EXPEEM system can give as high a spatial resolution as 0.1 μm.[10,11] The worse spatial resolution was due to the spherical aberration using a wide angle limiting aperture as well as ill-adjustment of imaging conditions due to limited beam time. Figure 2d shows the XPEEM image of photoelectrons with kinetic energy of 112 eV, which was higher than the kinetic energy of Ta $3p_{3/2}$. The Au islands were hardly observed. Thus, the brighter Ta substrate image in Figure 2c was due to the Ta $3p_{3/2}$ photoelectron. As far as we know, this is the first energy-filtered XPEEM image using a high energy X-ray with such a few μm-order spatial resolution. These results also demonstrated the possibility of the EXPEEM for chemical analysis with a retarding Wien-filter energy analyzer.

Successful energy-filtered XPEEM images were reported from the two groups, both of which used the hemispherical type of energy analyzer and the X-rays with photon energies less than 300 eV.[3–5] The EXPEEM system reported here adopted a Wien-filter energy analyzer which has advantages of a collinear arrangement of electron optics and possible corrections for the second and third order aberrations in the energy analyzer by adjusting the Fourier components of electric and magnetic fields.[15] A disadvantage of the Wien-filter consists in the difficulty to design the high sensitivity energy analyzer with a compact size. We have compared the sensitivity of the Wien-filter type EXPEEM system with the previous hemispherical type EXPEEM systems semiquantitatively and found that the sensitivity of the Wien-filter type energy analyzer is not fatally worse, probably one order of magnitude smaller than the previous hemispherical types. This low sensitivity can be overcome by the improvement of the objective lens and the Wien-filter. We can conclude that a Wien-filter will be a promising energy analyzer for the EXPEEM considering its advantages. Further developments in the EXPEEM using the Wien-filter energy analyzer will provide a new type of conventional nanoscale element (or chemical state)-specific spectromicroscopy.

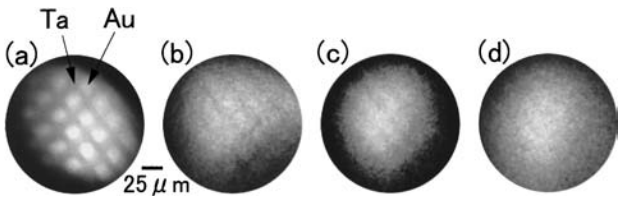

Figure 2. Energy-filtered XPEEM images of Au on Ta substrate. Kinetic energy = 0 eV (a), 60 eV (b), 102 eV (c) and 112 eV (d). The photon energy was 2300 eV. The photoelectron energy of (c) corresponds to Ta $3p_{3/2}$.

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