

Spectrochemical Analysis

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1. Introduction

The spectrochemical analysis group has dedicated two experimental instruments in the experimental hutch of BL39XU for research subjects of the spectrochemical analysis group and for general proposals. One (x-ray microprobe) is for x-ray fluorescence (XRF) analysis and spectroscopy and the other (grazing incidence x-ray spectro-reflectometer) is for grazing incidence spectroscopies. Beside the setup and preliminary operation of these instruments softwares have been developed mainly by Mr. T. Yamamoto of the spectrochemical analysis group, which enable various types of measurements combined with the beam energy and stage positions in one dimensional and two dimensional scans.

Performance of these two instruments and preliminary experimental results are described in this report.

2. Status of dedicated instruments for BL39XU

Instruments developed by the spectrochemical analysis group are placed on the bench in the experimental hutch. Two instruments can be easily adjusted to the x-ray beam by using the precise translation and adjustment mechanism of the bench. A limited space on the bench is reserved for the research subjects which require additional experimental setup without using these two instruments. Most of the beam time is utilized for the commissioning of the x-ray microprobe system and the commissioning of the grazing incidence x-ray spectro-reflectometer is now in progress.

2.1. X-ray microprobe system for XRF analysis and spectroscopy

Fig. 1 shows a schematic illustration of the x-ray microprobe system. The details of the beamline were described in the previous paper[1]. The chamber can be evacuated by

an oil-free evacuation pump, and atmospheric and vacuum environments can be selected. A pinhole of 10 to 50 micron placed approximately 50 m from the source is used to define the beam size. Owing to the extremely small beam divergence between the pinhole and the sample, the beam size on the sample is identical to the pinhole size under the normal incidence condition. The incident and transmitted x-ray intensities can be monitored by using ionization chambers. To collect x-ray fluorescence (XRF) signals, both a conventional energy dispersive spectrometer using a Si(Li) detector and the wavelength dispersive spectrometer are attached. These spectrometers can be switched by rotating the sample surface. In the wavelength dispersive spectrometer the central Bragg angle of the analyzer crystal is fixed to be 21 deg. 10 analyzer crystals can be mounted on the crystal revolver and an adequate analyzer crystal is remotely selected for the energy range of interest. The distance between the sample and the PSPC is 200 mm and the energy resolution, $\Delta E/E$, of 1/400 is expected around 8 keV when the PSPC is used.

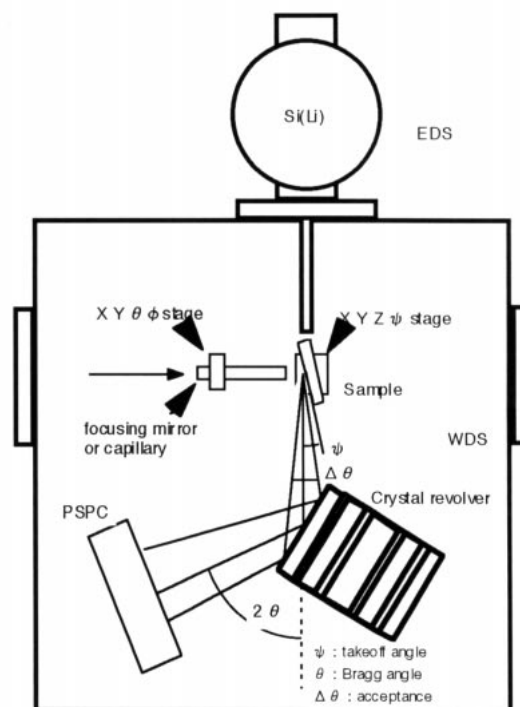


Fig. 1 Schematic view of the x-ray microprobe system with a wavelength-dispersive and an energy-dispersive XRF spectrometers.

Fig. 2 shows transmitted x-ray image of a nickel grid which has 2000 patterns per inch. The pinhole of 10 mm was used for this case.

Fig. 3 shows x-ray spectra measured from a commercial nickel foil of 8 mm in thickness by using the wavelength dispersive spectrometer with the Si(111) analyzer crystal. The foil contains iron and manganese as impurities, and the concentrations of these elements are evaluated to be 2530 ppm and 1480 ppm by using atomic absorption spectroscopy. The energy difference between the Mn K-M(Kb) and Fe K-L (Ka) is 91eV, and the practical energy resolution in these measurements was insufficient to resolve

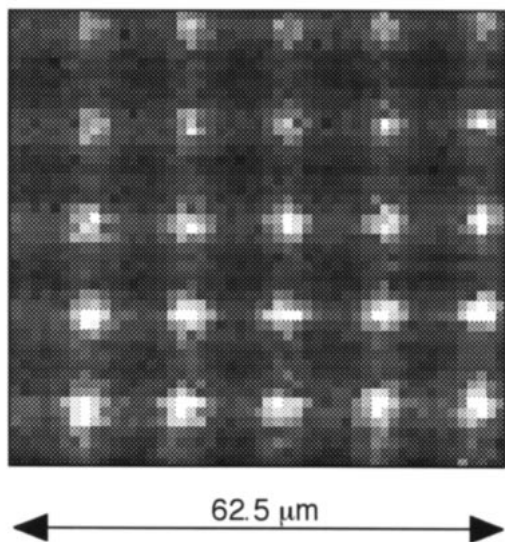


Fig.2 transmitted x-ray image of a Ni grid #2000.

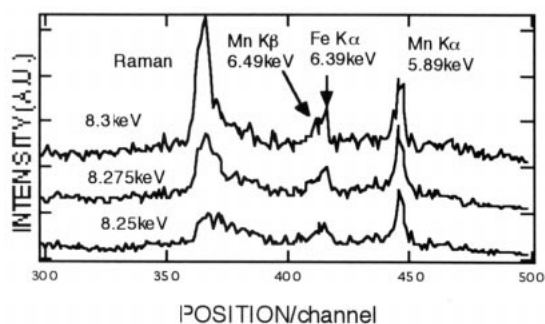


Fig.3. XRF and Raman spectra from a Ni foil.

these two peaks. The degrade of the energy resolution might be caused by the the electrical noise on the PSPC signals. The excitation x-ray energy was changed around Ni K absorption edge, and the peak which changes its position and intensity is the resonant inelastic scattering. (S.H.)

2.2. Grazing incidence x-ray spectro-reflectometer

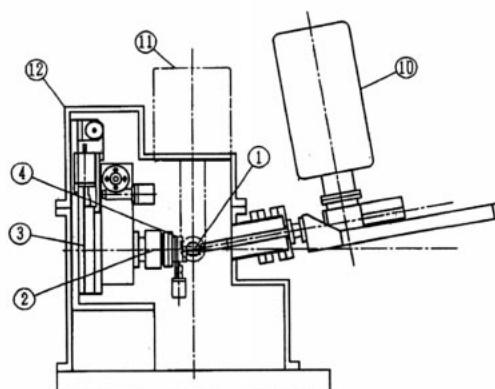
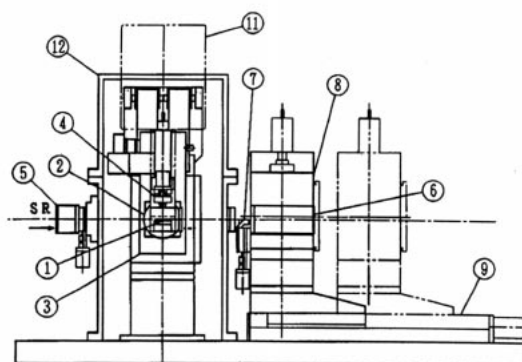
The recent remarkable progress made in total reflection x-ray fluorescence (TXRF) and grazing incidence x-ray reflectometry are significant from a viewpoint of bio-chemical analysis and materials characterization, especially in the ultra trace determination [2]. One of the most widely known TXRF applications is the evaluation of surface contamination of semiconductor wafers, and trace determination in the order of $10^9 \sim 10^8$ atoms/cm² are now in the bounds of reality [3]. Chemical characterization of trace metals in a small sample, e.g., a drop of liquid, is also important in biological and environmental analysis [4]. In this case, chemical shifts of absorption edges are detected by measuring fluorescence intensity as a function of incident x-ray energy. When a mirror is used as a sample support to improve the signal to background ratio, the chemical state of trace metals (~ 0.1 mM) in a drop of liquid (\sim ml) is determined. Another important application is nano-meter scale surface topography [5] using both x-ray specular and non-specular (diffuse) reflection, and when combined with angular resolved TXRF measurements, it contributes a unique probe for interface study by means of the interference effect caused by multiple reflection of x-rays [6]. We consider it possible to realize the further advanced analysis in those three types of experiments, if undulator x-ray radiation is appropriately applied.

Figures 4 (side view) and 5 (section view) show schematically the grazing incidence x-ray spectro-reflectometer [7] designed for the BL39XU. A high degree of accuracy and precision in angular scanning are essential for our research. In the present design, a single-axis goniometer (2 in Figs.) with 0.005 arcsec resolution [8] is employed for rotating the sample. The resolution is chosen not only

for conventional x-ray reflection/scattering experiments but also for future grazing incidence x-ray interference experiments using a partially coherent beam. For detector (6) scanning, an independent translational stage (8) is used instead of the second axis of the goniometer. Since the angle of incidence is shallow, typically in the order of mrad, straight motion gives exact angular change, and high resolution is easily achievable because of the rather long distance from the goniometer center (250~500 mm). The distance is controlled by the stage (9), and can be read out by a magnetic scale. Two linear stages are used for the precise alignment; one (3) for positioning the goniometer and the other (4) for the sample (1). For reliable positioning of the sample surface, a direct beam stopper (a knife-edge, 7) is required just in front of the receiving slit of the reflection detector.

Since the present reflectometer is intended for ultra trace analysis by TXRF, it is important to obtain a good signal to scattering background ratio and also to reduce fluorescent x-rays from the environment (outside the sample). A low-pressure chamber (12) is prepared to reduce air scattering and to avoid contamination from the airborne particles. An oil-free pump is used for the evacuation. A teflon surface finish is added to every part around the sample and the x-ray fluorescence detector (10 or 11). The distance between the sample and the detector (10) can be changed (0~250 mm). The detector is equipped with a collimator to limit the viewing area. This is useful in avoiding the influence of scattering at the edges of the sample. Another requirement is freedom for the sample environment. The ability to switch rotation axis (horizontal and vertical) is necessary. The upper part of the chamber can be removed, and if necessary, it is possible to connect different chambers or equipment. It is also possible to introduce gas (He, dry N₂, etc) for biological and materials research. In our research plan, a high-resolution x-ray fluorescence detector is important. A Si(Li) detector has been employed in the mean time, but in the future a superconductor tunneling junction detector

[9] or an efficient focusing crystal analyzer may be placed here. On the other hand, for x-ray reflection, a wide dynamic range is important, and an ionization chamber or an APD detector is used. Incident intensity is monitored by an ionization chamber (5)/(K.S.)



Figs 4 and 5

Drawings of the designed reflectometer (horizontal axis geometry), 1. Sample, 2. Goniometer, 3. Stage for positioning the goniometer center, 4. Stage for positioning the sample surface, 5. Incident x-ray monitor with entrance slit, 6. Reflection detector with receiving slit, 7. Direct beam stopper and the stage, 8. Stage for reflection detector scan, 9. Stage for adjusting angular resolution, 10. Fluorescence detector, 11. Fluorescence detector (direction convertible type), 12. Vacuum chamber.

References

- [1] S. Hayakawa, S. Goto, T. Shoji, E. Yamada and Y. Gohshi, to be appeared in J. Synchrotron Rad.
- [2] K.N. Stoev and K. Sakurai, to be appeared in Spectrochim. Acta Part B.
- [3] P. Wobrauschek et al., Nucl. Instrum. & Methods A363, 619 (1995).
- [4] K.Sakurai, A.Iida and H.Shintani, J. Phys. IV (France) 7, C2-713 (1997).
- [5] de Boer, D.K.G. (1996). Phys. Rev. B53, 6048.
- [6] K.Sakurai and A.Iida, Adv. in X-Ray Anal. 39, 695 (1997).
- [7] K.Sakurai, S.Uehara and S.Goto, to be appeared in J. Synchrotron Rad.
- [8] T.Ishikawa et al., Nucl. Instrum. & Methods A308, 356 (1991).
- [9] M.Kurakado et al., Rev. Sci. Instrum. 68, 3685 (1997).