Recent Advances and Perspectives in Synchrotron Radiation TXRF

K. Baur [1], S. Brennan [1], D. Werho [2], L. Moro [3] and P. Pianetta [1]

1 Stanford Synchrotron Radiation Laboratory, Stanford, CA 94309

2 Motorola, Inc., Mesa, AZ

3 SRI International, Menlo Park, CA 94025

Total reflection x-ray fluorescence (TXRF) using Synchrotron Radiation is likely to be the most powerful non-destructive technique for the analysis of trace metal impurities on silicon wafer surfaces. Of fundamental importance in TXRF is the achievable sensitivity as characterized by the minimum detection limit. This work describes the progress we achieved recently at the Stanford Synchrotron Radiation Laboratory (SSRL) in minimum detection limits for transition metals and will give an estimate of what can be achieved using a third generation synchrotron radiation source such as SPEAR3.

Keywords: Total reflection X-ray fluorescence, detection limit, Stanford Synchrotron Radiation Laboratory

Corresponding author: pianetta@stanford.edu (P. Pianetta)

Introduction.

TXRF for transition metal detection has matured to a point at which users from industry, national laboratories and universities are able to perform industrially relevant measurements at state of the art sensitivities at a dedicated facility at the Stanford Synchrotron Radiation Laboratory (SSRL). This facility features clean wafer handling and automated data acquisition making routine analytical measurements possible. The sensitivity that can routinely be achieved for Cu is about 8 E7 atoms/cm^2 for a standard 1000-second count time as determined from Fe, Ni and Zn standards [1,2,3,4]. This is about a factor of 50 better than what can be achieved with conventional laboratory TXRF using a rotating anode.

The minimum detection limit (MDL) is determined using an elemental standard and the equation:

$$\mathrm{MDL} = \frac{3\mathrm{C}}{\mathrm{I}_{\mathrm{Peak}}} \cdot \frac{\sqrt{\mathrm{I}_{\mathrm{BG}}}}{\sqrt{\mathrm{t}_{1000\,\mathrm{sec}}}} \qquad (1)$$

where C is the concentration of the elemental standard and t the measuring time in multiples of 1000 seconds. I_{Peak} is the integrated intensity of the respective fluorescence peak after subtracting the background intensity, I_{BG}, below that peak [5]. The equation implies that the sensitivity can be increased by either increasing the incoming photon flux and/or reducing the spectral background. Both have been exploited by applying synchrotron radiation which provides a high incident flux combined with low divergence and a linearly polarized beam. This leads to an increased fluorescence signal while simultaneously reducing the elastically scattered background. However, the Si(Li) semiconductor detectors which are generally used for fluorescence detection in TXRF

show a high counting rate load when exposed to high flux synchrotron radiation, especially from insertion devices. The main contributions giving rise of detector deadtime are the elastically and inelastically scattered primary photons. The counting rate load from the Si substrate signal on the other hand, can be efficiently reduced by a Teflon filter in front of the detector [1]. This paper will demonstrate the state of the art detection limits for transition metals and extrapolate to what can be achieved using a third generation synchrotron radiation source such as SPEAR3.

Experiment.

The experiments reported here were carried out on beamline 6.2 at SSRL which uses a high flux, 54 pole wiggler on the SPEAR storage ring. The beamline and the general experimental setup of the TXRF experiment have been described elsewhere [1]. For this work we have studied a wafer from Motorola with very low levels of unintentional Ni and Fe contamination resulting from a state of the art cleaning process. The wafer was measured for an extended counting time of 5000 seconds in order to determine the minimum detection limit accurately.

It is worthwhile to mention several points concerning the choice of samples for this experiment. As mentioned above, detection limits are determined by measuring standard wafers and using Equation (1). However, the relatively high contamination levels (i.e., 1E10 to 1E11 atom/cm^2) that are used as standards make it impractical to measure MDL's that are below the 1E8 atom/cm^2 level. As a result, for these measurements, a sample was used with very low yet detectable contamination levels. In this case the contamination

levels were a little less than two times the MDL at the 1000 second counting time. It should also be noted that the current state of the art cleaning processes do produce wafers with contamination levels that are below the SR-TXRF detection limits for 1000 second counting times. This is shown in Fig. 1 for a Si epilayer grown by CVD on a Si wafer. It demonstrates that the fluorescence detector used in the setup at SSRL shows no parasitic fluorescence lines from the detector housing as well as that there is no unintentional contamination added during wafer handling.

Results and Discussion.

Fig.2 shows the fluorescence spectrum of the Si wafer obtained after an integration time of 5000 seconds. The excitation energy of 11280 eV gives a high excitation cross section for transition metals such as Ni and Fe. The spectrum was measured for an angle of incidence of 0.09^{o}, which is below the critical angle for total external reflection (0.16^{o} at 11280 eV) and which resulted in the maximum acceptable count rate for the current detector setup of approximately 14 kHz and a deadtime of 50%. The dominant peak at 11280 eV is from elastic scattering of the incident synchrotron radiation. Next to it is its associated escape peak at 9540 eV. The intensity of the Si Kα substrate fluorescence at 1740 eV would normally dominate the spectrum except for the Teflon filter that was discussed above. Between 6-8 keV, the spectrum shows the signature of the unintentional contamination from Fe and Ni. The concentrations were determined to be 2.5 E8 atoms/cm^2 for Fe and 1.2 E8 atoms/cm^2 for Ni. The background below approximately 7 keV is dominated by the photoelectron bremsstrahlung emitted by the Si 1s photoelectrons which are created in the wafer by the primary photon beam [6]. In the higher energy region the background is

dominated by inelastic Compton scattering and the escape peak. Using equation (1) we derive the MDL for Ni to be 4.0 E7 atoms/cm^2 for a 5000 second counting time which corresponds to 8.9 E7 atoms/cm^2 for the standard counting time of 1000 seconds. The MDL for Fe is 7.4 E7 atoms/cm^2 for a 5000 second counting time and 1.6 E8 atoms/cm^2 for 1000 seconds. The MDL derived from the Fe peak is worse than that for Ni because the photoabsorption cross section for the primary photon energy is reduced by a factor of 0.8 relative to Ni and because of the higher contribution from the background in this energy region.

The ability to handle higher count rates from third generation synchrotron sources must clearly be preceded by significant detector developments which must include both multielement detector arrays as well as higher speed electronics. Multielement, high-speed detectors are now routine in other fields such as XAS so that it should be reasonable to expect that appropriate detectors could also be engineered for TXRF applications. The SPEAR3 upgrade at SSRL, which will be completed in 2003, will offer several opportunities for TXRF. The horizontal source size for an insertion device, which is the dimension of interest given the horizontal reflection geometry being used at SSRL, will be reduced from 2 mm to 0.43 mm and the current will be increased from 100 mA to 500 mA. This results in an overall increase in flux density of approximately a factor of 23 and should result in a MDL of about 2 E7 atoms/cm^2 for the standard 1000 second counting time.

Another exciting possibility is the use of a bending magnet line on SPEAR3. Although the flux of a bending magnets is less than that of an insertion device, the SPEAR3 bend will have at least a factor of 1.5 improvement over the existing SPEAR2 facility on the wiggler

beamline 6.2. This is mainly due to the expected horizontal source size of 164 μm which will be smaller by a factor of 12.5 than the current horizontal source size of the wiggler beamline 6.2 as well as the factor of 5 increase in current. Together with a higher degree of linear polarization, the bending magnet source on SPEAR3 will provide better performance than the current situation on beamline 6.2. This would result in detection limits in the mid-E7 range as well as enabling relatively inexpensive multiple stations on a single beam line realizing commercial activities in the future.

Conclusions.

We have demonstrated that the current TXRF experiment at SSRL is capable of achieving detection limits for transition metals below 1 E8 atoms/cm^2 for a standard integration time of 1000 seconds. Taking the expected source parameters of SPEAR3 into account a bend magnet beamline on SPEAR3 will improve the detection limit by about a factor of 1.5 as compared to the current wiggler beamline on SPEAR. This would make a dedicated TXRF experiment with routine detection limits in the mid-E7 atoms/cm2 range a reality.

Acknowledgments. We would like to thank the staff of SSRL for their expert technical assistance and especially M. L. Poligano, ST Microelectronics (Agrate, Italy), and P. Lazzeri, IRST (Trento, Italy), for providing the clean Si wafer. Part of this work was performed at SSRL, which is supported by the Department of Energy, Office of Basic Energy Sciences.

References

[1] P. Pianetta, K. Baur, A. Singh, S. Brennan, J. Kerner, D. Werho, J. Wang, Thin solid films, in press.

[2] P. Pianetta, N. Takaura, S. Brennan, W. Tompkins, S. S. Laderman, A. Fischer-Colbrie, A. Shimazaki, K. Miyazaki, M. Madden, D. C. Wherry, J. B. Kortright, Rev. Sci. Instrum. **66**, 1293 (1995).

[3] S. Brennan, W. Tompkins, N. Takaura, P. Pianetta, S.S. Laderman, A. Fischer-Colbrie, J. B. Kortright, M. C. Madden, D. C. Wherry, Nucl. Instrum. Meth. **347**, 417 (1994).

[4] S. Brennan, P. Pianetta, S. Gosh, N. Takaura, C. Wiemer, A. Fischer-Colbrie, S. Laderman, A. Shimazaki, A. Waldhauer, M. A. Zaitz, *in Application of Synchrotron Radiation to Materials Science* **IV 542**, in: S. M. Mini, D. L. Perry, S. R. Stock, L. J. Terminello, (Eds.), Materials Research Society, Boston, p. 125 (1993).

[5] E. P. Bertin, *Principles and Practice of X-Ray Spectrometric Analysis*, New York, Plenum Press, 1975.

[6] N. Takaura, S. Brennan, P. Pianetta, S. Laderman, A. Fischer-Colbrie, J. B. Kortright, D. C. Wherry, K. Miyazaki, A. Shimazaki, Advances in X-Ray Chemical Analysis, Japan **26s**, 113 (1995).

Figure Captions

Fig.1. TXRF spectrum of a clean Si wafer after a standard counting time of 3000 seconds. The contamination level is below the SR-TXRF sensitivity for 3000 seconds.

Fig.2. TXRF spectrum of a Si wafer unintentionally contaminated with Fe and Ni as measured for a 5000 second counting time resulting in a MDL for Ni of 4.0 E7 atoms/cm^2. The spectrum has been taken for an excitation energy of 11280 eV at an angle of incidence of 0.08^o.

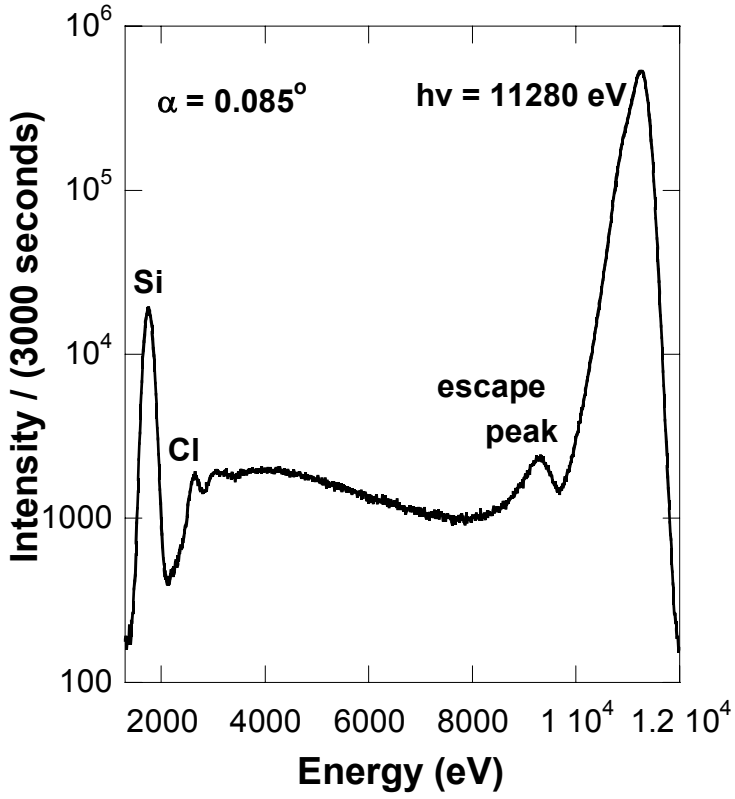
10^6
10^5
10^4
1000
100
α = 0.085°
hv = 11280 eV
Si
Cl
escape
peak
Intensity / (3000 seconds)
2000
4000
6000
8000
1 10^4
1.2 10^4
Energy (eV)

Fig.1

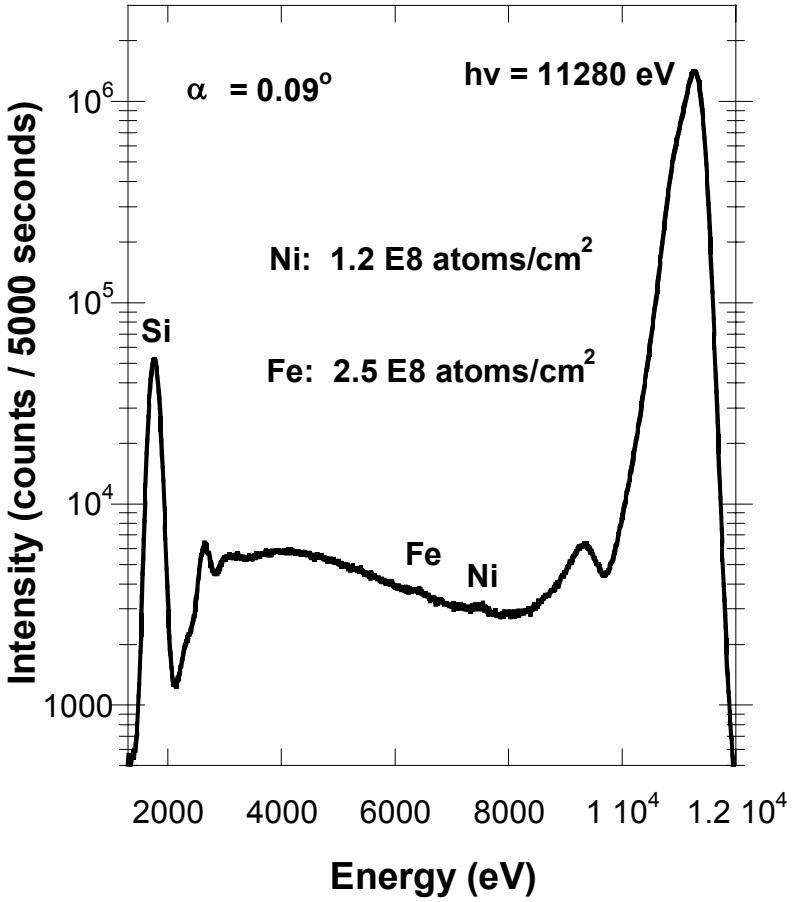
α = 0.09°
hv = 11280 eV
Ni: 1.2 E8 atoms/cm2
Fe: 2.5 E8 atoms/cm2
Si
Fe
Ni
Intensity (counts / 5000 seconds)
Energy (eV)
10^6
10^5
10^4
1000
2000
4000
6000
8000
1 10^4
1.2 10^4

Fig.2