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Proximity gettering of silicon wafers using CH₃O multielement molecular ion implantation technique

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We investigated the fundamental characteristics of a CH₃O-ion-implanted silicon epitaxial wafer with our previously developed multielement molecular ion implantation technique and compared this technique with a conventional implantation technique, i.e., “carbon cluster ion implantation”. We found that the CH₃O ion projection range has a 10-fold higher oxygen concentration than the carbon cluster ion projection range after epitaxial growth. We also found 50 nm silicon {111} stacking faults in the CH₃O ion projection range. Such defects were not observed in the carbon cluster ion projection range. From nickel gettering test results, proximity gettering of nickel contaminations by CH₃O ion implantation was found to be more effective than that by C₂H₃ ion implantation. Therefore, we speculate that the CH₃O ion projection range improves the gettering capability of metallic impurity contaminants through the formation of complex point defects formed by vacancies and that oxygen implanted at a high concentration and silicon {111} stacking faults are new gettering sinks. © 2018 The Japan Society of Applied Physics

1. Introduction

Advanced CMOS image sensors currently require high imaging sensitivity and device performance. However, one of the most important technological issues is the removal of metallic impurity contaminants from the device active range during CMOS image sensor fabrication.^{1–5} To address this issue, it is strongly required that a silicon wafer should have a high gettering capability.

To import the gettering capability of silicon epitaxial wafers, intrinsic gettering (IG) and extrinsic gettering (EG) techniques are mainly used in CMOS device fabrication. Figure 1 shows a schematic image of these gettering techniques. The IG technique involves the formation of an oxygen precipitate as a gettering sink during device heat treatment.^{6–9} The EG technique involves the deposition of a polysilicon layer used as a gettering sink on the back of a silicon wafer.^{10,11} However, the temperature of the current device fabrication process continuously decreases year by year. In the case of the IG technique, the oxygen precipitate cannot form sufficient amounts of gettering sinks. In the case of the EG technique, the polysilicon layer is far from the device active region. Thus, it is difficult to diffuse the metallic impurity to the gettering sinks. For these reasons, a conventional gettering technique cannot perform sufficient gettering in the CMOS image sensor manufacturing process.

To solve this technical issue, we developed proximity gettering wafers called “carbon-cluster-ion-implanted epitaxial silicon wafers”.^{12–16} In our previous study, we demonstrated that carbon-cluster-ion-implanted epitaxial silicon wafers have three useful characteristics for advanced CMOS image sensors, namely, strong gettering capability for metallic impurity contaminants, out-diffusion barrier effect on oxygen impurities from a silicon substrate, and hydrogen passivation effect.¹⁴

Although these wafers are useful for improving the performance of CMOS image sensors, the demand for high-performance wafers is expected to continue in the future.

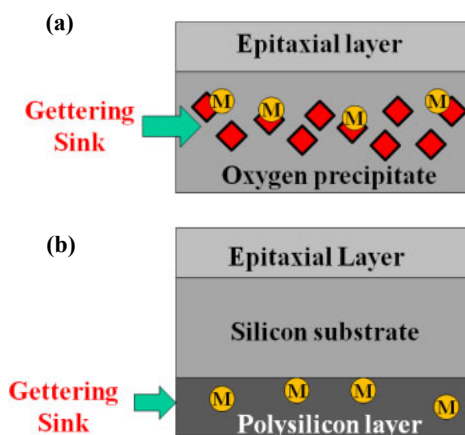


Fig. 1. (Color online) Simplified schematic of (a) IG and (b) EG techniques.

Therefore, silicon epitaxial wafers require a much higher metallic impurity gettering capability. To obtain epitaxial silicon wafers with higher gettering capability, we focused on ion implantation techniques.

In general, it is known that the defects formed by ion implantation function as gettering sinks. Kuroi and coworkers reported on a gettering technique involving high-energy ion implantation using various elements such as oxygen, silicon, and boron.^{17–19} The origin of this gettering sink is the secondary defect induced by high-energy ion implantation. On the other hand, Okuyama et al. reported that the carbon cluster ion implantation does not form secondary defects in the projection range after heat treatment.¹⁶ The gettering sink induced by carbon cluster ion implantation is a carbon and interstitial silicon complex formed in the carbon cluster ion projection range. From these studies, it is considered that ion implantation techniques can form various types of gettering sinks depending on implantation elements or conditions.



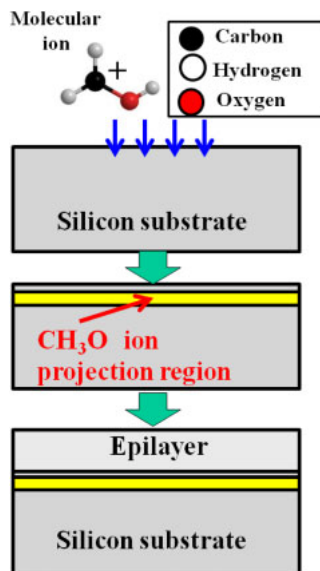


Fig. 2. (Color online) Fabrication process and characteristics of carbon-cluster-ion-implanted silicon epitaxial wafer.

The conventional carbon cluster ion implantation technique implants cluster ions consisting of carbon and hydrogen. To improve this technique, we have developed a new molecular ion implantation technique called “multi element molecular ion implantation”.²⁰⁾ This technique characterized that implant molecular ions consist of three elements with one additional element in addition to carbon and hydrogen. In this article, we use CH_3O ion implantation. We expect that a CH_3O -ion-implanted silicon epitaxial wafer will have a higher metallic impurity contamination gettering capability with the formation of new defects or complexes, while retaining the characteristics of conventional carbon-cluster-ion-implanted epitaxial silicon wafers.

In this study, we demonstrate the diffusion behavior of implanted elements and the defect formation behavior in the CH_3O ion projection range after epitaxial growth, and also the gettering capability test on nickel.²⁰⁾

2. Experimental methods

2.1 Sample preparation

Figure 2 shows the sample preparation process used in this study. 12 in. n-type (100) phosphorus-doped Czochralski (CZ) silicon single-crystal wafers were implanted with CH_3O multielement molecular ions and carbon cluster C_2H_3 ions at room temperature. The CH_3O and C_2H_3 ion implantations used Nissin's ion implanter “CLARIS®”.^{21–23)} The implantation energy was 80 keV/ion. The implantation dose of the CH_3O ions was 5.0×10^{14} – 2.0×10^{15} ions/cm² converted to a carbon dose of 5.0×10^{14} – 2.0×10^{15} carbon atoms/cm². The implantation dose of C_2H_3 ions was 3.75×10^{14} – 5.0×10^{14} ions/cm² converted to a carbon dose of 7.5×10^{14} – 1.0×10^{15} carbon atoms/cm². This carbon dose is the same as 7.5×10^{14} – 1.0×10^{15} ions/cm² in CH_3O ions. The ion beam currents of CH_3O and C_2H_3 were the same, i.e., 550 μA . The epitaxial growth of the samples was conducted after CH_3O ion and carbon cluster ion implantation. The epitaxial thickness was 9.0 μm . For the nickel gettering test, the sample wafers were contaminated with nickel metallic impurities (2.5×10^{13} atoms/cm²) by spin coating with a metallic-

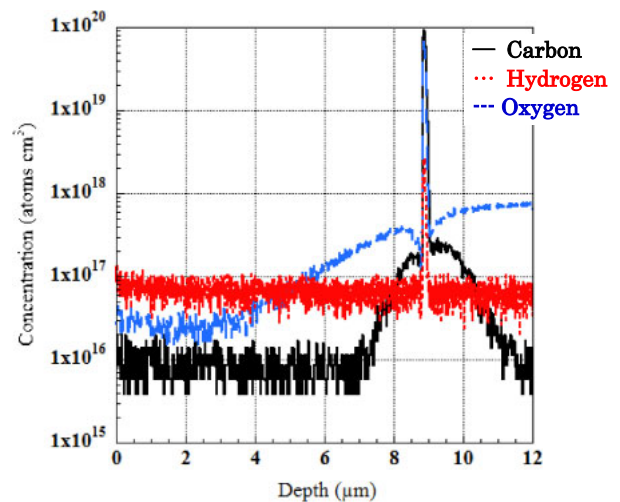


Fig. 3. (Color online) Depth-distribution profiles of carbon, hydrogen, and oxygen in CH_3O -ion-implanted epitaxial wafer obtained using SIMS. The blue line is carbon, the black line is hydrogen, and the red line is oxygen.

impurity-contaminated acid solution. The surface initial nickel concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS) after spin coating. After the metallic impurity contamination, the wafers were heated at 900 °C for 1800 s for nickel diffuse treatment.

The distributions of carbon, hydrogen, oxygen, and nickel were analyzed by secondary ion mass spectrometry (SIMS). The defects in the multielement molecular cluster ion projection range were analyzed by transmission electron microscopy (TEM).

3. Results and discussion

3.1 SIMS depth profile of carbon, hydrogen, and oxygen after epitaxial growth

Figure 3 shows the carbon, hydrogen, and oxygen distribution-depth profiles of CH_3O -ion-implanted silicon epitaxial wafers. The implantation energy was 80 keV and the implantation dose was 1.0×10^{15} carbon atoms/cm². The epitaxial layer thickness was 9 μm . From these results, the CH_3O ion projection range had concentration peaks of carbon, hydrogen, and oxygen.

The peak concentration of the carbon impurity in the CH_3O ion projection range was higher than the solid solubility of carbon in the silicon single-crystal wafers, which was the same as in the carbon cluster ion projection range.¹⁸⁾ Kurita and coworkers reported that a high concentration of carbon is observed after epitaxial growth in the carbon cluster ion projection range, and an aggregate of carbon is formed in this range as a gettering sink.^{14,16)} Therefore, it is speculated that the CH_3O ion projection range has almost the same characteristics as the carbon cluster ion projection range. In the CH_3O ion projection range, carbon and oxygen concentration peaks were approximately at the same concentration. Such a trend was not observed in the carbon cluster ion projection range.

Figure 4 shows the distribution-depth profiles of oxygen in CH_3O - and C_2H_3 -ion-implanted silicon epitaxial wafers. The carbon dose was the same in both CH_3O and C_2H_3 ions, i.e., 1.0×10^{15} carbon atoms/cm². As shown in Fig. 4, the oxygen peak concentration of the CH_3O -ion-implanted sample was

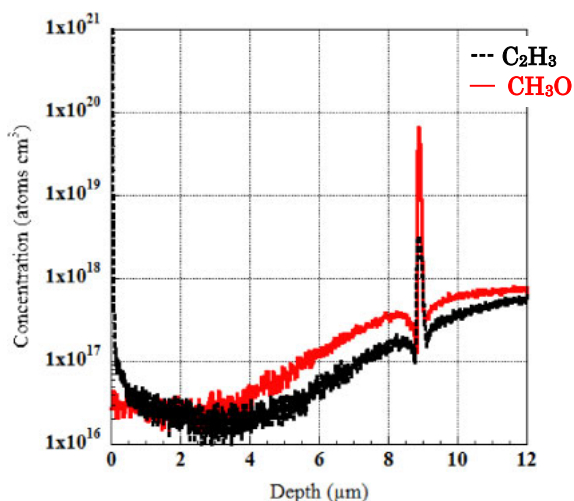


Fig. 4. (Color online) Oxygen distribution profiles of CH₃O- and C₂H₃-ion-implanted silicon epitaxial wafers. The red line is the CH₃O-ion-implanted silicon epitaxial wafer and the black line is the C₂H₃-ion-implanted silicon wafer. The epitaxial thickness was 9 μm.

6.5×10^{19} atoms/cm³. The oxygen peak concentration of the C₂H₃-ion-implanted sample was 3.1×10^{18} atoms/cm³. Thus, the oxygen peak concentration of the CH₃O-ion-implanted sample was up to more than 10-fold higher than that of the C₂H₃-ion-implanted sample. The oxygen concentration of the CH₃O-ion-implanted sample in the epitaxial layer was up to approximately 2-fold higher than that of the C₂H₃-ion-implanted sample. These results suggest that almost all the oxygen implanted by CH₃O ions is fixed in the CH₃O ion projection range. The detailed mechanism of the implanted oxygen behavior is not clear. However, it is assumed that there are two mechanisms.

First, the VO complex forms in the CH₃O ion projection range. Shirasawa et al. calculated, by DFT calculation, the possibility of VO complex formation in the carbon cluster ion projection range.^{26,27)} The multielement molecular ion implantation forms high-concentration vacancy by collision with the silicon crystal. Thus, the multielement molecular ion projection range is considered to have a high VO concentration. Therefore, owing to VO complex formation, it is assumed that implanted oxygen is fixed in this projection range.

Second, oxygen is gettered in the carbon projection range. A previous study reported that the carbon cluster ion projection range can getter oxygen impurity.¹⁴⁾ A carbon cluster ion contains carbon and hydrogen, and a CH₃O ion contains carbon and hydrogen. Thus, it is assumed that there is a possibility that oxygen is gettered in the CH₃O ion projection range. However, the oxygen concentration in the CH₃O ion projection range is more than 10-fold higher than that in the C₂H₃ ion projection range. Thus, we speculate that a new complex different from that in the carbon cluster ion projection range is formed after epitaxial growth in the CH₃O ion projection range.

3.2 TEM observation of CH₃O ion projection range

Figure 5 shows the cross-sectional TEM images of the CH₃O ion projection range. The implantation energy was 80 keV, and the implantation dose was 5.0×10^{14} – 2.0×10^{15} carbon atoms/cm². In these images, approximately 50 nm defects were observed in the samples with an implantation dose of 7.5×10^{14} – 2.0×10^{15} carbon atoms/cm² in the CH₃O ion

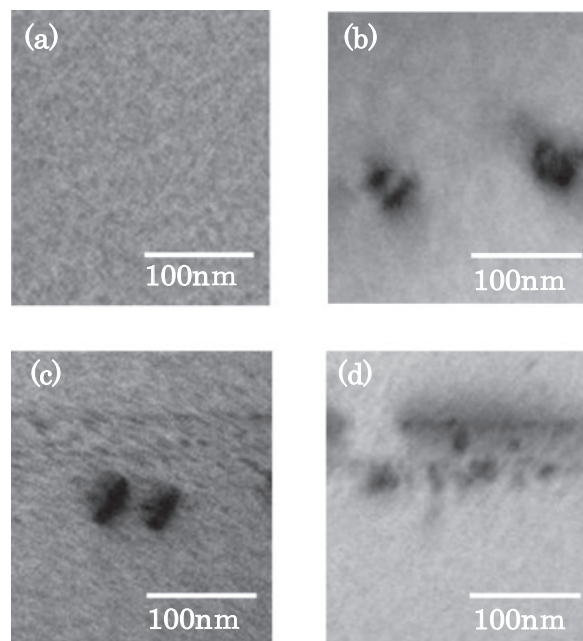


Fig. 5. Cross-sectional TEM images of CH₃O ion projection range. Implantation doses were (a) 5.0×10^{14} , (b) 7.5×10^{14} , (c) 1.0×10^{15} , and (d) 2.0×10^{15} ions/cm².

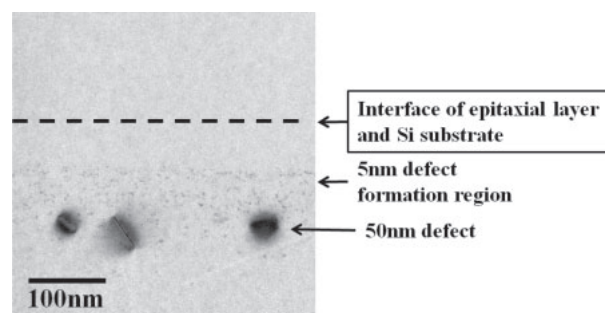


Fig. 6. Clear-resolution cross-sectional TEM image of CH₃O ion projection range with CH₃O ion dose of 1.0×10^{15} ions/cm².

projection range. However, there were no such large defects at the dose of 5.0×10^{14} carbon atoms/cm². These results suggest that approximately 50 nm defect formation has dose dependence. This tendency is thought to be related to ion-implantation damage. We previously reported that the critical dose of CH₃O ion implantation is approximately 1.0×10^{15} ions/cm².²³⁾ Thus, it is considered that excessive damage given to the silicon crystal by CH₃O ion implantation is one of the causes of secondary defects.

Figure 6 shows a high-resolution cross-sectional TEM image of the CH₃O ion projection range. The implantation energy was 80 keV/ion and the implantation dose was 1.0×10^{15} carbon atoms/cm². The interface of the epitaxial layer and Si substrate is indicated by the black dashed line in Fig. 6. As shown in Fig. 6, the projection range of CH₃O ions was observed at a depth of approximately 120 nm from the interface of the epitaxial layer and Si substrate. Furthermore, two types of defects (5 and 50 nm defects) were observed in the CH₃O ion projection range. The 5 nm defect was observed at a depth of approximately 80 nm from the interface of the epitaxial layer and Si substrate. On the other hand, the 50 nm defect was observed at a depth of approxi-

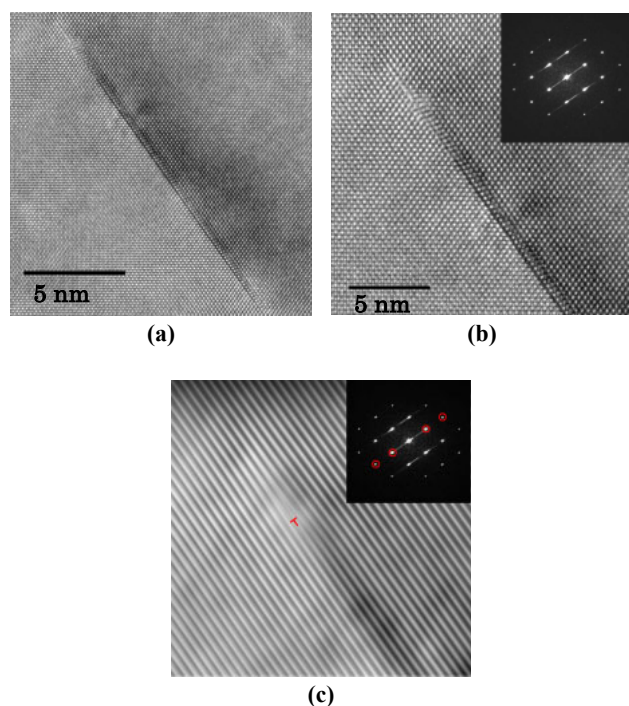


Fig. 7. (Color online) High-resolution cross-sectional TEM images of 50 nm defects in CH_3O ion projection range. (a) Overall image of 50 nm defects. (b) Expansion image of 50 nm defects. (c) FFT.

mately 160 nm from the interface of the epitaxial layer and Si substrate. Therefore, the 50 nm defect formation region was deeper than the 5 nm defect formation region in the CH_3O ion projection range.

Defects similar to the 5 nm defect were observed in the carbon cluster ion projection range.^{16,18)} The formation of such defects is due to carbon implantation and the defects act as gettering sinks. A CH_3O ion contains carbon atoms. Hence, the 5 nm defect in the CH_3O ion projection range is considered to be due to carbon implantation and to act also as the gettering sink. From this result, it is assumed that the CH_3O ion projection range has at least the same degree of gettering capability as the carbon cluster ion projection range. Defects different from those were observed in the CH_3O ion projection range. The 50 nm defect is the new type of defect. Okuyama et al. reported the defect formation in the carbon cluster ion projection range.¹⁶⁾ In the sample with high carbon cluster ion dose, the carbon cluster ion projection range forms a 40 nm defect after epitaxial growth. This defect is due to the recrystallization of the amorphous region formed by ion implantation and is located on the surface layer side of the carbon-cluster-implanted region. However, as shown in Fig. 6, the 50 nm defect is located at the back side of the CH_3O ion projection range. Thus, it is considered that 50 nm defects are peculiar to the CH_3O ion projection range. The formation of 50 nm defects is considered to be the effect of adding oxygen to the ions. To analyze the origin of 50 nm defects, we conducted high-resolution TEM observation and fast Fourier transform (FFT) analysis.

Figure 7(a) shows a high-resolution cross-sectional TEM image of 50 nm defects in the CH_3O ion projection range. There seem to be two types of 50 nm defects, i.e., round and linear in the silicon {111} direction. However, round defects are assumed to be silicon {111} stacking faults in the direction

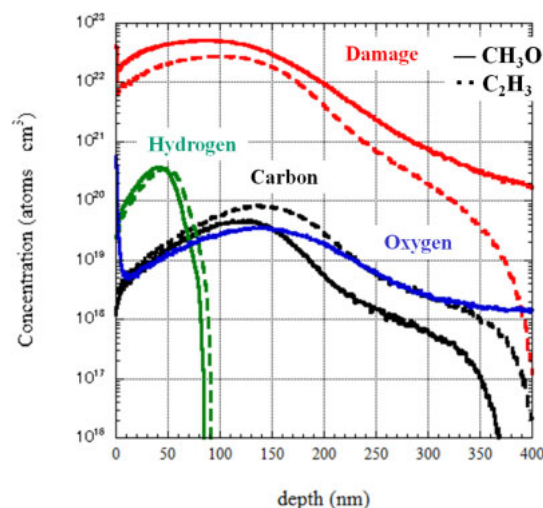


Fig. 8. (Color online) TCAD simulation results for CH_3O and C_2H_3 ion implantations.

perpendicular to the TEM analysis direction. Therefore, it is assumed that round and linear defects are the same. Therefore, we conducted a detailed analysis of linear defects.

For the detailed analysis of this type of defect, we examine an FFT pattern at the edge of a defect. An enlarged TEM image of the defect edge and FFT pattern is shown in Fig. 7(b).

Figure 7(c) shows a defect image obtained from the FFT pattern by extracting only the silicon {111} direction component. From Fig. 7(c), the 50 nm defects are the stacking faults inserted with one atomic layer in the silicon {111} direction. Okuyama et al. reported that the 40 nm defects in the carbon cluster ion implantation region are silicon single crystals from the electron diffraction pattern.¹⁶⁾ From the difference in diffraction pattern, the defect in the CH_3O ion implantation region is thought to be also different from that formed in the carbon cluster ion implantation region. A 50 nm defect is a defect peculiar to the CH_3O ion implantation region.

To consider the origin of 50 nm defects, we calculated and compared the damage distribution profiles after C_2H_3 and CH_3O ion implantations by technology computer aided design (TCAD) simulation with the Sentaurus process simulator from Synopsys.²⁴⁾ Figure 8 shows the distribution profiles of carbon, hydrogen, oxygen, and damage calculated by TCAD simulation. The implanted energy was 80 keV. CH_3O and C_2H_3 were implanted at a dose of 5.0×10^{14} ions/cm². Tilt and twist were 0 degrees. The damage concentration was calculated using the Frenkel pair model that defines interstitial silicon (I) and vacancy (V) concentrations generated by the ion implantation. At a high implantation dose, the damage concentration saturated owing to the supersaturated generation of I and V. In this situation, it was not possible to compare the damage profiles of CH_3O and C_2H_3 . Therefore, the distribution profiles were calculated at an implantation dose of 5.0×10^{14} ions/cm² to compare the damage profiles of the ion implantation regions. As shown in Fig. 8, the damage concentration increased in CH_3O ion implantation, even at the same ion dose. Since CH_3O is an ion in which one carbon atom of C_2H_3 is replaced with oxygen, the impact of oxygen in the ion implantation damage is extremely large.

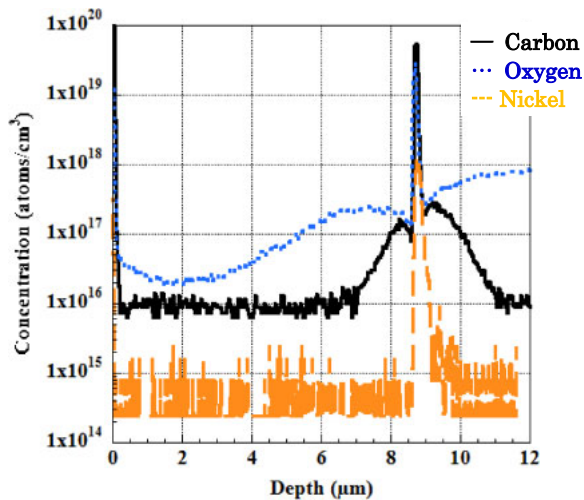


Fig. 9. (Color online) SIMS depth profiles measured on CH_3O -ion-implanted epitaxially grown sample after nickel metallic impurity contamination. The black line is the distribution profile of carbon, the blue line is the distribution profile of oxygen, and the orange line is the distribution profile of nickel.

From Fig. 8, it was found that CH_3O ion implantation has large damage in the region deeper than the carbon concentration peak of 160 nm depth as compared with C_2H_3 implantation. The damage profile indicated that CH_3O ion implantation results in higher I and V concentrations than C_2H_3 implantation. The increase in V concentration seems to form a VO complex with O of CH_3O . Therefore, it is considered that an excessive amount of I remained without recombination with V during heat treatment in epitaxial growth. A previous study indicated that an excessive amount of I induced by ion implantation forms the defect called the “end-of-range defect”.²⁵⁾ Therefore, the origin of 50 nm defects is considered to be aggregates of interstitial silicon formed in deep regions by additional oxygen implantation in CH_3O ion implantation. This inference is consistent with the finding that the 50 nm defect is an intrinsic stacking fault as shown in Fig. 7. Furthermore, it is in agreement with the finding that 50 nm defects are located behind carbon complex defects as shown in Fig. 6.

It is expected that the gettering capability of metallic impurity will be improved by the formation of 50 nm defects and a VO complex using CH_3O ion implantation.

3.3 Nickel gettering capability improvement using CH_3O ion implantation

Figure 9 shows the SIMS depth profiles measured on the CH_3O -ion-implanted epitaxially grown samples (CH_3O ions were implanted at 80 keV at a carbon dose of 7.5×10^{14} carbon atoms/cm²) after the nickel metallic impurity contamination.

As shown in Fig. 9, the carbon peak concentration was 6×10^{19} atoms/cm³ in the CH_3O ion projection range. Moreover, the oxygen peak concentration in this projection range was 3×10^{19} atoms/cm³. These results suggest that carbon and oxygen impurities remain at concentrations exceeding the solid solubility in the silicon single-crystal wafers after nickel metal impurity contamination. We also confirmed that nickel impurities are gettering in the CH_3O ion projection range. Therefore, the CH_3O ion projection range can getter nickel metallic impurities.

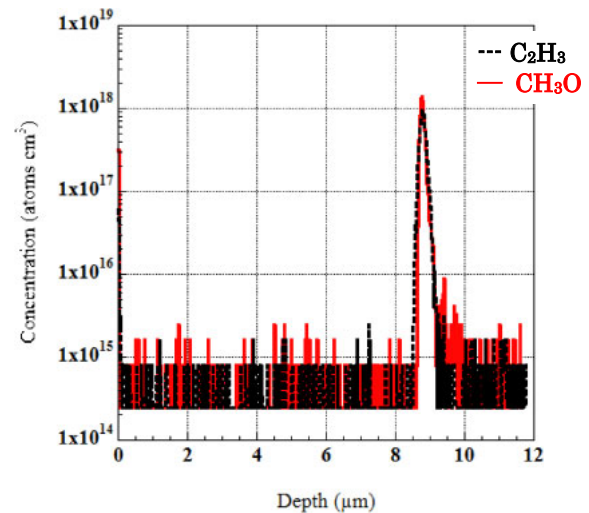


Fig. 10. (Color online) SIMS depth profiles of nickel metallic impurity contamination in CH_3O -ion-implanted epitaxially grown sample (red line) and C_2H_3 -ion-implanted epitaxially grown sample (black line).

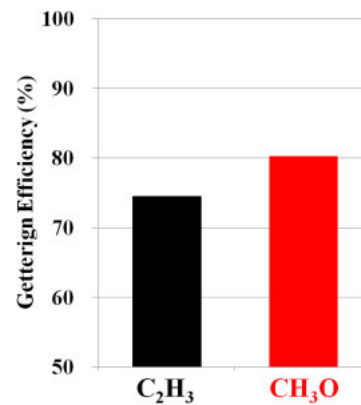


Fig. 11. (Color online) Comparison of nickel gettering efficiencies in C_2H_3 and CH_3O ion projection ranges.

Figure 10 shows the SIMS depth profiles measured on CH_3O - and C_2H_3 -ion-implanted epitaxially grown samples (CH_3O and C_2H_3 ions were implanted at 80 keV at a carbon dose of 7.5×10^{14} carbon atoms/cm²) after nickel metallic impurity contamination. The nickel contamination surface concentration measured by ICP-MS was 2.5×10^{13} atoms/cm². As shown in Fig. 10, nickel concentration peaks were observed in the CH_3O and C_2H_3 ion projection ranges. From these results, both CH_3O and C_2H_3 ion implantations could getter nickel contaminants. The nickel concentration in the CH_3O ion projection range was 2.0×10^{13} atoms/cm² and that in the C_2H_3 ion projection range was 1.8×10^{13} atoms/cm².

Figure 11 shows the nickel gettering efficiencies of the CH_3O - and C_2H_3 -ion-implanted samples after nickel contamination. The nickel gettering efficiency was calculated using the following equation, where η_{eff} is the gettering efficiency, C_{ni} is the nickel concentration in the ion projection range, and C_{init} is the initial surface nickel concentration.

$$\eta_{\text{eff}} = C_{\text{ni}}/C_{\text{init}}$$

As shown in Fig. 11, the nickel gettering efficiency of the CH_3O -ion-implanted sample improved by 5.7% compared with that of the C_2H_3 -ion implanted sample. Thus, CH_3O ion

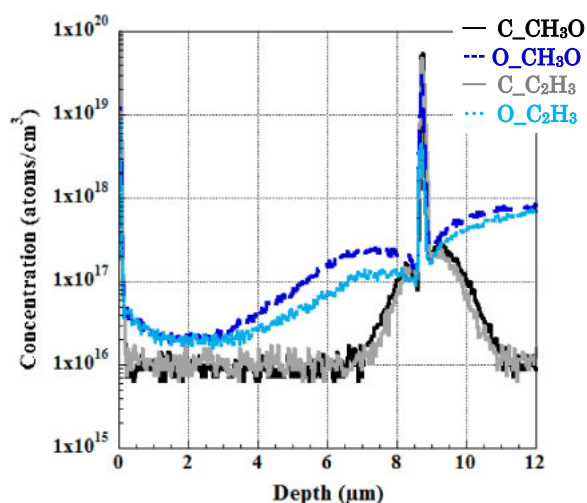


Fig. 12. (Color online) SIMS-depth profiles of carbon and oxygen measured on CH_3O - and C_2H_3 -ion-implanted epitaxially grown samples after nickel metallic impurity contamination. The black line is the distribution profile of carbon (CH_3O sample), the gray line is the distribution profile of carbon (C_2H_3 sample), the dark blue line is the distribution profile of oxygen (CH_3O sample), and the light blue line is the distribution profile of oxygen (C_2H_3 sample).

implantation can import a higher nickel gettering capability than C_2H_3 ion implantation. The details of the gettering mechanism in the CH_3O ion projection range are not clear, although this improvement in gettering efficiency is thought to be the effect of the three types of estimated gettering sinks below.

First, the carbon projection range has a gettering capability on nickel. Figure 12 shows carbon and oxygen distribution-depth profiles after nickel metallic contamination. As shown in Fig. 12, the carbon peak concentration in the CH_3O ion projection range was 5.5×10^{19} atoms/cm³ and that in the C_2H_3 ion projection range was 4.7×10^{19} atoms/cm³. These results suggest that implanted carbon remains in the C_2H_3 and CH_3O ion projection ranges after nickel metallic contamination. Kurita et al. reported that the high-concentration carbon region, which was formed by carbon cluster ion implantation, has a high gettering capability for various metals.¹⁴⁾ As shown in Fig. 12, the CH_3O ion projection range had the same ordered carbon concentration as in the carbon-cluster (C_2H_3) ion projection range. Furthermore, as shown in Fig. 6, the CH_3O ion projection range had the same defects as the carbon cluster ion projection range. Thus, it is conceivable that the CH_3O ion projection range has at least the same function as the carbon cluster ion projection range.

Second, the silicon {111} defects in the CH_3O ion projection range function as gettering sinks. As shown in Figs. 6 and 7, the CH_3O ion projection range had 50 nm defects. Kuroi et al. reported that secondary defects formed by high-energy ion implantation function as gettering sinks.¹⁹⁾ The CH_3O ion implantation condition is not high energy. However, it is sufficiently conceivable that defects, as shown in Fig. 9, function as new gettering sinks, and the nickel gettering capability improves.

Third, the VO-complex point defects in the CH_3O ion projection range function as gettering sinks. As shown in Fig. 12, carbon concentrations in the CH_3O and C_2H_3 ion projection range were almost the same. However, the oxygen

peak concentration in the CH_3O ion projection ranges was approximately 10-fold higher than that in the C_2H_3 ion projection range (oxygen concentration in the CH_3O ion projection range was 3.0×10^{19} atoms/cm³ and that in the C_2H_3 ion projection range was 1.5×10^{18} atoms/cm³). Shirasawa et al. used DFT to determine the binding energy between metallic impurity and point defects.^{26,27)} In the calculation results, the carbon-interstitial silicon (C-I), vacancy-hydrogen (VH_n , $n = 1$ to 3), or VO complex has a high binding energy with metallic impurities. In the case of CH_3O ion implantation, oxygen was implanted at a high concentration, and vacancy was formed by CH_3O ion implantation. Thus, it is expected that the CH_3O ion projection range will have a high-concentration VO complex and will improve the nickel gettering capability through VO-complex point defect formation.

From these types of gettering sinks, it is considered that the nickel gettering capability in the CH_3O ion projection range is improved by the coexistence of the carbon cluster ion projection range and silicon {111} or VO-complex point defects.

4. Conclusions

We succeeded in epitaxial growth on the top surface of a CH_3O -ion-implanted silicon wafer. From SIMS analysis results, the oxygen concentration peak in the CH_3O ion projection range was 10-fold higher than that in the C_2H_3 -ion projection range. These results also suggest that the CH_3O ion projection range forms different chemical bonding states from the carbon cluster ion projection range.

From TEM observation results, the CH_3O ion projection range had two types of defects. The first type is an approximately 5 nm defect, which is the same as that observed in the carbon cluster ion projection range. These results indicate that the CH_3O ion projection range has at least the same gettering capability for metallic impurity as the carbon cluster ion projection range. In the CH_3O ion projection range, approximately 50 nm defects, which were not observed in the carbon cluster ion projection range, were observed. From high-resolution TEM observation and FFT analysis results, it was found that the defects are silicon {111} one-layer stacking faults. From the nickel gettering test results, the CH_3O ion projection range was found to improve the nickel gettering capability compared with the C_2H_3 -ion projection range. We speculated that the CH_3O ion projection range improves the gettering capability through the formation of silicon {111} stacking faults as new gettering sinks.

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