B — 5 — 6 Quantitative Analysis of Semiconductor Materials with Secondary Ion Mass Spectrometer

Masaharu OSHIMA, Izumi Kawashima, and Shizuka YOSHII*

Musashino Electrical Communication Laboratory, NTT, Musashino-shi, Tokyo 180

*Ibaragi Electrical Communication Laboratory, NTT, Naka-gun, Ibaragi 319-11

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[1], 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) and electron density (N_e) to determine ionization yields[2], so the calculation is comparably 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 1μA current.

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

$$\frac{N^+}{N^o} = \left(\frac{2\pi}{h^2}\frac{m^+ m_e}{m^o}kT\right)^{3/2}\frac{B^+ B_e}{N_e B^o}\exp\left(-\frac{E-\Delta E}{kT}\right) \qquad (1)$$

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 ΔE is energy depletion. When N^+ is assumed to be negligibly small, compared with N^o, N_e and E in Eq.(1) can be eliminated by making a ratio of N^+/N^o for two elements.

$$\frac{(N^+/N^o)_A}{(N^+/N^o)_B} = \frac{(B^+/B^o)_A}{(B^+/B^o)_B}\exp\left(-\frac{E_A-E_B}{kT}\right) \qquad (2)$$

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

$$\frac{C_A}{C_B} = \sqrt{\frac{m_A}{m_B}}\frac{I_A}{I_B}\Bigg/\frac{(B^+/B^o)_A}{(B^+/B^o)_B}\exp\left(-\frac{E_A-E_B}{kT}\right). \qquad (3)$$

This procedure was applied to the quantitative analysis of $In_xGa_{1-x}As$ 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 EPMA, 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 2×10^{-7} torr, (2) Ar^+ primary beam with O_2 admission of 1×10^{-5} torr, and (3) O_2^+ primary beam at 2×10^{-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

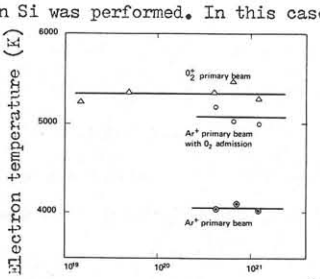

Fig.1 Electron temperatures.

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 Å) 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.

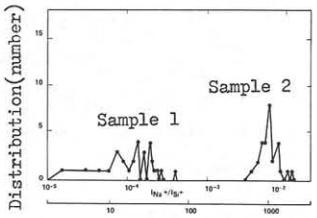

Fig.2 Distribution of C_{Na} measured with SIMS; Ar^+ primary beam,10 KV.

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 (2×10^{-7} torr) was adopted. This procedure was checked previously by the calculation of C_P in phospho-silicate glass (PSG), whose C_P was determined by spectrophotometry[3] beforehand. The electron temperature, determined from $\{I_{Si}, I_O$ and $I_{SiO}\}$, was 8630±310 K in the case of 10 KV Ar^+ beam. Using this value and $\{I_P, I_O$ and $I_{PO}\}$, 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 ppma. The validity of this calculation will be checked by chemical analysis of the total Na concentration in SiO_2 films using flame spectrometry[4].

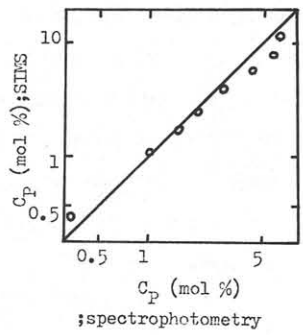

Fig.3 P concentration in PSG films determined with SIMS as a function of C_P determined by spectrophotometry.

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.

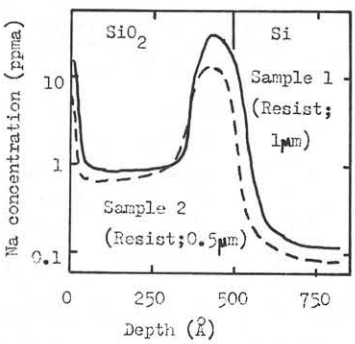

Fig.4 Na in-depth profiles in SiO_2 films on Si substrates.

References

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