Effect of ramping up rate on end of range defect in multielement molecular-ion (CH$_3$O)-implanted silicon wafers

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The dependence of the density of CH$_3$O ion-implantation defects on ramping up rate after annealing at 1100 °C for 300 s have been investigated using rapid thermal annealing. We found that the density of defects after annealing was highest at a ramping up rate of 15 °C s$^{-1}$. Furthermore, we also found that the diffusion behavior of implanted carbon and oxygen which were gittered by the CH$_3$O ion-implantation defects, was dependent on the annealing temperature. Therefore, the ramping up rate dependence of the density of CH$_3$O ion-implantation defects was considered to be caused by the difference between the formation behavior of CH$_3$O ion-implantation defects and the dissociative adsorption behavior of carbon and oxygen. An increase in the defect density led to an increase in the density of gittering sinks. The gittering capability of the CH$_3$O ion-implantation region is expected to be improved by optimizing the ramping up rate.

**1. Introduction**

The complementary metal oxide semiconductor (CMOS) image sensors with higher sensitivity are required for use in applications such as automobiles. To achieve higher sensitivity, the reduction in the density of white spot defects and dark current is necessary. The most important technical issue in reducing white spot defects and dark current is metallic impurity contamination introduced by the CMOS device fabrication process. The metallic impurity contamination in the device active region forms deep-level defects, generating white spot defects and dark current. Thus, the removal of metallic impurities from the device active region is important for achieving higher sensitivity. With this background, the development of a novel gittering technique with which metallic impurities can be removed from the device active region is required for silicon wafers.

Gittering techniques such as intrinsic gittering (IG) and extrinsic gittering (EG) are also used in current silicon wafer manufacturing processes. However, the thermal treatment is carried out at lower temperatures in recent device fabrication processes for shorter durations. This trend accounts for several issues encountered in IG and EG. In the case of IG, the size and density of the formed oxygen precipitate acting as gittering sinks are not sufficient for the device fabrication process. When using EG, metallic impurities cannot accumulate in gittering sinks because of the insufficient diffusion length after heat treatment at lower temperature. Therefore, a gittering technique that form gittering sinks near the device active region without an additional thermal process is required.

To this end, we developed a new proximity gittering silicon epitaxial wafer using a multielement molecular-ion-implantation technique based on carbon cluster ion-implantation. This technique involves CH$_3$O ion-implantation to improve the gittering capability on silicon epitaxial wafer. We previously reported that this technique provides the same three characteristics as those obtained in carbon cluster ion-implanted silicon epitaxial wafers to improve device electrical properties: high gittering capability for metallic impurities, the oxygen out-diffusion barrier effect, and the hydrogen passivation effect. In particular, CH$_3$O ion-implantation provides a much high capability for gittering metallic impurities via distinctive defect formation. This technique enables gittering by forming two types of defect, carbon-related defects and extended defects. The extended defects are assumed to be end-of-range (EOR) defects. Defects of this type act as gittering sinks. Therefore, understanding the formation behavior of extended defects is important to achieve higher gittering capability.

In previous studies on EOR defects generated by monomer ion-implantation, the formation behavior of EOR defects was found to depend on the temperature and duration of heat treatment. On the other hand, the defect formation behavior introduced by molecular-ion-implantation has so far not been reported. In our previous study of CH$_3$O ion-implantation, we demonstrated that EOR defects are formed after the heat treatment in the epitaxial growth process. This finding suggests that the EOR defects introduced by CH$_3$O ion-implantation are formed during ramping up or at 1100 °C annealing, which is the temperature for the epitaxial growth process. Therefore, understanding the formation behavior of extended defects is important to achieve higher gittering capability.
between 600 °C and 1000 °C can be changed by changing the ramping up rate. Because the annealing time affects the EOR defect formation behavior, changing the ramping up rate is considered effective for EOR defect formation. However, the effect of the ramping up rate on the defect formation behavior was not reported in previous studies. Thus, we focused on the dependence of the formation of EOR defects induced by CH₃O ion-implantation on the ramping up rate. To demonstrate this, we used the rapid thermal annealing (RTA) method which can simulate the heat treatment sequence of epitaxial growth. Therefore, the main objective of this study is to clarify the effect of the ramping up rate on the density of EOR defects introduced by CH₃O ion-implantation by RTA.

2. Experimental methods

In this study, n-type Si (100) wafers were implanted with CH₃O multielement molecular ions at room temperature using a CLARIS® ion implanter (Nissin Ion Equipment Co., Ltd). CH₃O was implanted at a dose of 1.0 × 10¹⁵ ions cm⁻². Tilting and twisting were performed at 0°. The implantation energy was 80 keV/ion. The CH₃O beam current was 550 μA. Samples were prepared after implantation and heat treatment by RTA in nitrogen ambient using AccuThermo Aw610 of HiSOL, Inc. The temperature during RTA was measured using a pyrometer. Figure 1 shows a typical heat treatment profile. To accurately control the ramping up rate, heating was carried out from 500 °C for 10 s because the pyrometer of AccuThermo Aw610 cannot measure temperature below 450 °C. With this setting, an accurate ramping up rate can be obtained from 500 °C to 1100 °C. The ramping up rates were 4, 8, 15, and 60 °C s⁻¹. Scanning transmission electron microscopy and transmission electron microscopy (TEM) were carried out to obtain images of the defects in the ion-implanted region in the projection range of the multielement molecular ions after RTA. The density of the defect was calculated from the six different TEM images in CH₃O ion-implantation region. The distributions of implanted carbon and oxygen were analyzed by secondary ion mass spectrometry (SIMS). The concentration depth profile of interstitials induced by CH₃O ion-implantation was calculated using the technology computer-aided design (TCAD) simulator of Sentaurus process from Synopsys.

3. Experimental results and discussion

3.1. Defect type in CH₃O ion-implanted region

Figure 2 shows the TEM images of the CH₃O ion-implanted region after (a) CH₃O ion-implantation at a dose of 1.0 × 10¹⁵ ions cm⁻² and (b) RTA at a ramping up rate of 15 °C s⁻¹, a temperature of 1100 °C and an annealing time of 300 s. Figure 3 shows the damage profile calculated by TCAD simulation after CH₃O ion-implantation at an energy of 80 keV and a dose of 1.0 × 10¹⁵ ions cm⁻².

As shown in Fig. 2(a), an amorphous region was formed at a depth of approximately 80 nm from the silicon surface. On the other hand, defects were formed after RTA at 1100 °C for 300 s at a depth of 120 nm from the silicon surface, as shown in Fig. 2(b). TCAD calculation results show that the damage concentration peak is observed at a depth of approximately 80 nm from the silicon surface as shown in Fig. 3. The damage in the TCAD calculation represents interstitial silicon and vacancies generated by CH₃O ion-implantation. Because of the depth at which the damage concentration peak in the TCAD calculation results is in the same as the depth of the amorphous layer, the damage profile calculated by TCAD is in good agreement with the TEM findings results. Furthermore, from the TCAD calculation results, the characteristics of the profile of CH₃O ion-implantation-generated damage, namely a damage concentration peak and decays with increasing depth, are similar to those of the profile of monomer ion-implantation.

Jones and Rozgonyi classified monomer ion-implantation defects into five types on the basis of their crystallinity after ion-implantation; the positional relationship among defects formed after heat treatment and the behavior of implanted elements after heat treatment. They classified the defects formed behind the a/c interface into type-II under ion-implantation conditions in which an amorphous layer is formed. They also reported that type-II defect is formed by aggregation of interstitial silicon introduced by ion-implantation. A comparison of TEM images after CH₃O ion-implantation and RTA. Figures 2(a) and 2(b), shows that the depth
of defects in the CH$_3$O ion-implanted region are larger than that in the amorphous layer. This defect morphology is in good agreement with the type-II defect reported by Jones and Rozgonyi. Thus, the defects introduced by CH$_3$O ion-implantation are considered to be type-II and are formed by aggregation of interstitial silicon. Furthermore, as shown in Fig. 2(b), the defects are a [111] stacking-fault. In our previous study, we observed defects with the same shape in the CH$_3$O ion-implantation region after the epitaxial growth of silicon.

To determine the shape of the defects formed in the CH$_3$O ion-implantation region, we performed a TCAD calculation with kinetic Monte Carlo (KMC) code. Figure 4 shows the TCAD calculation using KMC code for the CH$_3$O ion-implantation region after annealing at 1100 °C for 300 s. The CH$_3$O ions were implanted at a dose of $1.0 \times 10^{15}$ ions cm$^{-2}$, an implantation energy of 80 keV, and a tilt and twist of 0°, which were the same as the ion-implantation conditions for Fig. 2. As shown in Fig. 4, dislocation loops were formed in the CH$_3$O ion-implantation region, where a dislocation loop is defined as a planar circular defect lying on the [111] plane in the TCAD calculation. This result suggests the possibility of forming dislocation loops in the CH$_3$O ion-implantation region by annealing at 1100 °C and above. Thus, the defect formed by CH$_3$O ion-implantation is considered to be a stacking-fault-type dislocation loop in which interstitial silicon is inserted in the [111] direction. It is found that the morphology of the defects after RTA was the same as that of the defects after the silicon epitaxial growth process in the CH$_3$O ion-implantation region. Therefore, the mechanism of CH$_3$O ion-implantation defects in the RTA is considered to be the same as that in the epitaxial growth process.

3.2. Effect of ramping up rate on defect formation in CH$_3$O ion-implanted region

In Sect. 3.1, we demonstrated the morphology of CH$_3$O ion-implantation generated defects after RTA. We also confirmed that these defects are the type-II and correspond to those after epitaxial growth. In this section, we demonstrate the effect of
the ramping up rate during RTA at 1100 °C on the formation of CH₃O ion-implanted defects.

Figure 5 shows TEM images of a CH₃O ion-implanted Si wafer after RTA at 1100 °C for 300 s. The ramping up rate was 4–60 °C s⁻¹ between 500 °C and 1100 °C. As shown in Fig. 5, the density of the CH₃O ion-implanted defect after RTA is changed by the change of the ramping up rate. Figure 5 shows the density of CH₃O ion-implanted defects after RTA. The size of each defect was approximately 50 nm, as shown in Fig. 2(b). We calculated the defect density by the counting the defects larger than 50 nm from six different TEM images in CH₃O ion-implantation region. As shown in Fig. 6, the density of CH₃O ion-implanted defects is the lowest at 4 °C s⁻¹. On the other hand, the density of CH₃O ion-implanted defects is highest at 15 °C s⁻¹. These results suggest that the density of CH₃O ion-implantation defect is dependent on the ramping up rate.

Tamura et al. reported that the EOR defects introduced by monomer ion-implantation are formed during annealing at temperatures between 600 °C and 1000 °C. They also reported that EOR defects disassemble after annealing at 1100 °C. The ramping up during annealing at temperatures between 600 °C and 1000 °C in which range EOR defects are formed, is longest at 4 °C s⁻¹. If the density of defects remaining after annealing at 1100 °C depends on only the duration of annealing at 600 °C–1000 °C, the defect density at 4 °C s⁻¹ can be higher than those at other ramping up rates. However, the density of the defects was highest at 15 °C s⁻¹, which suggests that the density of the defects is affected by the defect behavior during both the ramping up and 1100 °C annealing.

Figure 7 shows the dependence of the density of defect on the 1100 °C annealing time and ramping up rate. As shown in Fig. 7, the defect density decrease with increasing 1100 °C annealing time. This finding indicates that the CH₃O ion-implanted defects disassemble during 1100 °C annealing. Additionally, it is observed that the density of CH₃O ion-implanted defects is dependent on the ramping up rate. In the case of 0 s annealing, the density of defects is almost the same at all ramping up rates. On the other hand, the density of defects in the 15 °C s⁻¹ sample is higher than those in the other samples annealed for longer. This finding suggests that the defects in the sample ramped up at 15 °C s⁻¹ more easily remain after 1100 °C annealing than the defects at other ramping up rates. Increasing the defect density may increase gettering capability. Therefore, it is assumed that the 15 °C s⁻¹ ramping up rate can increase the gettering capability of CH₃O ion-implanted silicon epitaxial wafer.

### 3.3. Mechanism underlying defect density dependence on ramping up rate

In previous sections, we showed that the ramping up rate contributes to the change in the density of CH₃O ion-implanted defects. In particular, the ramping up rate of 15 °C s⁻¹ provided the highest density of CH₃O ion-implanted defects remaining after 1100 °C annealing. This
finding suggests that the ramping up rate should not be too low or too high to obtain a sufficiently high density of CH₃O ion-implantation defects remaining. Then, why is it difficult for the defects formed at 15 °C s⁻¹ to disassemble? It is considered that this defect behavior was determined by the defect disassembly behavior during 1100 °C annealing and the defect formation behavior during ramping up.

Firstly, considering the mechanism of disassembly of CH₃O ion-implantation defects during 1100 °C annealing. Tamura et al. examined behavior of defects introduced by monomer ion-implantation and found that the defects were disassembled by 1100 °C annealing and the Bonafos reported that the EOR defects are disassembled owing to the release of interstitial silicon. However, the CH₃O ion-implantation defects remained after 1100 °C annealing as shown in Fig. 2(b). Thus, the defect disassembly behavior during 1100 °C annealing cannot be explained by only the interstitial silicon behavior. Figures 8(a) and 8(b) respectively show the SIMS depth profiles of carbon and oxygen after 300 s at annealing at temperatures of 800 °C, 900 °C, 1000 °C, and 1100 °C. The ramping up rate was set at 60 °C s⁻¹ to avoid the effect of the defect formation behavior during ramping up. After 800 °C annealing, only one concentration peak is observed. On the other hand, two peaks are observed at other annealing temperatures. In our previous studies, these two peaks corresponded to carbon-related defects and ion-implanted defects. These results suggest that the carbon and oxygen implanted by CH₃O ion-implantation are fixed around the CH₃O ion-implantation defects. It is previously reported that the EOR defects introduced by monomer ion-implantation were stabilized by the oxygen in the silicon wafer. The results of three-dimensional atom probe tomography analysis of the CH₃O ion-implantation region suggest that carbon and oxygen were segregated at the edge of the defect. The CH₃O ion-implantation defects are stabilized by the high concentrations of aggregated carbon and oxygen around ion-implanted defects. Therefore, the interaction between the CH₃O ion-implantation defect and carbon and oxygen is considered to be important for remaining the CH₃O ion-implantation defect after 1100 °C annealing.

The mechanism of the disassembly behavior during 1100 °C annealing is considered to be as follows. First, the CH₃O ion-implantation defects are destabilized by the release of carbon and oxygen from the defects during 1100 °C annealing. Then, interstitial silicon is released from CH₃O
ion-implantation defects. As a result, the defects disassemble during 1100 °C annealing. Therefore, the pinning of carbon and oxygen is important for the stabilization of CH$_3$O ion-implantation defects during 1100 °C annealing.

Second, we consider the dependence of the density of defects formed during RTA on the ramping up rate. In a previous report on the behavior of defects introduced by monomer ion-implantation, the defect morphology changed with the annealing temperature. Ito et al. reported that the size of EOR defects introduced by monomer ion-implantation is increased by annealing between 800 °C and 1000 °C. Thus, the morphology of CH$_3$O ion-implantation defects is considered to be dependent on the annealing temperature. Figure 9 shows the CH$_3$O ion-implantation defect morphology dependence on the annealing temperatures. The annealing temperatures were 800 °C, 900 °C, 1000 °C, and 1100 °C. The annealing time was 300 s. The ramping up rate was set at 60 °C s$^{-1}$ to avoid the effect of the defect formation behavior during the ramping up. As shown in Fig. 9, defects larger than 50 nm are observed at annealing temperatures higher than 900 °C. On the other hand, no defects of this size were observed after 800 °C annealing. Furthermore, the density of the defects after 1100 °C annealing was lower than those after annealing at 900 °C and 1000 °C. These results suggest that the CH$_3$O ion-implantation defects were formed by annealing at temperatures of about 900 °C, and it is assumed that the duration of annealing at temperatures of about 900 °C is important for the increasing the density of CH$_3$O ion-implantation defect.

Then, we demonstrated the defect behavior during RTA at 900 °C for various annealing durations. Figure 10 shows the TEM images of the CH$_3$O ion-implanted silicon wafer at 900 °C annealed for 0, 60, and 300 s. at a ramping up rate of 60 °C s$^{-1}$. As shown in Fig. 10, the defects appear extended with increasing annealed duration. As Bonafos et al. reported, the EOR defects become larger in only ten seconds order owing to the absorbance of interstitial silicon during annealing of around 900 °C. In the case of CH$_3$O ion-implantation, the defects are considered to also absorb the interstitial silicon and extend during the annealing at 900 °C. Furthermore, carbon and oxygen at high concentrations aggregated around the CH$_3$O ion-implantation defects formed during annealing at 900 °C, as shown in Fig. 8. Therefore, it is considered important that annealing at around 900 °C should proceed for some time to form stable CH$_3$O ion-implantation defects.

On the basis of the above mechanisms, we consider why the CH$_3$O ion-implantation defects formed at 15 °C s$^{-1}$ hardly disassembled during annealing at the 1100 °C. Figures 11(a)–11(c) show schematic images of CH$_3$O ion-implantation defects immediately after ramping up. As shown in Figs. 2(b) and 4, the CH$_3$O ion-implantation defects are considered to be dislocation loops and [111] stacking faults. The shape of the defect in this model is assumed to be a circular loop.

In the case of ramping up at a low rate of 4 °C s$^{-1}$, it is considered that the defects easily disassembled during the annealing at 1100 °C. As shown Fig. 11(a), the interstitial silicon concentration around the defects is assumed to decrease through diffusion during annealing at temperatures below 900 °C. Interstitial silicon is not sufficiently absorbed during annealing at temperatures higher than 900 °C. As a result, the CH$_3$O ion-implantation defects easily disassemble during annealing at 1100 °C. Furthermore, in the case of ramping up at a rate of 4 °C s$^{-1}$, the duration of annealing at over 1000 °C is longer than that at a ramping up rate of 15 °C s$^{-1}$. Because the CH$_3$O ion-implantation defects were disassembled by the annealing at over 1000 °C with the release of carbon and oxygen, as shown Figs. 8 and 9, the CH$_3$O ion-implantation defects are assumed to easily disassemble at 4 °C s$^{-1}$. This is also considered to be a factor causing the decrease in the density of CH$_3$O ion-implantation defects.

In the case of ramping up at a high rate of 60 °C s$^{-1}$, it is considered that no defects were formed with sufficient size and density during the ramping up process. The shorter the ramping up process, the shorter the times for defect formation during annealing. Thus, it is considered that interstitial silicon, carbon, and oxygen were not aggregated during the ramping up process as shown in Fig. 11(c). CH$_3$O ion-implantation defects are considered to easily disassemble during 1100 °C annealing because they were not sufficiently stabilized by carbon and oxygen. As a result,
the density of CH₃O ion-implantation defects was decreased by ramping up at 60 °C s⁻¹.

It is considered that interstitial silicon, carbon, and oxygen sufficiently aggregated during ramping up at 15 °C s⁻¹ in contrast to ramping at 60 °C s⁻¹, as shown in Figs. 11(b) and 11(c). On the other hand, more interstitial silicon is considered to remain in the case of ramping at 15 °C s⁻¹ than that at 4 °C s⁻¹, as shown in Figs. 11(a) and 11(b). Furthermore, the duration of annealing at over 1000 °C and 15 °C s⁻¹ is shorter than that at 4 °C s⁻¹. On the basis of these findings, it is considered that the defects formed at 15 °C s⁻¹ can hardly disassemble during 1100 °C annealing, resulting in a higher density of the defects at other rates.

We assumed that the dependence of the density of CH₂O ion-implantation defects on the ramping up rate is determined by the formation behavior of EOR defects, namely aggregation of interstitial silicon and the interaction of the carbon and oxygen with the EOR defects. Regarding the remaining CH₂O ion-implantation defects after annealing of 1100 °C, we found three important factors related to the ramping up process. Firstly, the duration of annealing at a temperature below 800 °C should be as short as possible. Secondly, the duration of annealing at a temperature of about 900 °C should be as long as possible. Finally, that of annealing at a temperature above 1000 °C should also be as short as possible. In summary, the interaction between the EOR defects and the diffusion behavior of carbon and oxygen determine the ramping up rate dependence of the density of CH₂O ion-implantation defects on the ramping up rate.

4. Conclusions

We investigated the dependence of the density of CH₂O ion-implantation defects on the ramping up rate in RTA. We found that the density of defects after annealing at 1100 °C for 300 s is the highest at a ramping up rate of 15 °C s⁻¹. We also found that carbon and oxygen implanted by CH₂O ion-implantation are interacted with CH₂O ion-implantation defects. Carbon and oxygen are assumed to pine those defects. Therefore, the dependence of the density of the CH₂O ion-implantation defects on the ramping up rate is considered to be due to the difference of the diffusion behavior of carbon and oxygen and the defect formation behavior in three annealing temperature zones of below 800 °C, about 900 °C and above 1000 °C. For the remaining CH₂O ion-implantation defects, it is important that the duration of annealing in the temperature at below 800 °C and above 1000 °C is as short as possible. Furthermore, it is desirable that the duration of annealing at about 900 °C is somewhat long.

In this study, we found that the balance between annealing duration and temperature at 15 °C s⁻¹ should be optimal for the CH₂O ion-implantation defects to remain after annealing at 1100 °C for 300 s. Therefore, it is expected that the gettering capability of CH₂O ion-implantation can be enhanced by 15 °C s⁻¹ as the ramping up rate. This finding may contribute to device fabrication processes through the enhancement of gettering capability.

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