Effect of low-oxygen-concentration layer on iron gettering capability of carbon-cluster ion-implanted Si wafer for CMOS image sensors

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The effect of oxygen (O) concentration on the Fe gettering capability in a carbon-cluster (C2H5) ion-implanted region was investigated by comparing a Czochralski (CZ)-grown silicon substrate and an epitaxial growth layer. A high Fe gettering efficiency in a carbon-cluster ion-implanted epitaxial growth layer, which has a low oxygen region, was observed by deep-level transient spectroscopy (DLTS) and secondary ion mass spectroscopy (SIMS). It was demonstrated that the amount of gettered Fe in the epitaxial growth layer is approximately two times higher than that in the CZ-grown silicon substrate. Furthermore, by measuring the cathodoluminescence, the number of intrinsic point defects induced by carbon-cluster ion implantation was found to differ between the CZ-grown silicon substrate and the epitaxial growth layer. It is suggested that Fe gettering by carbon-cluster ion implantation comes through point defect clusters, and that O in the carbon-cluster ion-implanted region affects the formation of gettering sinks for Fe. © 2018 The Japan Society of Applied Physics

1. Introduction

In fabricating CMOS devices, there are many chances for metallic impurities to be introduced, such as from plasma heat treatment and dry etching. Impurities introduced into silicon (Si) wafers degrade electrical device performance characteristics, such as junction leakage current, recombination lifetime, and generation lifetime.1,2) In particular, the performance of CMOS image sensors is markedly affected by metallic impurities related to the deep energy levels in the space-charge region of photodiodes.3,4) These impurities cause a fixed pattern noise, which is a key parameter in CMOS image sensors. Therefore, the gettering technique has been required for Si wafers in CMOS imaging sensors to reduce the amounts of metallic impurities in the device active region. Intrinsic gettering (IG) is an effective technique that involves oxygen (O) precipitation for the gettering sink in Si wafers.7–10) The IG effect depends on the size and density of oxide precipitates.9,10) However, sufficient O precipitation cannot be obtained with the low-temperature process used to fabricate CMOS devices. Furthermore, the durations of the processes for advanced CMOS image sensors are much shorter than those of conventional CMOS device thermal processes. Thus, it is difficult for metallic impurities to diffuse to the gettering sink from the device active region during the fabrication of advanced CMOS devices. Therefore, creating a gettering sink in the proximity of the device active region is required for CMOS image sensors; this is called “proximity gettering”.6,11–15)

Recently, we have reported on novel proximity gettering techniques that use a carbon (C)-cluster (C2H5) ion implantation technique.16–19) It was found that not only metallic impurities, such as Fe, Ni, and Cu, but also O and H are gettered in the C-cluster ion-implanted region after heat treatment in a device fabrication experiment conducted by secondary ion mass spectrometry (SIMS).

It was also demonstrated that the gettering mechanism in the C-cluster ion implantation technique is segregation-induced gettering.16–18) Gettering mechanisms are classified into relaxation-induced gettering and segregation-induced gettering. Relaxation-induced gettering9,20) is explained by the Cottrell effect. Metallic impurities are gettered in the strain field induced by extended defects. Segregation-induced gettering15,21–24) is considered as a local enhancement in the solubility of metallic impurities in Si bulk. It is also considered that this enhancement occurs owing to a dopant-induced Fermi-level shift, the interaction between metallic impurities and dopants, intrinsic point defects including implanted species, and so forth. Regarding the C-cluster ion implantation technique, it was suggested that the gettering sink is caused by intrinsic point defect-related complexes.18,19,25) However, the origin of the sink is not clear.

In the case of monomer ion-implanted Si wafers, a few studies of the impact of O on the gettering efficiency of metallic impurities were conducted. Wong and coworkers11,12) reported that the gettering efficiency of implanted MeV C is reduced by adding O atoms. Koveshnikov and Rozgonyi15) reported the gettering efficiency of Fe with MeV Si ion implantation to epitaxial Si wafers. The efficiency of Fe depends on both O concentration and ion implantation dose. It seems that the O concentration affects the gettering efficiency and implantation-related defect formation after heat treatment.

It is also not clear whether the O concentration in the C-cluster projected range affects the gettering effect for metallic impurities. The O concentration in an epitaxial growth layer (Epi-Si) is lower than that in a Czochralski (CZ)-grown Si substrate, and that the n-type epitaxial Si wafer is widely used for advanced CMOS image sensors. In this study, we therefore, investigated the effect of O concentration in the projected range of C-cluster ion implantation for Fe gettering using n-type Epi-Si and n-type CZ-Si substrates. We also studied the characteristics of defects, which contribute to Fe gettering in the C-cluster projected range.
2. Experimental procedure

N-type phosphorus (P)-doped CZ-Si and Epi-Si wafers were used for C-cluster ion implantation. The interstitial O concentration of CZ-Si was about $1.4 \times 10^{18}$ cm$^{-3}$, and that of the C-cluster projected range in Epi-Si was below $10^{16}$ cm$^{-3}$. The wafers were implanted with 80 keV C-cluster (C$_3$H$_5$) ions at C doses of $1 \times 10^{14}$, $2 \times 10^{14}$, $5 \times 10^{14}$, and $1 \times 10^{15}$ cm$^{-2}$. An 8-µm-thick epitaxial layer with 30Ω cm resistivity was grown using a SiHCl$_3$ gas source at 1100 °C. The samples were cleaned with HF (0.5%) and SC1 solutions and then contaminated with Fe at a concentration of $1 \times 10^{15}$ cm$^{-2}$ on their surfaces by spin coating. Fe was driven at 1050 °C for 2 h in N$_2$ ambient. Figure 1 schematically shows the experimental process and analysis technique used in this study.

The amount of gettered Fe in the C-cluster projected range was obtained by depth-dependent SIMS analysis by sputtering from the sample surface direction (CAMECA IMS7f). The concentration of ungettered Fe in the epitaxial layer was measured by deep-level transient spectroscopy (DLTS; SEMILAB DLS-1000). Au was evaporated onto the sample surfaces. The concentration of ungettered Fe was measured by DLTS and SIMS.

The defects induced by C-cluster ion-implanted after 1050 °C for 2 h annealing were analyzed by transmission electron microscopy (TEM) observation.

The implantation-related defects in the projection range before and after epilayer growth were investigated by measuring the cathodoluminescence (CL). CL measurements were performed at 37 K using an electron beam at 15 kV. The CL spectra of the implantation region were obtained by cross-sectional analysis.

3. Results and discussion

3.1 Gettering efficiency of C-cluster ion-implanted CZ-Si and Epi-Si

Figure 2 shows the typical DLTS spectra of C-cluster ion-implanted and reference samples contaminated with Fe. The C-cluster implanted samples were implanted with a dose of $1 \times 10^{15}$ cm$^{-2}$. Three Fe-related deep energy levels were obtained in the epitaxial layer of the reference samples without implantation (no gettering). After C-cluster ion implantation, the ungettered Fe-related deep levels were less than the DLTS detection limit in both the epitaxial layers of CZ-Si and Epi-Si. The results obtained here demonstrate that C-cluster ion implantation provides a sufficient gettering efficiency for Fe in both CZ-Si and Epi-Si.

Figure 3 shows the C implantation dose dependence of the ungettered Fe concentration measured by DLTS. For a low dose of $1 \times 10^{14}$ cm$^{-2}$, a slight decrease in the concentration of residual Fe in the epitaxial layer in the implanted CZ-Si was observed compared with the initial concentration. The concentration of residual Fe in the epitaxial layer decreased as the C-cluster ion implantation dose increased for both CZ-Si and Epi-Si wafer. The concentration of ungettered Fe in Epi-Si was less than the DLTS detection limit with a dose of $5 \times 10^{14}$ cm$^{-2}$. This result indicates that the gettering sink induced by implanted Epi-Si has a higher gettering efficiency for Fe than for CZ-Si.

Figures 4(a)–4(c) respectively show the C, O, and Fe concentrations obtained from SIMS profiles in the implanted CZ-Si and Epi-Si with a dose of $2 \times 10^{15}$ cm$^{-2}$ after annealing at 1050 °C for 2 h. The peaks of C concentration in the C-cluster ion projected range of both CZ-Si and Epi-Si matched, as shown in Fig. 4(a). O and Fe impurities were gettered in the C-cluster ion projected ranges in both CZ-Si and Epi-Si.
and Epi-Si, as shown in Figs. 4(b) and 4(c), respectively. Note that the amount of Fe in Epi-Si was higher than that in CZ-Si. That is, the gettering efficiency of Fe in implanted Epi-Si was higher than that in implanted CZ-Si. This higher efficiency was also confirmed for the dose of $1 \times 10^{15}$ cm$^{-2}$, as shown in Fig. 5. At this implantation dose, DLTS measurement did not reveal a difference between CZ-Si and Epi-Si, whose values were less than the DLTS detection limit. In comparison with the SIMS profile of the Fe peak concentration with O peak concentration, as shown in Figs. 4 and 5, it seems that the rate of the increase in the amount of gettered Fe correlates with that of the increase in O peak concentration. From these results, we expect that the low O concentration in the C-cluster ion implantation projected range will increase the number of gettering sites for Fe.

Figure 6 shows the peak concentration of Fe as a function of C-cluster dose. The higher gettering efficiency of Fe in Epi-Si depended on C implantation dose. The amount of gettered Fe in Epi-Si was approximately two times higher than that in CZ-Si at all doses.

The increase in the amount of gettered Fe was also confirmed by DLTS measurement as mentioned in Fig. 3. Thus, these data suggest that C-cluster ion implantation in the low O region markedly increases the gettering efficiency of Fe. The ratio of the increase in the gettering efficiency of Fe to that for CZ-Si remains constant without depending on C implantation dose.

### 3.2 Relationship of C-cluster ion-implanted defects with gettering capability

A previous work indicated two mechanisms for Fe gettering in MeV Si ion-implanted epitaxial wafers.\(^{15}\) It was demonstrated that two damage zones, that is, the vacancy (V)-rich region and buried layer of interstitial dislocation loops, were created in MeV Si ion-implanted epitaxial wafers. Fe gettering occurs in the V-rich region via segregation-induced gettering and in the buried layer via relaxation-induced gettering. The increase in the amount of gettered Fe in the implanted epitaxial wafer was stopped by interaction with V-related complexes. In comparison, in the C-cluster ion-implanted Epi-Si wafer, a double-peak profile for Fe gettering was not obtained by SIMS. C-cluster ion implantation-induced damage is less than that produced by the MeV high-energy ion implantation technique.\(^{18}\)

Why does the C-cluster ion implantation in Epi-Si cause the gettering efficiency of Fe to increase? Here, we give two possible explanations for the Fe gettering mechanism:

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**Fig. 4.** (Color online) SIMS depth profiles of (a) C concentration, (b) O concentration, and (c) Fe concentration in implanted CZ-Si and Epi-Si in C-cluster projected range with a dose of $2 \times 10^{14}$ cm$^{-2}$ after annealing at 1050°C for 2 h.

**Fig. 5.** (Color online) SIMS depth profiles of (a) C concentration, (b) O concentration, and (c) Fe concentration in implanted CZ-Si and Epi-Si in C-cluster projected range with a dose of $1 \times 10^{15}$ cm$^{-2}$ after annealing at 1050°C for 2 h.

**Fig. 6.** Fe peak concentration measured by SIMS in implanted CZ-Si and Epi-Si as a function of C dose.
Interaction with secondary defects such as dislocations (relaxation-induced gettering).

Local increase in the solubility of Fe due to interaction with point defects (segregation-induced gettering).

First, we investigated the secondary defect formation caused by C-cluster ion implantation in Epi-Si. Figures 7(a) and 7(b) show TEM cross-sectional images of C-cluster ion-implanted CZ-Si and Epi-Si, respectively, after epitaxial growth and annealing at 1050 °C for 2 h. The C-cluster implantation-related defect densities were about $1.4 \times 10^{17}$ and $1.0 \times 10^{14}$ atoms/cm$^2$, respectively. No clear difference in C-cluster implantation-related defect density was obtained between CZ-Si and Epi-Si. The C-cluster implantation-related defect morphologies on implanted CZ-Si are in good agreement with results of previous works.16–19 For the implantation on Epi-Si, no secondary defects that lead to a higher Fe gettering efficiency were observed in the C-cluster ion implantation range.

Moreover, as shown in Figs. 3 and 6, the gettering efficiency of Fe had a linear dependence on the C-cluster ion implantation dose for both implanted CZ-Si and Epi-Si. It was demonstrated that the gettering mechanism in C-cluster ion implanted CZ-Si is dominated by segregation-induced gettering.16–18 This is probably because the gettering efficiency of Fe on C-cluster ion-implanted Epi-Si does not show a linear dependence if the amount of gettered Fe in C-cluster ion-implanted Epi-Si increases owing to secondary defects.

Tamura et al.27 demonstrated that high-energy ion implantation induces the formation of secondary defects through self-interstitial (I) agglomeration by ion implantation.26 The formation of secondary defects, therefore, is sensitive to the ion dose. However, the density and morphology of the defects also depend on the implantation parameters, specific ion implantation, annealing conditions, and O concentration of Si crystal bulk. Benton et al.29 indicated that MeV high-dose boron (B) implantation induces the formation of secondary defects, and that the amount of gettered Fe increases with B dose. However, the gettering efficiency of Fe does not indicate a linear function of B implantation. This gettering dependence for ion implantation was not in agreement with our results for C-cluster ion-implanted Epi-Si.

Furthermore, regarding the interaction between secondary defects and O in Si bulk, Tamura and Suzuki reported that the density of these localized sites in CZ-Si is higher than that in FZ-Si because of the locking of O on defects in CZ-Si.30 The density of secondary defects in Epi-Si is probably lower than that in CZ-Si if the defects are created by C-cluster ion implantation. Therefore, the increase in the amount of gettered Fe in implanted Epi-Si cannot be explained by relaxation-induced gettering.

Next, we consider segregation-induced gettering. The solubility level of Fe at 1050 °C is $1.1 \times 10^{15}$ cm$^{-3}$.31 The SIMS peak concentration of Fe in the C-cluster ion implantation projected range is higher than that of the solubility levels of both CZ-Si and Epi-Si, as shown in Figs. 4(c) and 5(c). Under our experimental conditions, the Fe concentration of Si bulk is about $1 \times 10^{14}$ cm$^{-3}$, which is below the solubility level. Gettering by segregation-induced gettering does not require impurity supersaturation. Additionally, our experimental data show that the gettering efficiency is linearly dependent on the C-cluster ion implantation dose even in the case of C-cluster ion implanted Epi-Si. Wong et al.12 demonstrated that the linear dependence of the amount of gettered metallic impurity is observed even at a high C dose. In C implantation, no secondary defects are observed in the C-cluster ion-implanted region. It seems that the gettering efficiency for metallic impurities in C implantation is controlled by the C concentration in the implanted region. This is probably because the efficiency of segregation-induced gettering depends on the C-cluster ion implantation dose. Therefore, we assume that the increase in the amount of gettered Fe in C-cluster ion-implanted Epi-Si occurs owing to the same mechanism as that in CZ-Si.

We consider the possibility that the point defects induced by C-cluster ion implantation are the origin of Fe gettering. Figure 8(a) shows the CL spectra after epitaxial growth for both CZ-Si and Epi-Si. Two broad peaks at ∼1345 and ∼1550 nm were observed. It is considered that the broad luminescence peak after implantation is ascribed to the point defects of multiple configurations that involve various levels.31,32 The intensities of these broad peaks were higher in Epi-Si. This result indicates that the defects induced by C-cluster ion implantation remained after epitaxial growth.
and that the number of residual defects is larger in Epi-Si. We assume that the larger number of defects induced by C-cluster ion implantation causes the increase in the amount of gettered Fe in C-cluster implanted Epi-Si.

Pinacho et al. demonstrated that C in Si after annealing forms C and I clusters (CI clusters), and that the complex of two substitutional carbon (Cs) atoms and I, i.e., Cs–I–Cs, is a precursor of CI clusters.

The two peaks of CL spectra were observed in as-implanted CZ-Si, as shown in Fig. 8(b). There is a G-center at 1280 nm and a C-center at 1570 nm, which are attributed to Cs–I–Cs and interstitial carbon (Ci) and interstitial oxygen (Oi) pairs, respectively. The G-center was observed in both CZ-Si and Epi-Si, but the intensity of the center clearly increased in the implanted Epi-Si. Therefore, we consider that the broad CL peaks after epitaxial growth in C-cluster ion-implanted samples probably originated from CI clusters involving multiple configurations. We suggest that C-cluster ion-implanted Epi-Si has more CI clusters because the number of initial intrinsic defects of CI clusters in Epi-Si is higher than that in CZ-Si. These models are illustrated in Fig. 9.

Therefore, we mainly assume that the higher gettering capability of Fe in Epi-Si is achieved through interaction with point defect clusters, such as CI clusters. The SIMS profiles of Fe concentration in both CZ-Si and Epi-Si are wider than the C and O profiles, as shown in Figs. 4 and 5. The presence of Fe around the C-cluster ion-implanted region suggests that Fe gettering does not occur in the C-rich region attributed to CI clusters. It is considered that some C distributes at the substitutional site. The Cs atoms induce the tensile strain because the C tetrahedral radius is smaller than the Si tetrahedral radius, that is, 0.76 Å for C vs 1.17 Å for Si. These data suggest that Fe is gettered partially in the tensile strain region induced by Cs atoms. In the region around C-cluster ion implantation, Fe gettering might occur owing to relaxation-type gettering.

V-type defects, such as V clusters, generated by C-cluster ion implantation should contribute to the increase in the amount of gettered Fe. Recent calculations suggest that the gettering effect of Fe decreases with the increase in the number of O atoms in VO complexes.

This is probably because the increase in the amount of gettered Fe on C-cluster ion-implanted Epi-Si occurs through interaction with point defect clusters. The local increase in the solubility of the projected range of C-cluster ion implantation for Fe is also caused by the interaction between Fe and point defect clusters. We believe that C-cluster implantation in a low-oxygen-concentration region induces a gettering sinks for Fe, such as CI clusters and V clusters.

4. Conclusions

We investigated the effect of O concentration on the capability of Fe gettering in a C-cluster ion-implanted region by comparing Epi-Si with CZ-Si. We found that C-cluster ion implantation in Epi-Si increases the gettering efficiency of Fe, and that the high gettering efficiency is due to C-cluster ion implantation dose in the range from $10^{14}$ to $10^{15}$ cm$^{-2}$. The amount of gettered Fe in Epi-Si was approximately two times higher than that in CZ-Si.

Furthermore, we found that the number of residual defects after epitaxial growth in the C-cluster projected range was larger in Epi-Si by CL measurement. It was shown that the higher gettering efficiency for Fe on C-cluster ion-implanted Epi-Si was due to the difference in the number of point defects. Our experimental results suggest that Fe in the projected range of C-cluster ion implantation is gettered through point defects such as CI clusters, and Fe gettering occurs owing to segregation-type gettering.

It is concluded that Si wafers including a low O region with C-cluster ion implantation are effective for advanced CMOS image sensors.
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