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Effect of hydrocarbon molecular ion size for amorphous region formation analyzed by X-ray photoelectron spectroscopy

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We investigate the amorphous formation behavior on hydrocarbon molecular ion implantation conditions such as hydrocarbon molecular ion size by X-ray photoelectron spectroscopy (XPS). The cross-sectional radius of the amorphous region was obtained from the peak intensity of the amorphous component in Si 2p spectra analyzed by XPS, and using columnar formula for a model. We confirmed that the cross-sectional radius of the amorphous region formed by hydrocarbon molecular ions differs greatly from that formed by monomer carbon ions, and increases by 0.078 nm as the number of carbon atoms composing the hydrocarbon molecular ion increases. The dependence of amorphous formation on the hydrocarbon molecular size is related to the C–C binding distance, and the ratio of increase in the amorphous cross-sectional radius corresponds to half of the C–C binding distance. Therefore, the collision behavior of hydrocarbon molecular ions during implantation predominantly influence the size of hydrocarbon molecular ions. © 2020 The Japan Society of Applied Physics

1. Introduction

CMOS image sensors have been widely used in ubiquitous devices such as smartphones, smartwatches, and personal computer tablets. The consumer market requires high-sensitivity and high-speed imaging data processing for fabricating high-performance devices such as CMOS image sensors. However, there are some serious technical issues in the fabrication of CMOS image sensors. One very important issue is metallic impurities contaminants in the device active region during CMOS device fabrication process.1–10 Metallic impurities form deep energy level defects in a silicon bandgap. These defects lead to, for example, dark current,11 pn-junction leakage current, and a gate oxide breakdown voltage, which affect electrical device performance. Thus, CMOS image sensor manufacturers are attempting to eliminate metallic impurities from the device active region by using a gettering technique.1–3

CMOS image sensor manufacturers strongly demand epitaxial silicon wafers with the highest gettering capability. In regard to the above technical issues, we have investigated an epitaxial silicon wafer subjected to proximity gettering using a hydrocarbon molecular ion implantation technique.4,5 In earlier studies, Kurita and coworkers presented the production concept and three unique characteristics of hydrocarbon-molecular-ion-implanted epitaxial wafers for CMOS image sensor manufacturing process.6–8

In the production concept for hydrocarbon-molecular-ion-implanted epitaxial wafers, neither protective oxide film deposition process nor recovery thermal treatment process for recrystallization is necessary before epitaxial growth, which makes this production process extremely simple with high throughput.9,10 Regarding the three unique characteristics of hydrocarbon-molecular-ion-implanted silicon wafers, the first characteristic is that in such wafers, the hydrocarbon molecular ion implantation projection range has high getting capability for metallic impurities such as nickel,6,7,9 iron,6,7,13,14 and copper.7,9 Second, this range also has a barrier effect on oxygen impurities out-diffusing to the epitaxial layer from the silicon substrate during device fabrication process.6–10 Third, a passivation effect on process-induced defects is expected owing to the hydrogen of the hydrocarbon molecular ions trapped in the projection range diffusing during the CMOS image sensor fabrication process.6,9,10,15,16 Furthermore, we have demonstrated that these characteristics, particularly the gettering capability for metallic impurities, are enhanced by increasing the hydrocarbon molecule dose.6,8 However, a high hydrocarbon molecule dose results in the form of an amorphous layer in hydrocarbon molecular ion implantation projection range.10 This amorphous layer is formed by the generated epitaxial-growth-related defects, such as stacking faults, dislocations, and dislocation loops after the epitaxial growth process. It is important to clarify the process and implantation conditions leading to the formation of an amorphous top surface of a silicon wafer. Therefore, we focus on the origin of amorphous region formation by analyzing hydrocarbon molecular ion implantation induced damage by X-ray photoelectron spectroscopy (XPS).

Lai et al. previously reported the quantitative XPS analysis of a silicon surface damaged by irradiated ions.18,19 Their experimental results showed that the Si 2p spectrum of an amorphous sample bombarded monomer xenon ions is broader than that of nonbombarded sample. The broadening of the Si 2p spectrum is affected by deviations in the bond length and bond angle due to the amorphous formation.20 Morehead and coworker proposed that the amorphous formation model is defined by the columnar shape along the monomer ion track.21 They showed that the amorphous formation behavior occurs discretely at low ion dose, and continuously with increasing ion dose. They described the dependence of ion species and substrate temperature on the critical implantation dose for forming continuous amorphous layer. Moreover, Ishii et al. reported on the cross-sectional radius of an amorphous layer formed by implanted noble gas ion implantation and analyzed by XPS and using a columnar
form model. However, the hydrocarbon molecular ion implantation conditions leading to amorphous region formation have not been clarified. Hydrocarbon molecules such as C2H5, C3H5, and C5H5 consist of carbon and hydrogen atoms. Therefore, hydrocarbon molecular ions have unique parameters such as molecular size.

In this study, we clarified the amorphous formation behavior using a columnar form model and the effect of the hydrocarbon molecular ion size on amorphous formation.

2. Experimental methods

2.1. Sample preparation

The experimental samples used in this study were 12 inch Czochralski (Cz) silicon crystals of 755 μm thickness. Their resistivity was 10 Ω cm. The starting sample wafers were implanted with C5H5, C3H5, and C2H5 using CLARIS (Nissin ion equipment). The implantation conditions were an energy of 80 keV ion−1, and doses of 2.0 × 1013 to 5.0 × 1015 ions cm−2. The tilt and twist angles were set to 0° so as not to suppress the channeling effects.

To compare with the amorphous region formation by monomer carbon ion implantation, the implantation was carried out under the same energy and dose range as those for hydrocarbon molecular ion implantation, and in the same incident beam direction for silicon wafers. After ion implantation, each sample was cut and cleaned in 0.5% HF solution for 2 min to remove the native oxide film.

2.2. Evaluation procedure

Crystallinity of several nm in the hydrocarbon-molecular-ion-implanted silicon surface were measured by XPS using a PHI Quantera SXM which is equipped with a monochromated Al Kα X-ray source (1486.6 eV). We focused on the changes in the binding energy spectrum of the Si 2p core level. Figures 1(a)–1(c) respectively show XPS spectra of Si 2p and a cross-sectional transmission electron microscope (TEM) image with and without hydrocarbon molecular ion implantation. The implantation conditions are C3H5, 80 keV implantation energy, and dose of (a) 1.67 × 1014 and (b) 1.67 × 1015 ions cm−2. In the sample implanted at a dose of 1.67 × 1014 ions cm−2 no amorphous layer was formed, and the Si 2p1/2 and Si 2p3/2 peaks of the XPS spectrum are clearly formed; however, the spectrum is slightly broader than without hydrocarbon molecular ion implantation.

In contrast, the sample implanted at a dose of 1.67 × 1015 ions cm−2 formed an amorphous layer from the surface to a depth of 80 nm, and the peaks of XPS spectra are broad and not clearly formed. These results show the same tendency as those reported by Lu et al.19 The broadening of the spectra reflects the changes in the Si–Si bond length and bond angle in the amorphous region formed by hydrocarbon molecular ion implantation.

Then, peaks of Si 2p spectra obtained in the experiments were separated by taking the difference between the samples with and without hydrocarbon molecular ion implantation. Figure 2 shows the separation of Si 2p1/2 at about 99.2 eV and Si 2p3/2 at about 99.8 eV of the hydrocarbon molecular ion implanted sample. This peak intensity indicates amorphous and crystal components.

We chose the peak intensity of the amorphous component and defined the amorphous formation ratio as

\[ X_a = \frac{I}{I'(\text{saturated})}, \]

where I is the peak intensity of the amorphous component of an implanted sample each implantation condition, and \( I'(\text{saturated}) \) is the peak intensity of the amorphous component with the amorphous region completely formed from the certain depth to the outermost surface.

3. Results and discussion

3.1. Hydrocarbon molecular size and dose dependences of amorphous region formation ratio

Figure 3 shows a plot of the normalized amorphous formation ratios for all hydrocarbon molecular ion sizes as a function of hydrocarbon molecule dose. When the normalized amorphous formation ratio reaches 1.0, it indicates that a continuous amorphous layer is formed from a certain depth to the outermost surface. The amorphous formation ratio of C2H5 ions starts increasing from a dose of 1.00 × 1015 ions cm−2, and the amorphous layer is completely formed on the surface at a molecule dose of 4.00 × 1015 ions cm−2 or higher. The onset of the increasing amorphous formation ratio shifts towards a
lower ion dose region depending on the hydrocarbon molecular ion size. It is confirmed that amorphous formation is promoted depending on the hydrocarbon molecular ion size.

In contrast, the monomer carbon ion implanted sample did not show a noticeable increase in the amorphous formation ratio. Thus, it is considered that the monomer carbon ion does not contribute to the amorphous formation of the outermost surface in the range of dose used in this experiment. From these results, we consider that the impact of amorphous formation by hydrocarbon molecular ions is markedly different from that of monomer carbon ions.

Furthermore, in this experiment, the implantation energy per molecular ion is the same, so the volume of amorphous region is different because of the different amorphous formation depth. For that reason, we confirm the amorphous formation ratios by monomer carbon ion implantation at implantation energy per carbon atom equivalent to each hydrocarbon molecular ion to form the same volume of amorphous region. We simulated the amorphous formation ratios with surface layer by using the kinetic Monte Carlo (KMC) code in the technology computer-aided design (TCAD) simulator Sentaurus process from Synopsys Inc.23)

Figure 4 shows the normalized amorphous formation ratios for monomer carbon ion implantation equivalent to each hydrocarbon molecular ion implantation conditions using TCAD. The implantation energy per carbon atom equivalent to C₅H₅, C₃H₅, and C₂H₅ are 14.8 keV, 23.4 keV, and 33.1 keV, respectively. The dose equivalent to C₅H₅, C₃H₅, and C₂H₅ are 5.00 \times 10^{14} \text{ ions cm}^{-2}, 8.33 \times 10^{14} \text{ ions cm}^{-2}, and 1.25 \times 10^{15} \text{ ions cm}^{-2}. The amorphous formation ratio is defined as the concentration of generated interstitial silicon and vacancy formed by hydrocarbon molecular ion implantation divided by threshold concentration of amorphous formation. The amorphous formation ratios are no significant difference in case of monomer carbon ion implantation equivalent to each hydrocarbon molecular ion implantation conditions. Therefore, amorphous formation by hydrocarbon molecular ion implantation indicate a size effect that cannot be obtained monomer carbon ion implantation.

3.2. Fitting of experimental results using columnar model

We examined the origin of amorphous formation using a columnar model with experimental results and the following model formula:22)

\[ X_o = 1 - \exp\left(-\frac{\pi R_0^2 m_0}{m}\right), \tag{2} \]

where \( R_0 \) is the cross-sectional radius of the columnar model, \( m_0 \) is the dose, and \( m \) is the dose of saturated amorphous formation throughout the entire surface. We can estimate the cross-sectional radius \( R_0 \) of each hydrocarbon molecular ion and monomer carbon ion using the columnar model formula. The solid line in Fig. 3 indicates the curve fitting results with \( R_0 \) in Eq. (2) as the fitting parameter. Figure 5 shows the amorphous region using columnar shape models as a function of hydrocarbon molecular ion size.
single columnar shape of amorphous formation as a function of the size of the hydrocarbon molecular ion size obtained from the fitting parameter $R_0$ of Fig. 3. The cross-sectional radius of the amorphous region formed by hydrocarbon molecular ions are from 0.70 to 0.93 nm. On the other hand, the cross-sectional radius of the region formed by monomer carbon ion is 0.33 nm. The amorphous formation depths of $C_3H_5$, $C_4H_5$, $C_6H_5$, and C at 80 keV ion $^{-1}$ implantation energy are 50 nm, 80 nm, 120 nm and 155 nm, respectively. The height of the columnar model considers the energy of ion implantation. Because the energy distribution depends on the element and the number of hydrocarbon molecular ions, the projection range of large hydrocarbon molecular ions becomes small.\(^{2,24}\) The radius of the columnar amorphous region formed by $C_2H_5$ hydrocarbon molecular ions is roughly twice that of the region formed by monomer carbon ions. The columnar shape formed by hydrocarbon molecular ions demonstrates the tendencies of the cross-sectional area to increase and the height to decrease as the hydrocarbon molecular ion size increases.

The solid diamonds of Fig. 6 show the hydrocarbon molecular ion size dependence on the cross-sectional radius of the columnar form model. The cross-sectional radius increases linearly with increasing number of carbon atoms contained in the hydrocarbon molecule. We found from the results that the cross-sectional radius of the amorphous region was increased to 0.078 nm by increasing the number of carbon atoms of the hydrocarbon molecule by one. Increasing the radius indicates that the area of the amorphous region formed by one hydrocarbon molecular ion increase. On basis of the obtained results, the Eq. (2) is extend by considering the hydrocarbon molecular ion size as follows:

$$X_n = 1 - \exp\left(-\frac{\pi[0.078(M - 2) + R_{C2H5}^2 m]}{m}\right). \quad (3)$$

where, $M$ is the number of carbon atoms ($M > 2$), $R_{C2H5}$ is the cross-sectional radius of the amorphous region formed by $C_2H_5$ molecular ions on the basis of the columnar model. From these results indicate that the impact of the cross-sectional radius of amorphous region formed by hydrocarbon molecular ions is markedly different from that formed by monomer carbon ions.

3.3. Mechanism of amorphous formation by hydrocarbon molecular ion

We discuss the origin of damage to the amorphous region formed by the hydrocarbon molecular ions. It is well known that the extent of implantation damage is determined the mass number and diameter of the implanted ion.\(^{25-28}\) In the case of hydrocarbon molecular ion implantation, we consider which factor is dominant for amorphous formation.

As the first possibility, we considered that the cross-sectional radius of the amorphous region formed depends on the mass number of ion species. Ishii et al. confirmed that the cross-sectional radius of the amorphous region formed by heavy monomer ions such as xenon is 0.38 nm.\(^{22}\) In addition, they showed that the cross-sectional radius of the amorphous region decreases with increasing implantation energy. This is because the collision cross-sectional radius decreases with increasing implantation energy.\(^{25,28}\) However, in our present study, we obtained larger hydrocarbon molecular ions despite using a high implantation energy and a small mass number.

Therefore, we consider the second possibility, that is, the impact of the hydrocarbon molecular ion diameter. The diameter of the monomer carbon ion and xenon ion are approximately 0.140 and 0.216 nm from as determined the atomic radius, respectively. The cross-sectional radii of the amorphous region are 0.33 and 0.38 nm,\(^{22}\) respectively. No significant differences were found in these diameters and the amorphous cross-sectional radii. From these results, the diameter of monomer ions is smaller than the lattice constant of silicon (0.543 nm).\(^{29}\) Therefore, the monomer ions can easily pass through the silicon crystal lattice, and did not interact much with silicon atoms. In addition, the implantation conditions of this experiment can easily cause the channeling effect due to the tilt and twist angles being set to 0°. The channeling effect results in few collisions of ions with crystal atoms, resulting in the deep implant atom of the ion.\(^{30-32}\) Therefore, because as the displacement of silicon atoms by ion implantation does not easily occur, ion-implantation-induced damage and amorphous formation are minimized.

In the case of hydrocarbon molecular ions, the diameters of $C_2H_5$, $C_3H_5$, and $C_6H_5$ ions are estimated to be 0.42, 0.58, and 0.89 nm.\(^{33,34}\) The C–C and C–H bond distances were set to 0.154 and 0.110 nm, respectively.\(^{33}\) The size of hydrocarbon molecular ions is the same as or larger than the silicon lattice constant. As an explanation for this result, it is difficult for hydrocarbon molecular ions causes the channeling effect, and they affect the top surface of the silicon crystal even under implantation conditions where the channeling effect occur.

Thus, we compared the experimental results and the estimated hydrocarbon molecular size. The open diamonds of Fig. 6 show the hydrocarbon molecular ion size dependence on the estimated radius of the hydrocarbon molecular ion. The estimated size of the hydrocarbon molecular ion was increased by 0.077 nm each time one carbon atom is added. This trend is the same as that of the experimental result regarding the hydrocarbon molecular ion size dependence. It is considered that the C–C bond distance was increased by increasing the number of carbon atoms of the hydrocarbon molecule by one. The diameter of the hydrocarbon molecular...
ion is increased by 0.154 nm. That is, the radius of the hydrocarbon molecular ion is increase by 0.077 nm each time one carbon atom is added.

From these considerations, hydrocarbon molecular and monomer carbon ions are markedly different in terms of the ion collision process during amorphous formation by ion implantation owing to the impact of the hydrocarbon molecular ion size on the silicon surface.

4. Conclusions
We studied the amorphous region formation by hydrocarbon molecular ion implantation using the XPS method and a columnar model. It was confirmed that the cross-sectional radii of the amorphous region formed by ions of each hydrocarbon molecule are approximately from 0.70 to 0.93 nm and were expanded by 0.078 nm when the number of carbons in the hydrocarbon was increased by one. These results are considered to have a large impact on the silicon surface because the diameter of the hydrocarbon molecular ion considering the C–C and C–H bonds is larger than the lattice constant of the silicon crystal. Therefore, the implantation mechanisms are markedly different between hydrocarbon and monomer ions implantation, and amorphous region formation depends on the size of hydrocarbon molecular ions. In the case of the amorphous formation process based on the columnar model, an initially non-uniform region is considered to form into a continuous uniform region as the dose increases, and overlapping regions are formed.

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