Diffusion kinetic of hydrogen in CH3O-molecular-ion-implanted silicon wafer for CMOS image sensors

Ryosuke Okuyama*, Ayumi Onaka-Masada, Satoshi Shigematsu, Takeshi Kadono, Ryo Hirose, Yoshihiro Koga, Hidehiko Okuda, and Kazunari Kurita

SUMCO Corporation, Imari, Saga 849-4256, Japan

E-mail: rokuyama@suncosi.com

Received January 10, 2018; accepted April 24, 2018; published online July 10, 2018

The association and dissociation behavior of hydrogen in the implanted region of a CH3O cluster were investigated for high-performance CMOS image sensors. Two hydrogen peaks were observed in the CH3O-implanted region after epitaxial growth and heat treatment. The difference in the depths of the two peaks accords with the difference in the depth of carbon-cluster-related and new extended stacking fault defects. Thus, we calculated the activation energies of the association and dissociation of hydrogen, assuming a dissociation reaction for the first peak, formed at a small depth from the surface of the silicon substrate, and a simple reversible reaction for the second peak, formed at a large depth from the surface of the silicon substrate. The dissociation activation energy corresponding to the first peak was $0.75 \pm 0.03$ eV. This activation energy indicates that the hydrogen associated with the first peak forms a binding state with a carbon and silicon self-interstitial cluster (C/I cluster). On the other hand, the binding energy corresponding to the second peak was calculated to be $0.78$ eV, which was close to the C–H2 binding energy. Consequently, the CH3O-implanted region forms a binding state with hydrogen and a C/I cluster or a C–H2 binding state.

1. Introduction

CMOS image sensors have been used in ubiquitous devices such as smartphones, personal-computer-type tablets, and cameras for in-vehicle and monitoring systems. Therefore, the CMOS image sensor market strongly requires technological advances for high-speed animation imaging and many other functions. Advanced CMOS image sensors have serious technical issues including white spot defects, image lag, and control of the interface state density in the device fabrication processes.1–4) The cause of white spot defects is metallic impurity contamination during various CMOS device fabrication processes such as high-temperature rapid thermal annealing and ion implantation.1–3) In addition, the characteristic of image lag has been reported to be caused by oxygen out-diffused from a silicon substrate during device fabrication processes.1,4) Furthermore, dark current occurs with the junction leakage current components due to the interface state density in the isolation region and process-induced defects.1–3) In particular, the reduction in interface state density is an extremely important technical issue, because the metal impurity contamination has been controlled so as to be minimized. In addition, the concentration of out-diffused oxygen has also been decreased using a low-oxygen-concentration silicon wafer or a low-temperature device fabrication process. On the other hand, the interface state density has been reduced by hydrogen forming gas annealing (FGA).5,6) However, the FGA process is performed after the device fabrication process. Furthermore, the diffusion of hydrogen into the interface of the isolation region is difficult owing to the formation of a complicated structure, such as a multilayer device structure, and shallow trench isolation.6) Consequently, not only the gettering ability for metal impurities or oxygen but also the improvement in interface state density is an important issue for the high performance of advanced CMOS image sensors.

Therefore, we have developed a proximity gettering technology with carbon cluster-ion-implanted silicon epitaxial wafers for CMOS image sensors.7–9) The carbon-cluster-implanted wafers have three characteristics that help resolve the technical issues of CMOS image sensors. First, the implanted region of a carbon cluster ion has a high gettering capability for metal impurities.7–9) Second, this implanted region exhibits a barrier effect on oxygen.7–9) Third, the hydrogen that diffuses from the carbon-cluster-implanted region during the device fabrication process has a passivation effect, resolving in the reduction in interface state density.10–12) As mentioned above, the hydrogen diffusion behavior of a cluster-implanted region in terms of how it contributes to the reduction in interface state density via the hydrogen passivation effect is particularly important in these three characteristics. Our previous studies demonstrated the unique hydrogen diffusion behavior by performing an experiment and a technology computer-aided design (TCAD) analysis in the implanted region of a carbon cluster.10,11) In our previous studies, the CH3 cluster ion was used as the carbon cluster ion. In addition, the implanted region of CH3 traps hydrogen after epitaxial growth, and the dissociation behavior upon subsequent heat treatment has been demonstrated. The above hydrogen diffusion behavior has not been reported in previous studies.

Furthermore, we developed a molecular ion implantation technique that added oxygen to a carbon cluster to improve the gettering capability. Molecular ions were used in a CH3O cluster. The implanted region of a CH3O cluster reportedly has the same three characteristics as the implanted region of a carbon cluster.10) However, the formation of defects, unlike in the carbon cluster, was reported for the CH3O cluster after epitaxial growth.13,14) A previous study demonstrated that a {111} extended stacking fault defect is formed in the implanted region of a CH3O cluster after epitaxial growth owing to the increase in the number of silicon self-interstitials by CH3O cluster implantation.13) Hydrogen in the implanted region of the CH3O cluster is also trapped after epitaxial growth, similarly to that in the implanted region of the carbon cluster.13) However, our previous studies suggest that a carbon...
and silicon self-interstitial cluster (C/I cluster) in the implanted region of the carbon cluster significantly contributes to the trapping and diffusion behavior of hydrogen.\(^{10,11,15}\) In addition, the implanted region of a CH\(_3\)O cluster forming a high-concentration silicon self-interstitial can be larger than the implanted region of the carbon cluster. Thus, the formation of a highly concentrated C/I cluster is expected. Furthermore, a {111} extended stacking fault defect is formed in the implanted region of the CH\(_3\)O cluster. However, the detailed diffusion behavior of hydrogen trapped in the implanted region of the CH\(_3\)O cluster after heat treatment is not clear. Consequently, the hydrogen diffusion behavior of the CH\(_3\)O cluster should differ from the conventional hydrogen diffusion behavior of the carbon cluster. Therefore, we focused on the annealing diffusion behavior of hydrogen in the implanted region of the CH\(_3\)O cluster after epitaxial growth. Furthermore, the hydrogen diffusion behavior of the CH\(_3\)O cluster was compared with that of C\(_3\)H\(_5\), which was studied in detail in our previous studies.

On the other hand, hydrogen is known to have various effects on semiconductors.\(^{16-31}\) In previous studies, the formation of hydrogen-induced platelet defects was reported for the smart-cut process.\(^{32-35}\) In another study, Fukata and co-workers indicated that hydrogen is trapped in a silicon-hydrogen bond in {111} platelets in silicon.\(^{25-28}\) In addition, in previous papers, the binding state and diffusion behavior after heat treatment below 800 °C were reported. However, hydrogen is trapped in the implanted region of the CH\(_3\)O cluster after heat treatment above 1000 °C such as to induce epitaxial growth. Thus, we assume that the hydrogen diffusion behavior in the implanted region of the CH\(_3\)O cluster is different from that in previous studies.

Therefore, the main purpose of this study was to clarify the hydrogen diffusion behavior after high-temperature heat treatment and perform a kinetic analysis in the implanted region of the CH\(_3\)O cluster. This paper presents the hydrogen binding state in the implanted region of the CH\(_3\)O cluster. The hydrogen diffusion behavior in the implanted region of the CH\(_3\)O cluster should contribute to the high performance of advanced CMOS image sensors.

2. Experimental methods

CH\(_3\)O and C\(_3\)H\(_5\) cluster ions were implanted in n-type silicon (100) wafers at room temperature. The carbon dose of the CH\(_3\)O or C\(_3\)H\(_5\) cluster ions was 1.0 \times 10^{15} carbon atoms/cm\(^2\). The implantation energy was 80 keV/cluster. An epitaxial layer of 5.0 \(\mu\)m thickness was grown after cluster ion implantation. The epitaxial silicon layer was grown using a Si\(_3\)H\(_x\)Cl gas source at 1100 °C with a growth rate of 1.0 \(\mu\)m/min. Furthermore, the subsequent heat treatment was performed from 700 to 1100 °C for 30 to 240 min to evaluate the diffusion behavior of the hydrogen in the implanted region of a CH\(_3\)O cluster. The CH\(_3\)O cluster ion implantation was conducted using CLARIS (Nissin Ion Equipment).

Figure 1 shows the process and analysis flow. The distribution of hydrogen in the implanted region of the CH\(_3\)O cluster was analyzed using secondary ion mass spectrometry (SIMS; CAMECA IMS7f). Cross-sectional transmission electron microscopy (XTEM) was used for observing the implantation defects in the implanted region of the CH\(_3\)O cluster after epitaxial growth and heat treatment.

3. Results and discussion

3.1 Hydrogen diffusion behavior after heat treatment in the implanted region of a CH\(_3\)O-cluster-implanted epitaxial wafer

Figure 2 shows the SIMS profiles of carbon, oxygen, and hydrogen after epitaxial growth with a CH\(_3\)O dose of 1.0 \times 10^{15} cluster atoms/cm\(^2\). Hydrogen, carbon, and oxygen peaks were found in the implanted region of the CH\(_3\)O cluster. The hydrogen peak concentration was 2.4 \times 10^{18} atoms/cm\(^3\). The epitaxial growth temperature was high (approximately 1100 °C). The hydrogen diffusion velocity is well known to be high at high temperatures.\(^{16,17}\) However, a hydrogen peak could be observed in the implanted region of the CH\(_3\)O cluster. A previous study also found a hydrogen peak in the implanted region of a C\(_3\)H\(_5\) cluster after epitaxial growth.\(^{10,11}\) Figure 3 shows the hydrogen profiles of CH\(_3\)O and C\(_3\)H\(_5\) after epitaxial growth with a dose of 1.0 \times 10^{15} carbon atoms/cm\(^2\), plotted for comparison of the hydrogen peak concentration. The hydrogen peak concentration of the CH\(_3\)O cluster is higher than that of the C\(_3\)H\(_5\) cluster.

Figure 4 shows the depth profiles of hydrogen after heat treatment at temperatures of (a) 700, (b) 900, and (c) 1100 °C for 30 min (solid line), 120 min (broken line), and 240 min (dotted line) obtained by SIMS analysis. The hydrogen peak concentration decreased with increasing heat treatment temperature. The dependence on the temperature is larger than that on the heat treatment time. Figure 5 shows integral values in a 1.0 \(\mu\)m region around the hydrogen peak in the...
implanted region of the (a) CH₃O and (b) C₃H₅ clusters as a function of the heat treatment time at temperatures of 700, 900, and 1100 °C. In the case of the C₃H₅ cluster, the hydrogen concentration decreased with increasing heat treatment temperature and time. However, the reduction in the hydrogen concentration for the CH₃O cluster only slightly depends on the heat treatment time. These results revealed that the hydrogen diffusion behavior in the implanted region of the CH₃O-cluster- and C₃H₅-cluster-ion-implanted epitaxial wafer was observed using XTEM in order to compare the formation of implantation defects. Figure 6 shows low-magnification XTEM images in the implanted region of the (a) C₃H₅ and (b) CH₃O clusters, and high-magnification XTEM images in the implanted region of the (c) C₃H₅ and (d) CH₃O clusters after epitaxial growth. In Figs. 6(a) and 6(c), small defects of 5 nm were observed. Our previous study suggests that small defects are formed by the carbon and interstitial silicon cluster (C/I cluster) in the implanted region of the carbon cluster. However, in the implanted region of the CH₃O cluster, a different defect was observed with small defects. Hirose et al. demonstrated that this different defect is an extended stacking fault defect in the {111} direction. The extended stacking fault defect is formed deeper than the small defects because the CH₃O cluster implantation forms excess interstitial silicon in the implanted region. Therefore, we found that the different defect morphology in the implanted region of the CH₃O cluster caused the difference in the diffusion behavior of hydrogen.
Our previous study demonstrated that the dissociation activation energy of 0.76 ± 0.04 eV to dissociate hydrogen from the implanted region of the C\textsubscript{3}H\textsubscript{5} cluster is extremely close to the binding energy of the C–H\textsubscript{2} defect.\textsuperscript{(10)} However, we found that the implanted region of the CH\textsubscript{3}O cluster has two defects in its morphology. One is the same defect as that in the C\textsubscript{3}H\textsubscript{5} cluster, and the other is a new defect in the CH\textsubscript{3}O cluster. Thus, we assume that there are two types of hydrogen trapping state in the implanted region of the CH\textsubscript{3}O cluster. Figure 7 shows the SIMS profiles of hydrogen in the implanted region of the CH\textsubscript{3}O (solid line) and C\textsubscript{3}H\textsubscript{5} (dashed line) clusters after 30 min of 700 °C heat treatment with a dose of 1.0 × 10\textsuperscript{15} cluster atoms/cm\textsuperscript{2}.

![Figure 6](image1.png)

**Fig. 6.** Low-magnification XTEM images in the implanted region of the (a) C\textsubscript{3}H\textsubscript{5} and (c) CH\textsubscript{3}O clusters, and high-magnification XTEM images in the implanted region of the (b) C\textsubscript{3}H\textsubscript{5} and (d) CH\textsubscript{3}O clusters after epitaxial growth.

The peak separation was calculated by Lorenz function fitting. The first peak closes to the top surface and the second peak (dashed line) as well as the total hydrogen profile of the first and second peaks after (a) 30 min of 700 °C heat treatment and (b) 30 min of 1100 °C heat treatment with a dose of 1.0 × 10\textsuperscript{15} cluster atoms/cm\textsuperscript{2}. The hydrogen peak concentration of the C\textsubscript{3}H\textsubscript{5} cluster is the same as the hydrogen peak of the conventional C\textsubscript{3}H\textsubscript{5} cluster. However, the second peak is considered to be formed by the trapped hydrogen in the new extended stacking fault defect. In addition, the second peak concentration is higher than the first peak concentration even after heat treatment. Consequently, we assumed that the dissociation activation energy of hydrogen from the second peak region was different from that of the first peak region. Therefore, we calculated the dissociation activation energy of hydrogen from the first peak and second peak regions.

For the second peak, we calculated the dissociation activation energy from the dissociation reaction because this region seems to be the same as the conventional implanted region of...
the C\textsubscript{2}H\textsubscript{5} cluster. However, the second peak is calculated from the dissociation and association activation energies assuming a simple reversible reaction because the hydrogen concentration of the second peak seems to be at equilibrium in Fig. 5. To make the reaction of hydrogen from an implantation defect a reversible reaction, the concentration of dissociated hydrogen can be expressed using the following reaction equations:

\[
H_D \xrightarrow{k_i} H, \tag{1}
\]

\[
\frac{dC_{\text{HD}}}{dt} = -k_f C_{\text{HD}} + k_i C_H, \tag{2}
\]

\[
\frac{dC_H}{dt} = k_f C_{\text{HD}} - k_i C_H, \tag{3}
\]

where $H_D$ is the trapped hydrogen in the defect of the implanted region of the CH\textsubscript{3}O cluster. H is the diffused hydrogen from the defect of the implanted region after heat treatment. $C_{\text{HD}}$ is the concentration of $H_D$. $C_{\text{HD}}$ is the hydrogen concentration obtained using SIMS analysis. $C_H$ is the concentration of diffused hydrogen after heat treatment. The reaction rate constants of the forward reaction (dissociation reaction) and inverse reaction (association reaction) are $k_f$ and $k_i$, respectively. In the case of the first-peak calculation, $k_i$ is assumed to be zero by ignoring the inverse reaction. The heat treatment time is $t$. For the initial condition, the concentrations $C_{\text{HD}}$ and $C_H$ before heat treatment are assumed to be $C_0$ and zero, respectively. Consequently, Eq. (2) can be expressed using the following reaction equation:

\[
\frac{dC_{\text{HD}}}{dt} = -(k_i + k_f) C_{\text{HD}} + k_i C_0. \tag{4}
\]

From this equation, the ratio of $C_{\text{HD}}$ to $C_0$ can be expressed as

\[
\frac{C_{\text{HD}}}{C_0} = \frac{k_i + k_i \exp[-(k_i + k_f)t]}{k_i + k_f}. \tag{5}
\]

Figure 9 shows the time dependence of the ratio of $C_{\text{HD}}$ to $C_0$ obtained from the (a) first and (b) second peaks. In Fig. 9, each plot shows experimental data obtained by SIMS analysis after peak separation, and the dashed lines show curves fitted with Eq. (3). These results demonstrate that the hydrogen diffusion behavior of the CH\textsubscript{3}O cluster can be expressed using the dissociation reaction model of the first peak and the reversible reaction model of the second peak. The reaction rate constants $k_f$ and $k_i$ were derived in accordance with the fitting curves in Fig. 9. The error bars of $k_f$ and $k_i$ are 5%. Figure 10 shows Arrhenius plots of the reaction rate constants for the (a) first and (b) second peaks from Fig. 9. For the first peak, the dissociation activation energy was derived to be about 0.75 ± 0.03 eV. However, the dissociation and association activation energies for the second peak were estimated to be about 0.92 ± 0.05 and 0.14 ± 0.01 eV, respectively. We assumed a simple reaction model of the dissociation and association behavior based on a defect formed in the implanted region of the CH\textsubscript{3}O cluster. These results of the trapping and diffusion behavior demonstrate good agreement with Eq. (3).

### 3.2 Hydrogen diffusion mechanism in the implanted region of the CH\textsubscript{3}O cluster after heat treatment

Previous studies have reported the binding states and diffusion behavior of hydrogen in crystalline silicon.\textsuperscript{24–30} Fukata and co-workers indicated that vacancy and void defects form complexes with hydrogen in carbon-doped silicon after hydrogen atom treatment.\textsuperscript{36–38} However, other previous studies have demonstrated that hydrogen is trapped in voids or platelet defects by phosphorus ion implantation.\textsuperscript{25–28} They reported the analytical results of the Si–H binding state after heat treatment below 800 °C. Other studies have reported the C–H binding state in silicon bulk.\textsuperscript{39–42} They also analyzed the C–H\textsubscript{2} binding state after low-temperature heat treatment below 900 °C.\textsuperscript{36–42} However, we revealed that the implanted region of the CH\textsubscript{3}O cluster trapped hydrogen after epitaxial growth and subsequent heat treatment at a high temperature. Conventionally, hydrogen diffuses easily during high-temperature heat treatment above 1000 °C.\textsuperscript{16,17} However, we found that hydrogen gradually diffused from the implanted region of a CH\textsubscript{3}O cluster after the subsequent heat treatment. Consequently, we consider that the trapped hydrogen and diffusion behaviors are related to the implantation defects in the CH\textsubscript{3}O cluster. As shown in Fig. 6, a defect of approximately 5 nm size and a (111) extended stacking fault defect were observed in the implanted region of the CH\textsubscript{3}O cluster. Furthermore, the hydrogen peak of the CH\textsubscript{3}O cluster could be separated into two peak profiles.

For the first peak, we considered the binding state for hydrogen as that in the implanted region of the C\textsubscript{2}H\textsubscript{4} cluster. Our previous study demonstrated that the dissociation activation energy of H is 0.76 ± 0.04 eV.\textsuperscript{10} In this study, the dissociation activation energy of hydrogen from the implanted region of CH\textsubscript{3}O of 0.75 ± 0.03 eV is extremely close. These activation energies assume the binding energy of the C–H\textsubscript{2} defect and the activation energy for the diffusion of hydrogen molecules from tetrahedral interstitial sites in silicon as well as multiple vacancies.\textsuperscript{43–46} However, other studies inves-
tigated the binding energy in terms of the hydrogen diffusion behavior after low-temperature heat treatment. Consequently, the hydrogen binding state in the implanted region of a C3H5 or CH3O cluster is presumed to differ from the conventional C–H2 binding state.39–42) Pinacho et al. indicated that a carbon and silicon self-interstitial formed a CmI n (e.g., C3I3 and C3I2) cluster (C/I cluster) in carbon-rich silicon.15) In addition, our previous study indicated that the trapping behavior of hydrogen in the implanted region of a carbon cluster after epitaxial growth and subsequent heat treatment can be calculated using TCAD analysis with a reaction model in which hydrogen binds to a C/I cluster.11) This result demonstrates that the C/I cluster in the implanted region of a carbon cluster significantly contributed to the trapping behavior of hydrogen. Therefore, we hypothesize that the first peak of hydrogen in the implanted region of the CH3O cluster also corresponds to the binding state with the C/I cluster.

Then, the second peak seems to originate from a {111} extended stacking fault defect as shown in Fig. 6. Previous studies have reported hydrogen trapping and diffusion behavior in a {111} platelet defect.25–28) Other studies reported that the high-dose hydrogen implantation formed hydrogen-induced platelet defects.32–35) However, these studies reported hydrogen diffusion behavior during low-temperature heat treatment because hydrogen diffused out during high-temperature heat treatment. In this study, the dissociation and association activation energies were estimated to be about 0.92 ± 0.05 and 0.14 ± 0.01 eV, respectively. These activation energies were obtained from heat treatment at 700 to 1100 °C. We considered the binding energy for a reversible reaction model of the second peak. Figure 11 shows a schematic of the activation energy for the reversible reaction model of the second peak, from which the binding energy of the second peak was calculated as approximately 0.78 eV owing to the differences in the dissociation and association activation energies. The binding energy is close to that of the C–H2 defect.39) Therefore, we hypothesize that carbon contributes to the formation of the second peak. We used a kinetic Monte Carlo (KMC) code in the TCAD Sentaurus Process simulator from Synopsys in order to simulate the diffusion behavior of carbon to determine the distribution of defects and carbon in the implanted region of the CH3O cluster.49) Figure 12 shows the distribution of dislocation defects (black) and carbon (red) obtained by simulation using the KMC code of the TCAD for the implanted region of a CH3O cluster after epitaxial growth heat treatment with a CH3O dose of 1.0 × 1015 cluster atoms/cm².
the dislocation. The dislocation defect revealed by the KMC code of the TCAD is inferred to be an extended stacking fault defect in the implanted region of the CH$_3$O cluster as shown in Fig. 6. Furthermore, Fig. 13 shows SIMS profiles of carbon and hydrogen at depths of 4.5 to 5.5 µm from the epitaxial wafer surface after epitaxial growth with a CH$_3$O dose of 1.0 × 10$^{15}$ cluster atoms/cm$^2$. The carbon peak was also observed along with two other peaks. In addition, the carbon peak corresponded to the hydrogen peak. In Figs. 6, 12, and 13, the difference in the two peaks and defect depths was approximately 40 nm. Consequently, we hypothesize that the carbon trapped in the extended stacking fault defect contributes to the second peak of hydrogen in the implanted region of the CH$_3$O cluster. On the other hand, this extended stacking fault defect can disappear with subsequent heat treatment, because a silicon self-interstitial dissociates from the extended stacking fault defect. Therefore, the dissociated silicon self-interstitial can form a C/I cluster in the carbon trapped in the extended stacking fault defect or in the C/I cluster corresponding to the first peak. Consequently, an increase in the concentration of hydrogen trapped by the C/I cluster is assumed. This suggests that the binding state of hydrogen in the second peak region changes to that in the first peak region; thus, the diffusion of hydrogen also shows the same behavior as that for the first peak. However, the experimental results in the temperature range in this paper show that the diffusion behavior associated with the second peak does not change. Since the epitaxial growth is performed at 1100°C, a change in the binding state of hydrogen may occur owing to the disappearance of the extended stacking fault defect when heat treatment is performed at a temperature higher than 1100°C. Therefore, the extended stacking fault defect in the implanted region of the CH$_3$O cluster is stable under the heat treatment conditions in this study. The results indicate that the hydrogen in the implanted region of the CH$_3$O cluster is in the above two kinds of binding state with the C/I cluster or in the C–H$_2$ binding state with the carbon trapped in the extended stacking fault defect.

### 4. Conclusions

We demonstrated the trapping and diffusion behavior of hydrogen in the implanted region of the CH$_3$O cluster after epitaxial growth and subsequent heat treatment. The hydrogen peak concentration of the CH$_3$O cluster is larger than that of the C$_2$I$_3$ cluster. In addition, the hydrogen profile of the CH$_3$O cluster has two peaks. Such hydrogen diffusion behavior has not been reported in previous studies. TEM observations revealed that the difference in the depth of the two peaks accords with the difference in the depth of the two types of formed defects. TEM results indicated that the implanted region of the CH$_3$O cluster has conventional carbon-cluster-related defects and a [111] extended stacking fault defect. Consequently, the hydrogen peak can be used to separate the first and second peaks obtained from the silicon surface. In addition, we derived the dissociation and association activation energies assuming a simple reaction model on the basis of the dissociation and association behavior from each defect formed in the implanted region of the CH$_3$O cluster. The dissociation activation energy of the first peak was estimated to be about 0.75 ± 0.03 eV. This value is extremely close to the conventional dissociation activation energy of the C$_3$I$_2$ cluster. Therefore, the first peak corresponds to the binding state related to C/I clusters and hydrogen. However, the dissociation and association activation energies for the second peak were estimated to be about 0.92 ± 0.05 and 0.14 ± 0.01 eV, respectively. Regarding the second peak, the binding energy was calculated as approximately 0.78 eV owing to the differences in the dissociation and association activation energies. The value is also extremely close to the binding energy of the C–H$_2$ defect. The KMC code of the TCAD indicated the possibility of forming the carbon complexes in the extended stacking fault defect.

Furthermore, we consider that hydrogen in the implanted region of the CH$_3$O-cluster forms complexes comprising the C/I cluster defect related to the C–H binding state and extended stacking fault defect. Hydrogen diffusion behavior in the implanted region of the CH$_3$O cluster is considered to contribute to the high electrical performance characteristics of CMOS image sensors such as the low photodiode junction leakage current and dark current.

### Acknowledgements

The authors would like to thank Dr. Hisashi Furuya and Mr. Naoki Ikeda of the Technology Division, SUMCO Corporation, for their support and helpful advice.

---

1) H. Takahashi, CMOS Image Sensor (Corona, Tokyo, 2012) Chap. 3, p. 123 [in Japanese].
2) H. I. Kwon, I. M. Kang, B.-G. Park, J. D. Lee, and S. S. Park, IEEE Trans. Electron Devices 51, 178 (2004).
3) F. Russo, G. Moccia, G. Nardone, R. Alfonsetti, G. Polsinelli, A. D’Angelo, A. Patacchiola, M. Liverani, P. Pianetta, T. Lippa, M. Carlini, M. L. Polignano, I. Mica, E. Cazzinni, M. Ceresoli, and D. Codegoni, Solid-State Electron. 91, 91 (2014).
4) A. Ohtani and T. Kaneda, Ext. Abstr. 77th Autumn Meet. Japan Society of Applied Physics and Related Societies, 2016, 14p-P6-11 [in Japanese].
5) K. Ohyu, Dr. Thesis, Faculty of Engineering, University of Tokyo, Tokyo (1997) [in Japanese].
6) J. P. Carrière, S.PLACE, J.-P. Oddou, D. Bensot, and F. Roy, IEEE Int. Reliability Physics Symp. (IRPS), 2014, 3C 1.1.
7) K. Kurita, T. Kadono, R. Okuyama, R. Hirose, A. Onaka-Masada, Y. Koga, and H. Okuda, Jpn. J. Appl. Phys. 55, 121301 (2016).
8) K. Kurita, T. Kadono, R. Okuyama, S. Shigematsu, R. Hirose, A. Onaka-Masada, Y. Koga, and H. Okuda, Phys. Status Solidi A 214, 1700216 (2017).
