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Gettering mechanism in hydrocarbon-molecular-ion-implanted epitaxial silicon wafers revealed by three-dimensional atom imaging

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The interaction of iron (Fe) with defects induced by a high hydrocarbon-molecular-ion-implantation dose of $1 \times 10^{16} \text{ cm}^{-2}$ in a Czochralski-grown silicon substrate and an epitaxial growth layer was investigated using secondary ion mass spectroscopy, transmission electron microscopy, and laser-assisted atom probe tomography (L-APT). High-dose hydrocarbon-molecular-ion-implantation formed two types of defects in the projection range: stacking faults and carbon agglomerates. It was demonstrated that the dominant gettering mechanisms of the two types of defects differ. Carbon agglomerates formed by implantation of the epitaxial growth layer exhibited high gettering efficiency for Fe. The L-APT data indicated that the Fe gettering efficiency is strongly affected by the distribution of oxygen atoms in carbon agglomerates. It is suggested that Fe gettering on agglomerates is due to the strong electronic interaction between carbon agglomerates and Fe but suppressed by oxygen atoms in agglomerates.
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1. Introduction

Complementary metal oxide semiconductor (CMOS) image sensors have recently been mounted on electronic applications such as smart-phones and on-vehicle apparatus. CMOS image sensors have advantages over charge-coupled devices (CCDs) of lower power consumption, lower fabrication cost, and camera-on-a-chip integration.¹⁻³ Thus, the focus of the camera market has changed from CCDs to CMOS image sensors. This has led to demand for more advanced fabrication methods for CMOS image sensors. However, the noise in CMOS image sensors is a serious issue in the fabrication of advanced image sensors. Dark current has a strongly adverse effect on CMOS device performance and is caused by deep energy levels formed by metallic impurities in the space-charge region of photodiodes.⁴⁻⁶ Metallic impurities are easily introduced into silicon (Si) bulk during CMOS device fabrication, such as during high-temperature rapid thermal annealing. It is necessary to suppress and control metallic impurities in the space-charge region of photodiodes for Si wafers in CMOS image sensors. Therefore, the gettering technique is extremely important for controlling metallic impurities and suppressing metallic-related defect formation in the active region of devices during the fabrication process.

Regarding the physical phenomena observed in metallic-impurity gettering, the gettering mechanism can be divided into two types: relaxation-induced gettering and segregation-induced gettering. The gettering mechanism for MeV-ion-implanted Si wafers has been suggested to be the a relaxation-induced type because of the formation of dislocations by supersaturated Si self-interstitials (I).⁷⁻⁹ Gettering occurs owing to heterogeneous precipitation in the strain field. In contrast, the gettering mechanism for iron (Fe) in a p/p⁺ epitaxial wafer has been suggested to be the segregation-induced type.¹⁰⁻¹⁴ Gettering occurs via Fermi level shift and electronic interaction.

Recently, we demonstrated higher gettering efficiency for metallic impurities, such as Fe, nickel (Ni), and copper (Cu), by using a hydrocarbon-molecular-ion-implantation technique.¹⁵⁻¹⁸ Hydrocarbon molecular ions are formed from a hydrocarbon gas source using an electron impact ionization method. The hydrocarbon molecular ions used for implantation are low-molecular-weight hydrocarbons (e.g., C₃H₅, C₃H₆, and C₅H₅). It has been shown that the amount of gettering of metallic impurities in the hydrocarbon-molecular-ion-implantation projection range is higher than their solubility in Si bulk. Kurita et al.^{17,18} suggested that the gettering mechanism for metallic impurities in the hydrocarbon-molecular-ion-implantation projection range is the segregation-induced type.

In the case of Fe gettering in a p/p⁺ epitaxial wafer,^{10,13,14} the origin of Fe gettering is boron (B). Increasing the B concentration increases the gettering efficiency for Fe through the interaction between Fe and B. By contrast, it was suggested that the origin of metallic-impurity gettering sinks in the hydrocarbon-molecular-ion-implantation projection range is carbon (C) agglomerates.¹⁸ It is expected that the gettering efficiency for Fe will increase with the increasing number of C agglomerates if the origin of the gettering sinks for Fe is C agglomerates. However, it has not yet been clearly established whether C agglomerates contribute to Fe gettering.

Our previous studies demonstrated that hydrocarbon-molecular-ion-implantation with a dose in the range from 10^{14} to 10^{15} cm^{-2} in an epitaxial growth layer (Epi-Si) with a low oxygen (O) concentration, has higher gettering efficiency for Fe rather than in Czochralski (CZ) Si.¹⁹ We concluded that higher gettering efficiency for Fe in hydrocarbon-molecular-ion-implanted Epi-Si is due to segregation-induced gettering. It can be assumed from previous work that the gettering sinks that induce higher gettering efficiency are point-defect-related agglomerates. However, it is not clear whether the higher gettering efficiency for Fe is due to the



large number of C agglomerates observed in CZ-Si or to other C-related defects.

Atom probe tomography (APT) analysis is an extremely useful approach to directly obtaining three-dimensional information of the impurity distribution in metallic materials at the atomic scale.^{20–24} Moreover, information on semiconductor materials can also be obtained using a laser-assisted APT (L-APT) instrument.^{21–24} Investigation of the atomic distribution of defects can provide a better understanding of the origin of gettering sinks on hydrocarbon-molecular-ion-implanted Epi-Si. However, L-APT analysis is conducted using needle-shaped samples of approximately 100 nm diameter; thus, there is a limit to the number of C agglomerates that can be detected in one needle-shaped sample. To resolve this problem, we have introduced gettering layers with a dose of 10^{16} cm^{-2} . The density of C agglomerates induced by hydrocarbon-molecular-ion-implantation has been reported to depend on the C dose.¹⁸ In this study, therefore, we investigated the morphology of defects at the atomic level to reveal the gettering mechanism of Fe in hydrocarbon-molecular-ion-implanted Epi-Si in more detail.

This article is organized as follows. Section 3.1 discusses the gettering efficiency for Fe when the hydrocarbon-molecular-ion-implantation dose is $1 \times 10^{16} \text{ cm}^{-2}$ in CZ-Si and Epi-Si. Section 3.2 describes the difference in the morphology of defects induced by hydrocarbon-molecular-ion-implanted CZ-Si and Epi-Si at the atomic level. On the basis of these results, Sect. 3.3 discusses the gettering mechanism of Fe in hydrocarbon-molecular-ion-implanted Epi-Si substrates.

2. Experimental procedure

In this study, we used phosphorus-doped wafers with oxygen (O) concentrations of $1.4 \times 10^{18} \text{ cm}^{-3}$ (CZ-Si) and $<10^{16} \text{ cm}^{-3}$ (Epi-Si) for hydrocarbon-molecular-ion-implantation. Figure 1 schematically shows the experimental process and analysis techniques used in this study. 80 keV hydrocarbon molecular (C_3H_6) ions were implanted into the wafers at a C dose of $1 \times 10^{16} \text{ cm}^{-2}$. After C_3H_6 -molecular-ion-implantation, the samples were annealed at 1100°C for 30 min in nitrogen gas (N_2) ambient. The samples were then implanted with 180 keV ^{56}Fe ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ from the underside of the wafer at 1050°C for 2 h in N_2 ambient.

The amount of gettered Fe in the C_3H_6 -molecular-ion projection range was obtained by secondary ion mass spectrometry (SIMS) analysis. High-resolution transmission electron microscopy (HR-XTEM) was used for the structural characterization of C_3H_6 -molecular ion-implantation-induced defects after annealing at 1100°C for 30 min.

The L-APT analysis was carried out using an AMETEC LEAP 4000XSi atom probe microscope to examine the impurity distribution in the C_3H_6 -molecular-ion projected range after 30 min annealing at 1100°C . Needle-shaped samples were fabricated using a focused ion beam system then lifted out within 300 nm from the sample surface which is within the C_3H_6 -molecular-ion projected range. The field evaporation of atoms from the needle-shaped samples was induced by pulsed laser irradiation. We selected a wavelength of 325 nm, a laser power of 20 pJ, and an analysis temperature of 70 K. The APT data were analyzed using integrated visualization and analysis software (IVAS) from CAMECA.

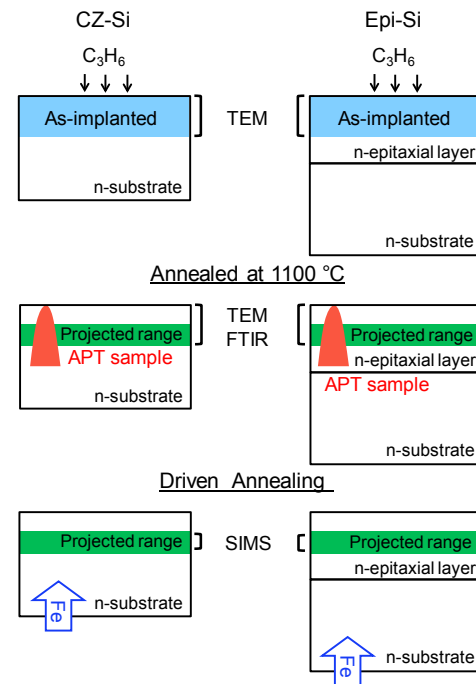


Fig. 1. (Color online) Schematic representation of experimental procedure in this study and regions of samples analyzed by TEM, FTIR, APT, and SIMS.

The bonding states of C in the C_3H_6 -molecular-ion projected range after annealing at 1100°C for 30 min were analyzed using Fourier transform infrared (FTIR) spectroscopy. The FTIR transmission spectra were obtained at room temperature. The absorbance spectra from the C_3H_6 -molecular-ion-implantation region were obtained by subtracting the reference spectra of the same wafer without implantation.

3. Results and discussion

3.1 Gettering efficiency in C_3H_6 -molecular-ion-implanted CZ-Si and Epi-Si with dose of $1 \times 10^{16} \text{ cm}^{-2}$

Figures 2(a)–2(c) respectively show the C, O, and Fe concentrations in the implanted CZ-Si and Epi-Si at a dose of $1 \times 10^{16} \text{ cm}^{-2}$ obtained from SIMS profiles after annealing at 1050°C for 2 h. The peaks of the C concentration of CZ-Si and Epi-Si matched in the C_3H_6 -molecular-ion projection range, as shown in Fig. 2(a). For the high dose of $1 \times 10^{16} \text{ cm}^{-2}$, the C depth profile exhibited two peaks at depths of approximately 60 and 90 nm from the sample surface in both CZ-Si and Epi-Si. The peak of C at the greater depth approximately corresponds to the projection range of C under the conditions of this study. The O and Fe depth profiles also exhibited two peaks, which mirrored the C peaks, as respectively shown in Figs. 2(b) and 2(c). The O profiles were identical between depths of the 60 and 90 nm for both CZ-Si and Epi-Si. In contrast, the amount of gettered Fe was higher in Epi-Si than in CZ-Si, even at a dose of $1 \times 10^{16} \text{ cm}^{-2}$. However, a difference in the gettering efficiency in the C_3H_6 -molecular ion-implanted Epi-Si was only observed at depths greater than 90 nm. The amounts of gettered Fe in C_3H_6 -molecular-ion-implanted CZ-Si and Epi-Si at depths from 80 to 200 nm were 5.9×10^{12} and $7.8 \times 10^{12} \text{ cm}^{-3}$, respectively; the value for Epi-Si is approximately 1.3 times higher than that for CZ-Si. Note that higher gettering efficiency for Fe in Epi-Si was observed despite same amount of gettered O in

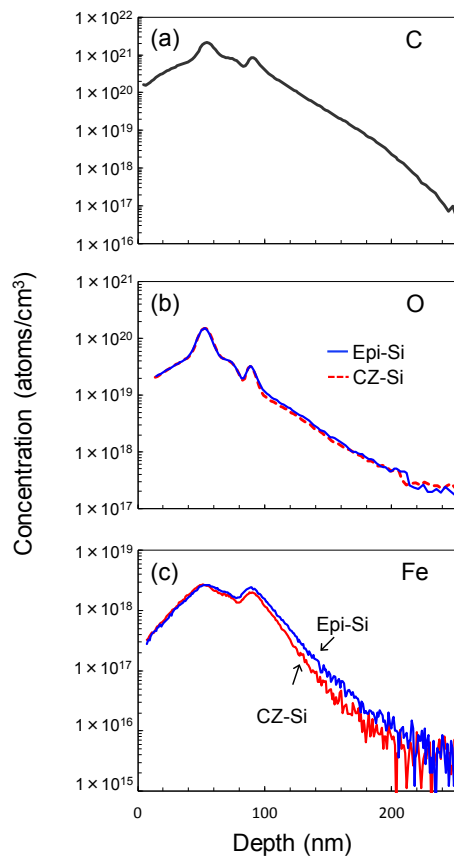


Fig. 2. (Color online) SIMS depth profiles of (a) C concentration, (b) O concentration, and (c) Fe concentration in CZ-Si and Epi-Si implanted at a C_3H_6 -molecular ion-implantation dose of $1 \times 10^{16} \text{ cm}^{-2}$ and gettered at 1050°C for 2 h.

the CZ-Si and Epi-Si. It was previously explained that for metallic-impurity gettering driven by a segregation mechanism, the metallic-impurity gettering in the projection range is in competition with the gettering of O.^{19,25,26} The high gettering efficiency for Fe in the Epi-Si observed in this study was a direct result of the increase in Fe gettering not only the amount of gettered O in the projection range but also the difference in defect formation induced by C_3H_6 -molecular-ion-implantation. The presence of O in C_3H_6 -molecular-ion-implantation directly affects defect formation.

Figures 3(a) and 3(b) respectively show TEM cross-sectional images of CZ-Si and Epi-Si as-implanted and after annealing at 1100°C in the case of C_3H_6 -molecular-ion-implantation. The TEM images obtained after annealing exhibited two types of defects: i.e., defects with a size of approximately 5 nm distributed approximately 90 nm below the surface and extended defects with a high density at a depth of approximately 60 nm. We refer to the 5-nm-sized defects as black point defects. These defects were distributed 200 nm below the sample surface. It appears that the distribution of black point defects corresponds to the region of the SIMS depth profile whose high gettering efficiency for Fe was observed, as shown in Fig. 2(c). In addition, the morphology of black point defects was similar to that in a previous study on lower-dose hydrocarbon-molecular-ion-implantation.^{17–19,27} Kurita et al.¹⁸ have suggested that black point defects are C-related defects such as C complexes. From these results, we considered that the high gettering efficiency

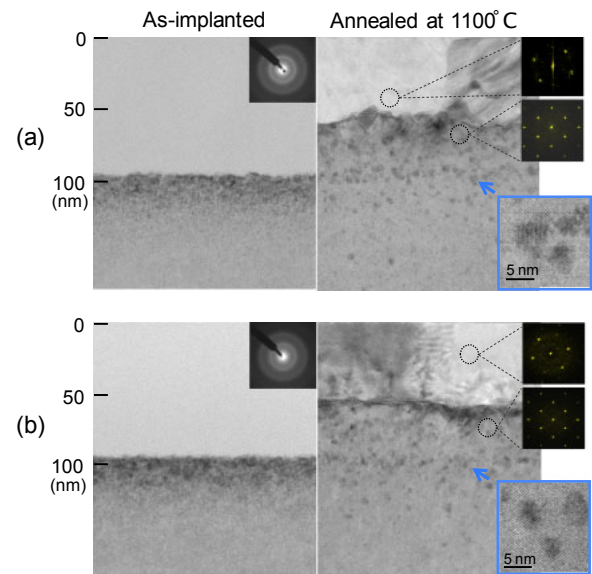


Fig. 3. (Color online) Cross-sectional TEM images and diffraction patterns of (a) CZ-Si and (b) Epi-Si as-implanted and after annealing at 1100°C for 30 min in the case of C_3H_6 -molecular ion-implantation at a dose of $1 \times 10^{16} \text{ cm}^{-2}$.

for Fe on implanted Epi-Si is related to the black point defects. However, no clear difference in black point defect density was obtained between CZ-Si and Epi-Si for which the values were 1.2×10^{17} and $1.3 \times 10^{17} \text{ cm}^{-3}$, respectively. This is also in good agreement with a previous study on lower-dose hydrocarbon-molecular-ion-implantation.¹⁹

On the other hand, the extended defects at the depth approximately 60 nm consisted of (111)-oriented microtwins and stacking faults. Similar defect formation has been reported for the solid-phase epitaxial (SPE) regrowth of an amorphous layer produced during implantation.^{28–30} Defect formation resulted from the different orientation dependence of the rate of SPE regrowth in different parts of the sample. The TEM images of as-implanted CZ-Si and Epi-Si exhibited amorphization from the sample surface; the amorphous layer was formed at a depth of approximately 90 nm. Subsequent annealing of these samples resulted in the formation of a recrystallized single-crystal layer from 60 to 90 nm, and the polycrystalline Si layer extended from 60 nm to the sample surface. A defective layer was observed around the interface of the polycrystalline Si layer. Calculation results obtained by the technology computer-aided design (TCAD) simulator³¹ indicated a high density of defects after C_3H_6 -molecular-ion-implantation at doses of 1×10^{15} , 2×10^{15} , and $1 \times 10^{16} \text{ cm}^{-2}$, with a peak concentration approximately 60 nm below the surface, as shown in Fig. 4. The damage concentration represents I and vacancy (V) generated by C_3H_6 -molecular-ion-implantation. At a dose of $1 \times 10^{16} \text{ cm}^{-2}$, the damage concentration saturated at $5 \times 10^{22} \text{ atoms/cm}^2$, which is the atomic density of Si. Presumably, from resulting at dose of 1×10^{15} , $2 \times 10^{15} \text{ cm}^{-2}$, the damage at a dose of $1 \times 10^{16} \text{ cm}^{-2}$ also has a maximum concentration at approximately 60 nm. This position corresponds to that of one of the C peaks after annealing, as shown in Fig. 2(a). We consider that at a depth of 60 nm, the segregation of C atoms in the damaged layer is induced by C_3H_6 -molecular-ion-implantation. The presence of supersaturated I and V facilitates C

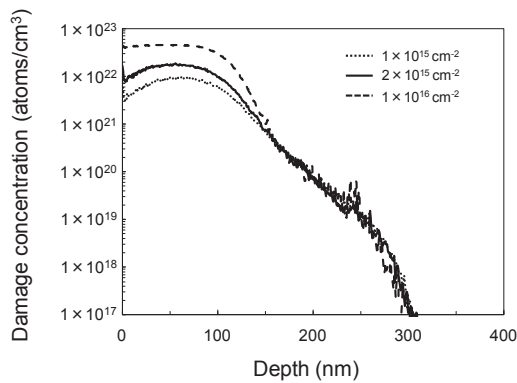


Fig. 4. Damage profiles of C_3H_6 -molecular ion-implantation at doses of 1×10^{15} , 2×10^{15} , and $1 \times 10^{16} \text{ cm}^{-2}$ calculated by TCAD simulation.

segregation.^{32,33} The large difference in the tetrahedral radius between Si (1.17 Å) and C (0.76 Å) leads to a huge lattice strain. As a result, the huge lattice strain induced by the highly concentration of C is assumed to be relaxed by, the formation of microtwins and stacking faults, followed by polycrystalline growth. In addition, it was demonstrated that a high C concentration in the amorphous region reduces the SPE growth rate.³⁴ The formation of the polycrystalline layer also demonstrated the contribution of C to recrystallization. The SIMS profile of Fe at a depth of 60 nm appears to match the C SIMS profile. We therefore assume that Fe at a depth of 60 nm is gettering in the strain field of the interface induced by the recrystallization of the amorphous layer, which segregates C atoms.

The polycrystalline layer, which is approximately 2 μm thick, is known to be an effective gettering sink for metallic impurities.^{35,36} We consider that the polycrystalline layer observed in our study is not an effective gettering sink owing to its insufficient thickness. It is considered that the profile of gettered Fe should have a uniform distribution from 60 nm to the sample surface if the Fe gettering is due to the polycrystalline layer.

These data suggest that Fe gettering at 60 and 90 nm is due to C; however, the nature of gettering for Fe at 60 nm differs from that at 90 nm. We assume that the difference in gettering efficiency for Fe induced by hydrocarbon-molecular ion-implantation in the low O-concentration layer is caused by the difference in the gettering efficiency on black point defects of 5 nm size and not by the extended defects.

3.2 APT map in C_3H_6 -molecular-ion-implantation region

Figures 5(a) and 5(b) show three-dimensional C-atom maps of the C_3H_6 -molecular-ion-implanted region in the CZ-Si and Epi-Si, respectively, after annealing at 1100 °C for 30 min. The L-APT map data show that at a depth of approximately 60 nm, there are a high density of C atoms in the damaged region induced by C_3H_6 -molecular-ion-implantation in both CZ-Si and Epi-Si. The C atoms appeared to form large clusters. No C segregation on microtwins or stacking faults were observed during the L-APT analysis. The L-APT map data also show that C atoms form C agglomerates below a depth of 60 nm. Presumably, C agglomerates correspond to black point defects.¹⁸ The cross-sectional images shown in Fig. 5 indicate that the size of the formed C agglomerates is approximately 5 nm in both CZ-Si and Epi-Si. This suggests

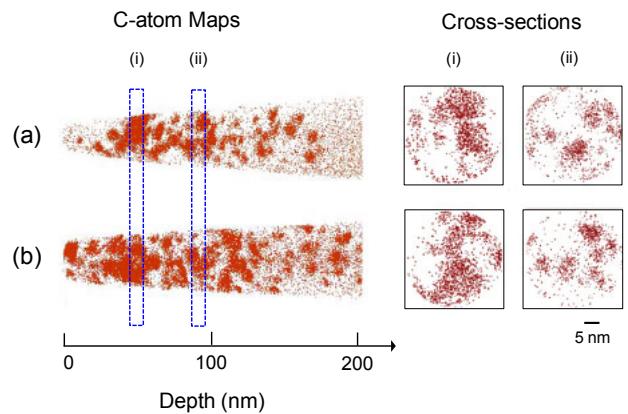


Fig. 5. (Color online) L-APT maps of C in C_3H_6 -molecular ion-implanted (a) CZ-Si and (b) Epi-Si. The implantation dose was $1 \times 10^{16} \text{ cm}^{-2}$ and the annealing was performed at 1100 °C for 30 min. Cross-section maps are also shown for areas indicated in blue boxes.

that the C_3H_6 -molecular-ion-implanted Epi-Si after annealing also formed C agglomerates, similarly to in CZ-Si.

The above results indicate that the effect of C_3H_6 -molecular-ion-implantation in the low-O-concentration layer during Fe gettering is associated with C agglomerates. The average number densities of the C agglomerates in CZ-Si and Epi-Si at depths from 80 to 200 nm were found to be about 1.1×10^{17} and $1.2 \times 10^{17} \text{ cm}^{-3}$, respectively, using IVAS data analysis software. These number densities are in good agreement with those of black point defects observed by TEM. No clear difference in the number densities of C agglomerates was observed between the CZ-Si and Epi-Si. Therefore, the increase in the gettering efficiency for Fe in the implanted Epi-Si cannot be explained by the increase in the C agglomerate density. In other words, C_3H_6 -molecular-ion-implantation in the low-O-concentration layer does not increase C agglomerate formation.

To reveal the distribution of O atoms on C agglomerates, L-APT maps showing 10 at. % C and 0.6 at. % O isoconcentration surfaces extracted from depths of 80 to 100 nm in the C_3H_6 -molecular ion-implanted CZ-Si and Epi-Si are shown in Figs. 6(a) and 6(b), respectively. These isoconcentration surfaces delineate regions containing more than 10 at. % C and 0.6 at. % O, and help visually clarify the atomic distributions. Focusing on the O-atom distribution, the presence of O atoms incorporated in C agglomerates was observed, as shown in Fig. 6(a). It was also observed that the O atoms in the C_3H_6 -molecular-ion-implanted region were segregated on C agglomerates, as shown in Fig. 6(b). The segregated O probably comprised O atoms diffusing from the Si bulk. Focusing on the C atoms, the composition of C agglomerates can be divided into two types: those that consist of only C atoms and those that include O atoms. The O segregation on C agglomerates was observed in both types of C agglomerates.

The concentration profiles of C and O in C agglomerates obtained in the depth direction also indicate the presence of two types of C agglomerates, as shown in Fig. 7. Both types of C agglomerates induced by C_3H_6 -molecular-ion-implantation are defects in which the C concentration of the agglomerates increased toward their center. However, the O-atom distribution in the C agglomerates differs. There are two types of defects, i.e., those containing O atoms in the region with

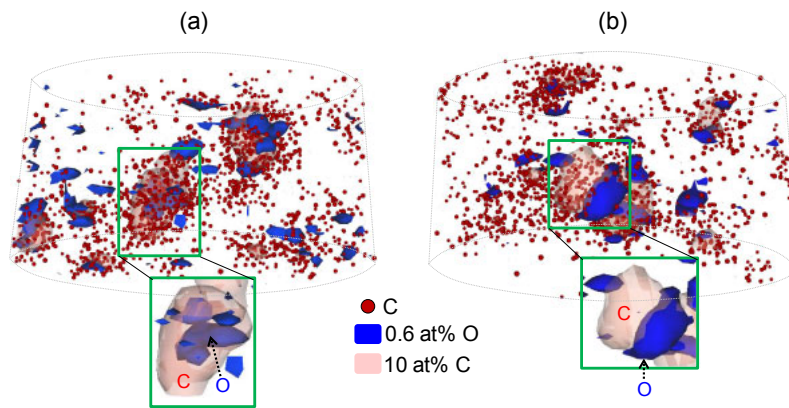


Fig. 6. (Color online) L-APT maps showing 10 at.% C isoconcentration-surface and 0.6 at.% O isoconcentration surfaces at depths of 80 to 100 nm in C_3H_6 -molecular ion-implanted (a) CZ-Si and (b) Epi-Si.

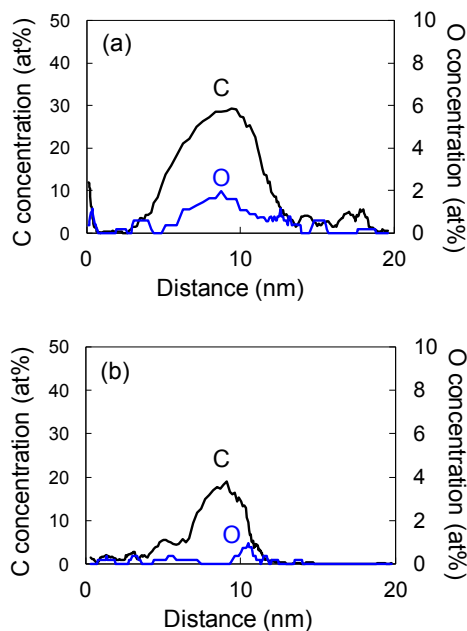


Fig. 7. (Color online) Depth profiles of C and O in C agglomerates (a) containing and (b) not containing O atoms determined through APT.

maximum C concentration and those not containing O atoms. These data suggest that, focusing on C- and O-atom distributions, the defects induced by C_3H_6 -molecular-ion-implantation consist of two types of C agglomerates, although they are regarded as the same defects in the TEM observation.

Figure 8 shows the presence ratio of the two types of C agglomerates, i.e., those containing O atoms and those not containing O atoms, induced by C_3H_6 -molecular-ion-implantation in CZ-Si and Epi-Si. The figure indicates that more C agglomerates in CZ-Si contain O atoms, whereas more C agglomerates in Epi-Si do not contain O atoms. This suggests that the atomic-level defect morphology differs in C_3H_6 -molecular-ion-implanted CZ-Si and Epi-Si, although the size and number density of defects appear to be similar. We assume that these differences in the defect morphology contribute to the gettering efficiency for Fe in the C_3H_6 -molecular-ion-implanted region.

3.3 Origin of gettering sinks in C_3H_6 -molecular-ion-implantation region

Why do the distributions of O atoms on C agglomerates

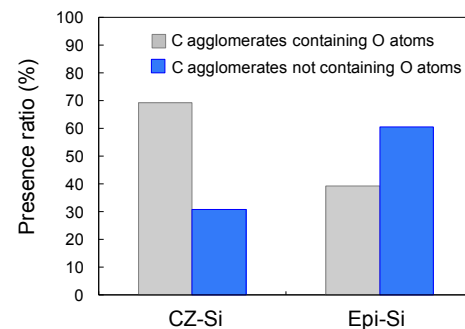


Fig. 8. (Color online) Presence ratio of C agglomerates containing and not containing O atoms in C_3H_6 -molecular ion-implanted CZ-Si and Epi-Si.

contribute to the gettering efficiency of Fe? We suggest that O atoms on C agglomerates play an important role in metallic-impurity gettering.

The formation of C agglomerates or precipitates can lead to a large decrease in volume because C atoms are smaller than Si atoms. This suggests that the formation of C agglomerates cannot occur without the relaxation of stress due to the incorporation of I.^{32,37,38} In other words, C atoms form CI clusters owing to the strong interaction with I. If C agglomerates without O atoms shown in Fig. 6(b) are formed by only C itself, Fe gettering can be induced by the strain field caused by the decrease in volume caused by the incorporation of C in the Si matrix. Because Epi-Si has more C agglomerates without O atoms, the increase in the amount of gettered Fe may be due to a relaxation-induced mechanism. However, the calculation results indicate that a high concentration of I is generated by C_3H_6 -molecular ion-implantation, as shown in Fig. 4. Thus, C agglomerates not containing O atoms are expected to be formed by CI clusters. We consider that Fe gettering on C agglomerates by the relaxation-induced mechanism is not a dominant reaction. We assume that Fe gettering associated with C agglomerates is induced by the strong interaction of C or CI clusters.

We consider the effect of O on C agglomerates containing O atoms, as shown in Fig. 6(a). Previous studies have suggested that C agglomerates are also formed in the presence of a high O concentration.³² The increase in stress caused by the decrease in volume due to the incorporation of C in the Si matrix is relaxed by the expansion due to the incorporation of O. A large amount of O is contained in the C_3H_6 -molecular-

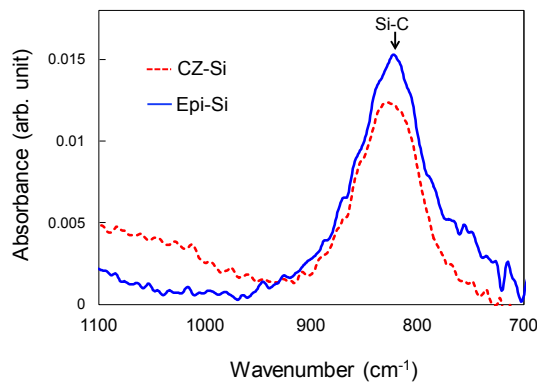


Fig. 9. (Color online) IR spectra of C_3H_6 -molecular ion implanted CZ-Si and Epi-Si at a dose of $1 \times 10^{16} \text{ cm}^{-2}$ after annealing at 1100°C for 30 min.

ion-implanted CZ-Si. Thus, the C agglomerates grow by incorporating O atoms. It is assumed that in the case of C agglomerates containing O atoms, the reduction in stress caused by the decrease in volume due to the incorporation of C is induced by the incorporation of O and I. Consequently, we suggest that C agglomerates containing O atoms suppress the formation of CI clusters.

Recent calculation results suggest that not only CI but also CI clusters can be effective gettering sinks for Fe.^{39,40} In short, CI clusters have a strong electronic interaction with Fe. We consider that C agglomerates consisting of CI clusters are effective gettering sinks for Fe. On the other hand, it is suggested that C_iO_i cannot be effective gettering sinks for metallic impurities.³⁹ It is considered that C_iO_i are nucleation centers that promote O precipitation, resulting in the co-precipitation or agglomeration of C and O.^{41,42} In the case of C agglomerates containing O atoms, the effect of the electronic interaction between C agglomerates and Fe is expected to be suppressed by the presence of O. Therefore, the driving force for the gettering of Fe on C agglomerates is reduced. Our experimental results shown in Fig. 8 indicate that C_3H_6 -molecular ion-implanted Epi-Si has more C agglomerates not containing O atoms than the ion-implanted CZ-Si. We consider that the presence of C agglomerates not containing O atoms increases the solid solubility of Fe in Epi-Si owing to the strong electronic interaction of C agglomerates. This is likely caused by the increase in the number CI clusters constituting C agglomerates.

To reveal the binding state of C agglomerates, the IR absorption spectra of C_3H_6 -molecular ion-implanted CZ-Si and Epi-Si after 1100°C annealing were obtained. The IR absorption spectra shown in Fig. 9 indicate only the absorption spectra around 824 cm^{-1} for both CZ-Si and Epi-Si. The peak in each IR absorption spectrum is attributed to the stretching mode of the Si-C bond.^{43,44} The IR data support the suggestion that C agglomerates consist of CI clusters. In addition, comparing the IR absorption of CZ-Si and Epi-Si at 824 cm^{-1} , the Si-C absorbance of Epi-Si was slightly higher than that of CZ-Si. These values for CZ-Si and Epi-Si are $0.012 (\pm 2\%)$ and $0.015 (\pm 3\%)$, respectively; the value for Epi-Si is approximately 1.3 times higher than that for CZ-Si. It is suggested that Epi-Si has more CI clusters in C agglomerates than CZ-Si. Table I summarizes the dose dependences of the Si-C absorbance and amount of gettered Fe in both CZ-Si and Epi-Si. The amount of gettered Fe represents

Table I. Dose dependences of Si-C absorbance at 824 cm^{-1} and the amount of gettered Fe measured by SIMS.

Implanted substrate	Dose (cm^{-2})	Absorbance	Amount of gettered Fe (cm^{-3})
CZ-Si	10^{15}	$0.001 (\pm 3\%)$	3.3×10^{12}
Epi-Si	10^{15}	$0.002 (\pm 2\%)$	6.0×10^{12}
CZ-Si	10^{16}	$0.012 (\pm 2\%)$	1.6×10^{13}
Epi-Si	10^{16}	$0.015 (\pm 3\%)$	1.8×10^{13}

the total Fe concentration in the hydrocarbon-molecular-ion-implanted region evaluated by SIMS. Even for the lower dose condition of 10^{15} cm^{-2} , a difference in the Si-C absorbance between CZ-Si and Epi-Si was confirmed. It is considered that this difference was due to not only the difference in the distributions of O atoms on C agglomerates but also the difference in density of C agglomerates. However, no difference in the density of black point defects was observed between CZ-Si and Epi-Si for doses of both 10^{15} and 10^{16} cm^{-2} .¹⁹ In contrast, the ratio of the Si-C absorbance between CZ-Si and Epi-Si is good agreement with the ratio of gettering efficiency for Fe in both dose conditions. We consider that the difference between the Si-C absorbance for CZ-Si and Epi-Si originates from the difference of the distribution of O atoms in C agglomerates observed by L-APT.

The L-APT data shown in Fig. 5 also indicate the presence of large C agglomerates at a depth of approximately 60 nm in both CZ-Si and Epi-Si. A difference in the gettering efficiency for Fe in CZ-Si and Epi-Si can also occur at 60 nm if Fe gettering contributes to C agglomerates consisting of CI clusters. However, no difference in the gettering efficiency for Fe was observed between C_3H_6 -molecular-ion-implanted CZ-Si and Epi-Si around a depth of 60 nm. At this depth, Fe gettering may be affected by both the strain field induced by the recrystallization of the amorphous layer and C agglomeration. It has been reported that Fe is readily gettered on partial dislocations.⁴⁵ Under our experimental conditions, Fe impurity exceeding the solid solubility existed in the C_3H_6 -molecular-ion-implanted region during annealing. Thus, Fe gettering can occur on the interfaces induced by recrystallization of the amorphous layer. We consider that the Fe gettering at a depth of 60 nm is dominated by the relaxation-induced mechanism.

We assume that the increase in the solid solubility of Fe is due to the presence of C agglomerates not containing O atoms, and we consider that the driving force for Fe gettering in the C_3H_6 -molecular-ion-implanted region is the electronic interaction of C agglomerates. This is determined by the amount of CI clusters constituting C agglomerates, suggesting that C agglomerates are effective gettering sinks of not only Fe but also O diffusing from the Si bulk.

4. Conclusions

We investigated the gettering mechanism of Fe in Epi-Si and CZ-Si induced by a high C_3H_6 -molecular-ion-implantation dose of $1 \times 10^{16} \text{ cm}^{-2}$. We demonstrated the gettering efficiency of Fe by SIMS, the defect morphology by TEM, and the distributions of C and O atoms on defects by L-APT. For the case of high dose C_3H_6 -molecular-ion-implantation, it was found that Fe gettering occurred in two damaged regions

in the projection range in both CZ-Si and Epi-Si. This was due to interfaces formed by recrystallization of the amorphous layer and C agglomerates. The amount of Fe gettering at interfaces induced by recrystallization of the amorphous layer was the same in both samples. However, the gettering efficiency for Fe at C agglomerates in Epi-Si was higher than that in CZ-Si.

Although the C agglomerate defects were regarded as the same type of defect in the TEM observation, the L-APT results indicated that they can be divided into two types. The C₃H₆-molecular-ion-implanted Epi-Si had more defects not containing O atoms inside the C agglomerates than the ion-implanted CZ-Si. It was shown that the distribution of O atoms in C agglomerates affects the gettering efficiency of Fe. We assume that Fe gettering on C agglomerate defects is due to strong electronic interaction of C agglomerates. The O atoms in C agglomerates strongly suppress the electronic interactions of C agglomerates themselves.

These results indicate that C agglomerates not containing O atoms are effective segregation-induced gettering sinks for metallic impurities and O diffusing from Si bulk. We believe that Si wafers in which the O distribution is controlled in the hydrocarbon-molecular-ion-implanted region will be effective for advanced CMOS image sensors.

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