New Products & Technologies

Small Area X-Ray Photoelectron Spectroscopy*

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1 Introduction

X-ray photoelectron spectroscopy (XPS or electron spectroscopy for chemical analysis, ESCA) is an analytical technique which determines the binding energies of elements constituting the surface of a specimen by measuring the kinetic energy of photoelectrons emitted by X-ray irradiation. If the chemical state of an element changes, the binding energy shifts and the chemical state of elements can be identified. Since the escape depth of the photoelectron is from a few to several tens of angstrom (top 1~30 Å), it is possible to analyze the chemical state of the outermost thin surface of materials. This form of spectroscopy uses X-rays as an excitation source so that there is far less damage to the specimen than is occasionally observed in methods employing an electron beam or ion beam. This method is, therefore, widely applied to the qualitative and semi-quantitative characterization of various materials such as metals, semiconductors, and organic compounds. Thus, XPS is regarded as one of the most commonly used surface analysis techniques. Kawasaki Steel introduced the model ESCALAB-5, made by V.G. Scientific in the U.K., in 1979 and has used it for the surface analysis of steel, especially coated steels.[1-3]

A conventional XPS instrument, however, can only analyse relatively large area, about 100mmϕ, and can not be applied to analysis of smaller area for which other surface analytical techniques such as Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) had to be used. These analytical techniques use charged-particle beams as an excitation source, making it difficult to apply the techniques to susceptible and/or insulating materials. Further, it is not easy to obtain information regarding chemical state using these techniques, and thus the demand for XPS analysis of smaller area has increased.

To meet such demand, XPS instrument manufacturers have since 1985 been supplying commercial instruments that collect photoelectrons either from a selected area (small area XPS), or from an area irradiated by focused X-ray (small spot XPS). Kawasaki Steel has recently introduced from Kratos in the U.K. a small area X-ray photoelectron spectroscope instrument (small area XPS, hereinafter referred to as SAX), model XSAM-800 and has used it for chemical analysis of area of a few hundred-μm diameter. This paper describes the general features of the instrument and examples of its application.

2 General Description of the Instrument

2.1 System Configuration

Photo 1 gives a general view of the SAX instrument and a schematic diagram of the system is shown in **Fig. 1**. The analyzer is a conventional 180° hemispherical analyser (HSA) with aberration-compensated input lens (ACIL), but is capable of analyzing small area with a high spatial resolution. Further, it is equipped with an electron gun for AES or SEM, a laser, a cone shaped aperture, and an optical microscope. The laser is located on the HSA and the beam axis coincides with the lens axis of the ACIL. This enables an operator to identify the analysis position. **Table 1** describes the general specifications of the instrument.

2.2 Analytical Method of SAX

This instrument has three analysis modes and the principle is shown in **Fig. 2**. For general XPS analysis, a LOW-MAG mode obtains the best sensitivity. For the AES analysis mode, a focused electron beam is used as an excitation source and the lens system is switched to HIGH-MAG mode which results in a large solid angle for collecting electrons with high efficiency, thereby increasing sensitivity to signals from submicron area. For SAX analysis, in order to improve spatial resolution, the HIGH-MAG mode is used in combination with an aperture. The aperture is necessary to cut signals from the outskirts of the lens focus because of the large radiation area of the X-ray. There are six apertures of different sizes for the purpose of choosing the analysis

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Photo 1 Small Area XPS KRATOS XSAM-800

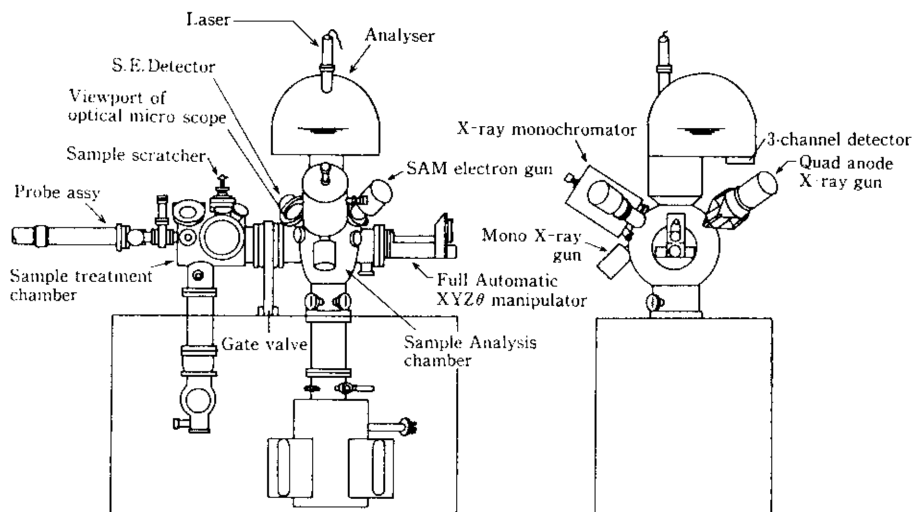

Fig. 1 Schematic representation of small area XPS XSAM-800 system

Table 1 Specifications of Small Area XPS, XSAM-800

Item	Specification
Vacuum	
Operating base pressure	to 7.5×10^{-11} Torr
XPS	
X-ray anode	Mg, Al, Ag, Ti
Maximum X-ray power	450 W
Resolution and sensitivity at Ag 3d 5/2 (MgK, 450 W)	0.82 eV···80 kcps 1.00 eV···650 kcps 1.40 eV···1 600 kcps
Small Area XPS	
Cone aperture size	94, 109, 238, 529, 650, 1 000 $\mu m\phi$
Monochrometer	
Resolution	0.65 eV
Maximum X-ray power	600 W
Attachment	Ion gun Electron gun Secondary electron detector Optical microscope

area.

To perform SAX analysis, it is necessary to place a specimen at the exact analysis position, while avoiding any change in the chemical state of the surface. It is possible to use SEM or AES for the positioning, but using an electron beam tends to damage the surface. Therefore, the following steps are taken to correctly set an analysis position:

(1) Bring the specimen to the focal position (Z-axis) of HIGH-MAG mode. The best Z-axis position was determined beforehand using a silver sample.

(2) Insert a cone aperture, place it above the specimen, and adjust the aperture position until the maximum signal is obtained from the specimen through the aperture.

(3) Using a laser beam which is coaxial with the ACIL lens system, adjust the specimen position on the horizontal plane in the X and the Y directions so that the laser beam passing through the aperture will illuminate the desired analysis area.

When using this method, a 260-μm-ϕ iron wire embedded in copper was analyzed using a 238$\mu m\phi$ cone aperture, but signals from the copper surrounding the iron wire could not be detected. In this case, the analysis area defined by a knife edge profile was 153 $\mu m\phi$.

3 Application

3.1 Analysis of the Ruptured Layer of Lacquered Riverwelt during T-Peel Testing

In this section an example is shown where SAX was used for the determination of a ruptured layer. In order to evaluate the lacquer adhesion of tinplate, it is important to know in which layer the rupture occurs. For the purpose of rupture layer determination, XPS has generally been used.[4] At Kawasaki Steel a lightly tin-coated steel, called River-welt,[5] was developed which provides sufficient weldability and corrosion resistance to welded cans. The coating layers consist of iron-nickel alloy, iron-tin-nickel alloy, free tin, and chromate film. In conventional tinplate, the reduction of tin coating weight results in the deterioration of corrosion resistance. However, Riverwelt has a new type chromate film, composed of chromium and chromium oxide, which contributes to improved corrosion resistance due to higher lacquer adhesion. The ruptured layer of lacquered Riverwelt was usually found to be in the lacquer film. Since the area not covered with lacquer in the rupture

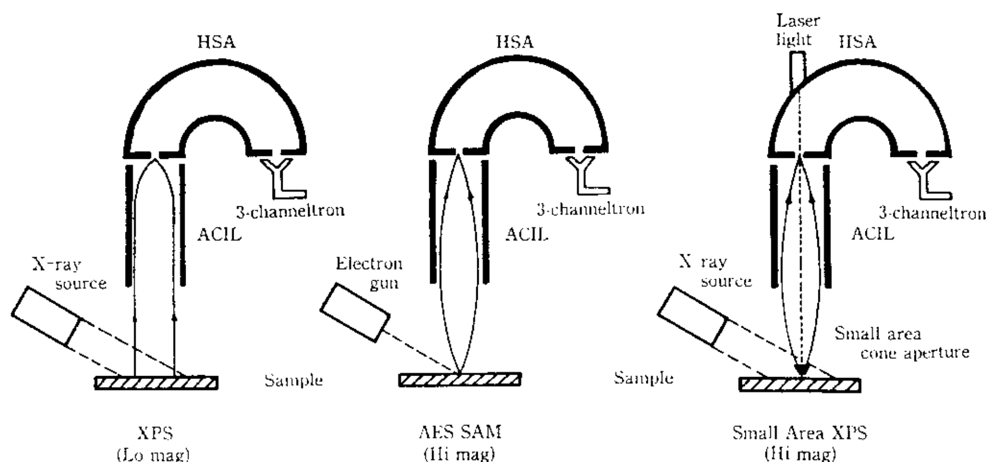

Fig. 2 Diagrams of the electron spectrometer constitution for conventional XPS, AES, and Small Area XPS

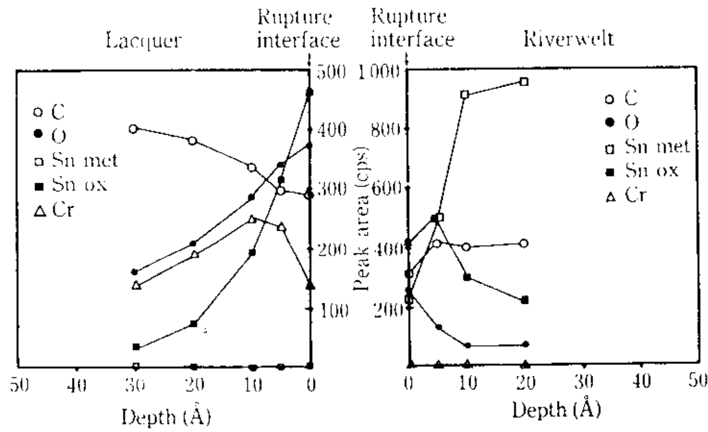

Fig. 3 Small Area XPS depth profiles of fracture surfaces after detaching the layer of lacquer from Riverwelt[5)]

layer was so small that conventional XPS could not be applied. Two small strips of lacquered Riverwelt were hot-glued with nylon adhesive and then separated into two specimens by T-peel test. The area without lacquer (River-welt side) and the corresponding area of another specimen with lacquer (lacquer side) were investigated by SAX depth profile analysis with Ar sputtering. The results are shown in **Fig. 3**.

Tin oxide was observed, on the surface of the lacquer and chromium underneath the tin oxide layer, but no free tin was observed. On the other hand, tin oxide and free tin were observed on the surface on Riverwelt, but not chromium. From these results, it was found that the rupture of the coating layer of Riverwelt occured in the tin oxide.

3.2 Analysis of LSI Device

Another application of SAX analysis was made on an LSI device. The specimen was prepared through dry etching of a partially masked silicon wafer, on which a SiO_2 layer (3000 Å in thickness) and an Si substrate were made in the pattern as shown in **Photo 2** by dry etching. SAX was applied to areas 1 and 2, as marked on the photo, in order to study the chemical state of each area. The results are shown in **Fig. 4**. Area 1 shows a peak of SiO_2 only, whereas area 2 shows peaks of metal silicon with a small amount of SiO_2. It is clear that the etching conditions in this case left a very thin film of SiO_2 on the silicon substrate.

4 Concluding Remarks

SAX has made it possible to analyze an area having a diameter that was not possible under conventional XPS. It is expected that SAX will expand its application to various fields of surface analysis.

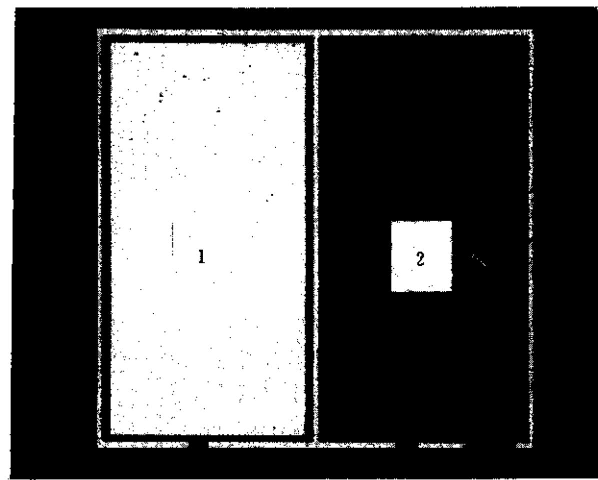

Photo 2 Si oxide/Si base pattern

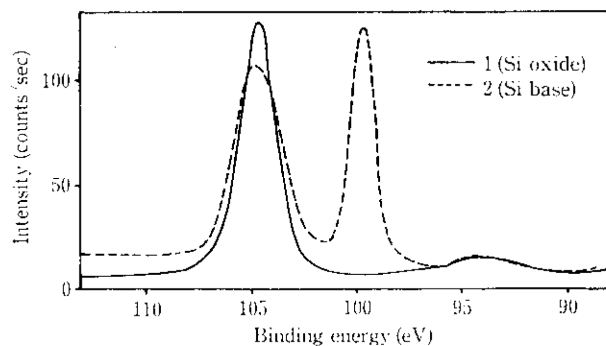

Fig. 4 Si2p spectra of Si oxide/Si base pattern (shown in Photo 2) by Small Area XPS

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