Quantitative Analysis of Semiconductor Materials

with Secondary Ion Mass Spectrometer

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The Secondary Ion Mass Spectrometer (SIMS) is an instrument for highly sensitive mass analysis of a microvolume near the surface of a solid sample. A method for quantitative analysis, proposed by Andersen and Hinthorne, assuming that the sputtering region resembles a dense plasma in Local Thermal Equilibrium (LTE), is convenient and useful. However, this procedure needs two parameters, namely electron temperature ($T_e$) and electron density ($N_e$) to determine ionization yields, so the calculation is comparatively complicated. The aim of this report is to propose a more convenient method based on a simplified LTE model, and calculate Na concentrations in Si and SiO$_2$. Experiments were carried out using a SIMS (Hitachi: IMA-2) with Ar$^+$ and O$_2^+$ primary beam of 10 kV accelerating voltage and about 1 mA current.

In LTE plasma, the Saha-Regge equation gives the ion to atom ratio for each element in plasma, as follows,

$$ \frac{N^+}{N^0} = \left( \frac{2\pi m_e^2}{h^2} \right)^{3/2} \frac{B^3 e^2}{N_e B^0} \exp\left(-\frac{E_{\text{ion}}}{kT_e}\right) $$

where $N$ is the density of particles, $h$ is Planck’s constant, $k$ is Boltzmann’s constant, $m$ is mass, $B$ is internal partition function, $E$ is ionization potential and $\Delta E$ is energy depletion. When $N^+$ is assumed to be negligibly small, compared with $N^0$, $N_e$ and $E$ in Eq.(1) can be eliminated by making a ratio of $N^+/N^0$ for two elements.

$$ \frac{(N^+/N^0)_A}{(N^+/N^0)_B} = \frac{(B^+/B^0)_A}{(B^+/B^0)_B} \exp\left(-\frac{E_{\text{ion}}}{kT_e}\right) $$

Then, the concentration ratio for element A to B is given by

$$ \frac{C_A}{C_B} = \sqrt{\frac{m_A I_A}{m_B I_B}} \left(\frac{(B^+/B^0)_A}{(B^+/B^0)_B}\right) \exp\left(-\frac{E_{\text{ion}}}{kT_e}\right) $$

This procedure was applied to the quantitative analysis of In$_x$Ga$_{1-x}$As to check the validity. The In concentration determined from Eq.(3), using Ga and As as standard elements, was in good agreement (within 10 %) with the composition determined by EMPA, regardless of primary ion and accelerating voltage. Then, the calculation of Na concentration in Si was performed. In this case, Si and As were adopted as standard elements for electron temperature determination. Figure 1 shows the electron temperatures as a function of As concentration under three SIMS conditions, namely (1) Ar$^+$ primary beam at 2x10$^{-7}$ torr, (2) Ar$^+$ primary beam with O$_2$ admission of 1x10$^{-5}$ torr, and (3) O$_2^+$ primary beam at 2x10$^{-7}$ torr. These results indicate the electron temperature increase by the O$_2$ admission effect, which is presumably chemical effect. Next, it was attempted to determine Na concentration.
using a Si wafer, whose \( C_{Na} \) was measured to be 4.3 ppba with activation analysis beforehand. The concentration was 8 ppba from Eq. (3) and \( I_{Na}/I_{Si} \) measured after 30 minutes' sputtering. The results of \( C_{Na} \) distribution on the surface (about 50 \( \AA \)) of the cleaned wafer (sample 1) and a contaminated wafer (sample 2) are shown in Fig. 2. This suggests that \( C_{Na} \) in the surface region can be reduced close to the bulk concentration (4.3 ppba) by means of an appropriate clean-up procedure.

For the quantitative analysis of Na in \( SiO_2 \) films, Si and O were used as standard elements. Accordingly, \( Ar^+ \) primary beam in high vacuum (2x10^{-7} torr) was adopted. This procedure was checked previously by the calculation of \( C_p \) in phospho-aluminate glass (PAG), whose \( C_p \) was determined by spectrophotometry \(^3\) beforehand. The electron temperature, determined from \( \{I_{Si}, I_0, I_{SiO}\} \), was 8650K at 10 KV primary beam. Using this value and \( \{I_{p}, I_0, I_{p0}\} \), \( C_p \) could be calculated. Figure 3 shows the results as a function of \( C_p \), determined by spectrophotometry. The good agreement between both values indicates that this simplified method is useful in impurity concentration determination in \( SiO_2 \), too.

Then, \( C_{Na} \) profiles in thermally grown \( SiO_2 \) films, resist films on which were eliminated by \( O_2 \) plasma ashing, were measured. Figure 4 shows the in-depth \( C_{Na} \) profiles having Na pile-up in the \( SiO_2-Si \) interfaces, where the maximum \( C_{Na} \) proved to be several tens ppba. The validity of this calculation will be checked by chemical analysis of the total Na concentration in \( SiO_2 \) films using flame spectrophotometry \(^4\).

Thus, the simplified quantitative analytical procedure can be applied to the determination of \( C_{Na} \) in Si and \( SiO_2 \). It also has a possibility of determining impurity concentrations in other materials.

References