Effect of dose and size on defect engineering in carbon cluster implanted silicon wafers

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Carbon-cluster-ion-implanted defects were investigated by high-resolution cross-sectional transmission electron microscopy toward achieving high-performance CMOS image sensors. We revealed that implantation damage formation in the silicon wafer bulk significantly differs between carbon-cluster and monomer ions after implantation. After epitaxial growth, small and large defects were observed in the implanted region of carbon clusters. The electron diffraction pattern of both small and large defects exhibits that from bulk crystalline silicon in the implanted region. On the one hand, we assumed that the silicon carbide structure was not formed in the implanted region, and small defects formed because of the complex of carbon and interstitial silicon. On the other hand, large defects were hypothesized to originate from the recrystallization of the amorphous layer formed by high-dose carbon-cluster implantation. These defects are considered to contribute to the powerful gettering capability required for high-performance CMOS image sensors. © 2018 The Japan Society of Applied Physics

1. Introduction

CMOS image sensor manufacturers strongly require a reduction in the dark current and white-spot defects for high-sensitivity performance.1) The dark current and white-spot defects are caused by deep energy levels in the silicon band gap formed by metallic impurities in the space-charge region during the device fabrication process.2–6) Therefore, an important requirement is that metallic impurities are eliminated from the active region of devices. Gettering techniques, such as intrinsic gettering (IG) and extrinsic gettering (EG), are necessary to address these issues.7–12) However, the thermal heat treatment of devices is tending toward short times and low temperatures.13) Thus, it is difficult for metallic impurities to diffuse to the gettering sink in the silicon bulk. Furthermore, it is difficult for IG sinks to grow an oxygen precipitate in the silicon bulk during the low-temperature thermal heating of devices.

Therefore, a proximity gettering technique is needed for CMOS image sensors. This technique forms sinks with the highest gettering capability under the epitaxial layer and substrate interface. We previously developed a proximity gettering technique by performing carbon-cluster-ion implantation in silicon wafers.14–16) Carbon-cluster ions can be obtained by the decomposition of a source gas containing carbon and hydrogen. For example, we can use C₂H₅ or C₃H₅. The implantation energy is very low because cluster ions distribute the implantation energy.17) We can perform very low energy implantation and form an implanted region around the projection range of carbon clusters near the top silicon wafer surface. Furthermore, we demonstrated that carbon-cluster-ion-implanted epitaxial wafers have three characteristics useful for achieving high-performance advanced CMOS image sensors.14–16) First, the silicon surface within the projection range of carbon clusters has a high gettering capability for metallic impurities.14–16) Second, this implanted region of carbon clusters also has a barrier effect on oxygen impurities diffusing out from the Si wafer bulk.14,15) Third, a passivation effect on process-induced defects is expected owing to the hydrogen in the carbon-cluster ions trapped in the implanted region during the device fabrication process.16,18) However, the formation behavior of the implantation defects considered to be the gettering sinks in the implanted region around the projection range of the carbon clusters is unclear.

Previous studies using a monomer-ion implantation technique for gettering have been reported.19–26) However, monomer-ion implantation usually requires high energy beyond 100 keV, and the projection range of a monomer ion is deep in the silicon substrate surface. Even if a monomer ion can be implanted with low energy, it is difficult to control the projection range because of the channeling effect. In addition, the previous gettering techniques by monomer ion implantation have mostly revealed that implantation defects such as dislocation loops make up the gettering sinks because high-energy implantation occurred.20–22) However, it is not preferable for defects such as dislocation loops to be formed under the interface of the epitaxial layer and substrate for proximity gettering.

Therefore, the main intention of this study was to demonstrate the structure of carbon-cluster-ion-implanted defects in silicon bulk. Several studies on carbon-cluster-ion implantation have been reported.27–30) However, there have been few studies reporting the effects of the carbon cluster size and carbon dose on defect formation or giving a comparison with monomer implantation. Furthermore, it is not clear what kinds of defects are formed after epitaxial growth. Therefore, understanding the properties of carbon-cluster implantation defects is important for both applied and fundamental material science. In this study, we compared the defect morphology after carbon-cluster implantation and carbon-monomer implantation. We also investigated the dependence of defect formation on the carbon cluster size and dose. We observed the implanted region around the projection range of carbon clusters after epitaxial growth by high-resolution cross-sectional transmission electron microscopy (HR-XTEM).
2. Experimental methods

In this study, n-type Si(100) wafers were implanted with C$_3$H$_5$ or C$_2$H$_5$ carbon-cluster ions at room temperature. The C$_3$H$_5$ doses were equivalent to carbon doses of 1.0 $\times$ 10$^{15}$, 2.0 $\times$ 10$^{15}$, and 3.0 $\times$ 10$^{15}$ carbon atoms/cm$^2$. The wafers were implanted with C$_2$H$_5$ of 2.0 $\times$ 10$^{15}$ carbon atoms/cm$^2$ for comparison. The tilt and twist condition was performed both in 0°. The implantation energy was 80 keV/cluster. For a carbon atom, the implantation energies of C$_3$H$_5$ and C$_2$H$_5$ were 23.4 and 33.1 keV, respectively. The C$_3$H$_5$ beam current was 800 µA (a factor of 3 is required to obtain the equivalent current per atom, i.e., 2400 µA/carbon atom) and the C$_2$H$_5$ beam current was 400 µA. Samples were prepared after implantation and after epitaxial silicon growth. Epitaxial silicon layers of 8.0 µm thickness were grown using a Si$_3$HCl gas source at 1100 °C. The epitaxial growth rate was 1.0 µm/min. Monomer-carbon-implanted samples were also prepared with the same carbon dose and energy as those for the C$_3$H$_5$-cluster-ion implantation. Carbon-cluster-ion implantation and monomer-carbon-ion implantation were conducted in CLARIS and EXCEED of Nissin Ion Equipment, respectively. HR-XTEM imaging was performed to study the evolution of damage due to carbon-cluster-ion implantation. Carbon-cluster-ion implantation and monomer-carbon-ion implantation were conducted in CLARIS and EXCEED of Nissin Ion Equipment, respectively. HR-XTEM imaging was performed to study the evolution of damage due to carbon-cluster-ion implantation and monomer-carbon-ion implantation. Selected-area electron diffraction (SAED) analysis was conducted after sample implantation to evaluate the amorphous layer. The distributions of the carbon-cluster ions, implanted carbon, and monomer-ion-implanted carbon were analyzed using secondary ion mass spectrometry (SIMS). HR-XTEM and nano-beam electron diffraction (n-ED) were used to observe the ion-implantation defects in the implanted region around the projection range of the carbon clusters after epitaxial growth.

3. Results and discussion

3.1 Defect formation behavior in the region implanted with carbon-cluster ions after implantation and epitaxial growth

Figure 1 shows XTEM images of the C$_3$H$_5$-cluster-ion-implanted Si wafers with carbon doses of (a) 1.0 $\times$ 10$^{15}$, (b) 2.0 $\times$ 10$^{15}$, and (c) 3.0 $\times$ 10$^{15}$ carbon atoms/cm$^2$. The region with a different contrast at a depth of approximately 60 nm is the damage region, as shown in Fig. 1(a). As the dose increased, the damage region changed to an amorphous structure, as shown in Figs. 1(b) and 1(c). The amorphous region was confirmed by SAED. The amorphous region was not formed from the silicon surface and it was observed in the silicon being formed inside. Rudawski et al. demonstrated that the formation of an amorphous region by C$_7$H$_7$ clusters is caused by the silicon surface. It was revealed that the formation process of amorphous regions varied in accordance with the difference in carbon-cluster size. Figure 2 shows the SIMS profiles of the C$_3$H$_5$-cluster-implanted (solid line) and monomer-carbon-implanted (dashed line) samples for a dose of 2.0 $\times$ 10$^{15}$ carbon atoms/cm$^2$. The projection range of the C$_3$H$_5$-implanted carbon was approximately 80 nm. For the following discussion, the projection range refers to the peak depth of the carbon profile obtained by SIMS analysis. Despite the same implanted energy of a carbon atom, the projection range of the monomer carbon was approximately
100 nm, as shown in Fig. 2. As a result, the projection range of the C₃H₅-implanted carbon was shallower than that of the monomer carbon. Figure 3 shows XTEM images of the carbon-monomer-implanted samples with doses of (a) 1.0 × 10¹⁵, (b) 2.0 × 10¹⁵, and (c) 3.0 × 10¹⁵ carbon atoms/cm². The amorphous region could not be observed even when the dose was 3.0 × 10¹⁵ carbon atoms/cm². However, an implanted region above the projection range at a depth of approximately 80 nm can be observed as the region with a different contrast in Figs. 3(b) and 3(c). This region is the monomer-implanted damage region. As shown in Figs. 1 and 3, the depth of the carbon-cluster damage region was also less than that of the carbon monomers. Consequently, from the difference between the depth of the damage layer of 80 nm for C₃H₅ and that of 60 nm for the carbon monomers, the depth of the C₃H₅-implanted damage region differed by approximately 20 nm. In addition, the formation depth of the amorphous region was less than the projection range of the C₃H₅-implanted carbon. These results indicate that a carbon cluster has a dechanneling effect and that the carbon-cluster damage to the silicon wafer is greater than that of carbon monomers. Furthermore, in previous studies, amorphization occurred from the silicon wafer surface.30 However, in this study, the C₃H₅-cluster ions formed an amorphous region inside the silicon wafer. Amorphization occurred from the C₃H₅-cluster-implanted region. This result suggests that epitaxial growth is possible after C₃H₅-cluster implantation.

Figure 4 shows XTEM images of the C₃H₅-cluster-implanted samples after epitaxial growth with doses of (a) 1.0 × 10¹⁵, (b) 2.0 × 10¹⁵, and (c) 3.0 × 10¹⁵ carbon atoms/cm², and Fig. 4(d) shows an XTEM image of the C₂H₅-cluster-implanted sample after epitaxial growth with 2.0 × 10¹⁵ carbon atoms/cm². The interface of the epitaxial layer and Si substrate is indicated by the white dashed line in Fig. 4. As shown in Fig. 4(a), the implanted region of the carbon cluster was observed at a depth of approximately 80 nm from the interface of the epitaxial layer and Si substrate after epitaxial growth. In addition, the defects in the carbon-cluster-implanted region are distributed over 20 nm around a depth of approximately 80 nm. Figures 4(b) and 4(c) show large defects at a depth of approximately 40 nm from the interface of the epitaxial layer and Si substrate, which appear with the increase in the dose. We call them black-point defects because of their appearance. The size of a large black-point defect is approximately 30 nm. These large defects were observed only when an amorphous region was observed before epitaxial growth. However, large black-point defects were not observed in the implantation region after epitaxial growth in Fig. 4(d). The amorphous region was not observed in the projection range of the C₂H₅-cluster implantation. These results indicate that the damage caused by C₃H₅ and C₂H₅ clusters depends on the size and dose. In addition, epitaxial defects, such as stacking faults, were not observed in the TEM images.

Figures 5(a) and 5(b) show high-magnification XTEM images of C₃H₅-ion-implanted samples with doses of 1.0 × 10¹⁵ and 3.0 × 10¹⁵ carbon atoms/cm² at a depth of approximately 40 nm from the interface of the epitaxial layer and Si substrate after epitaxial growth, respectively. As shown in Fig. 5(a), carbon-cluster-implantation defects due to the aggregation of small black-point defects of approximately 5 nm size were observed at high magnification. On the other hand, the 3.0 × 10¹⁵ carbon atoms/cm² samples were observed to have small and large black-point defects. We calculated the number of defects from the density of small black-point defects distributed in the implanted region around the projection range. The volume used for the calculation was assumed to be 40 × 40 nm² with a thickness of 100 nm in the TEM sample. With increasing dose, the density of the small black-point defects increased. For the 1.0 × 10¹⁵ and 3.0 × 10¹⁵ carbon atoms/cm² samples, the densities of the small black-point defects were 6.3 × 10¹⁶ and 1.2 × 10¹⁷/cm³, respectively. As shown in Fig. 4, large black-point defects formed in a region approximately 40 nm above the center of the distribution of small black-point defects. This result suggests that the large black-point defects form in the recrystallized region of the amorphous region.
3.2 Mechanism of defect formation behavior in the implanted region of the carbon clusters after epitaxial growth

We observed the projection range of the carbon clusters on the basis of the detailed analysis of small and large black-point defects by HR-XTEM and n-ED. Figure 6 shows the HR-XTEM and n-ED observation results. The lattice constant was not changed by ion implantation according to the HR-XTEM observation. In addition, we found that the electron diffraction patterns of small and large black-point defects show that of silicon single crystal. Other defects such as secondary extended dislocation defects and stacking faults were not observed. Small black-point defects were observed for the dose of $1.0 \times 10^{15}$ carbon atoms/cm², for which an amorphous layer was not formed. In contrast, large black-point defects were observed when the amorphous layer was formed. Consequently, we assume that the small black-point defects are carbon-related defects and that the large black-point defects are the effects of the amorphous region. Similar small black-point defects were observed during the formation of silicon carbide (SiC) structures in previous studies on monomer-carbon implantation. Thus, SiC precipitates formed as a result of high-temperature heat treatment. In this study, heat treatment of 1100 °C was carried out for about 10 min on a sample after epitaxial growth. However, small black-point defects were observed in the electron diffraction pattern of a silicon single crystal. Additionally, the lattice constant of the small black-point defects was the same as that of the silicon substrate. Because the dose in this study was smaller than that in previous studies, we considered that a SiC structure did not form. Consequently, we assume that the small black-point defects were formed by a complex of carbon. Pinacho et al. reported that the behavior of carbon impurities in Si bulk demonstrates that carbon and Si self-interstitial (C\textsubscript{I}) clusters are formed in carbon-rich Si. As shown in Figs. 1–3, the implantation damage and the dechanneling effect of carbon-cluster implantation are larger than those of monomer implantation. These results indicate that many vacancy and Si self-interstitial point defects are generated after carbon-cluster implantation. We consider that implanted carbon and Si self-interstitials generated by carbon-cluster implantation can form C\textsubscript{I} clusters of carbon and Si self-interstitials. We assume that these C\textsubscript{I} clusters were observed as the contrast in the HR-XTEM images. Therefore, we simulated the carbon-cluster-ion implantation and the silicon epitaxial growth process by using the kinetic Monte Carlo (KMC) code in the technology computer-aided design (TCAD) Sentaurus Process from Synopsys Inc. to confirm the formation of C\textsubscript{I} clusters. Note that the model for the formation of C\textsubscript{I} clusters is incorporated in the TCAD Sentaurus Process. This cluster model describes a complex of carbon and Si self-interstitials in the form of C\textsubscript{m}\textsubscript{I}\textsubscript{n} (e.g., C\textsubscript{6}\textsubscript{I}\textsubscript{6} and C\textsubscript{6}\textsubscript{I}\textsubscript{7}). The reaction of a C\textsubscript{m}\textsubscript{I}\textsubscript{n} complex can...
be expressed by the following tapping and emission reactions of interstitial carbon (C\textsubscript{i}) and Si self-interstitials (I):

\[
C_{m}I_{n} + C_{i} \leftrightarrow C_{m+1}I_{n+1}, \quad (1)
\]

\[
C_{m}I_{n} + I \leftrightarrow C_{m}I_{n+1}. \quad (2)
\]

Figure 7 shows the distribution of carbon (black) and Si self-interstitials (red) in the projection range of carbon clusters after epitaxial growth obtained using KMC code.

![Image](Fig. 6. HR-XTEM images and electron diffraction patterns obtained by n-ED observation of sample after epitaxial growth with carbon dose of 3.0 \times 10^{15} carbon atoms/cm\textsuperscript{2}.)

![Image](Fig. 7. (Color) TCAD result of distribution of carbon (black) and Si self-interstitials (red) obtained using KMC code.)

black-point defects are formed by the aggregation of C/I clusters.

On the other hand, the presence of large black-point defects was confirmed only under the condition in which the amorphous region was observed. Moreover, the large black-point defects formed in a region approximately 40 nm above the small black-point defects. This region is in agreement with the amorphous region. Therefore, we assume that the large black-point defects are formed by the recrystallization of the amorphous region.

We consider that the small and large black-point defects function as gettering sinks. Our previous study indicated that the gettering capability of a carbon-cluster-implanted region increased with the dose of carbon clusters. Similarly, the density of small black-point defects increases with the dose of carbon clusters. Consequently, the small black-point defects seem to have gettering capability. Furthermore, the large black-point defects were observed in the implanted region of carbon clusters at the dose for which an amorphous region was formed. The recrystallized amorphous region is also expected to demonstrate gettering capability. These results suggest that small and large black-point defects contribute to the gettering capability for the metallic impurities in a carbon-cluster-implanted silicon epitaxial wafer.

4. Conclusions

After carbon-cluster-ion implantation, we confirmed that damage due to carbon-cluster implantation is greater than that due to monomer implantation. This result means that carbon-cluster ions exhibit dechanneling effects and cause an amount of damage depending on the carbon-cluster size. We also analyzed samples after epitaxial growth, on which previous studies have not been reported. We observed that two types of defects are formed in the carbon-cluster-implantation region in silicon bulk. These defects show single-silicon electron-diffraction patterns. In addition, the structures of these defects do not form SiC structures. Therefore, we assume that these defects are C/I-cluster-related and amorphous-related defects. Amorphous-related defects also formed...
under high-dose conditions. We believe that these types of defects have powerful gettering capability for our proximity gettering technique.

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