

High-Precision Evaluation of Ultra-Shallow Impurity Profiles by Secondary Ion Mass Spectrometry

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As complementary metal oxide semiconductor (CMOS) processes evolve and device structures become finer, semiconductor manufacturers are having to form transistor gates with thin films 1–3 nm thick and ultra-shallow junctions of 40 nm or less. For better reliability and performance, these device structures must be controlled at the nanometer level. This requires the nanometer-level analysis and evaluation of the profiles of elements in thin films and the profiles of impurities in ultra-shallow junctions. Secondary ion mass spectrometry (SIMS) is ideal for analyzing compositions and impurity profiles. Although the latest developments in SIMS equipment do enable nanometer-level element profile analysis, this analysis method works by exploiting complex physical phenomena, so it is important to optimize the analysis conditions in order to obtain the profiles precisely. In this paper, we discuss the latest achievements in our study of analysis conditions where high precision is obtained by considering factors that degrade precision in the SIMS analysis of element profiles across surface regions ranging from 3–5 to 10–20 nm from the surface.

1. Introduction

With recent advances in the miniaturization of LSI devices, complementary metal oxide semiconductor (CMOS) transistors are now being made with ultrathin gate layers (a few nanometers thick) and very shallow junctions (40 nm or less).^{1,2)} To achieve reliable high-performance devices, it is essential to control the composition of thin films and the dopant profile at junctions and to analyze and evaluate the composition and dopant profile on the nanometer scale. A suitable technique for this sort of analysis is dynamic secondary ion mass spectrometry (SIMS).^{3,4)} Its principle is schematically illustrated in Figure 1.

One of the major benefits of SIMS is its ability to measure minute impurity concentrations of the order of parts per million or billion of any chemical element. It can also obtain

information about the profiles of elements in the depth direction because the ions emitted from the sample (secondary ions) are captured in sequence when the surface of the sample is sputtered by primary ions. In recent years, low-energy SIMS equipment has been developed to facilitate the analysis of ultra-shallow doping profiles. This

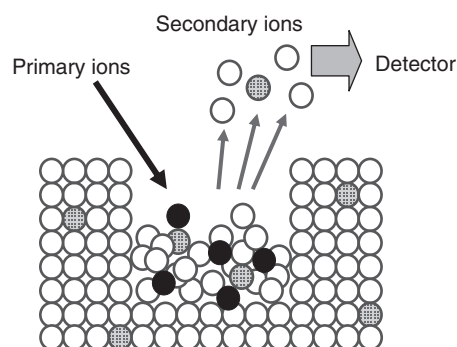


Figure 1
Principle of SIMS analysis (cross-sectional view).

equipment accelerates the primary ions to 1 keV or less (instead of the several kiloelectron volts of conventional SIMS equipment) and can achieve nanometer-order depth resolution.

However, one problem with the analysis of the region from 3–5 to 10–20 nm below the surface is that the impurity profiles obtained vary depending on the analysis conditions (primary ion species, energy, angle of incidence, oxygen flooding, etc.).⁵⁾ Moreover, some elements can sometimes undergo segregation towards the surface or deeper into the substrate during the analysis.⁶⁾ Consequently, to obtain the profiles precisely, one must perform a detailed investigation of how the profile varies with the analysis conditions and select analysis conditions under which high precision can be obtained by taking these factors into consideration.

In this paper, we discuss an analysis method established to obtain element concentration profiles with high precision in nanometer-scale SIMS analysis and evaluation.

2. Effects of native oxide film and transient region

During a subsurface evaluation, the main factors that affect the profiles are the native oxide film and the transient region affected by unstable sputtering (sputtering is initially unstable but then stabilizes).^{7,8)} Of these, the native oxide film has a different composition to that of the substrate and thus causes localized variations in the sputtering rate and secondary ionization rate. However, if the sample is bombarded with oxygen (O_2^+) primary ions at a near-normal angle of incidence, an oxide film is formed at the silicon substrate surface when a sufficient quantity of oxygen has accumulated,^{9,10)} and the sputtering becomes stable. By minimizing this transient region, one can obtain very precise data. The profile of silicon intensity in a silicon substrate bombarded with O_2^+ primary ions at an incidence angle of 0° (with respect to the surface normal) is shown in **Figure 2**. A depth of 0 nm corresponds

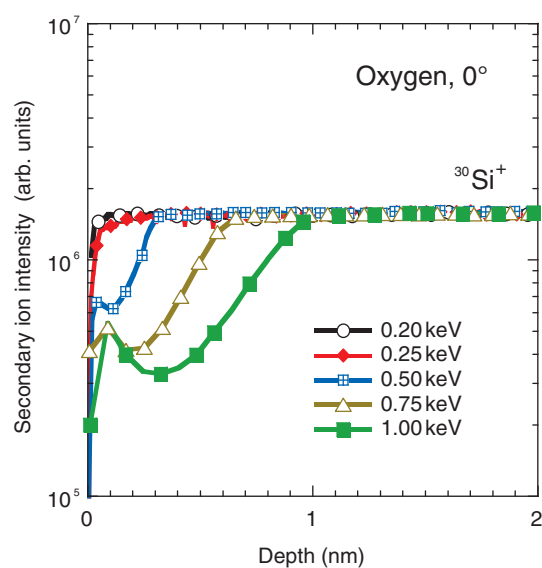


Figure 2
Variation in transient region with primary ion energy.

to the substrate surface. The region in which the silicon profile fluctuates is the transient region. In the results obtained for primary ion energy of 1.00 keV, the silicon intensity was affected more by the native oxide film closest to the surface, and after an initial drop it increased again to reach a fixed value. This occurred owing to the presence of an unoxidized region between the native oxide film and the oxide film formed by the primary ion bombardment. On the other hand, for primary ion energy of 0.20 keV, the silicon intensity remained more or less constant from the outermost surface. These results indicate that a subsurface analysis with O_2^+ primary ions accelerated to 0.20 keV at a near-normal angle of incidence gives an element profile closer to the true value with fewer effects from the native oxide film and transient region.

3. Impurity profile variation with analysis conditions

Next, taking as an example a silicon substrate implanted with arsenic (As) or gallium (Ga), we investigated how the profiles of impurity elements varied with primary ion energy. As and Ga profiles obtained in SIMS analysis with O_2^+

primary ions incident at 0° with energies ranging from 0.20–1.00 keV are shown in **Figure 3**. The As and Ga profiles obtained by high-resolution Rutherford backscattering spectrometry (HR-RBS) are also shown for reference. HR-RBS is an analysis method that works for only a limited range of elements and has a detection limit 2–3 orders of magnitude worse than SIMS. However, in recent years it has become possible to use this technique to acquire impurity profiles from shallow regions. Figure 3 (a) shows that for As, a lower primary ion energy produces results that are closer to HR-RBS: indeed, for 0.20 keV the profile is almost identical to that of HR-RBS. On the other hand, Figure 3 (b) shows that for Ga, a lower primary ion energy causes the profile to spread deeper into the substrate. The behavior observed for Ga has also been reported to occur with indium (In).¹¹⁾

4. Angle of incidence optimization

A possible cause of the spreading of Ga into the substrate is that Ga segregated deeper into the substrate from the oxide layer formed by the O_2^+ primary ions.¹²⁾ In the range of depths

to which the O_2^+ primary ions penetrate, the agitation causes a mixing layer to form, and sputter etching causes secondary ions to be emitted from the vicinity of this surface.^{3,4)} When the primary ion incidence angle is close to normal, an oxide film is formed in the mixing layer,^{9,10)} and it is thinner when the primary energy is lower.^{13,14)} Consequently, if impurity segregation does not occur, then lower primary ion energy increases the resolution in the depth direction. This is illustrated by the results for As in Figure 3 (a). However, for Ga, there was more spreading into the substrate as the primary ion energy was decreased. We assume that this was caused by a kind of segregation into the substrate from the oxide film formed by O_2^+ primary ions.

One possible factor causing this phenomenon is the reduced sputtering rate. Since the sputtering rate drops as the primary ion energy decreases,¹⁵⁾ this might have caused the Ga segregation to become more pronounced. On the other hand, the sputtering rate depends on the primary ion incidence angle, and up to about 70° , a higher incidence angle produced a higher sputtering rate.^{3,4)} We therefore investigated how the profiles varied with incidence angle for As

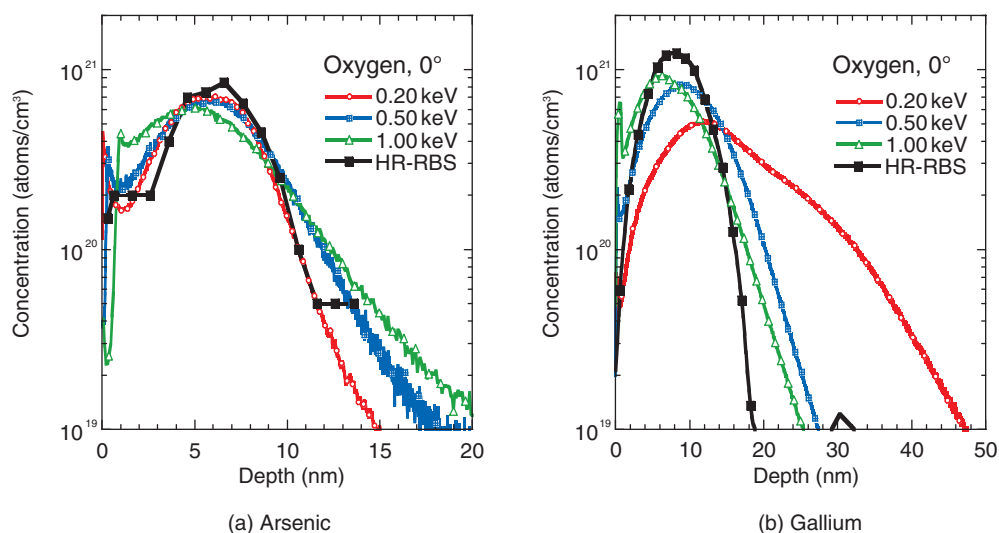


Figure 3
Variation in impurity profiles with primary ion energy.

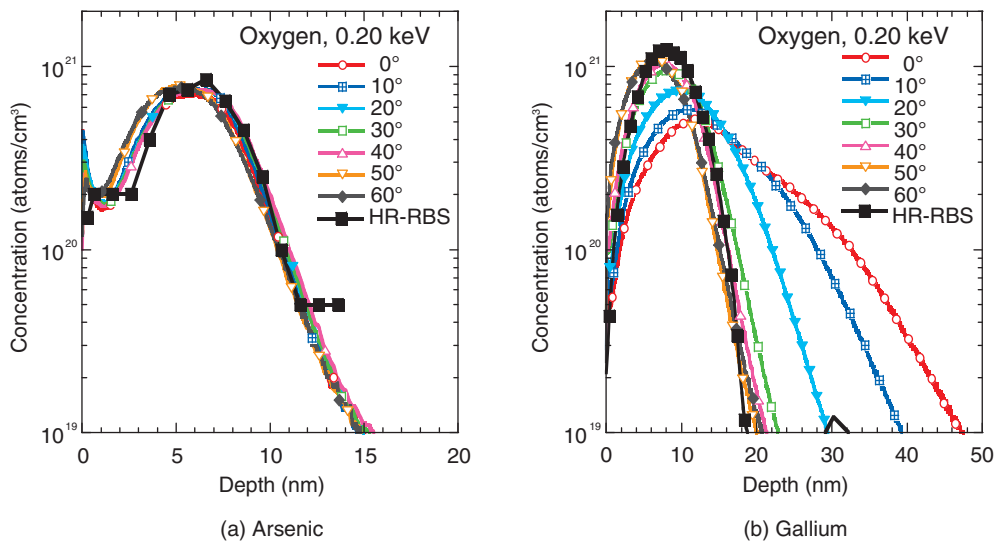


Figure 4 Variation in impurity profiles with primary ion incidence angle.

and Ga under O_2^+ bombardment with ion energy of 0.20 keV. The results are shown in **Figure 4**, together with the results obtained by HR-RBS. They show that profiles almost identical to those of HR-RBS were obtained at 0–40° for As and at around 40° for Ga, while at approximately 50–60°, the peak shifted towards the surface for both As and Ga.

The silicon profile obtained under the same analysis conditions as in Figure 4 is shown in **Figure 5**. The silicon intensity remained more or less constant over the range of 0–40°, while the profile peaked at the outermost surface above the range of 50–60°. As the incidence angle increased, the O_2^+ ions became unable to form an oxide layer because a smaller amount of oxide was deposited on the substrate.^{9),10)} On the other hand, the secondary ionization of silicon was higher in the oxide film than in the substrate.⁴⁾ Accordingly, the peak observed near the surface at incidence angles of 50–60° is thought to result from the effects of the native oxide film. The range of 50–60° is thought to correspond to the angle range where primary ions no longer form an oxide film.

From the above investigation, taking into

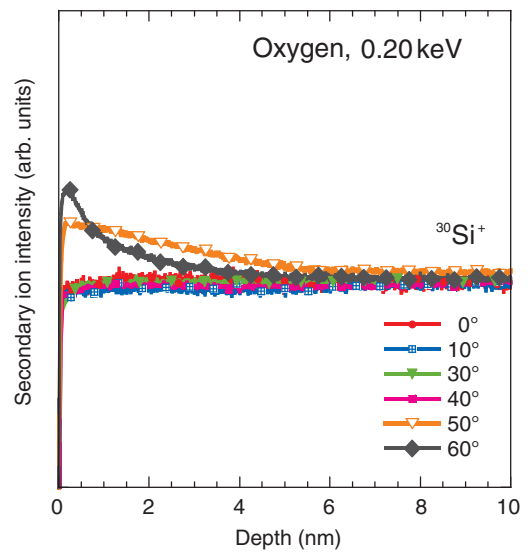


Figure 5 Variation in silicon profile with primary ion incidence angle.

consideration the effects of the native oxide film, transient region, segregation, and other factors, it seems that the best conditions for high-precision analysis are an angle of incidence of around 40° and O_2^+ ion acceleration energy of 0.20 keV.

5. Application to ultra-shallow impurity analysis

Next, we introduce an example where the optimized analysis conditions (O_2^+ primary ions acceleration of 0.20 keV and incidence angle of around 40°) were applied to the analysis of boron (B), which is used as a p-type dopant in CMOS transistors. **Figure 6** shows the B profiles obtained when ions were implanted in a silicon substrate under the following conditions (B ion acceleration energy, doping concentration, incidence angle: substrate tilt):

- 0.5 keV, $1 \times 10^{13} - 1 \times 10^{15} \text{ cm}^{-2}$, 7° (silicon substrate)
- 0.5 keV, $1 \times 10^{13} - 1 \times 10^{15} \text{ cm}^{-2}$, 0° (silicon substrate)
- 0.5 keV, $1 \times 10^{15} \text{ cm}^{-2}$, 7° (silicon substrate made amorphous by implantation of germanium (Ge) ions)

The shape of the B peak varied with the doping level in the near-surface region, and that the profile in the B tail region varied by about 1 nm depending on the tilt angle, so the B profile depended on the ion implantation conditions. Furthermore, the tail profile of B implanted into the amorphous substrate decreased rapidly, and

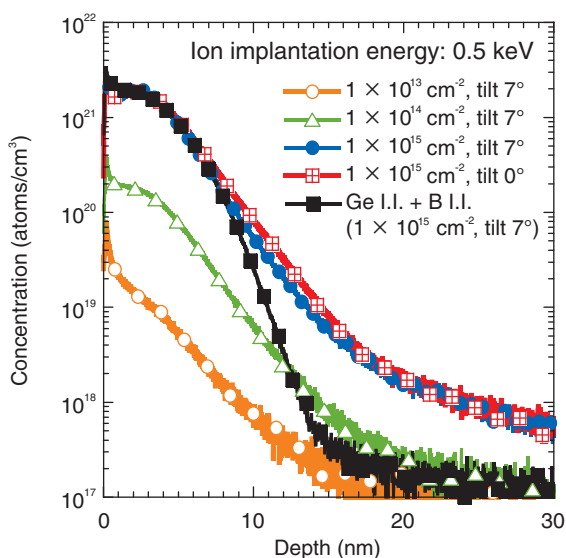


Figure 6
Change in B profile with ion implantation conditions.

that the tail profile of B seen in implantation into a silicon substrate was a channeling distribution, which is not a problem for SIMS analysis. By using optimized analysis conditions, one can ascertain differences in impurity profiles at the nanometer level caused by differences in fabrication conditions.

6. Topics for future study

It is possible to evaluate the atomic profile of any element at the nanometer level when the analysis is performed with O_2^+ primary ions accelerated to 0.20 keV and the incidence angle is around 40° . However, these conditions do not yield sufficient sensitivity for the analysis of elements that have a high negative secondary ionization rate or elements whose signals are subject to interference from molecular ions, including oxygen. Such elements are usually analyzed using cesium primary ions, for which optimized analysis conditions are also necessary, so an investigation of these conditions is a topic for future study.

7. Conclusion

In this paper, we introduced a technique for analyzing the profiles of elements in regions from 3–5 to 10–20 nm below the surface of a silicon substrate. The profile shape is affected by factors such as the transient region that exists until sputtering becomes stable, native oxide films, and impurity segregation occurring during analysis. These effects can be minimized by performing the analysis with O_2^+ primary ions accelerated to 0.20 keV with an incidence angle of around 40° . In the future, we will continue investigating methods for evaluating elements for which these conditions do not give adequate sensitivity.

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