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Review

Total reflection X-ray photoelectron spectroscopy: A review

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ABSTRACT

Total reflection X-ray photoelectron spectroscopy (TRXPS) is reviewed and all the published papers on TRXPS until the end of 2009 are included. Special emphasis is on the historical development. Applications are also described for each report. The background reduction is the most important effect of total reflection, but interference effect, relation to inelastic mean free path, change of probing depth are also discussed.

Contents

1. Principles and characteristics of TRXPS

The number of review papers on total reflection X-ray photoelectron spectroscopy (TRXPS) is quite a few; Iijia [1–4] and Kawai [5] before 2000. The present review on TRXPS is a revised and updated version of a Japanese review by Kawai [5].

The TRXPS is measured by a grazing incidence of X-ray beam whose glancing angle is below the critical angle of total reflection (Fig. 1). The characteristics of the TRXPS are, compared with conventional XPS, (i) more surface sensitive, usually the probing depth is 1/2 shallower, (ii) lower background of inelastic scattering, typically 1/2, (iii) stronger signal intensity by 10^2 due to the factor of X-ray projected area at grazing incidnce, (iv) possibility of multilayer analysis using X-ray standing wave, and (v) possibility of island structure or interface roughness analysis. Additionally, chemical state analysis is possible as ordinary XPS. Trace amounts of carbon, nitrogen, and oxygen can be detected; compared with total reflection X-ray fluorescence (TXRF) spectrometry, TXRF is only possible for heavier elements (such as transition metals) or Na, Mg, Al, and Si for vacuum type TXRF spectrometer.

The reasons that the advantage of the use of TRXPS for low atomic number elements ($Z < 10$) is as follows:

(i) The X-ray fluorescence yield is less than 2% of Auger electron yield, and thus photoelectron detection has a large advantage over X-ray fluorescence detection.
(ii) The K fluorescence energy for such low atomic number elements is below 1 keV and therefore increasingly difficult to observe because the X-rays are easy to be absorbed by detector windows.
(iii) The cross-sections for ionizing low atomic number elements are maximized by excitation by low-energy (Al Kα) X-rays, which is consistent with both the sources and electron spectrometers normally employed for X-ray photoelectron spectroscopy. Except for some recent hard X-ray XPS, the TRXPS is usually implemented with low-energy X-rays (1–3 keV) but TXRF is usually reserved to higher energy X-rays (8 keV and higher). As a result, the critical angle for TRXPS is much larger than the critical angle for TXRF, leading to a smaller spot size consistent with the use of an electron spectrometer. However we must note that at a larger angle such as a few degrees, simple approximations for very small angles

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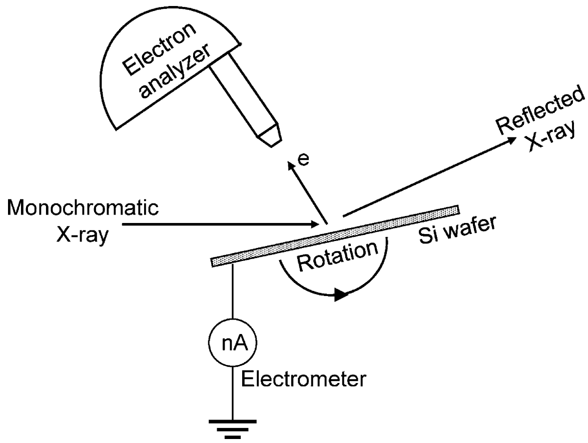

Fig. 1. Schematic illustration of experimental setup for TRXPS.

used for TXRF, are not sufficiently accurate: the work of de Boer [6], which is valid for larger incidence angles, has been crucial for quantitative TRXPS.

2. Terminology

The term TXRF is widely used in analytical chemistry. International conference on TXRF is periodically organized since 1986. The 13th International Conference on TXRF was held at Goteborg in June 2009. Von Bohlen summarized a history of the TXRF conference in his review paper [7]. However the term "total reflection" was not always accepted because the incident X-rays are not always totally reflected; sometimes a little bit higher angle than grazing incidence is used for excitation, in order to compare the difference between total and non-total reflections. This is the case for TRXPS, because the difference between total and non-total reflection XPS spectra by rotating the sample by say 0.5° just below and above the critical angle of total reflection are compared. Therefore, according to de Boer, "total reflection" method is sometimes called "GI method" [6].

De Boer used "GI" as the abbreviation of "glancing incidence" [6], but usually it is understood as "grazing incidence" [8]. Thus the TRXPS (or TR-XPS) is more precisely "grazing incidence/total reflection XPS" or GIXPS (or sometimes GI-XPS) if grazing incidence is emphasized. These are the keywords: for searching papers in database.

The TRXPS method uses non-linear phenomena crossing the critical angle of total X-ray reflection, such as the X-ray penetration depth changes over several orders of magnitude below and above the critical angle. Other related X-ray GI methods are X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray scattering, and X-ray absorption. Stoev and Sakurai published reviews on these GI methods [9,10].

Optically inverse GE (grazing exit) methods are also possible, but not exactly optically inverse because X-rays in and characteristic X-rays out for GI but electrons in and X-rays out for GE method. Review papers on "normal electron incidence – GE X-ray emission" were published by Ino [11], and on GE X-ray fluorescence yield XAFS by Kitajima [12], and on GE-XRF and GE-XRD by Noma et al. [13]. The GI and GE are complimentary, and merits of GI seem demerits of GE, but the shortcomings are the same; the sample surface should be flat.

The term "glancing angle" is sometimes confused with "incident angle". Mathematically the relation between the two angles is "glancing angle" + "incident angle" = 90° as shown in Fig. 2, but "incident angle" is often used as the meaning of glancing angle because the meaning is quite clear in case of X-ray total reflection experiment.

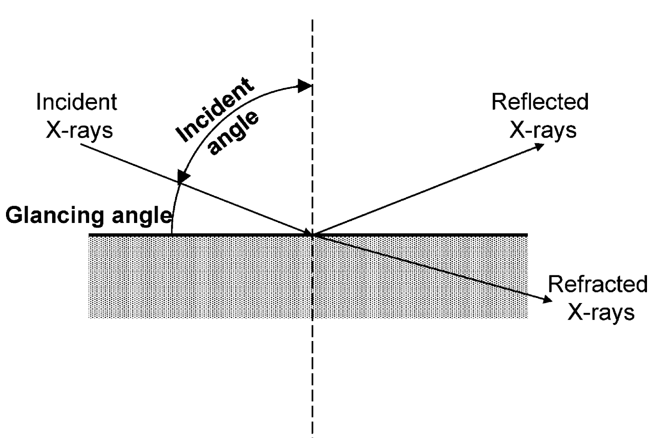

Fig. 2. Definitions of angles.

3. The development of TXRF

The first TXRF analysis experiment was done by Yoneda and Horiuchi [14]. The detection limit of transition metal elements on Si wafer is 10^9 atoms/cm^2 without preconcentration for laboratory TXRF spectrometers [15]. Synchrotron radiation TXRF is 1–3 orders of magnitude more sensitive. The first report on the physical phenomena on total X-ray reflection was the doctoral thesis by Stenström in Lund University [16], but practical theory was first published by Parratt [17], which is still now ready to be used for practical applications.

Yoneda and Horiuchi, in Kyushu University, Japan, found the trace analysis possibility of TXRF in 1971, and this method was not attracted any attention in Japan. After it was used in Europe, Gohshi and Iida imported to Japan from Europe and found that the monochromatic X-ray excitation is more sensitive for trace elemental analysis than continuous X-ray radiation [18]. After this paper, the TXRF became a practical elemental analysis method for Si wafer industry. The first ISO standard was published in 1999 using TXRF for surface analysis method of Si wafer [19]. About 300 TXRF spectrometers were in use for the Si wafer semiconductor processing industries all over the world at 1999 [15]. Recently, Kunimura et al. [20] pointed out that the non-monochromatic TXRF was more sensitive than monochromatic TXRF when the X-ray tube power was a few watts. They proved that the detection limit was down to 10^{11} atoms/cm^2 by using non-monochromatic 1 W X-ray tube, which is only 3 orders of magnitude worse than a 3rd generation synchrotron radiation TXRF analysis with monochromatic X-ray excitation. Before this research, it was believed that the stronger X-ray source was indispensable for lower detection limit, but the stronger X-ray source is not always the best solution for spectroscopic analysis.

4. The beginning of TRXPS in Japan

In the late 1980s, monochromatic TXRF spectrometers were commercially available and thus the basic research on TXRF had been almost finished. At around this instance, Gohshi gave several talks in Japan as well as international conferences on the possibility of TRXPS. Some of attendees to the Gohshi's talk were Y. Hashiguchi and M. Fujinami (Nippon Steel Corporation), K. Nisawa (Rigaku), Y. Iijima (JEOL), and the present author. This is the reason that TRXPS research has been active in Japan.