Corrigendum: “Proximity gettering technique using CH$_3$O multielement molecular ion implantation for white spot defect density reduction in CMOS image sensor” [Jpn. J. Appl. Phys. 58, 091002 (2019)]

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In our published paper, the STEM image in Fig. 12(b) is incorrectly the same as Fig. 12(a). The correct appearance of Fig. 12(b) is shown here. The discussions and conclusions are not altered by this correction.

Fig. 12. (Color online) Cross-sectional STEM images of needle-shaped samples and 3D-APT analysis results of atom maps and isoconcentration surfaces at 2.0 at% carbon and 10 at% oxygen on stacking fault defects in CH$_3$O ion-implanted range (a) before and (b) after device process.

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Proximity gettering technique using CH$_3$O multielement molecular ion implantation for the reduction of the white spot defect density in CMOS image sensor

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We have characterized CH$_3$O ion-implanted epitaxial wafers in device fabrication processes. We confirmed that the CH$_3$O ion-implanted wafers can reduce the density of white spot defects in CMOS image sensors. Evaluation of the CH$_3$O ion-implanted region before and after device fabrication processes which included heat treatment and ion implantation, showed that two types of defects, namely stacking faults and carbon-related defects, exist in the CH$_3$O ion implantation region. GETting metallic impurities from the Si/SiO$_2$ interface region is powerful gettering sinks for oxygen. Thus, it was considered that two types of gettering sink formed by CH$_3$O ion implantation contribute to the reduction in the density of white spot defects. We believe that these characteristics contribute to the improvement of fabrication processes for advanced CMOS image sensors.

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1. Introduction

In recent years, charge coupled device (CCD) and complementary metal oxide semiconductor (CMOS) image sensors have been used for various applications such as vehicle-mounted cameras and monitoring cameras. For these products, high-performance CCD and CMOS image sensors with a wide dynamic range and high-sensitivity are required. To manufacture highly sensitive CCD and CMOS image sensors, it is necessary to improve their electrical properties such as reducing the dark current and the density of white defects. However, there are three technical issues that should be addressed to improve electrical device parameters, as shown in Fig. 1.

The first technical issue is the increase in dark current caused by metal impurity contamination during CCD and CMOS image sensor fabrication processes, which involve many heat treatment steps and ion implantation. In these processes, metallic impurities easily contaminate the active region in a device. These contaminating metal impurities form deep-energy-level defects within silicon band gaps, which generate dark current and white spot defects. Thus, to obtain high-performance CCD and CMOS image sensors, metallic impurities should be removed from the device active region. To solve this issue, a gettering technique is used in silicon wafer fabrication. This technique is used to gather metallic impurities outside of the device active region, thus removing metallic impurities from the device active region. There are several techniques of gettering technique on silicon wafers. Intrinsic gettering (IG) is the most popular technique. The origin of the sinks in IG is oxygen precipitates. In order to form oxygen precipitates, a high-temperature treatment is required. However, the temperature in thermal treatment is lower and the duration shorter in recently developed device fabrication processes. In such processes, the amount of formed oxygen precipitates acting as gettering sinks is not sufficient. Therefore, IG is not necessarily compatible with the fabrication processes for CCD and CMOS image sensors.

The second technical issue is the deterioration of the interface characteristics caused by oxygen-related defects. Typically, a Czochralski (CZ) silicon wafer substrate is used in the epitaxial wafer for CCD and CMOS image sensors. CZ silicon wafers have high concentrations of oxygen in the bulk. Thus, oxygen in the silicon wafer substrate diffuses to the silicon epitaxial layer, which is the device active region, during heat treatment. The diffused oxygen forms deep-energy-level defects in the device active region. Thus, high-performance CCD and CMOS image sensors should have a reduced oxygen concentration in the bulk of the CZ silicon wafer substrate. However, the low-oxygen-concentration CZ wafers cannot form a sufficient amount of oxygen precipitates for IG. Therefore, the use of low-oxygen-concentration wafers should be combined with another gettering technique.

The third issue is the random telegraph signal (RTS) noise generated by the interface state defects in the Si/SiO$_2$ interface region. Silicon dangling bonds exist in the Si/SiO$_2$ interface region. The dangling bonds form energy levels in silicon band gaps and affect the electrical properties of CMOS image sensors. Therefore, the density of interface state defects should be decreased to improve CMOS image sensor fabrication. The most popular technique for this is hydrogen passivation. This technique involves annealing at low temperatures in a hydrogen atmosphere. In this process, silicon dangling bonds are terminated by hydrogen to form silicon–hydrogen bonds. As a result, the energy level in the silicon band gap due to dangling bonds disappears and RTS noise can be reduced. The hydrogen passivation technique can effectively reduce electrical noise generated by dangling bonds. However, it has been reported that the device structure in recent years has progressively become multilayered, for which it is difficult to utilize the techniques of all the multilayer films. Thus, a passivation technique applicable to a multilayer device structure should be developed.
As described above, various efforts are being made to solve the technical problems encountered in CMOS image sensor fabrication processes. On the other hand, techniques that can solve all these problems have not yet been developed. A new gettering technique is required for silicon wafers in advanced CMOS image sensor fabrication processes.

To address these problems, we developed a multielement molecular ion implantation technique as a proximity gettering technology. This technique involves implanting molecular ions of three elements. We previously reported that the CH₃O ion implantation technique, which is used for implanting molecular ions of multiple elements, provides a higher gettering capability for nickel contamination by forming two types of gettering sink. One is implanted carbon-related defects and the other is stacking fault defects. As Kurita and coworkers reported in their study on proximity gettering using hydrocarbon molecular ion implantation, implanted carbon forms carbon-related defects which function as gettering sinks for metallic impurities. Furthermore, Kuroi et al. reported that the crystal defects generated by ion implantation function as gettering sinks. Taken together, it is considered that both types of defect formed by CH₃O ion implantation function as strong gettering sinks. Therefore, CH₃O ion implantation can markedly remove metallic impurities from the device formation region. We also believe that this technique can contribute to the reduction in the density of white spot defects in CMOS image sensors.

However, there are two aspects that should be verified with regard to whether the CH₃O ion implantation technique can indeed contribute to the improvement of the characteristics of CMOS image sensors. One is the gettering behavior in device fabrication processes. In experiments on gettering capability in previous studies, a contamination gettering test was carried out using a standard aqueous solution with a high concentration of contaminating nickel. Thus, it is not clear whether the gettering capability within the CH₃O-implanted region affects the metallic impurity contamination in the fabrication processes for CMOS image sensors.

The other aspect is the effect of implanted oxygen on white spot defects. It is not clear how oxygen added in CH₃O ion implantation affects the white defect characteristics of CMOS image sensors. In this study, we demonstrate the gettering capability within the CH₃O-implanted region for metallic impurities generated during the fabrication processes for CMOS image sensors. To determine the effect of CH₃O ion implantation on CMOS image sensors, we compared wafers with and without CH₃O ion implantation in wafers using IG, which is the most basic gettering technique. Moreover, we investigated whether the technique can getter the oxygen diffusing during the device fabrication process and reduce the oxygen concentration in the epitaxial layer despite implanting oxygen in the CH₃O-implanted region. Furthermore, we investigated whether the CH₃O ion-implanted silicon epitaxial wafer can reduce the density of white spot defects in CMOS image sensors.

2. Experimental methods
We used 12 inch n-type (100) phosphorus- and carbon-doped CZ single-crystal silicon wafers. The concentration of phosphorus was $5.0 \times 10^{14}$ atoms cm$^{-3}$. The concentration of carbon was $2.7-3.0 \times 10^{16}$ atoms cm$^{-3}$. The wafers used in this experiment were prepared from the same crystal silicon ingot. These wafers were implanted with CH₃O multielement molecular ions at room temperature. The CH₃O ions were implanted using a CLARIS® ion implanter, (Nissin Ion Equipment Co,. Ltd.). The implantation energy was 80 keV/ion. The implantation dose of the CH₃O ions was $7.0 \times 10^{14}$ ions cm$^{-2}$. The ion beam current of CH₃O was 550 μA. The samples were epitaxially grown after CH₃O multielement molecular ion implantation.

To analyze the effect of the CH₃O ion implantation technique on the electrical properties of CMOS image sensors, we evaluated the density of white spot defects that are larger than 145 ele/s in samples with and without CH₃O ion implantation by dark current spectrometry (DCS). DCS analysis enables the measurement of the density of electrical defects due to metallic impurity contamination and that of interface state defects in the CMOS device structure. In this study, DCS analysis was carried out using a CMOS...
image device structure, which is a four-transistor-type pinned photodiode fabricated by a CMOS device process line. After the DCS analysis, we measured the physical properties such as the density of defects and the concentration-depth profiles of implanted atoms and metallic impurities in the same sample as that used for DCS analysis. The density of bulk micro defects (BMD) was measured using a BMD analyzer (MO-441\textsuperscript{®}, Raytex Optima Incorporated). The distribution profiles of carbon, hydrogen, oxygen, nickel, and copper were analyzed by secondary ion mass spectrometry (SIMS). For high-sensitivity analysis, we mechanically polished the surface layer a depth of about 1 μm before SIMS analysis. The concentration profiles before and after the device processes were compared considering the polishing depth in samples after the device processes. A sample before the device processes refers to the sample after silicon epitaxial growth. The defects within implantation range of the multielement molecular cluster ions were analyzed by transmission electron microscopy (TEM). The distribution profiles of carbon and oxygen within the CH\textsubscript{3}O ion-implanted region were analyzed by three-dimensional atom probe tomography (3D-APT) using a LEAP4000XSi (AMETEC CAMECA).\textsuperscript{31,32} In 3D-APT analysis, it is necessary to prepare needle-shaped samples using a focused ion beam. The samples for 3D-APT analysis were lifted out within 5 μm from their surface, which is within the CH\textsubscript{3}O ion-implanted region. The 3D-APT data collected were analyzed using integrated visualization and analysis software from CAMECA.

3. Experimental results and discussion

3.1. Metallic impurity gettering behavior during device fabrication processes

Figure 2 shows the distribution profiles of carbon, hydrogen, oxygen, nickel, and copper as a function of concentration after the device processes. CH\textsubscript{3}O ions were implanted at a dose of 7.0 \times 10^{14} ions cm\textsuperscript{-2}. The concentration peaks of carbon, hydrogen, and oxygen were observed at the same depth; thus, these concentration peaks are assumed to be attributable to CH\textsubscript{3}O ion implantation. Furthermore, the nickel and copper concentration peaks were observed at the same depth within the CH\textsubscript{3}O ion-implanted region. These results suggest that within the CH\textsubscript{3}O ion-implanted region, various metallic impurities aregettered. Furthermore, the CH\textsubscript{3}O ion-implanted wafer forms two types of gettering sink, the BMD and CH\textsubscript{3}O ion-implanted regions. Nevertheless, the nickel and copper concentration peaks were observed in the CH\textsubscript{3}O ion-implanted region. This result suggests that the CH\textsubscript{3}O ion-implanted region can getter metallic impurities during the device process.

To analyze the amount of nickel gettered during the device process, we analyzed the nickel concentration-depth profiles by SIMS before and after the device process. Figure 3(a) shows the nickel concentration-depth profile before the device process. Figure 3(b) shows the nickel concentration-depth profile after the device process. As shown in Fig. 3(a), no nickel impurities were observed in the epitaxial layer and CH\textsubscript{3}O ion-implanted range. On the other hand, a nickel
concentration peak was observed within the CH$_3$O ion-implanted region as shown in Fig. 3(b). The nickel concentration in the CH$_3$O ion-implanted range after the device process was $1.2 \times 10^{11}$ atoms cm$^{-2}$. Thus, this result suggests that within the CH$_3$O ion-implanted regions at least $1.2 \times 10^{11}$ atoms cm$^{-2}$ nickel impurities are gettered during the device processes.

3.2. Diffusion behavior of implanted atoms during device fabrication processes

As shown in Sect. 3.3.1, the gettering by CH$_3$O ion implantation is effective for metallic impurities during the device fabrication processes. In our previous study, we confirmed that the concentration peaks of carbon, oxygen and hydrogen occur within the CH$_3$O-implanted region, which are higher than their solid solubility owing to two types of defect “stacking fault and carbon-related defect.” We also confirmed that this range functions as the gettering sink for metallic impurities. Thus, understanding the diffusion behavior of implanted atoms and defect behavior during the device fabrication processes is important for understanding the effect of the CH$_3$O ion-implanted range. As reported in this subsection, we investigated the diffusion behavior of carbon, oxygen, and hydrogen, which are implanted by CH$_3$O ion implantation.

3.2.1. Carbon diffusion behavior.

Figure 4 shows the carbon distribution profiles in CH$_3$O ion-implanted wafer and non-ion-implanted wafer (a) before and (b) after device process. In the CH$_3$O ion-implanted epitaxial layer of the CH$_3$O ion-implanted wafer, the carbon concentration near its peak was decreased by the device process. On the other hand, the carbon concentration in the epitaxial layer after the device process decreased in the CH$_3$O ion-implanted wafer, as shown in Fig. 5(b). The amount of oxygen gettered in the CH$_3$O ion-implanted region before the device processes was $1.7 \times 10^{14}$ atoms cm$^{-2}$ and that after the device process was $3.4 \times 10^{14}$ atoms cm$^{-2}$. The amount of oxygen gettered increased during the device process. This suggests that the CH$_3$O ion-implanted region can getter oxygen atoms diffusing from the silicon substrate during the device heat treatment.

3.2.2. Oxygen gettering behavior.

Figures 5(a) and 5(b), respectively, show the oxygen distribution profiles of oxygen before and after the device process. From these results, oxygen concentration peaks were observed in the CH$_3$O ion-implanted range. This indicates that the CH$_3$O ion-implanted range gettered oxygen before and after the device process. As Fig. 5(a), the oxygen concentration in the epitaxial layer of the CH$_3$O ion-implanted wafer is higher than that in the non-ion-implanted wafer after epitaxial growth. This difference was assumed to be due to the diffusion of implanted oxygen into the epitaxial layer from the CH$_3$O ion-implanted range during the epitaxial layer growth process. On the other hand, the oxygen concentration in the epitaxial layer after the device process decreased in the CH$_3$O ion-implanted wafer, as shown in Fig. 5(b). The amount of oxygen gettered in the CH$_3$O ion-implanted region before the device processes was $1.7 \times 10^{14}$ atoms cm$^{-2}$ and that after the device process was $3.4 \times 10^{14}$ atoms cm$^{-2}$. The amount of oxygen gettered increased during the device process. This suggests that the CH$_3$O ion-implanted region can getter oxygen atoms diffusing from the silicon substrate during the device heat treatment.

Figure 6 shows the oxygen concentrations at a depth of 1.4 $\mu$m from the surface layer to the interface of the silicon substrate and epitaxial layer where can be measured by SIMS. The oxygen concentration in the epitaxial layer without CH$_3$O ion implantation was increased from $4.5 \times 10^{13}$ to $1.0 \times 10^{14}$ atoms cm$^{-2}$ by the device heat
treatment. However, in the CH₃O ion-implanted epitaxial wafer, the oxygen concentration decreased from $6.8 \times 10^{13}$ to $6.7 \times 10^{13}$ atoms cm$^{-2}$. These results suggest that most of the oxygen atoms that diffused from the silicon substrate were getters in the CH₃O ion-implanted regions. Furthermore, the difference in the oxygen distribution depth profile in the epitaxial layer was due to the diffusion of oxygen that already existed in the silicon epitaxial layer before the device process. Therefore, the CH₃O ion implantation technique does not increase the oxygen concentration in the epitaxial layer, but rather decreases the oxygen concentration by gettering oxygen during the device fabrication processes.

3.2.3. Hydrogen gettering behavior. Figure 7 shows the hydrogen distribution profiles before and after the device process. Before the device process, the hydrogen concentration in the CH₃O ion-implanted range was $8.6 \times 10^{12}$ atoms cm$^{-2}$ and that after the device process was $1.2 \times 10^{12}$ atoms cm$^{-2}$. The amount of hydrogen that diffused from the CH₃O ion-implanted range was $7.4 \times 10^{12}$ atoms cm$^{-2}$. We confirmed that hydrogen diffused from the CH₃O ion-implanted range during the device process. Okuyama et al. reported the diffusion behavior in a CH₃O ion-implanted silicon epitaxial wafer during isothermal annealing. In their study, almost $7.4 \times 10^{12}$ atoms cm$^{-2}$ hydrogen diffused. Thus, the same amount of hydrogen diffused during the device process. Therefore, it is expected that the CH₃O ion-implanted silicon epitaxial wafer can passivate the interface state defects by the diffusion of hydrogen from the CH₃O ion-implanted range.

3.3. Defect morphology observation in CH₃O ion-implanted range

In Sect. 3.3.2, we investigated the diffusion behavior of ion-implanted atoms during the device fabrication process. Typically, the diffusion behavior of atoms and defect behavior are closely related. Furthermore, understanding the
defects in silicon crystals is important for understanding the gettering effect because the defects function as gettering sinks. The \( \text{CH}_3\text{O} \) ion-implanted epitaxial wafer is expected to have two regions of the gettering sinks. One is the \( \text{CH}_3\text{O} \) ion-implanted region and the other is BMD region. As shown in Fig. 5, the \( \text{CH}_3\text{O} \) ion-implanted region is located near the interface of silicon epitaxial layer and silicon substrate. On the other hand, the formation region of BMDs is the bulk of the silicon substrate about 30 \( \mu \text{m} \) in depth from the surface of the substrate. Thus, the \( \text{CH}_3\text{O} \) ion-implanted region is located nearer to the device active region than the BMD region. In this section, we investigate the defect behavior in the \( \text{CH}_3\text{O} \) ion-implanted epitaxial wafer during device fabrication process.

3.3.1. BMD formation behavior. Figure 8 shows the BMD densities in the \( \text{CH}_3\text{O} \) ion-implanted silicon epitaxial wafer and non-ion-implanted silicon epitaxial wafer analyzed using MO-441. \( \text{CH}_3\text{O} \) ions were implanted at a dose of \( 7.0 \times 10^{14} \text{ ions cm}^{-2} \) and the BMD density in the non-ion-implanted silicon epitaxial wafer was \( 2.7 \times 10^{9} \text{ cm}^{-3} \). The BMD density in the \( \text{CH}_3\text{O} \) ion-implanted silicon epitaxial wafer was \( 3.4 \times 10^{9} \text{ cm}^{-3} \). The BMD density of \( \text{CH}_3\text{O} \) ion-implanted wafer is slightly higher than that of the non-ion-implanted wafer. The reasons for the increase in BMD density are considered to be as follows. One is the difference between initial carbon and oxygen concentrations in the silicon substrate. The other reason is the effect of carbon and oxygen introduced by \( \text{CH}_3\text{O} \) ion implantation. However, the depth of the BMD region is over 30 \( \mu \text{m} \) the interface of the silicon substrate and silicon epitaxial layer. Thus, the \( \text{CH}_3\text{O} \) ion-implanted region is far from the BMD region. It is

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**Fig. 6.** (Color online) Oxygen concentrations in epitaxial layer of wafers with and without \( \text{CH}_3\text{O} \) ion implantation before and after device process.

**Fig. 7.** (Color online) Hydrogen distribution profiles before and after device process.

**Fig. 8.** (Color online) BMD densities in \( \text{CH}_3\text{O} \) ion-implanted wafer and non-ion-implanted wafer.
considered that the impact of CH₃O ion implantation on BMD formation is small. We speculated that the difference in BMD density between the CH₃O ion-implanted wafer and the non-ion-implanted wafer is due to the difference between the oxygen and carbon concentrations in the substrate. It is considered from the results shown in Fig. 8 that the BMD density in the non-ion-implanted wafer and CH₃O ion-implanted wafer is almost the same and the gettering capability of the BMD region in these wafers.

3.3.2. CH₃O ion-implanted defect behavior. Figures 9(a) and 9(b) show cross-sectional TEM images of the CH₃O ion-implanted region before and after the device process, respectively. CH₃O ions were implanted at a dose of \(7.0 \times 10^{14} \text{ ions cm}^{-2}\). In Figs. 9(a) and 9(b), two types of defect were observed: carbon-related defects of almost 5 nm size and large ion implantation defects. The 5 nm size defects were observed as black points in Figs. 9(a) and 9(b). In a previous study, ion implantation defects were determined to be Si \{111\} stacking faults.\(^{15}\) We assumed that these two types of defect functioned as gettering sinks. Focusing on stacking fault defects, their density did not change as a result of the device process. Therefore, we assumed that the gettering capability for stacking fault defects was not changed during the device process.

Figure 10 shows the densities of 5 nm size carbon-related defects. The defect density before the device process was \(3.4 \times 10^{16} \text{ cm}^{-3}\) and the defect density after the device process was \(2.9 \times 10^{16} \text{ cm}^{-3}\). The density of the 5 nm size defects did not change as a result of the process. In a study of the hydrocarbon molecular ion implantation technique, the gettering capability increased with increasing 5 nm size defect density.\(^{20}\) Thus, we assumed that the gettering capability of the CH₃O ion-implanted range was maintained during the devices process.

Figures 11(a) and 11(b) show cross-sectional SEM images of samples for carbon-related defect analysis by 3D-APT before and after the device process along with their carbon and oxygen distribution maps. These samples were prepared for analyzing 5 nm size defects, which were located far from stacking fault defects. As shown in Figs. 11(a) and 11(b), the aggregation of carbon and oxygen was observed.

To reveal the distribution of carbon and oxygen atoms, the maps showing 2 at% carbon and 5 at% oxygen isoconcentration surfaces extracted from the CH₃O ion-implanted range before and after the device process are shown in Figs. 11(a) and 11(b), respectively. As shown Figs. 11(a) and 11(b), the regions with high concentrations of carbon and oxygen are almost overlap. Furthermore, the oxygen concentration in the oxygen aggregation region after the device process was higher than that before the device process. This result indicates that the carbon aggregation region can gather oxygen that diffused from the CZ silicon substrate during the device process.

STEM images and 3D-APT analysis results of the samples before and after the device fabrication process for stacking fault defects are shown Fig. 12. As shown in Fig. 12, STEM images stacking fault defects in the samples. Figures 12(a) and 12(b) show the carbon and oxygen distribution map before and after device process, which, respectively, show the aggregation of carbon and oxygen assumed to be located around the stacking fault defects.
To reveal the distribution of carbon and oxygen atoms, the maps showing 2 at% carbon and 10 at% oxygen isoconcentration surfaces extracted from the CH₃O ion-implanted range before and after the device process are, respectively, shown in Figs. 12(a) and 12(b). As shown in Figs. 12(a) and 12(b), the regions with high concentrations of carbon and oxygen are almost the overlap. Furthermore, the region with 10 at% oxygen after the device process was wider than that before the device process. This result suggests that the oxygen concentration in the CH₃O ion-implanted range around the stacking fault defects after the device process was significantly higher than that before the device process. It is considered that the stacking fault defects function as gettering sinks for oxygen impurities that diffused from the silicon substrate during the device process. In particular, the oxygen concentration around the stacking fault defects is higher than that around the carbon aggregation region near the stacking fault defects. It is indicated that the stacking fault defects are stronger gettering sinks for oxygen than the carbon aggregation region.

As mentioned above, the CH₃O ion-implanted region can getter various elements. It is assumed that this characteristic contributes to the reduction in white spot defect density. Then, why can the CH₃O-implanted region getter various elements? What is the mechanism underlying the gettering effect in the CH₃O ion-implanted region?

Generally, there are two mechanisms underlying the gettering effect in silicon wafers. The first is segregation gettering. Segregation gettering is induced by the difference in the solid solubility for metallic impurities. If gettering sinks have higher solid solubility than the bulk of the silicon crystal, the gettering sinks can gather the metallic impurities. The second is relaxation gettering. This type of gettering is caused by the stress field. For example, the stress field induced by the defect such as dislocations can getter metallic impurities.
The CH$_3$O ion-implanted range has two types of defect functioning as gettering sinks, as shown in Fig. 9. Figure 11 also shows that carbon-related defects arise from carbon and oxygen aggregation. This type of defect is similar to that generated by hydrocarbon molecular ion implantation. Previously, Kurita et al. reported that the mechanism of gettering carbon-related defects is segregation. Therefore, it is considered that the mechanism of gettering the carbon-related defects in the CH$_3$O ion-implanted range is segregation.

On the other hand, a different mechanism of gettering stacking fault defects is assumed. In general, the mechanism of gettering the secondary defects generated by ion implantation such as high-energy ion implantation is relaxation. Because the ion-implanted defects in the CH$_3$O ion-implanted range are stacking fault defects, it is considered that the mechanism of gettering these defects is relaxation. However, as shown in Fig. 12, the carbon complexes exist around the stacking fault defects. Moreover, the oxygen atoms that diffused during the device heat treatment are gettered by the carbon complexes. Thus, it is considered that the carbon complexes around the stacking fault defects function as the gettering sinks for metallic impurities. The mechanism of gettering the carbon complexes existing in the silicon crystal bulk is segregation. Additionally, Shirasawa et al. reported that the carbon complexes in silicon crystal have high binding energy for various metallic impurities, as determined by density functional theory calculation. Therefore, the mechanism of gettering the carbon complexes around the stacking fault defects is considered to be segregation. In conclusion, it is considered that the mechanism of gettering the stacking fault defects in the CH$_3$O ion-implanted range is a combination of the relaxation type for secondary defects and the segregation type for the carbon and oxygen complexes. As shown by the isoconcentration surface analysis results in Fig. 11, the oxygen concentration increased around the carbon-related defects existing far from stacking fault defects after the fabrication processes. On the other hand, the oxygen concentration did not increase around the carbon-related defects existing near the stacking fault defects after the fabrication processes, as shown by the isoconcentration surfaces analysis result in Fig. 12. It can be considered that stacking fault defects are stronger gettering sinks and contribute to the reduction in the density of white spot defects.

![Fig. 12.](Color online) Cross-sectional STEM images of needle-shaped samples and 3D-APT analysis results of atom maps and isoconcentration surfaces at 2.0 at% carbon and 10 at% oxygen on stacking fault defects in CH$_3$O ion-implanted range (a) before and (b) after device process.

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can getter oxygen that diffused from the silicon substrate during the device heat treatment. The oxygen in the device structure region accounts for the lag characteristics of CMOS image sensors. Furthermore, Kaneda and Ohtani reported that the oxygen–boron complex generates the energy level in silicon band gaps. Boron is used to form the p-type region in device structures such as photodiodes. Thus, it is considered that oxygen concentration reduction reduces the white spot defect density via the reduction in the concentration of the oxygen–boron complex.

Third, hydrogen gettering occurs in the CH$_3$O ion-implanted range. In general, Si/SiO$_2$ interface states form the electrical state in silicon crystal band gaps. This electrical state easily forms holes and electrons by thermal energy without photo-irradiation. As a result, Si/SiO$_2$ interface states increase the density of white spot defects.

As shown in the Fig. 7, the concentration of hydrogen that diffused during the device process was $7.4 \times 10^{12}$ atoms cm$^{-2}$. In general, the density of Si/SiO$_2$ interface states is almost $10^{13}$ atoms cm$^{-2}$. Although the amount of hydrogen that diffused was over ten times higher than that of the Si/SiO$_2$ interface state, we assumed that the amount of hydrogen was sufficient to passivate the Si/SiO$_2$ interface states. It is expected that hydrogen that diffused from the CH$_3$O ion-implanted range passivated the interface state in device structures such as the Si/SiO$_2$ interface state.

In conclusion, it is considered that white spot defect density reduction was realized through these three mechanisms, accounting for the high gettering capability of the CH$_3$O ion-implanted region for metallic impurities.

4. Conclusions

We demonstrated the reduction in white spot defect density in CMOS image sensors using the CH$_3$O ion implantation technique. We assumed that this reduction was achieved through to three mechanisms. The first mechanism is the metallic impurity gettering in the CH$_3$O ion-implanted range. The CH$_3$O ion-implanted range forms two types of defect, carbon-related defects and stacking fault defects. We assumed that these defects function as gettering sinks for metallic impurities generated during the device fabrication process. The second mechanism is the reduction in the amount of oxygen in the epitaxial layer during the device heat treatment. Although the CH$_3$O ion implantation technique implants oxygen, it is presumed that the oxygen gettering capability can be further enhanced by forming stacking fault defects. As a result, it was confirmed that the oxygen concentration in the epitaxial layer after the device process can be reduced by gettering oxygen. The third mechanism is the hydrogen passivation effect. We confirmed that hydrogen out-diffused to device active region from the CH$_3$O ion-implanted range during the device heat treatment. We found that the amount of hydrogen that diffused from the CH$_3$O ion-implanted range was over ten times higher than the general density of Si/SiO$_2$ interface states. Therefore, it is expected that out-diffused hydrogen also contributes to the reduction in the density of Si/SiO$_2$ interface-related white spot defects. It is considered that these mechanisms are effective in reducing the density of white spot defects in CMOS image sensors. Therefore, it is considered that the reduction in the density of white spot defects by CH$_3$O ion

![Fig. 13. (Color online) Density of white spot defects in wafers with CH$_3$O ion implantation and without implantation.](image)
implantation was accomplished by a combination of these mechanisms. We believe that this wafer can contribute to the improvement of device electrical performance for advanced CMOS image sensor manufacturing.

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1) T. Kuroda, Essential Principles of Image Sensors (CRC Press, Tokyo, 2014), Chap. 5, p. 55.
2) H. Takahashi, CMOS Image Sensor (Corona, Tokyo, 2012), Chap. 3, p. 123 [in Japanese].
3) K. Graff, Metal Impurities in Silicon-Devices Fabrication (Springer, Cham, 2000).
4) C. Claey and E. Simoen, Metal Impurities in Silicon-and Germanium-Based Technologies (Springer, Cham, 2018), Chap. 7, p. 332.
5) E. R. Weber, Appl. Phys. A 30, 1 (1983).
6) A. A. Istratov and E. R. Weber, Appl. Phys. A 66, 123 (1998).
7) J. S. Kang and D. K. Schroder, J. Appl. Phys. 65, 2974 (1989).
8) D. Gilles, E. R. Weber, and S. Hahn, Phys. Rev. Lett. 64, 196 (1990).
9) M. Aoki, A. Hara, and A. Ohawa, J. Appl. Phys. 72, 895 (1992).
10) T. Kameda and A. Ohtani, Ext. Abstr. (77th Autumn Meet. 2016); Japan Society of Applied Physics and Related Societies, (2016), 14p-P6-10 [in Japanese].
11) A. Ohtani and T. Kaneda, Ext. Abstr. (77th Autumn Meet. 2016); Japan Society of Applied Physics and Related Societies, (2016), 14p-P6-11 [in Japanese].
12) F. Shimura, Semiconductor Silicon Crystal Technology (Academic, Cambridge, 1989).
13) J.-P. Carrère, S. Place, J.-P. Oddou, D. Benoit, and F. Roy, IEEE Int. Reliability Physics Symp. (IRPS), 2014, (2014), p. 3C.1.1.
14) J. L. Regolini, D. Benoit, and P. Morin, Microelectron. Reliab. 47, 739 (2007).
15) R. Hirose, T. Kadono, R. Okuyama, S. Shigematsu, A. Onaka-Masada, H. Okuda, Y. Koga, and K. Kurita, Jpn. J. Appl. Phys. 57, 096503 (2018).
16) K. Kurita, T. Kadono, R. Okuyama, R. Hirose, A. Onaka-Masada, Y. Koga, and H. Okuda, Jpn. J. Appl. Phys. 55, 121301 (2016).
17) R. Okuyama, T. Kadono, A. Masada, R. Hirose, Y. Koga, H. Okuda, and K. Kurita, Jpn. J. Appl. Phys. 56, 025601 (2017).
18) K. Kurita, T. Kadono, R. Okuyama, R. Hirose, A. Onaka-Masada, Y. Koga, and H. Okuda, IEEE Electron Device Technology and Manufacturing Conf., 2017 Vol. 6M-A, p. 105.
19) R. Okuyama, S. Shigematsu, R. Hirose, A. Masada, T. Kadono, Y. Koga, H. Okuda, and K. Kurita, Phys. Status Solidi. C 14, 1700036 (2017).
20) K. Kurita, T. Kadono, R. Okuyama, S. Shigematsu, R. Hirose, A. Onaka-Masada, Y. Koga, and H. Okuda, Phys. Status Solidi. A 217, 1700216 (2017).
21) T. Kuroi, Y. Kawasaki, S. Komori, M. Inuishi, K. Tsukamoto, H. Shinyaishi, and T. Shingyoji, Jpn. J. Appl. Phys. 32, 303 (1993).
22) I. Yamada, Materials Processing by Cluster Ion Beams, History, Technology, and Applications (CRC Press, Tokyo, 2015), Chap. 2, p. 21.
23) I. Yamada, M. Matsuo, N. Toyoda, and A. Kirkpatrick, Mater. Sci. Eng. R 34, 231 (2001).
24) M. Tanjyo, N. Hamamoto, T. Nagayama, S. Umixedo, Y. Koga, N. Maehara, H. Une, T. Matsumoto, N. Nagai, and J. O. Borland, ECS Trans. 18, 1059 (2009).
25) F. Russo et al., Solid-State Electron. 91, 91 (2014).
26) F. Russo et al., ECS J. Solid State Sci. Technol. 6, 217 (2017).
27) T. Yamaguchi, T. Yamashita, T. Kamin, Y. Goto, T. Kuroi, and M. Matsuura, 2016 IEEE Symp. on VLSI Technology, (2016).
28) T. Yamaguchi, T. Kamin, Y. Goto, M. Kimura, M. Inoue, and M. Matsuura, The 8th Forum on the Science and Technology of Silicon Materials 2018, (2018), p. S6.
29) H. Takahashi, M. Kinoshita, K. Morita, T. Shirai, T. Sato, T. Kimura, H. Yuzuihara, and S. Inoue, ISSCC Dig. Tech. Pap., 2004, (2004) Vol. 78.
30) M. Mee, M. Katsumo, S. Kasuga, T. Murata, and T. Yamaguchi, ISSCC Dig. Tech. Pap., 2004, (2004) Vol. 80.
31) T. P. Kelly and M. K. Miller, Rev. Sci. Instrum. 78, 031101 (2007).
32) D. Blavette, E. Cadel, A. Fraczkiewicz, and A. Menand, Science 286, 2317 (1999).
33) L. Baldi, G. F. Cerofolini, G. Ferla, and G. Frigerio, Phys. Status Solidi A 48, 525 (1978).
34) S. Shirasawa, K. Suseoka, T. Yamaguchi, and K. Maekawa, J. Electrochem. Soc. 4, P351 (2015).
35) S. Shirasawa, K. Suseoka, T. Yamaguchi, and K. Maekawa, Ext. Abstr. (76th Autumn Meet. 2015); Japan Society of Applied Physics and Related Societies, 2015, (2015), 14p-PB7-2 [in Japanese].
36) S. Shirasawa, K. Suseoka, T. Yamaguchi, and K. Maekawa, Mater. Sci. Semicond. Process. 44, 13 (2016).