Photoelectron Nano-spectroscopy of Reactive Ion Etching-Induced Damages to the Trench Sidewalls and Bottoms of 4H-SiC Trench-MOSFETs

Masaharu Oshima†
School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan and
Tokyo City University, 1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

Daisuke Mori, Aki Takigawa, and Akihiko Otsuki
Fuji Electric Co., 1 Fuji-cho, Hino City, Tokyo 191-8502, Japan

Naoka Nagamura
NIMS, 1-2-1 Sengen, Tsukuba City, Ibaraki 305-0047, Japan

Shun Konno, Yoshinobu Takahashi, and Masato Kotsugi
Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku, Tokyo 125-8585, Japan

Hiroshi Nohira
Tokyo City University, 1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

(Received 28 December 2017; Accepted 25 April 2018; Published 9 June 2018)

SiC trench structures having a width of 0.6 μm and a depth of 2.0 μm are fabricated by reactive ion etching (RIE) using a gas mixture of SF₆, Ar, and O₂. Further, SiC trench structures are cleaved to expose the sidewall for the channel region of a trench MOSFET. These structures were analyzed by pin-point photoelectron spectroscopy using a 100 nm soft-X-ray beam. It is observed that around 2 nm-thick homogeneous carbon-rich layer containing 1–2% F forms on the SiC sidewalls. This may be caused due to the re-deposition of RIE reaction products, CF₄ and SiF₄, under appropriate conditions to fabricate the trench walls that are approximately vertical using RIE. Further, a carbon-rich layer having a thickness of about 2.4 nm is also formed on the bottom of the SiC trench, suggesting the possibility of selective etching of Si from the SiC substrate. The position of the dominant peak that is associated with the SiC component remains constant regardless of the trench depth, suggesting homogeneous band bending due to the RIE defects, which may explain the reason for no variation being observed in the gate oxide/SiC interface trap density values. Further, the band bending of 1.50 eV that is observed on the sidewall can be attributed to a positively charged carbon vacancy (VₓC). [DOI: 10.1380/ejssnt.2018.257]

Keywords: Pin-point photoelectron spectroscopy; Reactive ion etching; SiC trench MOSFET; SiC sidewall damage; Band bending; Trench formation mechanism

I. INTRODUCTION

Silicon carbide has attracted great attention in order to be applied to high-power devices for devices that depict low power consumption, low on-resistance, and high blocking voltage [1], because of its superior material properties such as high voltage endurance and saturation velocity. Recently, 4H-SiC metal-oxide-semiconductor field-effect transistors (MOSFETs), especially trench-gate MOSFETs have been regarded as one of the most promising device structures to reduce on-resistance because of their high cell density and the lack of a junction-FETing device structures to reduce on-resistance because of MOSFETs have been regarded as one of the most promising device structures to reduce on-resistance because of their high cell density and the lack of a junction-FET region. [2] Furthermore, the non-polar 1100 plane (m-plane) of 4H-SiC can offer the highest channel mobility among various SiC crystal planes [3] and can be used as a channel plane for the trench sidewall in trench-gate MOSFETs. [4] However, we observe that only a few reports have been published regarding the effects of MOS channel planes, considerably affecting the MOS channel properties and the overall MOSFET performance. [5] Till date, several studies have been conducted to investigate the influences of etching conditions [6–8], etched contamination, and damages [9–11] on RIE etching performance. Further, the relationship between damages and device performance [12, 13] has also been investigated. Ahn et al. [13] reported that an SiC trench with a verticality of 85° was obtained by optimizing the etching conditions. Further, Schottky barrier diodes exhibited considerably less contamination and damage on the etched surface. However, MOSFETs are more sensitive to interfacial damage and defects than the Schottky barrier diodes. Further, the sidewall crystallinity (or damage) and surface contamination (or residue) caused by RIE have not been analyzed yet. Although the RIE-induced damage and contamination can be eliminated by annealing and chemical etching prior to gate oxide formation, these factors have critical influences on the channel properties of MOSFETs. Because it is difficult to investigate the chemical changes of the surface and the electronic band bending in the small region of the m-plane that is etched on the sidewall of the 4H-SiC epitaxial layers by conventional X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM), a pin-point photoelectron spectroscopic system is used to conduct this investigation in the current study.
II. EXPERIMENTAL

SiC trench structures that were fabricated by ICP (Inductively coupled plasma)-RIE with a gas mixture of SF₆ + Ar + O₂ were analyzed for the very first time using pin-point angle-resolved photoelectron spectroscopy with a 70 nm soft-X-ray beam in order to investigate the chemical and electrical damage on the SiC sidewall which is critical for the subsequent formation of gate oxide in comparison with the bottom plane (the 0001 plane of the SiC trench structure). The depth and width of the trench were fixed to be 2.0 μm and 0.6 μm, respectively. The RIE etching rate of SiC was approximately 350 nm/min. The cross-sectional SEM observations revealed that the verticality, (i.e., the tilted angle of the trench sidewalls was about 85°, which is approximately at a distance of 5° from the m-plane. Further, the trench structures were mechanically cleaved, and thinned. We performed scanning photoelectron emission microscopic (SPEM) measurements using a three-dimensional nanoscale electron-spectroscopy chemical analysis (3D nano-ESCA) system that was installed at BL07LSU of SPring-8. [14–17] The lateral and energy resolutions were set to 100 nm and 300 meV, respectively, at an excitation photon energy of 1000 eV.

III. RESULTS AND DISCUSSION

Figure 1 depicts wide scan photoelectron spectra that are obtained from four different positions (X = 0.1, 0.7, 1.2, and 1.8 μm from the SiC c-plane surface) of the trench sidewall, respectively. It was observed that F 1s and O 1s were detected in addition to the dominant SiC components, namely Si 2p, Si 2s, and C 1s. However, it should be noted that the S 2p peaks were not observed on the trench sidewall or the bottom plane at a binding energy of approximately 164 eV almost completely, even though SF₆ gas was used. This is probably caused because the sulfur residue is eliminated during RIE as a form of volatile SO₂ or SO₃ species, which is the reason why the admission of O₂ into the gas mixture is inevitable for the RIE of SiC. Casady et al. [10] used Auger electron spectroscopy to reveal that RIE of 4H-SiC containing NF₃ gas caused N contamination; conversely, no F contamination was observed on the etched SiC surface. However, this was probably caused because a part of SiC was nitrided during RIE, unlike the results that have been obtained, which depicts no S contamination probably due to the lack of Si-S bond formation.

In order to investigate the detailed chemistry of the trench sidewall, C 1s, Si 2p, F 1s, and O 1s photoelectron spectra were measured in a narrow scan mode. Among these spectra, the most important chemistry was observed in the F 1s spectra, that are depicted in Fig. 2(a). From the deepest point (X = 1.8 μm) to the shallowest point (X = 0.1 μm), the intensity ratio of F 1s peak to Si 2p peak (Si-C component) increased, and reached the maximum at X = 0.7 μm. Subsequently, the intensity was about half of this value at X = 0.1 μm. This decrease in the intensity of F 1s at X = 0.1 μm may be due to the SiO₂ protective layer on the SiC substrate as the RIE etching mask, since the interface between the SiO₂ protective layer and the SiC cannot be clearly discriminated by the SPEM image with about 0.1 μm spatial resolution. Furthermore, the F 1s peak shifts from 686.2 eV (probably the Si-F component) at X = 1.8 μm to 687.8 eV (the C-F component) at X = 0.1 μm. Thus, the distribution of re-deposited chemical components can provide critical information about the mechanism of trench formation in SiC using RIE. These results suggest that among the RIE products (CF₄ and SiF₄) the heavier SiF₄ may be re-deposited near the bottom of the sidewall, while the lighter CF₄ component is more likely to be re-deposited near the exit or surface, resulting in the maximum intensity of F 1s at X = 0.7 μm.

In the C 1s spectra that are depicted in Fig. 2(b), the dominant SiC and Si-H/C-C components were located at 283.1 eV and 285.0 eV, respectively. Additionally, two components were observed at 286.9 eV and 289.5 eV, which means the chemical shifts from the C-C components are 1.9 eV and 4.5 eV, respectively. Jiang et al. [12] reported that various kinds of C-F bonds have been detected on the SiC surface that is etched by RIE using SF₆/O₂ gas and that the relative intensities of these bonds vary based on etching conditions. The peaks at 287.8, 289.8, and 292.5 eV were assigned to CF, CF₂, and CF₃ species, respectively, while the SiC component is located at 282.3 eV. Oshima [18] reported that on the Si(001) bottom surface etched by RIE with the C₂F₆ gas both CF and CF₂ components were clearly detected at approximately 287.5 eV and 288.8 eV of binding energy, respectively, along with a dominant C-C bond at approximately 284.2 eV, indicating that the chemical shifts of the CF and CF₂ components from the C-C component are approximately 3.3 eV and 4.6 eV, respectively. Therefore, the 289.5 eV peak can be allocated to the CF₂ component, whereas the peak at 286.9 eV may be attributed to the CF component. However, the possibility that the formentioned peaks are caused due to the CO and COO components, respectively, cannot be ignored, because the intensity of F 1s is very small as compared to the intensity of O 1s.

It is possible to estimate the thickness of the C-H/C-C layer because the dominant SiC and C-H/C-C components in C 1s can be deconvoluted. For example, the peak intensity ratio of C-H/C-C to SiC is approximately 3 at X = 0.7 μm. The escape depth of C 1s photoelectron

FIG. 1. The wide scan photoelectron spectra from four different positions (X = 0.1, 0.7, 1.2, and 1.8 μm from the surface) of the trench sidewall. The photon energy was 1000 eV.
having a kinetic energy of 710 eV can be evaluated to be about 2 nm. Since the VG-Scien tia R3000 analyzer was fixed to a take-off angle of 60°, the average escape depth, λC, was about 1 nm. By assuming a homogeneous overlayer model of carbon (thickness: d) on the SiC substrate, the peak intensity ratio (R) of C-H/C-C can be expressed using the following equation;

\[
R = \frac{\lambda_C \sigma_{\text{C}} \left[1 - \exp(-d/\lambda_C)\right]}{\lambda_{\text{SiC}} \sigma_{\text{SiC}} \exp(-d/\lambda_{\text{SiC}}) N_{\text{SiC}}(\text{SiC})},
\]

where \(\sigma_{\text{C}}\) is the photoionization cross section of C 1s at a photon energy of 1000 eV, and \(N_{\text{SiC}}(\text{SiC})\) represents the carbon composition in SiC. Although the densities of carbon in the carbon layer and SiC substrate are different, it can be assumed that \(N_{\text{SiC}}(\text{SiC})\) is 0.5. We additionally assume that both \(\lambda_C\) and \(\lambda_{\text{SiC}}\) are equal to 1 nm for simplicity. Further, we calculate the carbon thickness (d) to be 2.0 nm at \(X = 0.7\) μm. As depicted in Fig. 2(b), the thickness of the protective layer mainly consists of carbon that remains almost constant as a function of depth and ranges from 0 μm (surface) to 2 μm (bottom). However, the quantities of other re-deposited components, especially the Si-F and C-F components were slightly altered.

Figure 3(a) depicts Si 2p spectra, in which the dominant peak can be attributed to the SiC component reflecting the SiC substrate. The shoulder peak is located around a binding energy of 104 eV that mainly appeared near the surface, when the \(X = 0.1\) μm point is assigned to the SiO2 component. This component may be formed partly due to the exposure to the air after completion of RIE. However there is also a possibility that the point at \(X = 0.1\) μm may be near the interface between the SiO2 protective layer and the SiC substrate, as mentioned above. In the deeper region of the trench, small shoulder peaks were detected that can be assigned to the SiO component. Jiang et al. [12] reported that no obvious Si-Si and Si-F bonds were detected on the etched SiC surface, which is in close agreement with Fig. 3(a). Furthermore, it should be noted that the peak variation of the dominant SiC component remains almost constant regardless of the trench depth. This suggests that the variation of local band bending or Fermi level pinning caused by the RIE-induced surface defects at different positions, which may inhomogeneously change the gate oxide/SiC interface trap density did not occur.

It is important to characterize the RIE-induced defects on the as-etched and annealed surfaces of the trench sidewalls in order to fabricate trench MOSFETs that depict high channel mobilities. In this study one of our objectives was to characterize the properties of defect, such as the energy level on the as-etched surface by measuring the band bending features using point-point photoelectron spectroscopy. Band bending features can be evaluated by measuring the Si 2p binding energy of the SiC components, because the energy difference between the Fermi level and valence band maximum (VBM) for the n-type 4H-SiC is calculated to be 3.06 eV and the energy difference between VBM and the Si 2p binding energy is reported to be 99.5 eV for 4H-SiC [19]. Therefore, the Si 2p binding energy of 101.1 eV that is measured for the sidewall corresponds to a band bending of 1.50 eV, as depicted in Fig. 3(b). In the previous study, deep-level transient spectroscopy (DLTS) analysis of 4H-SiC irradiated with 9 MeV electron beam has revealed mainly four traps: EH1 [0.41 eV below the conduction band minimum (CBM)], Z1/Z2 (0.68 eV), EH3 (0.71 eV), and EH7 (1.54 eV) [20]. Among them EH7 was dominant in 4H-SiC caused by electron irradiation and ion implantation. Further, theoretical calculations using DFT (density functional theory) reportedly revealed that the dominant EH7 trap can be attributed to the presence of positively charged carbon vacancies (V\(^{+}\)) whose energy level is 1.73 eV less than the CBM [21]. Based on these experiments and calculations the observed band bending of 1.50 eV may be attributed to the dominant EH7 trap or to the positively charged carbon vacancy (V\(^{+}\)). Further study including DLTS and other defect characterization techniques is required to reach definitive conclusions. Furthermore, it is important to characterize both before and after the growth of the gate oxide film for MOSFET fabrication using nano-ESCA.

Based on these results, we discuss the RIE mechanism for the SiC trench formation. Thus, the overall chemical reaction can be represented as follows:

\[
4 \text{SF}_6 + 4 \text{O}_2 + 3 \text{SiC} \rightarrow 4 \text{SO}_2 \uparrow + 3 \text{SiF}_4 \uparrow + 3 \text{CF}_4 \uparrow. \tag{2}
\]
In this reaction, all the products are volatile at room temperature, which means that no residues are left on the trench sidewall or bottom plane. However, it is well known that CF\textsubscript{4} species are likely to form polymer-like protective layers during the RIE process using Si and other substrates, resulting in the enhancement of the etching selectivity of Si to SiO\textsubscript{2}, SiN, and so on. It has additionally been reported that the thickness of polymer-like layers is drastically decreased as the ratio of O\textsubscript{2} in the etching gases of CF\textsubscript{4} and C\textsubscript{2}F\textsubscript{6} increases. These polymer-like layers that are observed during the SiC trench formation are assumed to be formed during the re-deposition of CF\textsubscript{4} or CF\textsubscript{x} species from the etched bottom plane. Further, we observed that the etching was enhanced using O\textsubscript{2} admission, suggesting the importance of O\textsubscript{2} to eliminate or reduce other residues such as SF\textsubscript{6}, SiF\textsubscript{x}, and CF\textsubscript{x} compounds from the etched bottom surface. This result corresponds to Kahn’s results \[8\] showing that the addition of O\textsubscript{2} to SF\textsubscript{6} increased the etching rate of SiC. Furthermore, upon mixing Ar in the SF\textsubscript{6} and O\textsubscript{2} mixed gas, the etching rate of SiC drastically increased, suggesting that the physical sputtering of Ar weakened the Si-C bonds.

Sugiura et al. \[6\] reported that the etching rate of SiC depends on the ion bombardment energy as a physical reaction, while the etching of Si is controlled by a chemical reaction rate. Thus, the effect of the addition of Ar (50\%) to the etching gas can be explained as an enhancement of a physical reaction. It was observed that the thickness of the polymer-like layers on the sidewall remains approximately constant throughout the entire depth (X) from the surface to the bottom. If the successive re-deposition process of CF\textsubscript{x} components takes place continuously, the carbon protective layer in the shallow region will become thicker than that in the deeper region. However, the homogeneous thickness of the carbon protective layer suggests that RIE proceeds as a competitive process between the re-deposition of CF\textsubscript{x} (and SiF\textsubscript{x}) and the removal, and that the elimination of the carbon protective layer by O\textsubscript{2} is necessary to form volatile CO\textsubscript{x}.

Thus, the chemical profiles of the trench sidewall provide us with critical information to reveal the RIE mechanism. In order to confirm the preceding discussion, Si trenches were fabricated using RIE with SF\textsubscript{6} + Ar + O\textsubscript{2} gas. The expected overall chemical reaction can be represented as follows:

\[
2 \text{SF}_6 + 2 \text{O}_2 + 3 \text{Si} \rightarrow 2 \text{SO}_2 \uparrow + 3 \text{SiF}_4 \uparrow, \quad (3)
\]

where neither the CF\textsubscript{4} nor CF\textsubscript{x} component is formed. Additionally, a trench structure with a width of 1 \(\mu\)m and a depth of 5 \(\mu\)m was fabricated, and cleaved. Further, the trench sidewall was analyzed using the pin-point photoelectron spectroscopy for observing the sidewall and bottom of the SiC trench. Although it was revealed that the concentration of F increased near the surface, the amount of F contamination on the Si sidewall was quite small as compared to that on SiC. Further, the Si 2p spectra that are depicted in Fig. 4 (a, b) indicate the presence of only the Si and SiO\textsubscript{2} components, but not the SiF\textsubscript{x} component. Furthermore, there was no S contamination on either the sidewall or the bottom, that is similar to the scenario of SiC, which may also be caused due to the O\textsubscript{2} mixing effect.

![FIG. 3. (a) Si 2p photoelectron spectra in a narrow scan mode with the deconvoluted components from four different positions (X = 0.1, 0.7, 1.2, and 1.8 \(\mu\)m from the surface) of the SiC trench sidewall, and (b) schematic of a band diagram for the m-plane SiC sidewall caused by RIE.](image)

![FIG. 4. F 1s (a) and Si 2p (b) photoelectron spectra from four different positions (X = 0.1, 0.7, 1.2, and 1.8 \(\mu\)m from the surface) of the Si trench sidewall.](image)
IV. CONCLUSION

In this study, SiC trench structures having a width of 0.6 μm and a depth of 2.0 μm were fabricated by RIE using a gas mixture of SF₆, Ar, and O₂. The sample was cleaved to expose the sidewall and to allow it to be analyzed by pin-point photoelectron spectroscopy using a 100 nm nano soft-X-ray beam. The observations depict that a homogeneous carbon-rich layer was formed on SiC sidewalls with a thickness of approximately 2 nm and that this layer contained 1–2 % F in the form of CF and CF₂. This probably occurred due to the re-deposition of RIE reaction products, CF₄ and SiF₄, which can additionally explain the fabrication of the trench walls that are almost vertical using RIE with an appropriate gas composition, particularly in terms of the O₂ ratio. The carbon-rich layer with a thickness of approximately 2.4 nm was further formed on the bottom of the SiC trench, suggesting the possibility of selective etching of Si from SiC substrates. Further, the fact that almost no S contaminants were detected on the bottom of the SiC trench, suggesting the formation of a homogeneous band bending due to the RIE defects, which may explain the reason for no variation in the gate oxide/SiC interface trap density. For the initial calculations, band bending of 1.50 eV was observed on the trench sidewall, using pin-point photoemission. This band bending of 1.50 eV can be attributed to the dominant EH7 trap or to the presence of positively charged carbon vacancies (V⁺C).

ACKNOWLEDGMENTS

This work was supported by Japan Science and Technology Agency (JST) through its “Core Research for Evolutional Science and Technology (CREST).” This work was performed using a facility of the Synchrotron Radiation Research Organization, the University of Tokyo (Proposal No. 7419 for 2016-2018).