QUANTITATIVE ANALYSIS OF LOW-Z ELEMENTS IN TOTAL REFLECTION X-RAY FLUORESCENCE SPECTROSCOPY

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ABSTRACT

In trace analysis of low-Z elements by a TXRF system, a correct estimation of the backgrounds is very important. The backgrounds from the tailing of a large Si-Kα peak are undesirable especially for the analysis of Al. Thus, X-ray radiation with excitation energies below the Si K absorption edge should be used to eliminate the Si-Kα peak. The W-Mα line from a W target and a radiation from a SR source are best for this purpose. The radiations with energy below the Si K absorption edge, however, create a background due to inelastic scattering from the existence of resonant X-ray Raman scattering. During an analysis of low-Z elements, the backgrounds caused by Raman scattering must be eliminated. We estimated theoretically the profile of the continuous spectrum of Raman scattering and applied the profile fitting technique to analyze thin films deposited on Si to determine simultaneously the concentrations of low-Z impurities and the Raman backgrounds. We found that the Raman backgrounds are significantly different depending on the X-ray incident angles and the film materials.

INTRODUCTION

Total reflection X-ray fluorescence spectroscopy (TXRF) has become one of the most powerful nondestructive techniques for the detection of very low concentrations of metal impurities on Si wafer surfaces. For the analysis of transition metals such as Fe, Ni and Zn, TXRF has achieved a remarkable sensitivity to the order of 10^9 atoms/cm^2. For low-Z elements with Z<14, the fluorescence signal are about one order of magnitude smaller than those of medium-Z elements because of a reduced fluorescence yield and a reduced detection efficiency of a solid-state detector (SSD). In addition to these restrictions, the detection of low-Z elements on a Si substrate is especially difficult because of the presence of much stronger Si fluorescence signals at 1.74 keV. Thus, X-ray radiations with excitation energies below the Si K absorption edge should be used to eliminate the Si-Kα fluorescence signal. The W-Mα line (1.78 keV) from W target and synchrotron radiation are best for this purpose. Another problem for the analysis of low-Z elements with excitation energies below the Si K absorption edge is that the background spectrum depends on the materials of the film (e.g., SiO₂ film, SiON film, low-k film and so on) and the incident angle of the primary X-ray beam. Therefore, it has been necessary to prepare background data from a blank substrate, before measuring the film. For low-k films, however, it is difficult to prepare a proper blank substrate.

K. Baur et al [1] recently demonstrated that X-ray radiation with excitation energies below the Si K absorption edge created a background due to inelastic scattering from the existence of resonant...
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X-ray Raman scattering, and they were successfully determined the concentrations of Al impurity on a Si wafer by a profile fitting method.

Recently, we has developed a new profile fitting technique to determine the true backgrounds for TXRF analysis of low-Z elements.

**METHOD OF ANALYSIS**

Figure 1 shows the two typical fluorescent spectra from a blank Si wafer. One is the case of W-Mα line excitation and the other is that of W-Lβ line excitation. The spectrum for the W-Lβ excitation is the Si-Kα line. On the other hand, the spectrum for W-Mα line excitation includes Raman scattering and elastic scattering of W-Mα line.

Raman scattering is represented by the process in Fig. 2, which is described by the second order time-dependent perturbation theory. First the X-rays of W-Mα excite the electron in K-shell state into an unoccupied state high above the Fermi level. The intermediate state is unstable, and then it immediately decays by the transmission of an electron from an inner shell (e.g. L-shell) to the K-shell vacancy and the energy difference is emitted as the scattered photon (X-ray). From the energy conservation, the energy of the scattered x-rays ($h\nu'$) is expressed by the following equation,

$$h\nu' = E(W-M\alpha) - E(e) - E(\text{inner-shell}) ,$$

where $E(W-M\alpha)$ is the energy of W-Mα line (1780eV), $E(e)$ is the energy of the scattered electron into the unoccupied state and $E(\text{inner-shell})$ is the binding energy of the electron in the inner shell which has a hole at final. The E(e) can be a positive and continuous value ($E(e) > 0$). Therefore the energy of the scattered X-rays is in the range from zero to $E(W-M\alpha) - E(\text{inner-shell})$. The cross section of Raman scattering is generally very low compared to Rayleigh scattering, which is elastic scattering. However, if the energy of the incident photon is close to an absorption threshold (i.e. the
Si K edge), the Raman process is resonantly enhanced. This resonance process is called "Resonant X-ray Raman scattering". Figure 3 (a) shows the differential cross section for this process that is calculated from the Kramers-Heisenberg formula[2], where we adopted the nonrelativistic Hydrogen-like atom model as Si atom. The differential cross section as shown in Fig. 3(a) has the threshold at the energy of 1680eV(=E(W-Mα)-E(Si-LIIshell)) and a low energy tail. From the energy conservation, you can see that the threshold energy for the differential cross section depends on the energy of the incident photon linearly. This dependence in TXRF analysis has been observed by K. Baur et al using a SR source [1].

The spectrum detected by SSD for the Raman scattered X-rays is obtained by convoluting the differential cross section with the detector response function [3] as well as taking account of the transmission function of the Be filter in front of the detector (Fig.3 (b)). The Profiles for elastic scattered x-rays of the primary beam and each fluorescent X-rays are directly described by SSD response function. Thus we can analyze the measured data by using the least square fitting method.

RESULT AND DISCUSSION

The TXRF system used in this work was RIGAKU TXRF 300. This system has triple beams from a W-target by exchanging monochromator in order to analyze a wide range of elements. For low-Z elements, W-Mα line is monochromatized by a double multilayer monochromator. The optical configuration is sketched in Fig. 4. Figure 5 shows the spectra from a blank Si wafer for different incident angles of the primary X-ray beam. Each spectrum...
can be deconvoluted into the elastic scattering part of W-Mα line and the Raman scattering part by the least-square fitting. The percentages of Raman scattering to the total integration of X-rays detected are shown in Fig. 6. Not only the absolute intensities of Raman scattering but also the percentages of it in the background intensity increase with the angle of incidence. The reason for the increase in the absolute Raman intensity is the increasing penetration of the primary X-rays into a Si wafer involving more Si atoms in the process. The percentages of Raman intensity in the background cannot, however, be explained by the increase of Si atoms. It can be attributed to a natural oxide layer on a Si wafer, that is, Raman scattering by silicon oxide occurs less likely than that by pure silicon as shown in the analysis below.

The analysis of thin films on Si is given in Fig. 7 and Fig. 8. They are a 100-nm SiO₂ film, a 10-nm SiON film and two low-k films denoted by "low-k film 1" and "low-k film 2". All of the measurements are fitted very well with the profiles described in the preceding section. Both the
SiO$_2$ and the Si ON film are found to be free of contamination with low-Z elements. Two low-k films have small amounts of low-Z impurities. The percentages of Raman scattering intensity in the background are different for different films (Fig. 8). The percentages of Raman scattering for 100-nm SiO$_2$ film and the "low-k film 2" film are obviously different from that for a bare Si wafer. Particularly, the probability to create Raman scattering for "low-k film 2" is nearly zero. The suppression of Raman scattering for SiO$_2$ film is partially attributed to reduction of Si concentration in SiO$_2$ than that in pure Si. Another possible cause for this suppression is a difference in the electron structure between pure Si and

![Fig. 7. Least square fits of the fluorescence spectra from SiO$_2$, SiON and Low-k films on Si wafer. The measured data are denoted as dots, Raman scattering as long dashed lines, W-Mα as short dashed lines, fluorescent x-rays of impurities as dash-dotted lines and the sum of all contributions as solid lines.](image)

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![Fig. 8. Percentages of Raman scattering intensity in backgrounds for different film samples.](image)
SiO$_2$. The origin of this suppression for SiO$_2$ film as well as low-k film will be future studied.

Finally we applied to spin coated samples and obtained the net Al-K$\alpha$ intensities. The concentrations of Al were also determined quantitatively by Atomic Absorption Spectrophotometer (AAS). The AAS concentrations were 0, $10^{12}$, $10^{13}$ and $10^{14}$ atoms/cm$^2$. The Al-K$\alpha$ intensities obtained by the profile fitting method are in good agreement with those by AAS (Fig. 9).

**CONCLUSION**

TXRF with excitation energies below Si K absorption edge is one of the most powerful techniques for determining low-Z element impurities on Si wafer. The background has been attributed to resonant X-ray Raman scattering and elastic scattering. We have demonstrated that the difference on background profiles for different incident angles of the primary X-ray beam and/or for different materials of films on Si came from the difference between their probabilities to create Raman scattering. We have successfully determined the Al-K$\alpha$ intensities for spin-coated samples. The Al-K$\alpha$ intensities obtained by our profile fitting method have a good linear correlation with the results obtained by Atomic Absorption Spectrophotometer. Our technique does not require a blank sample to estimate the background.

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