Feature Article

Masao Horiba Award

Ultra-Trace Analysis by X-Ray Fluorescence

— Instrumentation of Novel Efficient Wavelength-Dispersive X-Ray Spectrometer and its Application to TXRF Experiments with Brilliant Synchrotrons —

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The present research is concerned with the instrumentation required to achieve extremely high detection rates for trace elements using X-ray fluorescence (XRF), which is a powerful non-destructive technique for element analysis. In total-reflection X-ray fluorescence (TXRF), which is known as a metrology tool for gauging the contamination of semiconductor surfaces, the use of an energy-dispersive system typically with a Si (Li) detector has been the only way so far to analyze trace elements. For many years, it had been believed that the wavelength-dispersive method was unsuitable for trace analysis. This is no longer the case, because of the advent of the present highly efficient XRF spectrometer. By combining TXRF with brilliant synchrotron radiation at the SPring-8, detection power has been upgraded to at least 10 times the prevailing world record. The detection limit is in the 10^{-16} g and/or ppt (10^{-12} g/g) range.

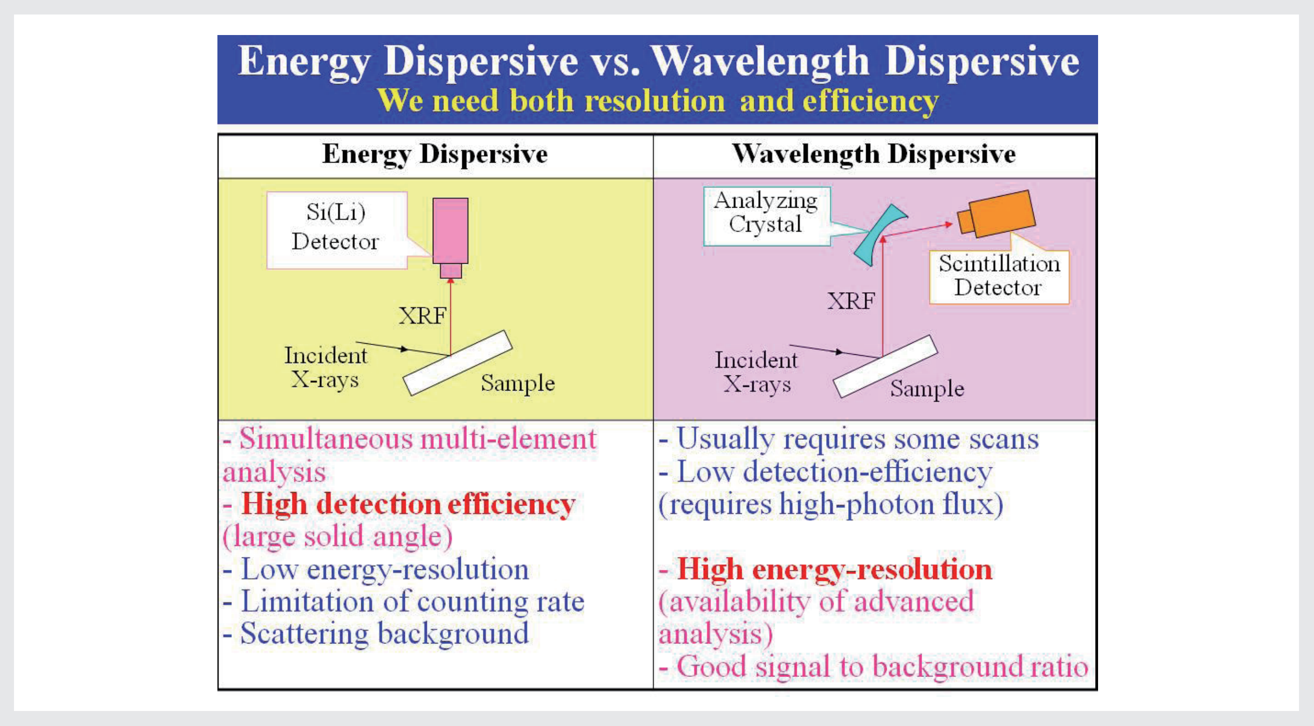
Introduction

Sometimes, only very small traces of materials play extremely important roles in industrial products, and bio-systems. It is often necessary to control and monitor such traces of materials in public life and in industry. In the semiconductor business, large-scale integrated circuit (LSI) technology needs ever finer wiring, which requires a reduction of the level of contamination of the surface of the Si wafer. Analytical methods for measuring trace materials are thus becoming increasingly important nowadays. X-ray fluorescence (XRF) spectroscopy, which can provide reliable non-destructive quantitative analysis for many elements, has so far not been suitable for the detection of trace elements. However, the advent of synchrotron radiation has changed this situation. All X-ray analytical methods including XRF have become very powerful. In Japan, the SPring-8, which is one of the brightest sources in the world, became available in 1997, thereby giving a significant boost to research into trace analysis. Even so, upgrading detection efficiency is not as straightforward as simply employing a brilliant X-ray source. It is also extremely important to devise novel spectrometers and detectors in order to have the instrumentation necessary to draw on the excellent properties of the X-ray source.

Conditions for Measuring Trace Materials

As XRF intensity is proportional to that of the incident X-ray, if a very brilliant X-ray source such as synchrotron radiation is available, this can boost a faint signal from trace systems. However, this is insufficient for detection. Because of strong incident X-rays, the background and other unnecessary X-ray spectra from major elements are also boosted. The detector has some limits in terms of maximum counting rate, and cannot count extremely strong X-rays. Therefore, to see trace systems, it is extremely important to improve the signal-to-background (S/B) ratio.

Total reflection X-ray fluorescence (TXRF) spectroscopy, which was first developed by Yoneda and Horiuchi in 1971, is one of the most promising ways to improve the S/B ratio. As synchrotron radiation provides a parallel



Energy Dispersive vs. Wavelength Dispersive

We need both resolution and efficiency

Energy Dispersive	Wavelength Dispersive
- Simultaneous multi-element analysis - **High detection efficiency** (large solid angle) - Low energy-resolution - Limitation of counting rate - Scattering background	- Usually requires some scans - Low detection-efficiency (requires high-photon flux) - **High energy-resolution** (availability of advanced analysis) - Good signal to background ratio

Figure 1 Two ways to conduct X-ray fluorescence spectroscopy
Energy-dispersive system using a Si (Li) detector (left) and wavelength-dispersive system with an analyzing crystal (right).

beam and is therefore suitable for TXRF, the ability to detect trace elements can be greatly strengthened. Synchrotron-based TXRF is fairly powerful for the analysis and evaluation of surface contamination of semiconductor wafers. It tells us the number and amount of elements in any part of a large silicon wafer. An Austrian research group carried out a series of studies on this topic and, in 1998, reported their best detection limit, 13 femtogram Ni on a Si surface. The aim of the present research is to pursue further advanced analysis of trace systems against the background set out above.

Application of Wavelength-Dispersive Spectrometer to TXRF

As illustrated in Figure 1, there are 2 ways to conduct XRF spectroscopy; either an energy-dispersive system using a Si (Li) detector (left) or a wavelength-dispersive system with an analyzing crystal (right). The choice of spectrometer simply depends on the type of analytical application and X-ray source to be used. The wavelength-dispersive system has higher energy resolution (and therefore a better S/B ratio), but detection efficiency is pretty low. In terms of detection efficiency at least, the energy-dispersive system is superior to the wavelength-dispersive system, and for many years it had been believed that the latter cannot outperform the former when it comes to detecting trace elements. Even after the completion of 3rd generation synchrotron sources such as ESRF, APS and SPring-8, quite a few scientists continued to use the energy-dispersive system (though this depended on the aim of the research and the type of the experiment and samples). Wavelength-dispersive XRF had not been considered as a method for trace analysis.

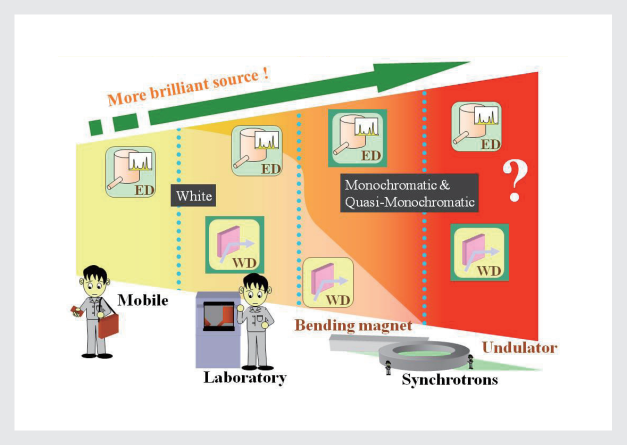


Figure 2 Why wavelength-dispersive?
The choice of spectrometer depends on the type of analytical application and X-ray source to be used. If highly brilliant synchrotron sources are available, the use of wavelength-dispersive spectrometer becomes promising, though so far it has not been used in synchrotron-based XRF analysis for trace systems.

However, is the above belief really correct? Generally, the performances of both the spectrometer and detector depend very much on the light source. When the source is replaced with a very different one, it is necessary to reconsider the design of the spectrometer and the detector (Figure 2). If highly brilliant synchrotron sources are available, the use of a wavelength-dispersive spectrometer becomes promising, though so far it has not been used in synchrotron-based XRF analysis for trace systems. As mentioned earlier, pulse-counting detectors, such as a Si (Li) detector, have some limits in terms of the maximum counting rate of X-ray photons. When combined with extremely strong X-ray sources, background and other unnecessary spectra can occupy the counting rate, leading to saturation of the detector. To solve such problems, it is necessary to come up with a completely different method that ensures at least 10 times better energy-resolution in order to both reduce background and avoid rapid saturation when strong X-rays hit the sample.

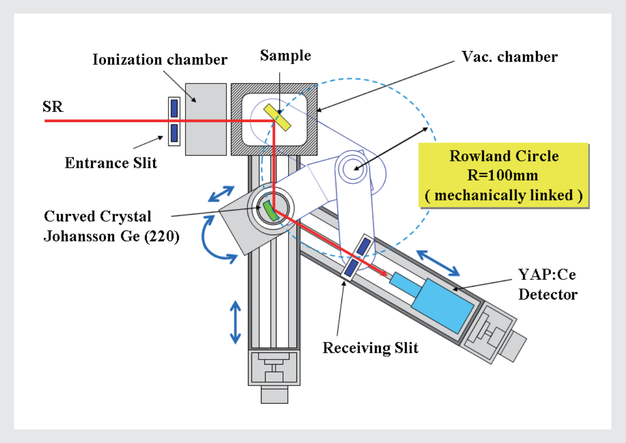


Figure 3 A compact high-efficiency XRF spectrometer
Let's make the smallest X-ray spectrometer – you might agree with me, but at that time, building a large spectrometer to gain high-resolution was the trend, and the idea of downsizing was not easily accepted. The instrumentation was first devised in 1996, even before the start-up of SPring-8, and the initial spectrometer had a Roland circle radius of 350 mm. Subsequently, this was shrunk to 200 mm, 150 mm, and then 120 mm. It is now 100 mm (the left figure)

The conclusion was to downsize the wavelength-dispersive XRF spectrometer (Figure 3). The instrumentation was first devised in 1996, even before the startup of SPring-8. A fast YAP:Ce scintillation detector and accompanying electronics, which were developed in our laboratory, were employed as a detector. Although the figure shows the case for 45 degree incidence and exit, switching to TXRF is done very easily by simply replacing the sample holder.

Ultra Trace Analysis

Let's look at some XRF spectra obtained with the present spectrometer. Figure 4 shows XRF spectra for NIST standard samples, which include many kinds of trace metals. The data were collected by ordinary geometry (not by TXRF layout). The energy resolution is 30 times higher than conventional XRF spectra obtained from a Si (Li) detector, and therefore the number of peaks are effectively resolved. Because of this, the signal to background ratio has been significantly improved. Figure 5 shows TXRF spectra of trace metals in micro-droplets on a Si wafer. The concentration for Ni, Co and Fe is 20 ppb, and the amount of the droplet is 0.1 micro liter. In spite of such extremely small amounts, as seen in the figure, good XRF spectra corresponding to those 3 elements were obtained with sufficient energy resolution (ca. 6~ 7 eV) and an extremely low background. If one measures similar samples with a Si (Li) detector, it is not possible to separate Co Kα and Fe Kβ. As has been frequently discussed, when iron contamination is significant, it has not been easy so far to detect small amounts of Co because of peak overlapping. On the contrary, the present spectra are not influenced by the neighboring lines and the scattering background. They show good linearity between concentration and XRF intensity. It is possible to conduct quantitative analysis, even for samples for which the amount and/or concentration ranges over several decades. The detection limit has been significantly improved. It was 0.31 femtogram, or the ppt (1 part per trillion) concentration level in the liquid drop.

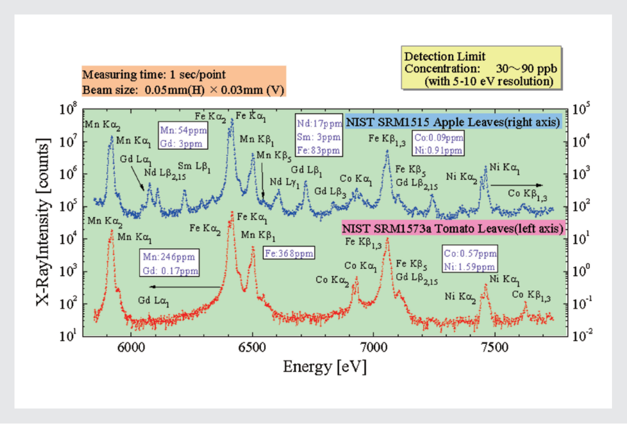


Figure 4 XRF spectra of trace elements for NIST standard samples (Apple and Tomato Leaves)

One should note that a clean environment is crucial for ultra trace analysis. The data such as shown in Figure 5 cannot be obtained with only an X-ray source and X-ray spectrometer. It is absolutely necessary to reduce contamination from air particulates and other sources in the experimental environment. Therefore, a special beamline equipped with a clean room is extremely important for ultra trace analysis. Unfortunately, such experimental conditions were not available at that time at the SPring-8 in Japan, because the beamlines were designed for much more general purposes. In the present research, to solve the problem, two fairly large clean booths were prepared for TXRF experiments, and each one was placed inside and outside of the experimental hutch of the beamline. Each clean booth has a double-folded structure. That is, we put a small clean booth inside a large clean booth, where all instruments can be installed. The data shown here were obtained by using such an experimental setup.

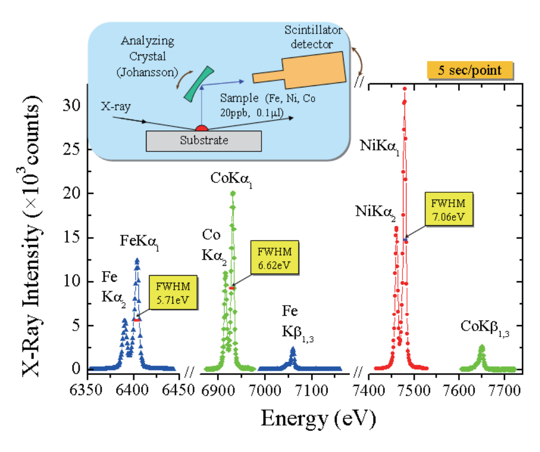


Figure 5 TXRF spectra obtained by the present wavelength dispersive XRF spectrometer (R=120 mm)
The sample is a droplet containing 20 ppb Fe, Co and Ni, and is prepared on a Si wafer. Look at the Fe and Co K spectra. You can see some satellite lines, which give chemical information, even though the data are from extremely small amounts of elements.

Chemical State Analysis

As the wavelength-dispersive X-ray spectrometer has far superior energy resolution compared with conventional Si (Li) detectors, it is possible to obtain chemical information on trace elements. In Figure 5, one can see that the shape of the Kβ spectra of Fe, Co and Ni is asymmetric and that they have some fine structures, even for such tiny samples. The intensity ratio of Kβ' (low energy side shoulder of Kβ) and Kβ$_5$ (a weak peak at the high energy side) lines can be used for chemical speciation. This procedure has been successfully applied to the determination of site occupancy and spin state analysis. At the beginning of the research, a new spectrometer was developed for detecting trace elements by improving the signal to background ratio. But later we found that the same spectrometer can be used for time-resolved XRF, which can follow changes in chemical states. One of the future directions of the research is time-resolved analysis (Figure 6), which can make analysis more attractive and useful in understanding how chemical reactions proceed from the viewpoint of changes to elements.

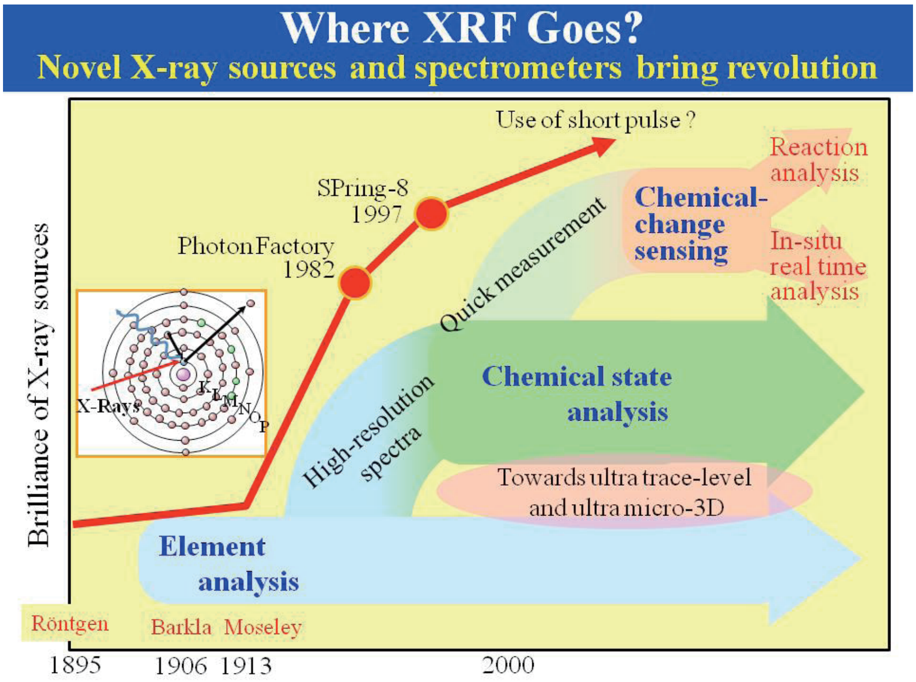


Figure 6 Future of XRF spectroscopy
Element analysis and chemical state analysis mature, enabling many interesting scientific applications. In addition, quick measurements and the use of pulsed sources assume greater importance. One future direction is following chemical changes by time-resolved XRF spectroscopy.

Summary

One of the advantages of TXRF is that it requires a much smaller sample compared with other methods of chemical analysis. This feature would aid the simultaneous measurement of identical samples using several methods. The technique can also analyze the widest variety of elements (almost all except for some light elements). Other attractive features are the short measuring time, ease of sample preparation and simple operation of the instrument. The X-ray spectrometer developed during the present research can conduct extremely difficult analysis when used in combination with a brilliant synchrotron X-ray source. Ultra trace element analysis could reveal previously unknown worlds by understanding the specific role of trace elements in materials and life systems. In addition to being capable of contributing to basic sciences, the technique could have many broad applications such as the evaluation of contamination on semiconductor surfaces and environmental analysis.

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