Investigation of Na impurities on Si wafer surfaces using TXRF

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Abstract. Synchrotron Radiation from the Stanford Synchrotron Radiation Laboratory (SSRL) has been used as an excitation source for Total Reflection X-ray Fluorescence Analysis (TXRF) of Na impurities on Si wafer surfaces. A wafer intentionally contaminated by a droplet containing 1.4×10^{14} atoms/cm^2 of sodium and a wafer uniformly contaminated with 4.4×10^{12} atoms/cm^2 of Na were investigated. The minimum detection limit for this element has been found to be 1.1×10^{11} atoms/cm^2 for the blanket sample and 3×10^{11} atoms/cm^2 for the droplet sample. Theoretical considerations show that the detection limit for Na can be further improved by at least a factor of 2 by exploiting the tunability of synchrotron radiation to even lower excitation energies.

INTRODUCTION

Total reflection x-ray fluorescence spectroscopy (TXRF) in combination with synchrotron radiation has developed into one of the most powerful non-destructive techniques for detecting trace concentrations of transition metal impurities on Si wafer surfaces (1, 2). To date, SR-TXRF has achieved remarkable sensitivity for transition metals of 3.4×10^7 atoms/cm^2, as determined for Fe, Ni and Zn standards (3).

A new challenging area for TXRF is the analysis of light elements such as Na on Si wafer surfaces. This becomes increasingly important to semiconductor industry as even very low levels of Na trace impurities can cause problems in integrated circuits such as drifts in FET threshold voltages.

Detection of Na poses a considerable challenge compared to transition-metal elements due to the low fluorescence yield and low photon absorption cross-section. A further complication for detection of light elements with $Z < 14$ results from the close proximity of the Si K fluorescence line, which cannot be suppressed by filters as is done for detection of transition metals (2).

The use of synchrotron radiation as a primary excitation source offers several advantages to compensate for these inherent restrictions. The tunability of synchrotron radiation to energies below the Si K absorption edge allows the elimination of the fluorescence from the Si substrate. The high incident flux combined with low divergence gives strong fluorescence signals, and due to the linear polarization, the elastic scattering of the primary radiation can be reduced by detection normal to the orientation of the electric vector resulting in a lower background. So far the lowest

detection limits reported in literature for Na droplets using synchrotron radiation are better than 200 fg (4).
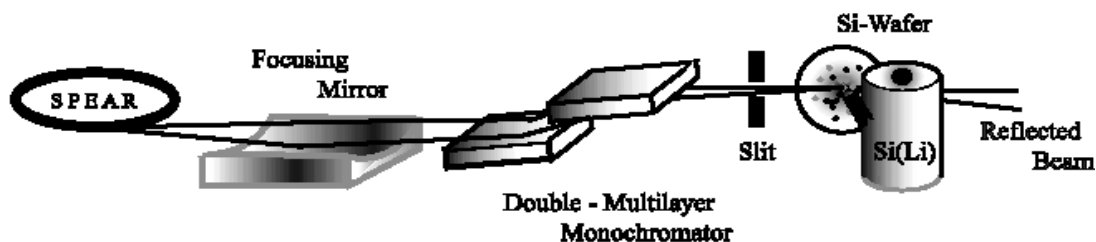
Figure 1. Experimental TXRF set-up installed on beam line 3.3 at the SSRL.

In this study we present our first results on the sensitivity of Na on Si wafer surfaces obtained at the Stanford Synchrotron Radiation Laboratory (SSRL). These results indicate that the droplet preparation method can be effectively used for preparation of Na standards.

EXPERIMENT

The measurements were carried out at the soft x-ray bending magnet beamline 3-3 at SSRL. The experimental configuration is shown in Fig. 1. Details about the experimental components and the wafer alignment are published elsewhere (3,5).

The sample was prepared at Balazs Analytical Laboratory. After cleaning the Si wafer with dilute HF, 300 pg of Na was deposited on the wafer by applying a 80 μl droplet with Na concentration of 4 ppb in a 2% nitric acid matrix. This corresponds to a nominal surface concentration of 5.6×10^{13} atoms/cm^2 within the droplet assuming a 2 mm x 7 mm acceptance area of the detector. In addition a wafer from Hewlett-Packard Co. with an intentional Na contamination of 4.4×10^{12} atoms/cm^2 was used as an external standard.

RESULTS AND DISCUSSION

Fig. 2 shows a typical fluorescence spectrum from the droplet sample measured for 1000 seconds for an excitation energy of 1730 eV. This is sufficiently below the Si K absorption edge, thereby eliminating Si K fluorescence. The spectrum was obtained for an angle of incidence of 0.1^o which is below the critical angle of total external reflection (0.9^o at 1730 eV). The peak at 1730 eV is due to elastic scattering of the

primary synchrotron radiation. At 1041 eV the fluorescence signature of Na is found. Between these two peaks the spectrum shows a third structure that is due to resonant x-ray Raman scattering (6), *i.e.* inelastic scattering of the incoming x-rays which will be discussed in detail in a forthcoming publication (7). Generally, the cross section of Raman scattering is low compared to elastic Rayleigh or inelastic Compton
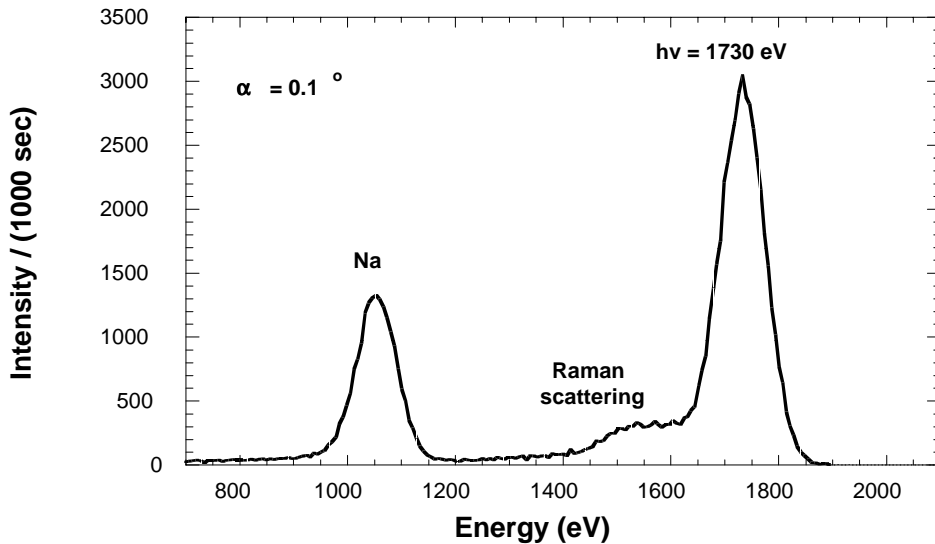
Figure 2. Fluorescence spectrum of a wafer intentionally contaminated by a droplet containing a Na concentration of 1.4×10^{14} atoms/cm^2.

scattering. It can, however, become significant due to resonant enhancement if the incident photon energy is close to an absorption edge of the substrate (8, 9), *e.g.,* the Si K edge at 1840 eV. The spectrum demonstrates that Raman scattering dominates the background behavior in the energy region between 1400 eV and 1600 eV but it does not significantly affect the Na Kα signal.

An independent calibration of the Na concentration within the droplet can be done by comparing the Na peak intensity with the one measured under the same conditions for an external Na standard. Therefore, the fluorescence spectrum of the 4.4 x 10^{12} atoms/cm^2 Na contaminated blanket wafer is shown in Fig. 3. This spectrum has been measured for 10000 seconds under the same experimental conditions, *i.e.* an excitation energy of 1730 eV and 0.1° angle of incidence. At 1730 eV one finds again the peak due to elastic scattering of the primary radiation and at 1041 eV the fluorescence line of Na. In addition this wafer also shows an Al fluorescence line at 1487 eV. This indicates an unintentional contamination of the wafer. This clearly demonstrates that unlike Na the sensitivity for Al detection is strongly limited by the occurrence of the inelastic Raman scattering background (7).

The cross-calibration gives a concentration of 1.4×10^{14} atoms/cm^2 of Na within the droplet. This corresponds reasonably with the calculated Na concentration of 5.6 x

10^{13} atoms/cm^2 taking uncertainties into account which arise from working at these low concentrations.

The minimum detection limit (MDL) is defined by (10)

$$MDL = 3C\sqrt{I_{BG}}\Big/I_{Peak} \, ,$$
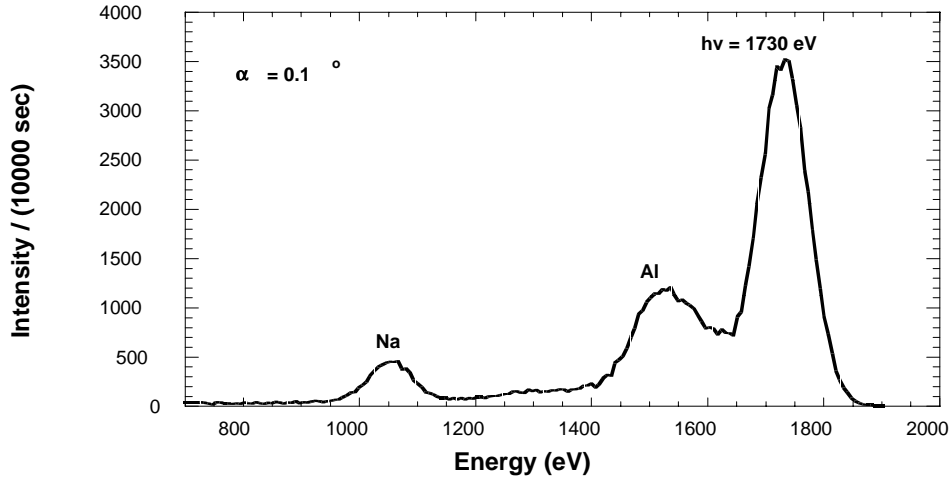
Figure 3. Fluorescence spectrum from a standard wafer contaminated with Na at a concentration of 4.4 x 10^{12} atoms/cm^2. In addition the spectrum shows the signature of Al due to an unintentional contamination.

with C being the Na concentration of the standard, I_{BG} the integrated linear background intensity under the peak of interest and I_{Peak} the integrated intensity of this peak on top of the background. We find the MDL to be 1.1. x 10^{11} atoms/cm^2 for the standard sample (and a 1000 sec counting time) and 3 x 10^{11} atoms/cm^2 for the droplet corresponding to a sensitivity of about 600 fg and 2 pg, respectively.

We expect that the MDL can be further reduced at least by a factor of two under the present experimental conditions by tuning the excitation energy closer to the Na absorption edge and thereby optimizing the photoionization cross-section. The maximum Na signal can be achieved when the incident photon energy is equal to the Na K absorption edge at 1071 eV. However, it has to be considered that the background has two contributions: a linear background which is in good approximation independent of the primary excitation energy in the energy region considered, and a contribution from the tail of the elastic scattered peak that increases with decreasing excitation energy.

The dots in Fig. 4 show calculated values for the minimum detection limit for Na as a function of the excitation energy between 1070 eV and 2000 eV. The signal intensity was calculated using the absorption cross-section of Na in this energy region. The intensity of the peak background was assumed to be independent of the incident x-

ray energy in this energy region. Fig. 4 clearly demonstrates that the minimum detection limit increases for an excitation energy around the Na K edge as a result of the strong overlap between the lines. It can be seen that the minimum detection limit can be further improved by about a factor of two by tuning the primary energy down to 1300 eV which will be exploited in the near future.
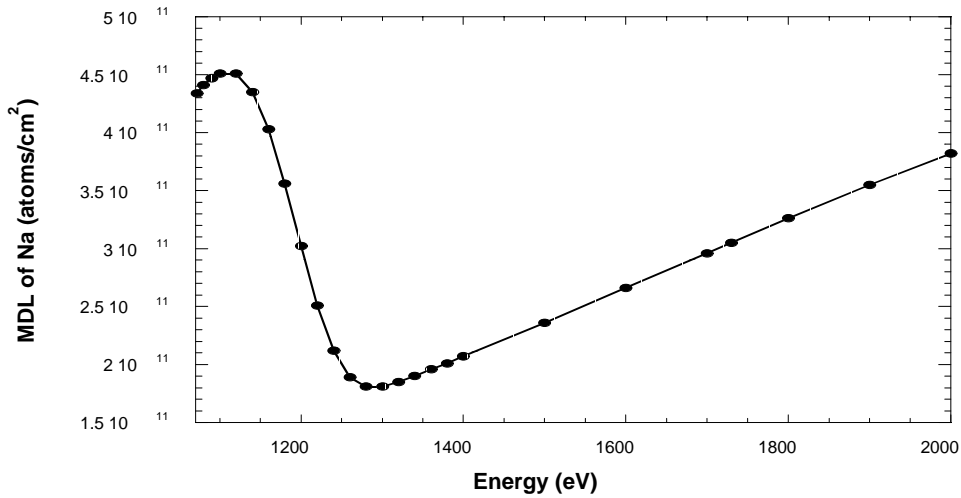
Figure 4. The MDLs of Na as a function of the primary beam energy. The calculated value at 1730 eV is normalized to 3×10^{11} atoms/cm^2.

CONCLUSION

We have demonstrated that TXRF in combination with synchrotron radiation has been developed as a powerful technique for the detection of low Z impurities on Si wafer surfaces. Using a Na blanket standard as an independent control for the droplet preparation method, consistent results for the Na concentration in the droplet have been achieved. This indicates that the droplet preparation method may be a promising technique for preparation of Na standards.

In addition the minimum detection limit could be determined for the standard wafer to be 1.1×10^{11} atoms/cm^2 and 3×10^{11} atoms/cm^2 for the droplet. Calculations of the minimum detection limit as a function of the primary excitation energy demonstrate that a reduction of the primary excitation energy to 1300 eV can further decrease the detection limit by a factor of 2.

Using the TXRF geometry, only about 10 μm of the horizontal width of the incoming beam is in the detector's field of view, which is much smaller than the actual horizontal beam size of about 7000 μm. This indicates that with better horizontal focussing, better sensitivities could be achieved. The MDL changes with the square-root of the observed incident photon flux. Assuming the source size and current from SPEAR3, SR-TXRF would benefit from the five times higher beam current compared to SPEAR as well as from the reduction in the horizontal beam size by about a factor of

7. This would result in a MDL of about 3×10^{10} atoms/cm^2 for the Na droplet. This could still be improved by using in addition an undulator source for primary excitation increasing the overall flux density by at least a factor of 250. This would result in an MDL of about 2×10^9 atoms/cm^2 for the Na droplet. This would be much lower than what may be achieved by conventional TXRF using a rotating anode.

ACKNOWLEDGMENTS

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