

## UPDATE ON SYNCHROTRON RADIATION TXRF: NEW RESULTS

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### ABSTRACT

Synchrotron-based total-reflection x-ray fluorescence (SR-TXRF) has been developed as a leading technique for measuring wafer cleanliness. It holds advantages over other techniques in that it is non-destructive and allows mapping of the surface. The highest sensitivity observed thus far is  $3 \times 10^8$  atoms/cm<sup>2</sup> ( $\approx 3$ fg) for 1000 second count time. Several applications of SR-TXRF are presented which take advantage of the energy tunability of the synchrotron source or the mapping capability.

### INTRODUCTION

Integrated circuits continue to increase in complexity as the widths of the critical dimensions continue to shrink. With decreasing linewidths the acceptable level of metal contamination decreases as well. Residual metal contamination on the wafer surface can be a source of defects in the integrated circuit, if the contamination level is too high. Some of the defects known to result from metal contamination are increased leakage current, poor threshold voltage control and gate insulator breakdown. All of these can result in device failure or reliability problems. The ability to measure low levels of contamination is crucial for developing techniques to remove these contaminants. The Semiconductor Industry Association (SIA) 1997 National Technology Roadmap for Semiconductors (NTRS) projects that the required sensitivities for transition metals will be  $3 \times 10^8$  atoms/cm<sup>2</sup> in the year 2001<sup>1</sup>. For comparison, a monolayer of silicon atoms is  $10^{15}$  atoms/cm<sup>2</sup>. Thus the requirements for surface cleanliness are below the part-per-million (ppm) level of contaminants.

There are a variety of techniques which can be used to measure low levels of surface contamination on wafers. The two most prevalent are Wafer Surface Analysis (WSA)<sup>2</sup> (also known as Vapor Phase Decomposition, or VPD) and Total-reflection X-Ray Fluorescence (TXRF)<sup>3,4</sup>. The former uses a range of wet chemistry techniques to remove the residual metals on the surface by concentrating them into a droplet, which is then either studied using X-ray Fluorescence or inductively-coupled plasma mass spectroscopy (ICPMS). For many years, TXRF using a rotating anode has been available to the semiconductor industry. Some of these units are installed in the manufacturing facility, while others are in the analytical groups associated with the manufacturing process. The TXRF technique has several advantages over the WSA-ICPMS procedure. It is non-destructive, and can be used to map the distribution of contaminants on the wafer. The biggest disadvantage of the conventional TXRF technique is that it does not have the sensitivity of the WSA-ICPMS, which has demonstrated a sensitivity of  $10^8$  atoms/cm<sup>2</sup>, whereas conventional TXRF has only recently demonstrated sensitivities of  $5 \times 10^9$  atoms/cm<sup>2</sup>. The TXRF technique consists of a beam of x-rays incident on the wafer surface at an angle of incidence below the

critical angle for total external reflection<sup>5</sup>. With this requirement the x-ray penetration depth is approximately 30 Å, which reduces the scattered and fluorescence intensity from the substrate. For comparison, bulk metallic impurity levels are comparable to a surface contamination of  $\sim 10^7$  atoms/cm<sup>2</sup>.

Several years ago a collaboration of Hewlett-Packard, Intel and the Stanford Synchrotron Radiation Laboratory (SSRL) was formed to explore the possible utility of synchrotron radiation for TXRF. This collaboration is now coordinated by Sematech and involves a number of semiconductor manufacturers, including AMD, Applied Materials, IBM, Lucent, and Motorola. Although the actual list of metals known to cause problems includes low-Z materials (Al, Na), 3-D transition metals (Fe, Ni, Cu, Zn) and other metals (W), our group has emphasized the 3-D transition metals as the focus of our research. Because the fluorescence process is not strongly dependent on the incident photon energy as long as the energy is greater than that of the absorption edge, we have chosen to use multilayers rather than silicon single crystals for our monochromatization. This has resulted in a roughly 2 order-of-magnitude increase in flux<sup>6,7</sup>.

## EXPERIMENTAL

The data were collected on beam line 6-2 at SSRL using a focused beam from a 1-1 focusing bent cylindrical platinum coated fused silica mirror with a critical energy of 21 keV. Multilayers consisting of alternating layers of tungsten and B<sub>4</sub>C with a d-spacing of 29 Å were installed in the monochromator and tuned to pass 11.1 keV radiation with a band pass of 280 eV. Because two multilayers are used in a +/- geometry it is a simple matter to change the photon energy entering the experiment. For most of the wafers 11.1 keV is a good energy because it positions the escape peak between the Zn K<sub>α</sub> and Zn K<sub>β</sub> peaks. There are times when the energy is increased to excite a higher-Z material (e.g. As) or lowered to reduce the fluorescence from a film on the wafer (e.g. Cu, see below). The vacuum chamber<sup>8</sup> in which the measurements are made is equipped with a pair of translation stages for positioning any part of both 150 and 200 mm wafers in front of the single element Si(Li) detector. The vacuum chamber is enclosed in a "mini-environment" inside the experimental enclosure, which uses ULPA filters and is surrounded by clear plastic sheeting. With these precautions, wafers can be routinely measured without adding contamination. Wafers are loaded remotely using a robot arm. In the near future cassette-to-cassette loading will be achieved. The primary reason the measurements are performed under vacuum is to eliminate the air scatter and Ar fluorescence which would otherwise add to the total count rate in the detector. The entire vacuum chamber is mounted on a large rotary bearing and driven by a motorized micrometer to define the grazing angle of incidence of the photon beam on the wafer. The wafer is mounted vertically with its surface normal nearly perpendicular to the incident beam. This is done so that the fluorescence detector is positioned along the E-vector of the incident beam, which minimizes the scattered radiation into the detector (the incident beam is  $\sim 95\%$  linearly polarized in the horizontal plane). At each measurement position of the wafer (horizontally and vertically) an angle scan is performed monitoring the scattered light intensity vs. angle. These data are fit to a standard theory<sup>5</sup> and the angle of incidence is set based on that fit.

## RESULTS

Of fundamental importance in TXRF is the minimum detection limit, or MDL<sup>3</sup>. For a given count time the instrument is incapable of detecting levels of contamination below this value. The typical counting time used for TXRF is 1000 seconds. Assuming stochastic

noise, the MDL will improve with the square root of the count time. The MDL is determined by measuring the signal from a wafer with a known level of contamination (typically one cross-calibrated using other techniques such as ICP-MS). The MDL is calculated as:

$$MDL = \frac{3C\sqrt{I_B}}{I_p}, \quad (1)$$

where  $C$  is the known concentration of the sample being measured,  $I_B$  is the background under the fluorescence peak of interest, calculated by a linear fit to the background on either side of the peak, and  $I_p$  is the integrated peak intensity after the background has been subtracted. Figure 1 shows two spectra, one with a known concentration of  $1 \times 10^{11}$  atoms/cm<sup>2</sup> of three elements, Fe, Ni and Zn. The other spectrum is of a very clean wafer. The two spectra have been normalized so that their intensity is the same at  $\approx 5$  keV. The clean spectrum was measured for a total of 5741 seconds in order to increase the sensitivity. There are no discernable peaks in the region between iron and zinc, indicating that at the MDL of  $3 \times 10^8$  atoms/cm<sup>2</sup> there is no metal contamination. It should also be noted that the "clean" spectrum also indicates that there is no parasitic fluorescence in the Si(Li) detector down to this same MDL<sup>8</sup>. There are several peaks in the "clean" spectrum. Starting on the low energy side, they are the silicon fluorescence peak, followed by a chlorine peak. Because of the emphasis of this program on the transition metals a 25  $\mu$ m teflon foil was placed over the detector. It reduces the silicon fluorescence by a factor of 500, and reduces the intensity of the Cl, S and Ar peaks. By the Ti fluorescence energy it transmits 67% of the intensity. The other significant peak in the clean spectrum is the "escape" peak, which is due to a small fraction of the elastically scattered photons absorbed by the detector which result in the emission of a Si K $\alpha$  photon. Thus the escape peak is 1.74 keV below the elastic peak at 11 keV. This escape peak is observed with any peak of sufficient intensity.

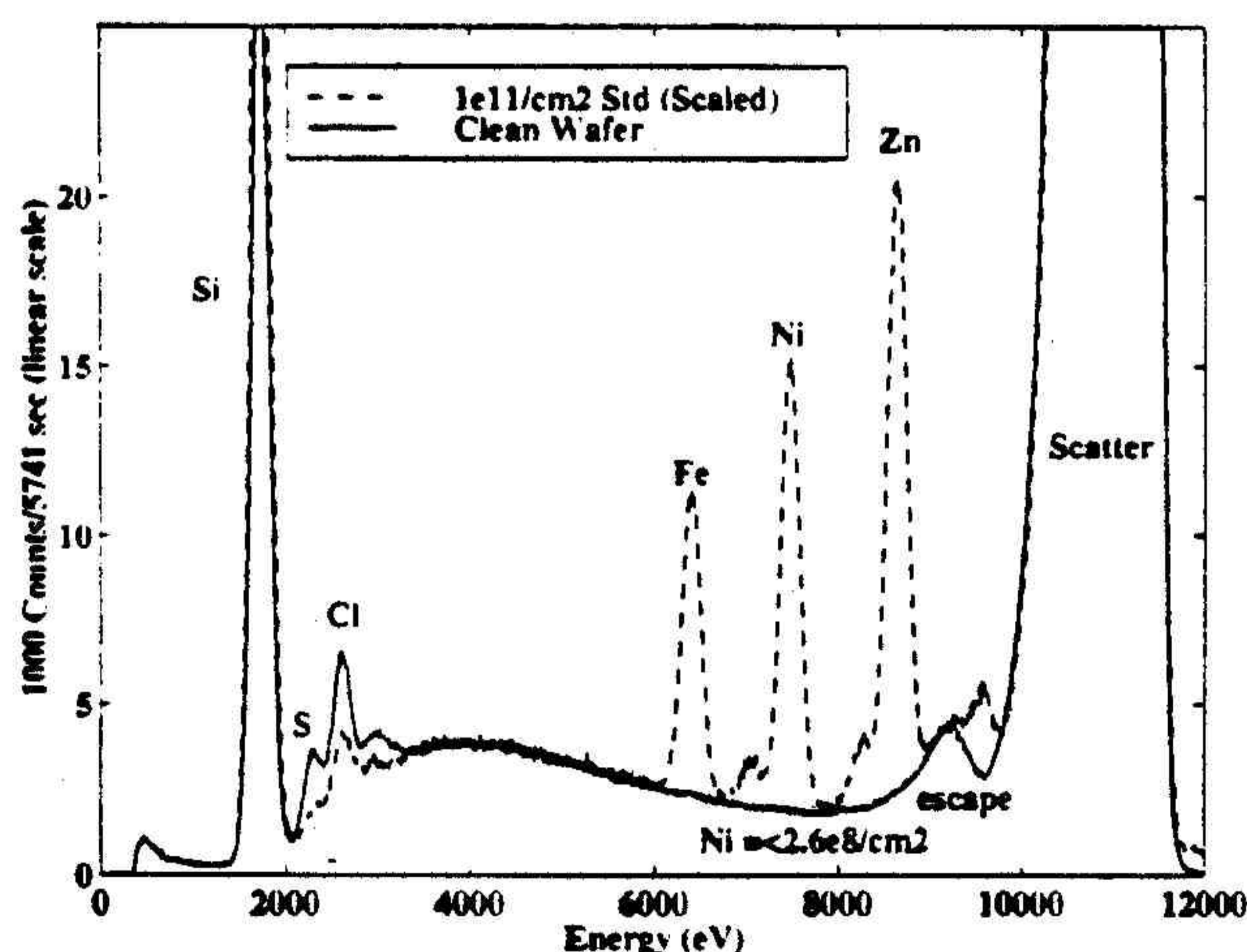


Figure 1: Fluorescent intensity from a silicon wafer intentionally contaminated with  $1 \times 10^{11}$  atoms/cm<sup>2</sup> of Fe, Ni and Zn. Also displayed is the spectrum from a clean wafer, showing no Fe, Ni, Cu or Zn contamination at a sensitivity of  $3 \times 10^8$  atoms/cm<sup>2</sup>.

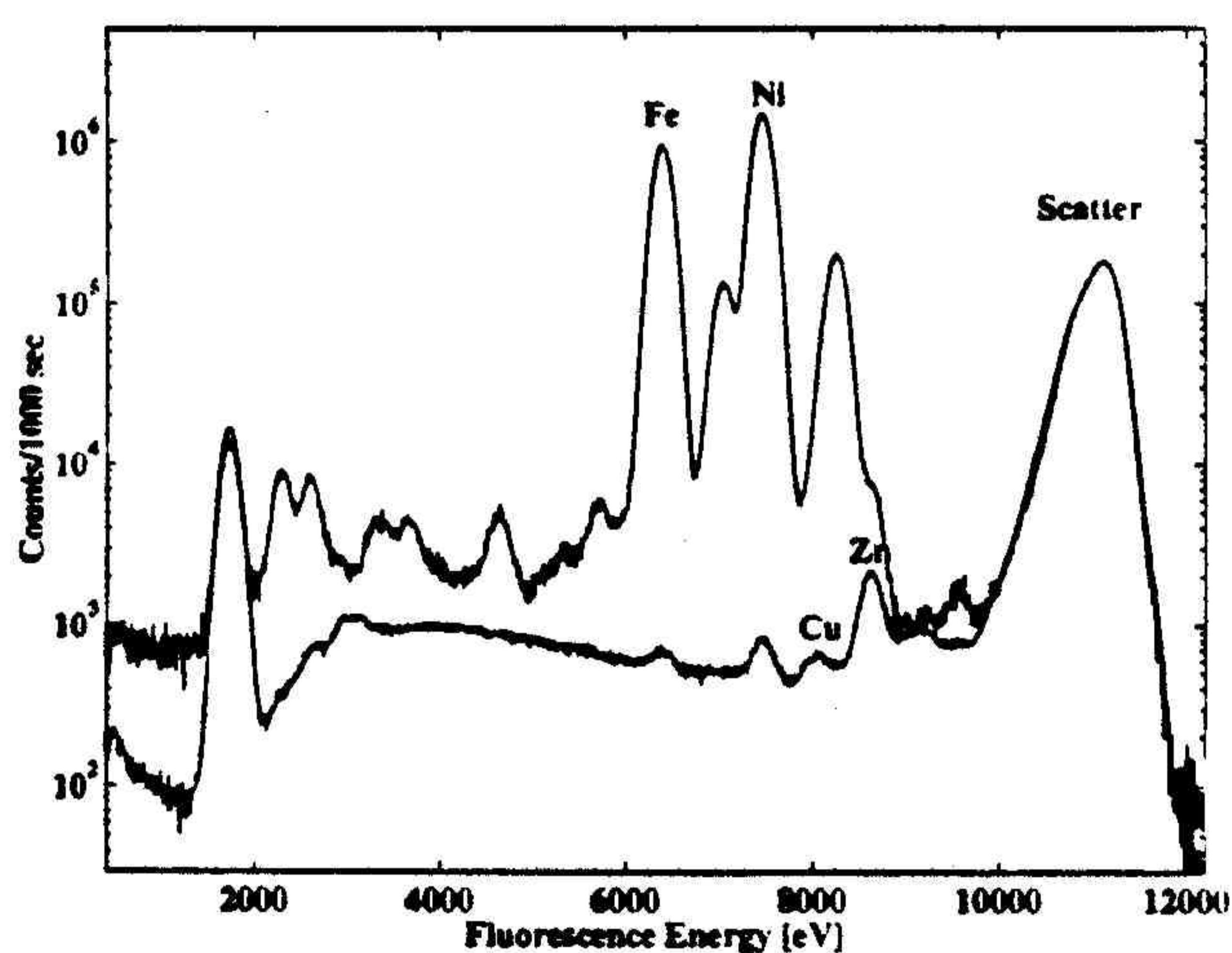


Figure 2: Fluorescent intensity from a droplet collected using the WSA technique and dried on the center of the wafer (upper curve). The lower curve shows the residual contamination not collected by the technique.

The WSA technique can also be used in conjunction with TXRF. By concentrating the contaminants in a droplet and drying the droplet on the wafer, there are several advantages. The mass of contaminant atoms in the view of the detector has increased by  $> 2000$ . An additional advantage is that the contaminant atoms consist of particles on the surface rather

than mono-dispersed as they are under normal conditions. The particles can be excited by the incident beam even at a nominal x-ray angle of incidence of zero degrees, which greatly reduces the background signal from the silicon wafer. Figure 2 shows two spectra from a wafer on which WSA has been performed. The upper curve was measured on the residual droplet, and a concentration of  $2 \times 10^{13}$  atoms/cm<sup>2</sup> of Fe and Ni is observed. Because of the concentration factor, the entire surface was contaminated with  $10^{11}$  atoms/cm<sup>2</sup> of those elements, which is a level observable with conventional TXRF. Although there are a variety of additional peaks in the region between 4000 and 8500 eV, they are either escape peaks or  $K_{\beta}$  peaks from the Fe and Ni signal, with the exception of the shoulder at 8400 eV, which is probably due to Zn. This is more clearly observed in the lower spectrum, which was measured at a position away from the residual droplet. One can still see significant levels of contamination on the wafer. These levels are: Fe,  $7 \times 10^9$ , Ni,  $1 \times 10^{10}$ , Cu,  $3 \times 10^9$ , and Zn,  $3 \times 10^{10}$  atoms/cm<sup>2</sup>. In other WSA wafers we have measured the residual contamination levels are much lower, although copper is often difficult to collect completely. Note also that as a result of concentration, the Fe and Ni have masked the presence of Cu on the surface, and the Zn concentration is difficult to quantify. For this figure the two spectra were normalized to have the same scattered beam intensity.

One of the strengths of the synchrotron radiation-based TXRF program is the ability to tune the incident beam energy to enhance the sensitivity to a particular element. Figure 3 shows the results of one study where one of the users was interested in determining whether there was bromine on the wafer. Bromine is a chemical analog of fluorine and chlorine, both of which are regularly used as the acids HCl and HF. Figure 3 has two spectra, one with the photon energy at the standard value near 11 keV. One can see small amounts of nickel and copper contamination on the wafer ( $2-4 \times 10^9$  atoms/cm<sup>2</sup>). However, with the incident photon energy set to 14 keV, a very clear Br peak is visible, with a concentration of  $4 \times 10^{11}$  atoms/cm<sup>2</sup>. Note that the Cl peak at 2620 eV is also visible, and is  $2.6 \times 10^{12}$  atoms/cm<sup>2</sup>. The teflon filter reduces the apparent intensity of the Cl peak. The 14 keV data were collected for 500 seconds, vs. 1000 seconds for the 11 keV data, so for the

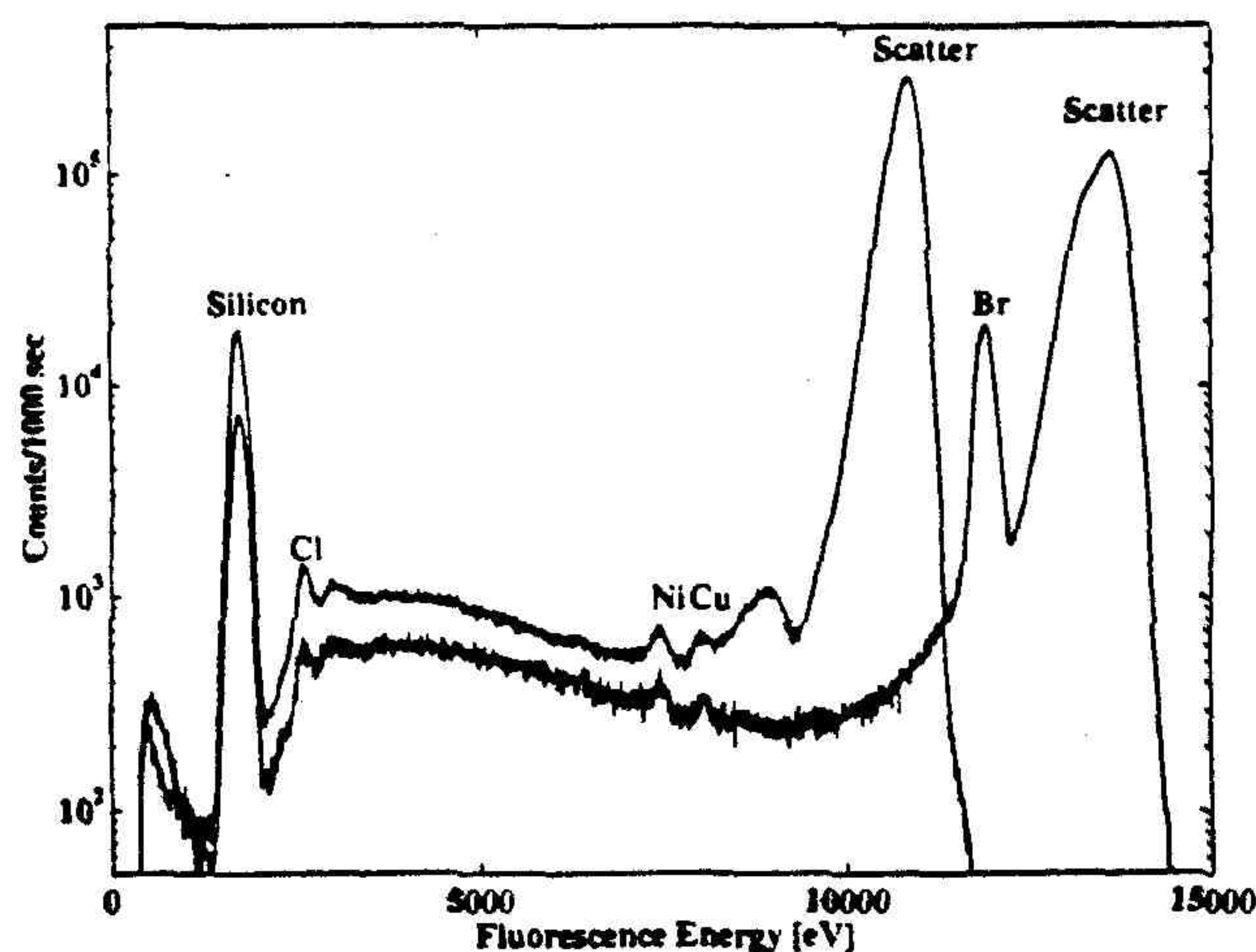


Figure 3: Fluorescent intensity from a silicon wafer using either 11 keV or 14 keV radiation to excite the fluorescence. The higher incident photon energy reveals the presence of bromine on the sample, probably a contaminant in the HCl used to clean the wafer. Low levels ( $2-4 \times 10^9$  atoms/cm<sup>2</sup>) of Ni and Cu are also present.

figure the 14 keV data are doubled. The lower incident intensity for the 14 keV spectrum is primarily due to the lower angle of incidence of the beam onto the multilayer monochromator. The incident beam overfills the vertical acceptance of the multilayers and the intensity decreases. The shoulder on the scatter peak for the 14 keV data is due to a weak diffraction peak from the silicon substrate.

There is increasing interest in copper films for metallization within the semiconductor industry. This poses a particular problem for conventional TXRF, as the typical excitation energy is greater than the Cu K-absorption edge, creating excessive Cu  $K_{\alpha}$  radiation. Our preliminary work on Cu films has shown that one can see concentrations below

$10^9$  atoms/cm<sup>2</sup> of elements from Ti to Ni. This is made possible by setting the incident photon energy directly on the Ni K-absorption edge at 8.3 keV, which is below the K-absorption edge of copper. Due to higher order harmonics in the incident beam, there is still some Cu K<sub>α</sub> fluorescence, but it is dramatically reduced. There is also a peak due to resonant Raman scattering from the Cu film<sup>9</sup>. However, by positioning the incident energy at the Ni edge, the Ni K<sub>α</sub> peak can be observed if present, and the escape peak from the incident beam rests on the high-energy shoulder of the Fe K<sub>α</sub> peak.

## CONCLUSIONS

Synchrotron-based TXRF has been demonstrated to be a very effective technique for measuring a wide range of analytical problems of interest to members of the semiconductor processing industry. The combination of very high sensitivity, non-destructiveness, mapping and incident beam energy tunability makes this a unique research tool. It is in regular use by semiconductor industry groups at SSRL, being used for a variety of studies including materials and equipment qualification and measurement of process cleanliness. Although the emphasis has been on silicon and oxidized wafers, blanket films, ion implanted films and GaAs wafers have also been measured. We expect new applications of the technique to continue to occur.

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