High depth resolution SIMS analysis using metal cluster complex ion bombardment

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Abstract. SIMS depth profiles were measured using metal cluster complex ions of Ir\textsubscript{4}(CO)\textsubscript{7}\textsuperscript{+} as a primary ion beam in order to obtain high depth resolution. Depth resolution was evaluated as a function of primary ion species, energy and incident angle using a multiple boron delta-doped silicon sample. The depth resolution obtained using cluster ion bombardment was considerably better than that obtained by oxygen ion bombardment under the same bombardment condition due to reduction of atomic mixing in the depth. The best depth resolution was 0.9 nm under the bombardment condition of 5 keV, 45° with oxygen flooding, which approaches the value measured with state of the art SIMS analyses. However, depth resolution was not improved by decreasing the cluster ion energy (less than 5 keV), even though the roughness of the sputtered surface was suppressed. The limit of depth resolution improvement may be caused by a carbon cover-layer that prevents the formation of surface oxide that buffers atomic mixing. To overcome this issue, it will be necessary to eliminate carbon from the cluster ion.

1. Introduction

Junction depths of ultra-large scale integration (ULSI) are becoming shallower (~10nm). Secondary ion mass spectrometry (SIMS) has been utilized for depth profiling of impurity distribution of the shallow junction in order to develop ULSI devices. However, it is difficult to acquire accurate depth profiles of ultra-shallow junctions in advanced devices even if conventional ion beams (O\textsubscript{2}\textsuperscript{+}, Cs\textsuperscript{+}, etc.) of a few hundred eV are used, because of the degradation of the depth resolution caused by atomic mixing. One of the solutions for improving the depth resolution is cluster primary ion bombardment. Since the energy of the constituent atoms of a cluster ion that includes many atoms becomes low, the use of cluster ions with comparable energy as conventional ions is expected to reduce the length of atomic mixing. This means that the cluster ion bombardment may exceed the limit of depth resolution in the current sputter depth profiling. It should be noted that cluster ion bombardment is considered to increase the depth of atomic mixing compared to the case of atomic ion bombardment at the same energy per atom [1]. However, we discuss the depth of atomic mixing by cluster ion and atomic ion (including molecular ion with two atoms such as O\textsubscript{2}\textsuperscript{+} ion) bombardments at comparable kinetic energies of incident projectiles.
Some SIMS depth profiles using cluster ions have been reported [2, 3]. SF$_5^+$ ion bombardment with oxygen flooding obtained good depth resolutions of 0.53 nm and 1.35 nm [2]. However, with SF$_5^+$ there is a problem concerning long-time running due to corrosion of the ion gun. With regard to C$_{60}^+$ ion bombardment, it is difficult to utilize C$_{60}^+$ ions at impact energies below ~10 keV for silicon sputtering because of carbon deposition [3]. For these reasons, we have developed a prototype cluster ion source that emits the metal cluster complex ion Ir$_4$(CO)$_7^+$, because the cluster ion has 18 atoms including heavy atoms of iridium, and its molecular weight is very large (964.9) [4-10]. In view of these features, this cluster ion is expected to reduce the thickness of the mixed layer, thus providing high depth resolution in SIMS analysis compared to the other cluster ions and conventional ions.

In this paper, SIMS analyses of a boron delta-doped silicon sample were carried out using the cluster ions under oxygen flooding condition, and the influence of primary ion species, energy and incident angle on depth resolution was investigated. The result showed decreasing primary ion energy improved depth resolution, and an appropriate cluster ion bombardment condition with a good depth resolution was found [7]. Furthermore, we encountered a limit to the improvement of the depth resolution at less than 5 keV. Hence, the causes and a solution of the issue concerning the depth resolution were investigated [10].

2. Experimental

SIMS measurements were carried out with an Atomika 4000 SIMS instrument equipped with the cluster ion (Ir$_4$(CO)$_7^+$) source. Details of the ion source mechanics and performance of the cluster ion beam have been described elsewhere [5, 8]. The cluster ions with impact energies from 3 keV to 10 keV, incident angles from 0° to 60° and a beam diameter of ~150 µm [6] were scanned over an approximately 1-mm$^2$ area on the sample surface and $^{11}$B$^+$ ions ejected from the center of the sputter crater (an approximately 250 × 250 µm$^2$ area) were detected. During the SIMS measurements, oxygen flooding with a pressure of 1 × 10$^{-6}$ Torr was used (the base pressure of the SIMS chamber was 1 × 10$^{-9}$ Torr when the cluster ion source was operated) to oxidize the sputtered silicon surface, and to increase secondary ion yields and suppress atomic mixing [11]. For the purpose of evaluating the depth resolution in our SIMS analysis, a multiple boron-delta-doped silicon sample with four layers having a 5-nm interval and four layers having a 20-nm interval was measured [12]. The area density of boron atoms for one delta-doped layer was approximately $1 \times 10^{14}$ atoms/cm$^2$. Depth scales for the measured depth profiles were calibrated using the distance of the known interval of the delta-doped sample in the constant sputtering rate region. After sputtering, surface topographies of crater bottoms were measured with an atomic force microscope (AFM, Dimension 3000 Nanoscope IIIa by Digital Instruments), compositional depth profiles of the surfaces modified by the ion bombardment were measured with a high resolution Rutherford backscattering spectrometer (HR-RBS, HRBS500 by Kobe Steel), and chemical information of atoms at the sputtered surface was analyzed with an X-ray photoelectron microscope (XPS, Quantum-2000 by ULVAC-PHI).

3. Results and Discussion

3.1. High depth resolution analyses using the cluster ion (Ir$_4$(CO)$_7^+$)

SIMS depth profiles of the boron delta-doped sample were measured by the cluster ion with the energy of 10 keV, incident angle of 45° and with and without oxygen flooding. Depth resolution ($1/e$ decay length) from the trailing edge of the eighth delta layer from the delta-doped sample surface under the oxygen flooding (2.2 nm) is significantly better than that without flooding (5.0 nm). The oxygen flooding also increased the boron ion yield by a factor of 40. Gillen et al. explained improvement of the depth resolution in SF$_5^+$ bombardment by using oxygen flooding, which causes the suppression of surface roughness [2]. However, in the cluster ion case, sputtered surface roughness (root mean square (RMS) roughness by AFM measurements) with oxygen flooding (0.4 nm) is even larger than that without flooding (0.3 nm). Therefore, the improvement of the depth resolution by oxygen flooding is not caused by the topography change, but may be caused by the silicon oxide growth on the sputtered
surface, which buffers atomic mixing [11]. Subsequently, the following depth profiles were measured with oxygen flooding condition.

In figure 1, SIMS depth profiles of the boron delta-doped sample are plotted, which were measured with the cluster ion and oxygen ion \((O_2^-)\) with the energy of 10 keV, incident angle of 45° and oxygen flooding. Obviously depth resolution measured at the fifth delta-layer by the cluster ion bombardment (2.2 nm) is better than that by oxygen ion bombardment (4.7 nm). Roughness of the two sputtered surfaces is not large (0.4 nm by cluster ion and 0.2 nm by oxygen ion bombardment) and the influence on the depth resolution is negligible. The first and second delta-layer profiles by the cluster ion bombardment were broadened by sputtering rate change [10]. The cluster ion energy was decreased to 5 keV in order to improve depth resolution. Figure 2 shows the dependence of depth resolution on the energy of projectile ions, both the cluster and oxygen ions. The depth resolution \((1/e\) decay length) was evaluated from the trailing edge of the fourth delta layer from the delta-doped sample surface (the fifth delta layer in the oxygen ion case because of coalescence of 5-nm interval delta-layer profiles). Decreasing the energy of both projectiles causes improvement in depth resolution at comparable incident energies. The depth resolution obtained by cluster ion bombardment is certainly better than that obtained by oxygen ion bombardment. The best depth resolution was 0.9 nm under the condition of 5 keV, 45° with oxygen flooding in this experiment. The value approaches the depth resolution (0.6 ~ 0.7 nm) measured by state of the art SIMS analysis (250-eV oxygen ion with normal incidence in Atomika 4500 instrument) using the same boron delta-doped sample.

![Figure 1](image1.png)

**Figure 1.** SIMS depth profiles of the boron delta-doped sample measured by the cluster ion and oxygen ion with the energy of 10 keV, the incident angle of 45°, and oxygen flooding.

![Figure 2](image2.png)

**Figure 2.** Depth resolution \((1/e\) decay length) as a function of energy of the cluster ion and oxygen ion with the incident angle of 45° and oxygen flooding.

In order to investigate the reason for the improvement, depth profiles of target atom (silicon) displacement collisions by the bombardment of the projectiles, which are the cluster ion \((Ir_4(CO)_{7}^{+})\) and oxygen ion \((O_2^-)\), were calculated using the SRIM-2003 simulation software [13]. Displacement collision profiles by the cluster ion (iridium) bombardment were located much closer to the surface than those by oxygen ion bombardment at the same kinetic energy. Decreasing the energy of ion bombardment is also effective for making the displacement collision profile shallow. Therefore, since the depth resolution dependence on a species of projectile and its kinetic energy is caused by atomic mixing, the use of the cluster ions with low energy evidently provides high depth resolution for SIMS depth profiles [7].

### 3.2. Causes of the limit of the depth resolution improvement

At less than 5 keV of the cluster ion bombardment, however, the depth resolution was degraded with decreasing energy, as shown in figure 2. Figure 3 shows that RMS roughness of the sputtered surface
with various energies of the cluster ions at 45° incidence, which was measured by AFM. The lengths in the figure indicate sputtered depths. It is confirmed that the sputtered surface by the 3 to 6 keV cluster ions have significant roughness of more than 0.8 nm, and the roughness grew in the depth direction. Comparing depth profiles of the top four boron delta-doped layers measured with the 3-keV and 5-keV cluster ions at 45° incidence in figure 4, the roughness must start to grow at a shallower depth with lower energy ion bombardment, since the profiles of the third and the following delta layers by the 3-keV cluster ion bombardment was broadened. The first delta-layer profile by the 5-keV cluster ion bombardment was broadened by sputtering rate change [10], not by the surface roughness.

Searching for sputtering conditions of the cluster ions that provide small roughness of the sputtered surface in which better depth resolution should be achieved, RMS roughness of the sputtered surface and the depth resolution at the fourth boron delta-doped layer were measured, and they were plotted against the incident angle of the cluster ions in figures 5 (a) and (b), respectively. We found that surface roughness was suppressed in the case of an incident angle of less than 40°. Nevertheless, the

![Figure 3. RMS roughness of a sputtered surface that depends on energy of the cluster ion with incident angle of 45°. The lengths in the figure indicate sputtered depths.](image)

![Figure 4. Depth profiles of the boron delta-doped sample measured by the cluster ions with energies of 5 keV and 3 keV, incident angle of 45° and oxygen flooding. The figure shows only the top of four delta layers.](image)

![Figure 5. (a) RMS roughness of a sputtered surface measured by AFM and (b) depth resolution at the forth delta-doped layer (b) that depends on the incident angle of the cluster ions.](image)
depth resolution did not improve although the cluster ions with low energy (less than 5 keV) were used. Increase of the depth resolution by decreasing incident angle (0° ~ 35°) may be caused by an increase of atomic mixing normal to the surface direction. However, it is surprising that there is little or no improvement of the depth resolution by decreasing the cluster ion energy.

In order to investigate the reason for the limit of depth resolution improvement, composition depth profiles of silicon surfaces, which were sputtered with 10 keV cluster ions at 45° and 60° incidences under oxygen flooding condition, were measured with HR-RBS. The reason for using the 10-keV cluster ions (not for using less than 5-keV ions) is that large area sputtering (~2 mm square) for HR-RBS measurements needs high-energy cluster ions with high sputtering yield. The sputtered depths by the cluster ions were 40~50 nm, where sputter equilibrium was obtained. The HR-RBS compositional depth profile of the 60°-sputtered surface in figure 6 (a) indicated that the top surface was composed of silicon dioxide with thickness of ~4 nm, and iridium from the cluster ion was placed at the interface between the silicon dioxide film and the substrate. The peak position of iridium derived from the bombarded cluster ion is slightly deeper than that calculated by SRIM-2003 [13]. It may be caused by the Gibbsian segregation of iridium to the interface during the cluster ion bombardment, because of high electronegativity of iridium [14].

In the 45°-sputtered surface as shown in figure 6 (b), the HR-RBS profile showed that the thickness of the silicon oxide was almost the same as that in the 60°-sputtered surface, however, the stoichiometric coefficient of the oxide is clearly less than 2.0, and furthermore ~40 at% carbon existed at the top of the surface. XPS measurement showed that some part of the carbon (~15%) has a Si-C bond. The carbon measured by XPS includes contamination from the air during transportation from SIMS instrument to XPS instrument, so that the ratio of carbon with Si-C bond to the total carbon derived from the cluster ion may be higher than 15%. The cover-layer of carbon including SiC can suppress taking of oxygen to the sputtered surface from flooding O₂ and thus prevents the growth of a surface oxide layer. In fact, the HR-RBS profiles in figures 6 (a) and (b) show that the total amount of oxygen for the 45°-sputtered surface is significantly less than that for 60°. The difference of carbon contents between 60° and 45° incidence must be related to sputtering yield. Therefore, low sputtering yield caused by lower energy and smaller incident angle must increase the content of carbon derived from the cluster ion on the sputtered surface. The cover-layer of carbon can suppress surface oxide growth that buffers atomic mixing [11], and therefore, it can degrade the depth resolution. Moreover, we found that the 2 keV, 0° cluster ion bombardment yields the deposition of iridium [6]. The carbon cover-layer results in a drastic decrease of the sputtering yield, because carbon has a large surface binding energy of 7.37 eV [6].

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**Figure 6.** HR-RBS compositional depth profiles of the sputtered surface by the cluster ions (a) with 10 keV, 60° and (b) with 10 keV, 45° under oxygen flooding condition. The arrows in the figures indicate the calculated peak positions of iridium profiles by SRIM-2003.
We showed that decreasing of CO ligand number in the cluster ion \( \text{Ir}_4(\text{CO})_n^+ \) increased the sputtering yield \([9]\). Therefore, in order to prevent formation of the carbon cover-layer to improve the depth resolution, the use of \( \text{Ir}_4^+ \) cluster ion that does not include carbon atoms may be effective. The \( \text{Ir}_4^+ \) cluster ion is also expected to increase the sputtering yield, and thereby improve the depth resolution further, because cluster ions with lower energy can be used. \( \text{Ir}_4^+ \) cluster ions are produced by electron ionization of \( \text{Ir}_4(\text{CO})_{12} \) \([5]\), and we intend to develop a new ion source for emitting \( \text{Ir}_4^+ \) cluster ions.

4. Conclusion

Using a metal cluster complex ions of \( \text{Ir}_4(\text{CO})_7^+ \), SIMS depth profiles of a multiple boron delta-doped sample were measured with the cluster ion impact energies from 3 keV to 10 keV and incident angles from 0° to 60°. Depth resolution was evaluated from the 1/e decay length of the delta layer profiles and roughness of the sputtered surface was measured with AFM. The cluster ion bombardment provided better depth resolution than that by oxygen ion bombardment at comparable impact energies and impact angles. The best depth resolution of 0.9 nm was obtained under the cluster ion bombardment condition of 5 keV, 45° with oxygen flooding due to reduction of atomic mixing. At less than 5-keV ion bombardment, the depth resolution was not improved by decreasing the cluster ion energy, even though the roughness of the sputtered surface was suppressed with using small incident angle conditions. HR-RBS measurements showed that the bombardment condition with low sputtering yield formed a carbon cover-layer on the sputtered surface. The limit of depth resolution improvement may be caused by the cover-layer that prevents the formation of surface oxide that buffers atomic mixing. The use of cluster ion that does not contain carbon may solve the issue.

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