UDC 669 . 782 : 621 . 382 : 593 . 219

Gettering of Metallic Impurities in SIMOX Wafers

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Abstruct

The gettering mechanism of copper was studied as an example of metallic impurities of SIMOX wafers. The authors developed a dual ion beam SIMS (Secondary Ion Mass Spectrometry) for quantifying distribution of the buried oxide/silicon boundaries along the depth of SIMOX wafers and the developed method successfully identified gettering sites. Changes during the heat treatment process suggest that priority sites of gettering are stacking fault tetrahedra (SFT) and that excessive copper segregates at the buried oxide/silicon substrate boundaries or around the SFTs.

1. Introduction

Gettering refers to the operation whereby heavy metal elements, such as Fe and Cu, that adversely affect device characteristics are confined outside of the device formation region. Gettering is designed to form gettering sites in given positions in a wafer and to absorb impurities to these sites by annealing in the device manufacturing process. SIMOX wafers have a SOI (silicon on insulator) structure and are considered to have gettering behavior different from that of conventional wafers. Zhang et al. have reported that Cu is gettered at the buried oxide (BOX)/substrate interface[1)], while Jablonski et al. have reported that Cu gettering sites are stacking fault tetrahedra (SFTs)[2)].

The purpose of this study was to clarify the gettering capability of SIMOX wafers by focusing attention on Cu as an example of contaminant element. It was also designed to estimate gettering sites on which consensus had not been reached in past papers. The silicon/oxide interface is a system where the sensitivity of SIMS exceedingly changes, and it is considered difficult to ensure the quantifiability of the silicon/oxide interface by SIMS. For the purpose of assuring this quantifiability, a new dual-ion beam method was developed to verify its validity by using actual samples.

2. Experiments

2.1 Sample preparation

Each sample was prepared by etching the surface oxide layer of a SIMOX wafer, applying a copper-containing aqueous solution to the top or bottom surface of the SOI layer, and quantitatively contaminating the surface with copper to a concentration of 1E13 atoms/cm^2 by using the spin coating process. Using an infrared image furnace, the sample was annealed in a 100% nitrogen, 1 atm ambient at 900°C. To estimate the diffusion coefficient of Cu in the BOX layer, the samples were prepared by changing the annealing time to 1, 2, 4 and 8 h, and were evaluated for the depth profile of Cu by secondary ion mass spectroscopy (SIMS).

To enhance the accuracy of quantification at the BOX/substrate interface, the SOI and BOX layers were sequentially removed by using a 5% hydrofluoric acid (HF) aqueous solution and a 40% potassium hydroxide (KOH) aqueous solution.

The dual-ion beam method was evaluated by using as samples the SIMOX wafers that were implanted with $^{54}Fe^+$ at 300 keV and 1E15 ions/cm^2.

2.2 Development of dual-ion beam method

The dual ion beam method improves the secondary ionization efficiency of the sample surface with a low-energy active ion beam, and efficiently sputters the sample surface with a high-energy ion beam, as shown in **Fig. 1**. Reducing the oxygen ion beam energy increases the sample surface coverage by oxygen, which in turn sharply improves the secondary ionization efficiency. On the other hand, the sputtering yield drastically drops, and the SIMS sensitivity suffers as well. For example, when O_2^+ is used as the primary ion, the sputtering yield at a beam energy of 250 eV drops to 1/50 to 1/60 of that at 2 keV as shown in **Fig. 2**[3)]. To make up for this condition, the second Cs^+ beam efficiently sputters the sample surface. This study tried to completely control the matrix effect by supplying a sufficient amount of oxygen to the sample surface layer with a low-energy oxygen ion beam.

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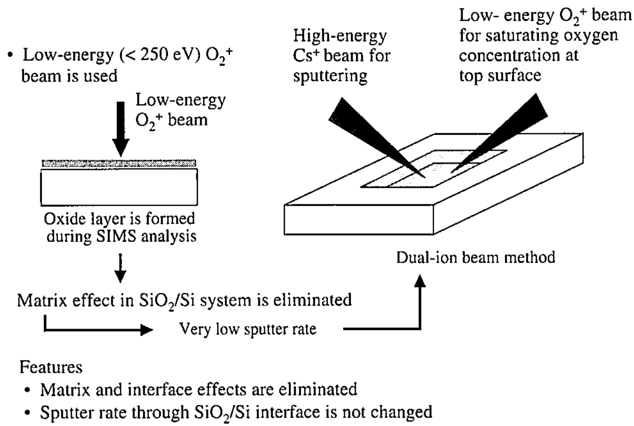


Fig. 1 Principle of dual-ion beam method

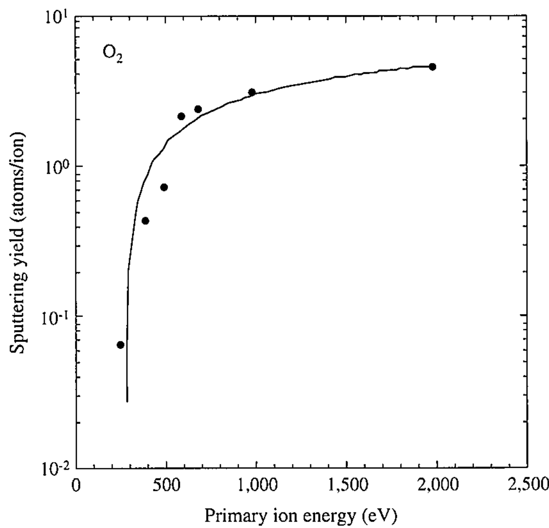
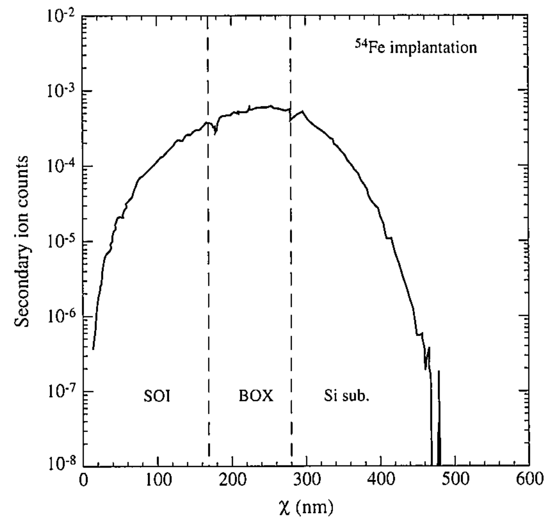


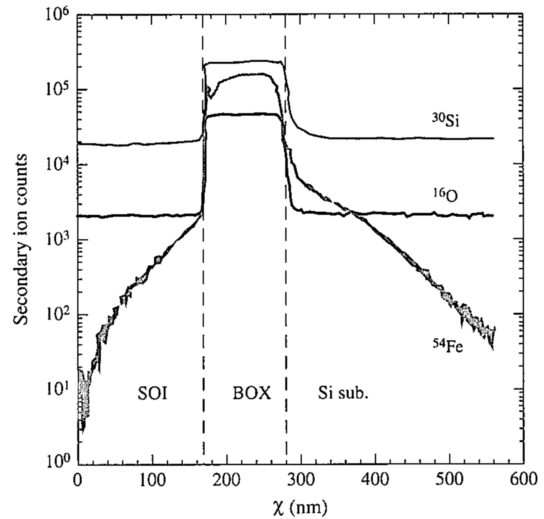
Fig. 2 Primary ion (O_2^+) energy dependence of sputtering yield

Using as the sample a SIMOX wafer implanted with $^{54}Fe^+$ ions, we studied the dual-ion beam optimum conditions for the quantification of sputtering in the SIMOX wafer. To clarify the oxygen enrichment effect in the dual-ion beam method, we evaluated the dual-ion beam method with the $^{18}O_2^+$ beam using the $^{18}O_2$ gas. The Monte Carlo simulation results of the ion implantation distribution of the prepared sample is shown in **Fig. 3**(a). It is evident that ^{54}Fe is distributed throughout the SOI/BOX/substrate interfaces of the SIMOX wafer. The depth profiles obtained by using the conventional O_2^+ beam are shown in Fig. 3(b). When the O_2^+ beam alone is used (acceleration voltage of 1 keV, 30 nA, raster scan area of 300 μm), the $^{16}O^+$ secondary ion intensity in the BOX layer exhibits a value larger by more than one order of magnitude. It is evident that the $^{54}Fe^+$ sensitivity is also enhanced by more than one order of magnitude as compared with the Monte Carlo simulation results of Fig. 3(a).

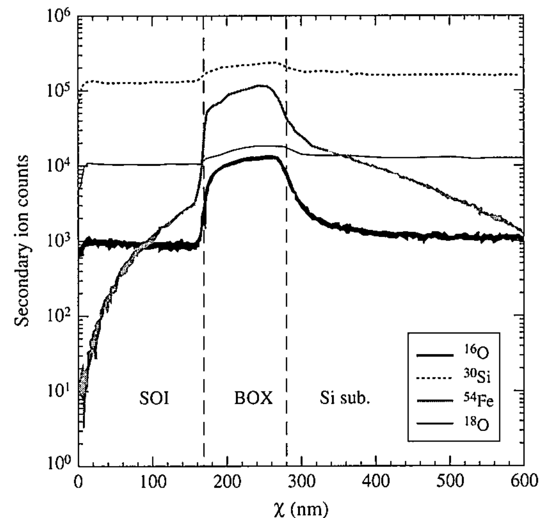
The evaluation results of the sample by the dual ion beam method (O_2^+ beam: 300 eV, 100 nA, raster scan area of 200 μm, Cs^+ beam: 10 keV, 1 nA, raster scan area of 300 μm) are shown in Fig. 3(c). The $^{18}O^+$ secondary ion intensity is almost uniform throughout the SOI/BOX/substrate interfaces. The SIMS conditions under which oxygen is uniformly present in the depth direction and the matrix effect



(a) Monte Carlo simulation



(b) O_2^+



(c) Dual-ion beam method

Fig. 3 SIMS depth profile analysis results of ^{54}Fe implanted into SIMOX wafers

is eliminated were thus established. At the same time, observation of the $^{16}O^+$ secondary ion intensity helped to clearly locate the SOI/BOX interface and the BOX/substrate interface. The enhancement of the $^{54}Fe^+$ secondary ion intensity in the BOX could not be fully controlled, but the distribution of interfaces between different phases could be evaluated more quantitatively than by the conventional O_2^+ ion beam method.

3. Results and Discussion

Fig. 4 shows the depth profiles of Cu present throughout the SOI/BOX/substrate interfaces as analyzed by the above-mentioned dual-ion beam SIMS method. It is evident that 4 h of annealing drove Cu trough the SOI and BOX layers, and concentrated Cu near the BOX/substrate interface. More Cu is detected near the BOX/substrate interface in the sample contaminated with Cu from the top surface than in the sample contaminated with Cu from the bottom surface. The Cu concentration peaks at the BOX/substrate interface in the sample contaminated with Cu from the bottom surface. There is the high possibility that Cu in the substrate segregated to the BOX/substrate interface during heat treatment.

Jablonski et al. have reported that Cu is highly concentrated from the BOX/substrate interface to the bulk of the substrate and that very large strains are present at the BOX/substrate interface or high-density gettering sites are distributed from the interface to the substrate. A SIMS analysis problem may also be considered. That is, there is the possibility that the depth profile is distorted by the measurement made to compensate for the surface charge by electron beam bombardment. To avoid the effect of this charge-up, we removed the SOI and BOX layers by chemical etching, and analyzed the substrate just below the BOX layer for Cu in the depth direction.

Fig. 5 shows the SIMS depth profiles of Cu in the substrate just below the BOX layer as obtained by the SIMS measurements made on the samples after removal of the SOI and BOX layers. Cu exhibits a depth profile peaking at a depth of about 100 nm below the BOX layer after 1 h of annealing at 900°C, and the Cu concentration at the BOX/substrate interface is extremely low. To know the reason why Cu exhibits such a depth distribution, the cross-section of each sample by transmission electron microscopy (TEM) was examined.

Fig. 6 shows the cross-sectional TEM image of a sample from the BOX layer to the substrate (×100,000). Contrast, probably due to stacking fault tetrahedra (SFTs), was detected just below the BOX layer. This depth is about 100 nm and approximately coincides with the peak position of Cu observed in the SIMS depth profile for the diffusion time of 1 h.

Fig. 7 shows the depth profile of oxygen from just below the BOX layer to the substrate as measured by SIMS. It is evident that an oxygen-denuded zone is present from 5 to 10 μm below the BOX layer. The measurement made to 10 μm beneath the BOX/substrate interface did not observe appreciable oxygen precipitation at all. The possibility of gettering by oxygen precipitates, which are major intrinsic gettering sites, is considered to be low. Therefore, Cu is esti-

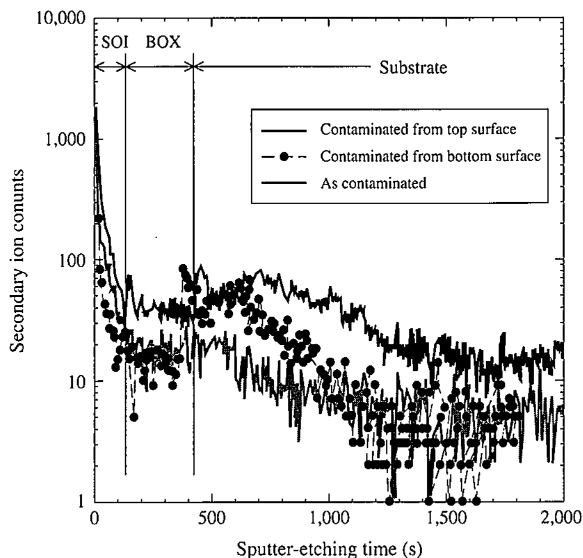


Fig. 4 Depth profiles of Cu applied to sample surface and measured by SIMS: SIMOX wafer contaminated with Cu from top surface and given 900°C/4h anneal, SIMOX wafer contaminated with Cu from bottom surface and given 900°C/4h anneal, and SIMOX water as contaminated with Cu

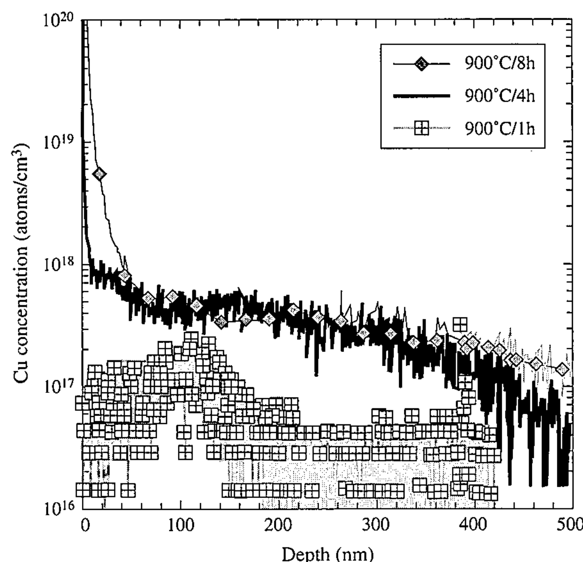


Fig. 5 Depth profiles of Cu gettered below BOX (annealing time: 1, 4, 8 h)

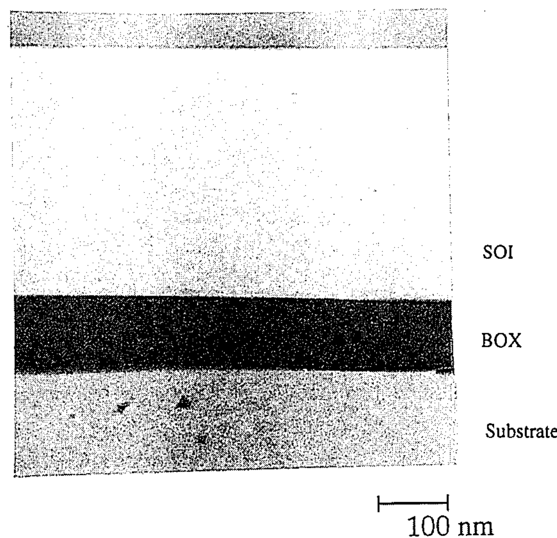


Fig. 6 Cross-sectional TEM image of BOX/substrate interface

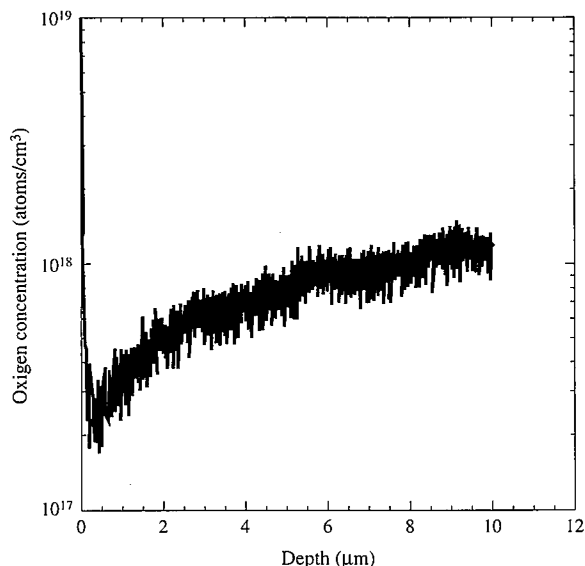


Fig. 7 SIMS depth profile of oxygen below BOX

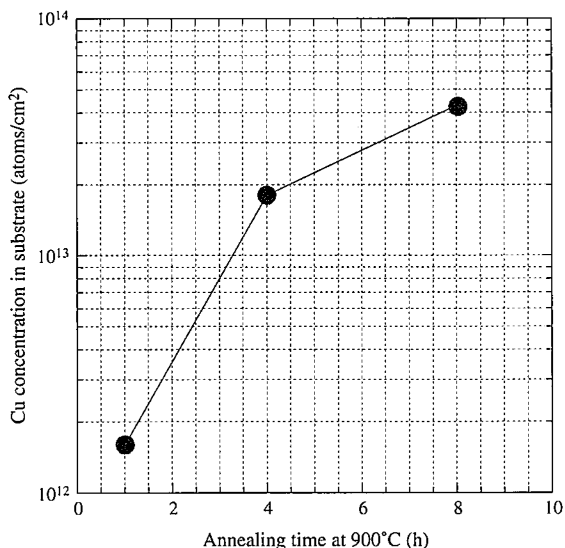


Fig. 8 Annealing time dependence of total amount of Cu reaching substrate below BOX after annealing at 900°C for 1, 4, or 8 h

mated to be gettered by SFTs. This agrees with the report of Jablonski et al[2].

As the annealing time increases to 4 and 8 h, the distribution of Cu expands to 500 nm or more below the BOX layer. Also, Cu is segregated to a very high concentration at the BOX/substrate interface. This may be explained as follows: Cu passes the BOX layer in a larger amount, resulting in the shortage of SFTs as preferred gettering sites. Consequently, Cu is segregated to strain-containing regions around the SFTs and to the BOX/substrate interface.

Fig. 8 shows the diffusion time dependence of the total amount of the contaminant Cu reaching the substrate from the SOI surface. The total amount of Cu introduced from the surface through the SOI and BOX layers into the substrate increases exponentially with increasing diffusion time in the diffusion time range of 1 to 4 h and increases linearly with increasing diffusion time in the diffusion time range of 4 to 8 h. If the concept of flat plate transmission is introduced here, the value of 5×10^{-11} cm^2/s is obtained as the apparent diffusion coefficient (including both the SOI and BOX layers) for Cu present on the SOI surface to diffuse through the SOI and BOX layers and reach the substrate. This value is regarded as the diffusion coefficient of Cu practically in the BOX layer, because the diffusion coefficient of Cu in Si is very large.

The diffusion coefficient of 5×10^{-11} cm^2/s is about three orders of magnitude larger than the diffusion coefficient of 3×10^{-14} cm^2/s that Kononchuk et al[4]. obtained for Fe in the BOX layer. This is probably because the diffusion coefficient of Cu in the BOX layer is predicted to be much larger than the diffusion coefficient of Fe in the BOX layer or is increased under the influence of oxygen-depleted defects existing to a high density in the BOX layer[5].

4. Conclusions

Development of the dual-ion beam method enabled the quantification of the SOI/BOX/substrate interfaces by SIMS, which was difficult to perform in the past. From the SIMS and TEM observation results just below the BOX layer, it was estimated that preferred Cu gettering sites are SFTs and that the maximum allowable amount of Cu to be gettered by SFTs is a level of 1E12 atoms/cm^2. When the amount of Cu to be gettered by SFTs exceeds this level, Cu begins to be segregated to the BOX/substrate interface or gettered by the strain fields around the SFTs. From the diffusion time dependence of the amount of Cu detected in the silicon substrate, the value of 5×10^{-11} cm^2/s was obtained as the apparent diffusion coefficient (including both the SOI and BOX layers) for Cu present on the surface to reach the substrate through the SOI/BOX interface.

This study has found the presence of gettering sites just below the BOX layer in the SIMOX wafers. The surface metal contamination in an amount of 1E12 to 1E13 atoms/cm^2 is large enough to degrade the gate oxide integrity (GOI) of the SIMOX wafers. Efficient gettering of this surface metal contamination will allow the SIMOX wafers to be strategically differentiated from the competing bonded SOI wafers.

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