Evaluation of Depth Distribution Function for AR-XPS using Synchrotron Radiation Hard X-ray

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It is well-known that angle–resolved X-ray photoelectron spectroscopy (AR-XPS) is a powerful tool for the nondestructive depth profiling of nanometer-scaled thin layers. Recently, high energy XPS (HX-XPS) using hard X-rays reveals the deeper layers up to 20 nm, and enables to clarify the electronic structure and chemical reaction in the nano-materials. Combination of AR-XPS and HX-XPS is going to be a frontier of the analysis of practical nano-devices of which working depth is several tens of nanometer. Emission Depth Distribution Function (EDDF) is a fundamental function for the quantitative nondestructive depth-profiling by using AR-XPS and HX-XPS. We evaluated the EDDF of HX-XPS by the angle-resolved and photon-energy-resolved XPS analysis for Ni 1s photoelectrons excited by synchrotron radiation (SR) linearly-polarized X-rays from 8.5 keV to 14 keV.

1. Introduction

It is well-known that the angle–resolved X-ray photoelectron spectroscopy (AR-XPS) is a powerful tool for the nondestructive depth profiling of nanometer-scaled thin layers. Recently, high energy XPS (HX-XPS) using hard X-rays reveals the deeper layers up to 20 nm, and enables to clarify the electronic structure and chemical reaction in the nano-materials [1,2]. Combination of AR-XPS and HX-XPS is going to be a frontier of the analysis of practical nano-devices of which working depth is several tens of nanometer.

Noted that present driving force behind this frontier is the developments of the hardware of brilliant X-ray sources and high-efficiency & high-voltage XPS analyzer. Photoionization cross-section of shallow core-level electrons excited by hard X-ray is considerably smaller than that by excited by usual soft X-ray (Al Kα or Mg Kα X-ray). Brilliant hard X-ray from the 3rd generation synchrotron radiation (SR) source is the most powerful to overcome this small photoionization cross-section for HX-XPS. It can be expected that the progress of the spectral analysis software for HX-XPS combined with the development of HX-XPS hardware advances the nondestructive deep depth profiling of practical devices.

It is well-known that Emission Depth Distribution Function (EDDF) is a fundamental function for the quantitative nondestructive depth-profiling by using AR-XPS. EDDF is the probability that electrons originate from a specified depth and leave the surface in a given direction. EDDF is affected by complex factors; asymmetry parameter, elastic scattering effects and so on. EDDFs have been evaluated for usual XPS spectra given by the laboratory XPS machine [3]. These factors depend on the X-ray source. For example, special X-ray source like SR light have additional

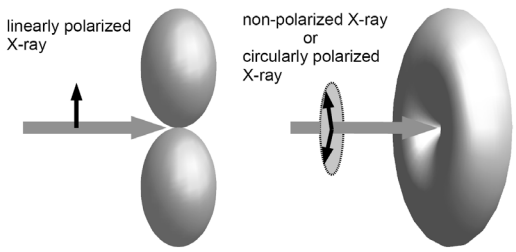

Fig. 1 Schematic diagram of asymmetry parameter for non-polarized X-ray and linearly polarized X-ray. Horizontal arrows show the direction of incident X-rays and the arrows orthogonal to incident X-rays show the direction of the electric field of X-rays.

functions; polarization, parallel beam, energy tunability and pulsed light.

Important factor discussed here is an asymmetry parameter. The asymmetry parameters of photoelectrons excited by non-polarized X-ray from the usual X-ray tube and linearly polarized X-ray from the SR source are different in space, which are illustrated in Fig.1. The shape of asymmetry parameter and the geometrical layout of the X-ray beam, sample tilt, and analyzer affect the quantitative performance of the depth profiling analysis with AR-XPS.

In this work, we demonstrate the evaluation of the EDDF for angle-resolved (AR) & photon-energy-resolved (PR) hard-X-ray XPS using SR X-rays. Present work has been done by the combination of the AR & PR XPS measurements by the rotatable analyzer and Monte Carlo simulation. Since the situation of elastic scattering events are strongly dependent on the kinetic energy of photoelectrons, flexible Monte Carlo simulation can demonstrate well the plural elastic/inelastic scattering events of electrons running in a solid.

2. Experimental

Experiment was done at the BL15XU NIMS beamline of SPring-8. This beamline has the revolver undulator X-ray sources, which can switch the helical undulator and the planar undulator with the revolving mechanics. X-rays monochromatized by Si (111) double crystals can be tuned in the 2 - 20 keV energy range. Its energy resolution ΔE/E of X-rays is about 10^{-4}, and X-ray flux density at the sample is about 10^{12} photons/mm^{2}sec.

XPS machine shown in Fig.2 is based on the ULVAC-PHI model 10-360 hemispherical analyzer

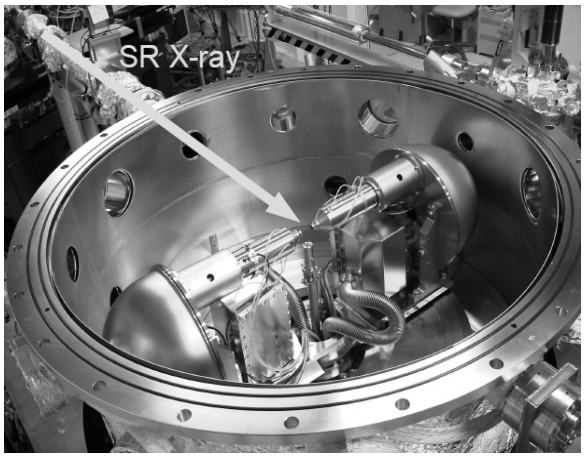

Fig. 2 Photograph of the angle resolved XPS machine. Two analyzers can rotate independently around the sample center in the UHV. On experiment, a manipulator is put on the center pillar.

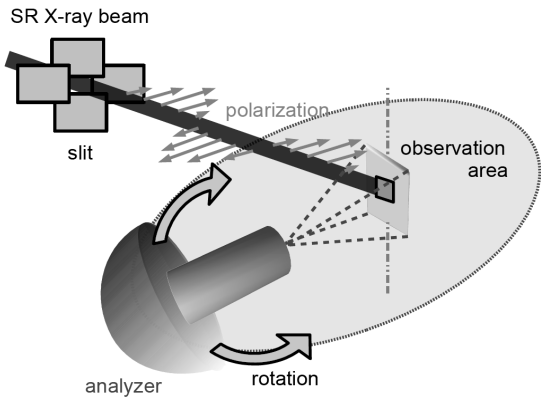

Fig. 3 Layout of the XPS measurement. The X-ray beam profile is formed by the slit to fit the beam within the observation rectangular area on a sample.

mounted in a large UHV chamber (base pressure of $6x10^{-8}$ Pa) with 1400 mm in diameter and put on a turntable for the rotation around the sample center [4].

In this work, we select the planar undulator, which produces the linearly polarized X-rays. The incident SR X-ray axis and the electric field vector of X-ray polarization are on the horizontal plane where analyzer rotates (see Fig.3). Key to make precise AR-XPS measurement is to limit the X-ray beam profile within the observation area of the analyzer wherever the analyzer rotates around a specimen. For this, X-ray beam size was controlled by the X-ray slit with 4 blades.

3. Results and discussion

We observed the AR & PR XPS analysis for Ni 1s photoelectrons excited by SR linearly-polarized X-rays between 8.5 keV and 14 keV from the planar undulator. X-ray energies and kinetic energies of photoelectrons are listed in Table 1. The reason why we chose the *s* orbital of Ni in this work is that the main component of asymmetry parameter β is almost 2 at any X-ray energies. This simple β is advantageous for us to analyze the AR & PR XPS for the first time

Experimental angular distributions are shown in Fig.4 The inset of Fig.4 indicates the top view of the geometrical layout of the XPS experiment. The sample tile angle was fixed at 20 degree. The angular distributions are normalized at the maximum intensity. Abscissa axis θ is the XPS analyzer angle relative to the direction of the electric field vector of X-rays (see the inset in Fig,4). Fig.4 indicates that there is a peak shift by about 10 degree between 146 eV and 3 keV photoelectrons.

Table 1 X-ray energies and kinetic energies of photoelectrons of Ni 1s (binding energy 8333 eV).

X-ray energy	kinetic energy of photoelectrons
8479.4 eV	146.4 eV
8575.7 eV	242.7 eV
8734.4 eV	401.4 eV
8996.1 eV	663.1 eV
9427.6 eV	1094.6 eV
10139.0 eV	1806 eV
11312.0 eV	2979 eV

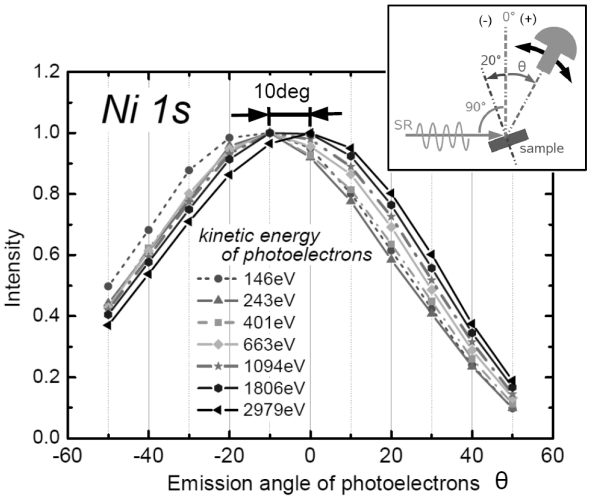

Fig. 4 Experimental angular distributions of Ni 1s photoelectrons of which kinetic energies are listed in Table 1. XPS analyzer rotates around the sample center.

After we performed Monte Carlo simulation including an asymmetry parameter for linearly polarized X-ray to evaluate the experimental data in Fig.4, we can recognize that this angular peak shift originates from the asymmetry parameter of the multipole transition term of photoelectrons.

Schematic view of asymmetry parameter of photoelectrons excited by dipole and multipole transition is shown in Fig.5. This *multipole transition* means the sum of the dipole transition and the higher-pole transitions. Peak direction of angular distribution of photoelectrons excited by the simple dipole transition faces to the direction of polarization vector (that is electric field vector). But peak direction of the angular distribution of photoelectrons excited by the multipole transition is inclined from the polarization vector, and the inclined angles are dependent on the X-ray energy.

Fig.6 shows the example result of Monte Carlo analysis of angular distributions of Ni 1s

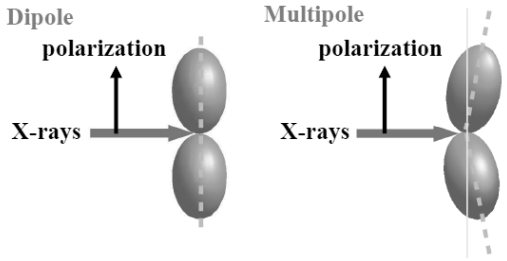

Fig. 5 Schematic view of asymmetry parameter of photoelectrons excited by dipole transition and multipole transition.

photoelectrons of which kinetic energy is 1094.6 eV. Filled circles in Fig.6 are the corresponding experimental data shown in Fig.4. Dashed-dotted line is a theoretical asymmetry parameter of the multipole transition [5]. Dashed line is a result of the combination of this theoretical asymmetry parameter and the intensity decay by inelastic scattering. Solid line is a result of Monte Carlo simulation with plural inelastic and elastic scatterings. In Monte Carlo simulation, the differential cross-section of elastic scattering is calculated with Dirac-Hartree-Fock potential. IMFP of the inelastic scattering events are estimated by TPP-2M formula [6]. Refraction effect when photoelectrons pass across the sample surface is also considered. Simulated result is in excellent agreement with the experiment. The result in Fig.6 indicates that the elastic scattering effect does not affect considerably the angular distribution in this 1 keV energy range. This is explained by the fact that angular distribution consists almost entirely of the 1 keV photoelectrons which undergo the small-angle forward elastic scattering. In conclusion, the

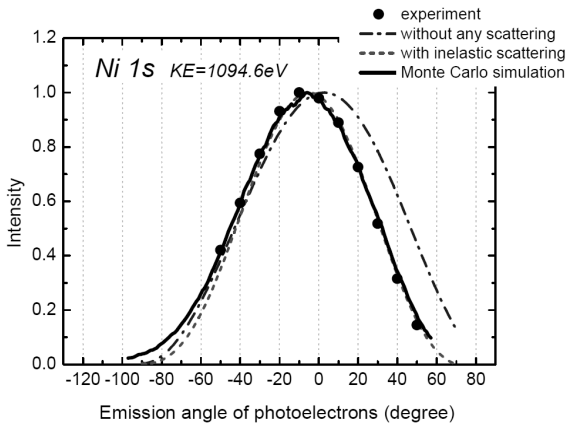

Fig. 6 Angular distributions of Ni 1s photoelectrons of which kinetic energy is 1094.6 eV. Filled circle is experimental data and solid line is a result of Monte Carlo simulation with plural inelastic and elastic scatterings.

angular distribution of 1keV photoelectrons can be estimated if one knows the precise asymmetry parameter. It should be noted that this simple explanation is valid under the condition photoelectrons are generated uniformly at any depth.

However, one has to consider the effect of elastic scattering carefully in order to estimate EDDF dependent on the generation depth. EDDFs corresponding to the experimental conditions of Fig.6 were calculated by Monte Carlo simulation including the precise asymmetry parameter with

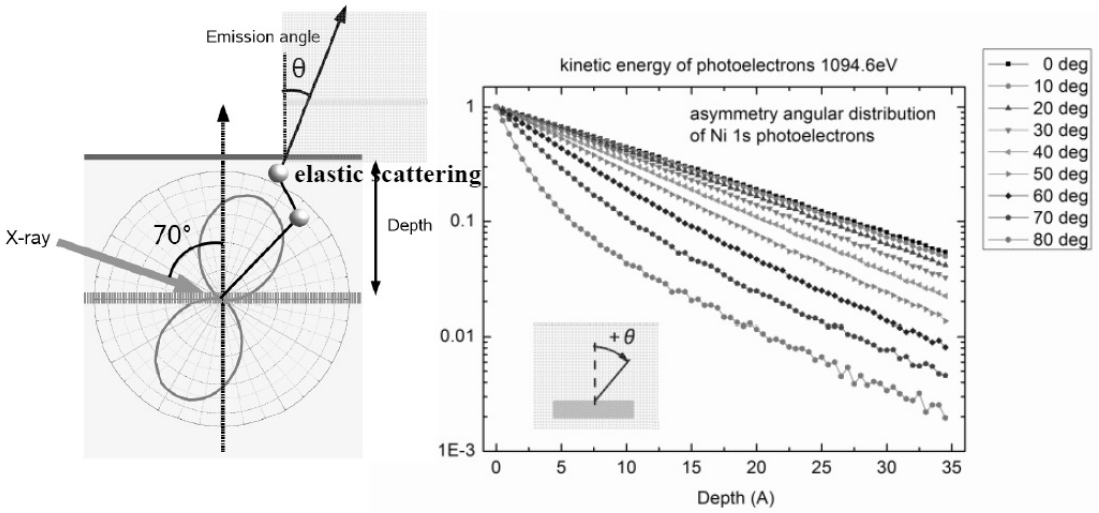

Fig. 7 Forward emission depth distribution function (EDDF) of Ni 1s photoelectrons calculated by Monte Carlo simulation. The forward emission angle θ is in the range between the sample normal-axis and the sample surface-axis close to the incident X-ray. The inset shows the schematic diagram of the asymmetry parameter of the angular distribution excited by linearly polarized X-rays. Kinetic energy of photoelectrons is 1094.6 eV.

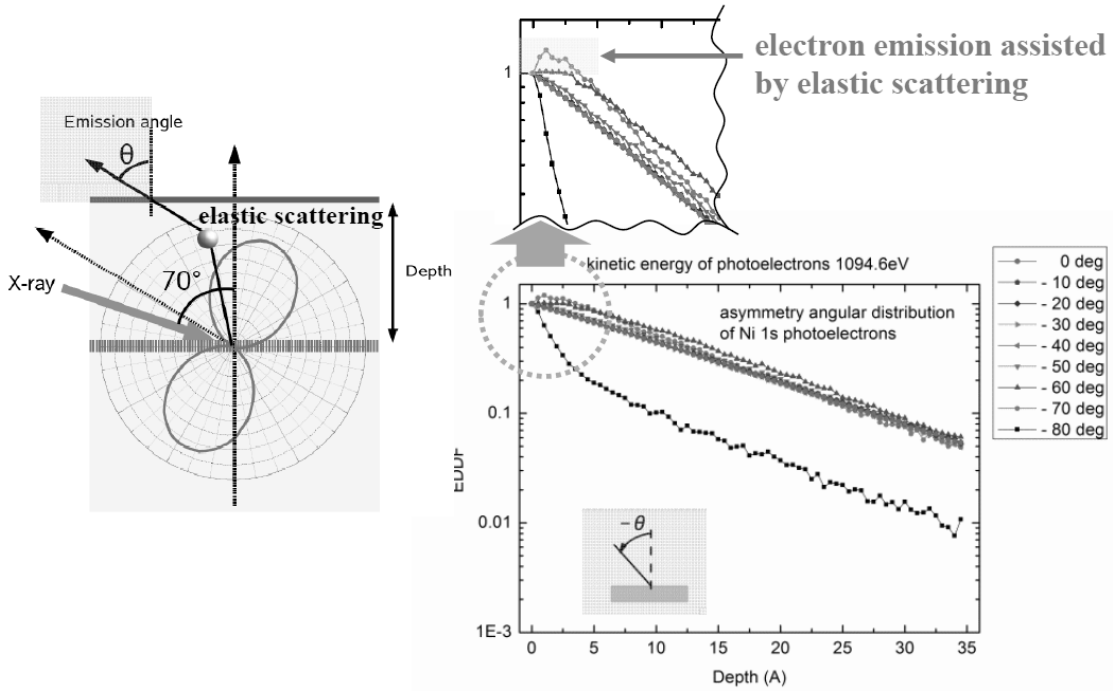

Fig. 8 Backward emission depth distribution function (EDDF) of Ni 1s photoelectrons calculated by Monte Carlo simulation. The backward emission angle θ is in the range between the sample normal-axis and the sample surface-axis reversely directed to the incident X-ray. The inset shows the schematic diagram of the asymmetry parameter of the angular distribution excited by linearly polarized X-rays. Kinetic energy of photoelectrons is 1094.6 eV.

multipole transition term and are shown in Fig.7 and Fig.8. Directions of emitted photoelectrons are different between these figures (see the insets of Fig.7 and Fig.8). Results of EDDF are considerably dependent on the angular shape of asymmetry parameter. In the case of the forward direction in Fig.7, the EDDF is similar to the result of homogeneous asymmetry parameter. On the other hand, in the case of the backward direction in Fig.8, the EDDF is quite different.

Fig.8 indicates that EDDF around the direction (θ = -70 degree) of the valley of the asymmetry parameter appears strange. This is caused by the following phenomenon. The photoelectrons generated to the direction of the valley of the asymmetry parameter is very few. Then, there are indirect paths that photoelectrons are generated into the directions inclined from the valley, undergo the elastic scattering, are finally emitted to the direction of the valley. This means the electron emission assisted by the elastic scattering. Fig.8 shows that one has to consider this process at the angle range of 30 degree relative to the valley of the asymmetry parameter. This phenomenon is observed for the XPS excited by non-polarized usual X-rays. This phenomenon should be more noticeable in the AR-XPS case using the linearly polarized X-ray, since the angular shape of asymmetry parameter of linearly polarized X-rays is sharper than that of non-polarized X-rays.

4. Conclusion

It is well-known that angle–resolved X-ray photoelectron spectroscopy (AR-XPS) is a powerful tool for the nondestructive depth profiling of nanometer-scaled thin layers. Emission Depth Distribution Function (EDDF) is a fundamental function for the quantitative nondestructive depth-profiling by using AR-XPS. We have aimed to expand AR-XPS toward the hard X-ray XPS technique. For this, we performed AR-XPS measurements using linearly polarized hard-X-rays at the synchrotron radiation NIMS beamline BL15XU in SPring-8. AR-XPS with a rotatable analyzer clearly revealed the asymmetry parameter of the multipole transition term by the data analysis with Monte Carlo simulation. This simulation also evaluated the effect of elastic scattering on the EDDF.

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