An investigation to determine the interface condition between graphene and aluminum oxide

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The interface condition between the graphene channel and aluminum oxide (Al₂O₃) gate insulator in a graphene field-effect transistor (FET) has been analyzed. The hard X-ray photoelectron spectroscopy technique was employed to analyze the interface. In the obtained C1s spectra, a small peak was found at 284.2 eV, which was considered to be derived from a covalent bond between the graphene and Al₂O₃. In the pulsed S-parameter measurements, it was found that the direction of the Dirac voltage shift matched the polarity of the applied voltage stress. The Dirac voltage shift demonstrated that there were electron traps at the interface, degrading the FET performance such as the cutoff frequency. It was concluded that the unexpected bond at the interface formed electron traps whose energy level located near the conduction band minimum and that the Dirac voltage shift occurred in accordance with carrier capturing or emitting by the traps.

1. Introduction

The data rate required for wireless communication is increasing rapidly year by year, and will soon reach 100 Gb/s in the 2020s. To realize such a high-speed and high-capacity communication system, we must develop devices that are able to operate in the terahertz frequency region. However, it seems to be impossible to realize a terahertz transistor using conventional materials.

A graphene field-effect transistor (GFET), which utilizes graphene as the channel material, is expected as a key component for next-generation high-speed and high-capacity communication systems due to the extremely high carrier mobility of graphene. In fact, the intrinsic carrier mobility of suspended exfoliated graphene reportedly amounts to 100 000 cm² V⁻¹ s⁻¹, which is expected to realize high carrier mobility performance compared to SiO₂. Several authors reported GFET using Al₂O₃ as the gate insulator, which is expected to realize high carrier mobility performance compared to SiO₂. Carrion et al. measured drain current decreases of GFETs with an Al₂O₃ gate insulator, with nanosecond-range pulsed gate and drain voltage, which occurred with a charge trapping mechanism. However, there has been no attempt to study the interface condition between graphene and the gate insulator.

In this study, we employed the hard X-ray photoelectron spectroscopy (HAXPES) technique to find the origin of the defect which deteriorates the high-frequency performance of GFETs. From conventional photoelectron spectroscopy (XPS) measurement using soft X-rays, we can only analyze the surface chemical states of graphene. From a HAXPES measurement, however, we can analyze not only the surface states but also the buried interfaces such as the interface between graphene and insulator in the device, since the photoelectron escape depth is an order of magnitude larger than that of the conventional XPS. We also performed the pulsed S-parameter measurement immediately after the voltage stress was applied to the GFET. The pulsed S-parameter measurement enabled us to analyze how transistor performance deteriorates in relation to the interface condition.

2. Experimental methods

2.1. GFET fabrication

Figure 1 shows the schematic cross-sectional view of the GFET with Al₂O₃ gate insulator layer, which was fabricated as follows. First, a bilayer graphene was formed on a semi-insulating SiC substrate using thermal sublimation. Then, the graphene except the activation area was etched using O₂ plasma and nickel (Ni) was evaporated on the graphene as an ohmic metal. We prepared two kinds of samples, #1 and #2. In sample #1, Al₂O₃ layer was formed by a natural oxidation of a metallic aluminum ultrathin film deposited by an electron beam evaporation technique. In sample #2, the Al₂O₃ layer was formed by the atomic layer deposition (ALD) method.
this process, O$_3$ was supplied at the beginning, then trimethylaluminum and the O$_3$ were supplied alternately. For both samples, Ni and gold (Au) were evaporated on top of the Al$_2$O$_3$ as the gate metal. The gate length was 1.6 $\mu$m and the gate to ohmic distances was 1.7 $\mu$m.

### 2.2. HAXPES sample preparation and measurement

Figure 2 illustrates the cross-section of the sample for the HAXPES measurements. The fabrication processes of the graphene and Al$_2$O$_3$ layers were the same as those for the GFET described above. On the Al$_2$O$_3$ layer, 5 nm thick Au was evaporated, in order to suppress the charge up effect during the measurements and to calibrate the measured kinetic energies of photoelectrons.

The HAXPES measurements were carried out at BL46XU and BL16XU in SPring-8, a synchrotron radiation facility in Hyogo Prefecture, Japan. The incident X-ray energy was around 8000 eV and the take-off angles (TOAs) were 80, 30, and 15 degrees. Both the back and front sides of the specimen were connected to ground level via carbon tapes to reduce the charge up effect during the measurements and to calibrate the measured kinetic energies of photoelectrons.

### 2.3. Pulsed S-parameters measurement

In the pulsed S-parameter measurement, the applied gate bias to the GFET was changed periodically from a stress bias, $V_{\text{STRESS}}$, to a measurement bias, $V_{\text{GS}}$. As shown in the timing chart in Fig. 3, pulsed S-parameters were measured simultaneously, which was synchronized to the applied bias cycle. Then, cutoff frequencies were calculated and the equivalent circuit parameters were extracted from the measured S-parameters. Using the pulsed S-parameters technique, we could investigate the device condition immediately after the stress bias was applied.
3. Results and discussions

3.1. HAXPES measurement

We measured the C1s spectra taken at a TOA of 30 degrees as shown in Fig. 4 for sample #1 and in Fig. 5 for #2. In both of the spectra, we found peaks at 284.8 eV which are from the sp² sigma-bonding of graphene, and the peak at 282.8 eV which are from the Si–C bonding of the SiC bulk. For purposes of comparison, the C1s spectrum of graphene which has no Al₂O₃ insulator layer is shown in Fig. 6. In this measurement, the incident energy of X-rays is 350 eV, and this spectrum was taken at SAGA Light Source, a synchrotron radiation facility in Saga Prefecture, Japan. In the spectrum, a peak at 285 eV was considered to be carbon contamination. At first, we noticed that the values of the binding energies determined by HAXPES are higher than the values measured by XPS by 0.3 eV. Generally speaking, a binding energy shift toward higher energy is considered to be the charge up effect. In this experiment, we also measured the Si1s spectra and confirmed that the peak value of SiC measured by HAXPES was the same as the value measured by XPS. Then the binding energy shift in this experiment is not attributable to the charge up effect.

Figure 7 compares the C1s spectra for a pair of incident photon energies. We found that as we increase the incident energy from 350 to 8000 eV, the sp² graphene peak shifts to a higher energy by 0.33 eV, as shown in Fig. 7. This apparent shift in value is due to the recoil effect. In the HAXPES measurement, light element atoms such as carbon are easily kicked aside by incident X-rays, and their photoelectrons lose part of their kinetic energies due to this effect.²⁵,²⁶)

The important message from Figs. 4 and 5 is the presence of the peak at 284.2 eV whose peak was not found in Fig. 6. This binding energy strongly suggests that it is a covalent bond of carbon atoms embedded in Al₂O₃, namely Al₂C₂O₃. Stoyanov et al. reported the binding energy of Al₂C₂O₃ as 283.7 eV,²⁷) the value of which is close to that of our HAXPES experiment corrected by recoil effect.

To confirm that this new peak is really related to the chemical bond between graphene and the Al₂O₃ gate insulator, the TOA dependence of the C1s spectrum for sample #1 was taken. When the TOA decreases from 80 degrees to 30 degrees and further to 15 degrees, the measurement becomes more and more surface-sensitive. As the measurement becomes more surface-sensitive, the fractional area of the new peak increases as shown in Fig. 8. We,

![Fig. 7.](Color online) The comparison of the C1s spectra between the data taken by 350 eV soft X-ray and the data taken by 8000 eV hard X-ray.

![Fig. 8.](Color online) The take-off angle dependence of the C1s spectrum. The take-off angle is (a) 80 degrees, (b) 30 degrees, (c) 15 degrees.
therefore, conclude that the new peak is related to chemical bonds that sit above the graphene layer and is thus attributed to an Al$_2$C$_2$O$_3$ covalent bond.

Next, to exclude the possibility that the Al$_2$C$_2$O$_3$ peak came from the bulk portion or surface contamination of the Al$_2$O$_3$ layer, by using normal XPS measurement we took the C1s spectra of the samples in which Al$_2$O$_3$ formed directly on SiC without graphene. As shown in Fig. 9, we found no peak around 283.9 eV (284.2–0.3 eV, corrected by recoil effect).

We also confirmed that there is not an Al$_2$C$_2$O$_3$ peak in the Al1s spectrum as shown in Fig. 10. We then concluded the Al$_2$C$_2$O$_3$ peak did not come from the bulk portion or surface of the Al$_2$O$_3$ layer. In the case of the TOA of 15 degrees shown in Fig. 8(c), we cannot find the SiC peak despite being able to find the peak of Al$_2$C$_2$O$_3$. This is because photoelectrons can escape from the Al$_2$O$_3$/graphene interface and cannot escape from the graphene/SiC interface despite the bilayer graphene being quite thin in the case of the surface sensitive measurement such as a TOA of 15 degrees.

Figure 10 shows the Al1s spectra of sample #1 measured at three levels of TOA. It has been confirmed that the Al$_2$O$_3$ peak energy becomes higher as the TOA gets smaller. This trend demonstrates that there is a potential gradient in the Al$_2$O$_3$ layer. Besides the main peak of the Al$_2$O$_3$, it is also recognized that another small peak exists at the lower binding energy, which corresponds to the metallic aluminum. Some unoxidized Al is considered to remain in the Al$_2$O$_3$ layer. From the viewpoint of electrical property, the metallic Al in the Al$_2$O$_3$ layer works as a floating electrode in the gate insulator of the device, which deteriorates the current modulation characteristic.

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Fig. 9. (Color online) The C1s spectrum of the samples in which Al$_2$O$_3$ formed directly on SiC without graphene. The Al$_2$O$_3$ layer was formed by natural oxidation method for sample #1, and was formed by ALD for sample #2. The spectra were taken by XPS.

Fig. 10. (Color online) The take-off angle dependence of Al1s spectrum of sample #1.

Fig. 11. (Color online) The stress voltage dependence of the cutoff frequency of sample #1 (a) and sample #2 (b). The drain voltage was fixed at 5 V.
Comparing Figs. 4 and 5, we found that sample #1 shows a higher peak intensity of Al$_2$C$_3$O$_3$. From the results, it is suggested that dangling bonds in graphene at the domain edge or crystal defects were almost terminated by the oxygen from O$_3$ in sample #2. On the other hand, in sample #1, C–Al–O bonding was fabricated at the interface along with the natural oxidation process of aluminum. We thus concluded that the interface state of the graphene can be effectively improved by using the ALD technique.

### 3.2. Pulsed measurement

We measured the pulsed S-parameters for two samples. In Fig. 11, we show the dependency of cutoff frequency, $f_T$, on the gate voltage. The drain voltage was set to 5 V. In the figures, the blue lines represent a stress voltage of $-8$ V, orange lines represent 0 V, i.e. no stress, and green lines represent +8 V. From the figures, we found that with negative stress voltage, the $f_T$–$V_{GS}$ relation curve shifts in a direction toward the negative voltage, and with positive stress, $f_T$–$V_{GS}$ shifts in a direction toward the positive voltage. We thought the curve shifts resulted from Dirac voltage shifts. In Fig. 12, the drain current dependency on the gate voltage of sample #1 is shown. As shown in the figure, we found that with negative stress voltage, the Dirac voltage shifts in a direction toward the negative voltage. And with positive stress, the Dirac voltage shifts toward the positive voltage. As described in the final part of this section, we considered the bulk or interface trap can be the cause of the Dirac voltage shifts.

Comparing Figs. 11(a) and 11(b), we found that sample #2 shows smaller voltage shifts and has a higher cutoff frequency. Then, we concluded that the carrier trap can be decreased by using the ALD technique. However, the voltage shift of sample #2 still remains.

To discriminate the impact between the bulk and the interface trap, we measured the capacitance–voltage characteristics. As shown in Fig. 13, sample #2 shows less hysteresis. Therefore, we considered the interface trap can be decreased by the ALD technique, and the remaining voltage shift of sample #2 resulted from the bulk trap of Al$_2$O$_3$. From the result, we consider that the covalent bond between graphene and aluminum oxide behaved as an electron trap which deteriorates the high-frequency characteristics of GFET.

In the case of positive stress voltage, the cutoff frequency around a $V_{GS}$ of 7 V decreased. The cutoff frequency degradation resulted from the mobility degradation with the increase of $V_{GS}$.

Finally, we measured the RF pulse width dependency of sample #1, the result of which is shown in Fig. 14. In the experiment, the gate stress voltage, $V_{STRESS}$, was set to $-8$ V, and the pulse widths were changed from 1 to 5 $\mu$s, and further to 10 $\mu$s. As is shown in the figures, we found that the peak cutoff frequency decreased with an increase in the duration of time of RF. To investigate why the cutoff frequency decreased with increasing pulse width, we performed an equivalent circuit analysis. As is shown in Fig. 15, the
extracted transconductance, $g_{m}$, decreased with increasing pulse width.

In Fig. 14, a voltage shift like that in Fig. 11 was not observed. We considered the potential increase during 10 microseconds was relatively small as much as the voltage shift can occur.

From these results, the curve shift mechanism is considered to be as described in Fig. 16. At first, the electron trap exists near the conduction band minimum in the vicinity of the Al$_2$O$_3$ layer, and, with negative stress voltage, electrons in the traps were emitted. Immediately after the bias voltage shifts to the measurement bias, the conduction band energy decreased in the vicinity of the Al$_2$O$_3$ because the electrons were emitted. The electrons in the graphene were gradually trapped with time, then the conduction band energy near the interface increased, so the cutoff frequency changed with the increase in the pulse width.

4. Conclusions

We measured the interface condition between graphene and an insulator using HAXPES. In the C1s spectrum, we found the peak of Al$_2$C$_2$O$_3$ to be between sp$^2$ and SiC and it is considered to be a covalent bond between carbon atoms and Al$_2$O$_3$. These covalent bonds behaved as carrier traps. The electrons which were captured in these traps were emitted when the stress voltage was applied. By using the ALD technique, the interface state of the graphene can be effectively improved and carrier traps can be decreased.

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References

1) F. Schwierz, Proc. IEEE 101, 1567 (2013).
2) F. Schwierz, Nat. Nanotechnol. 5, 487 (2010).
3) D.-H. Kim, B. Brar, and J. A. del Alamo, Tech. Dig. Int. Electron Devices Meeting, 2011, p. 319.
4) D.-H. Kim and J. A. del Alamo, IEEE Electron Device Lett. 31, 806 (2010).
5) S. Lee et al., Tech. Dig. Int. Electron Devices Meeting, 2007, p. 255.
6) L. D. Nguyen, P. J. Tasker, D. C. Radosavljevic, and J. F. Eastman, IEEE Trans. Electron Device 36, 2243 (1989).
7) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
8) A. S. Mayarov et al., Nano Lett. 11, 2396 (2011).
9) J. L. Tedesco, B. L. VanMil, R. L. Myers-Ward, J. M. McCrate, S. A. Kitt, P. M. Campbell, G. G. Jernigan, J. C. Culbertson, C. R. Eddy Jr, and D. K. Gaskill, Appl. Phys. Lett. 95, 122102 (2009).
10) W. Norimatsu, J. Bao, T. Tarasawa, and M. Kusunoki, Int. Symp. Epitaxial Graphene, 2017, p. 40.
11) K. Nagashio, T. Yamashita, T. Nishimura, H. Kita, and A. Toriumi, J. Appl. Phys. 110, 024513 (2011).
12) S. Kim, J. Nah, I. J. Jo, D. Shahzadri, L. Colombo, Z. Yao, E. Tutuc, and S. K. Banerjee, Appl. Phys. Lett. 94, 062107 (2009).
13) B. Fallahazad, K. Lee, G. Lian, S. Kim, C. M. Corbet, D. A. Ferrer, L. Colombo, and E. Tutuc, Appl. Phys. Lett. 100, 093112 (2012).
14) L. Liao, J. Bai, Y. Qu, Y. Huang, and X. Duan, Nanotechnology 21, 015705 (2010).
15) Y. Zhang, Z. Qiu, X. Cheng, H. Xie, H. Wang, X. Xie, Y. Yu, and R. Liu, J. Phys. D: Appl. Phys. 47, 055106 (2014).
16) J. S. Moon et al., IEEE Electron Devices Lett. 30, 650 (2009).
17) N. Y. Garces, Y. D. Wheeler, J. K. Hite, G. G. Jernigan, J. L. Tedesco, P. Riyadh, C. E. R. D. Jr, and D. K. Gaskill, J. Appl. Phys. 109, 124304 (2011).
18) T.-E. Bae, H. Kim, J. Jung, and W.-J. Cho, Appl. Phys. Lett. 100, 153506 (2014).
19) E. A. Carrion, A. Y. Serov, S. Islam, A. Behnam, A. Malik, F. Xiong, M. Bianchi, R. Sordan, and E. Pop, IEEE Trans. Electron Device 61, 1583 (2014).
20) J. Rubio-Zuzua and G. R. Castro, J. Phys.: Conf. Ser. 100, 012042 (2008).
21) S. Tanuma, H. Yoshikawa, H. Shinotsuka, and R. Ueda, J. Electron Spectrosc. Relat. Phenom. 190, 127 (2013).
22) Y. Tateno, T. Yonemura, M. Okada, F. Mitsuhashi, H. Fukidome, M. Suemitsu, M. Ueno, and T. Nakabayashi, Int. Symp. Epitaxial Graphene, 2017.
23) Y. Tateno, T. Kochi, T. Komatani, H. Yamamoti, T. Yonemura, J. Ihara, T. Saito, and T. Nakabayashi, IEEE Comp. Semicond. Integrated Circuit Symp., 2016.
24) Y. Tateno, Y. Kurachi, H. Yamamoto, and T. Nakabayashi, IEEE Int. Reliability Phys. Symp., 2018.

25) T. Fujikawa, R. Suzuki, and J. Kover, J. Electron Spectrosc. Relat. Phenom. 151, 170 (2006).

26) Y. Takaka et al., Phys. Rev. B 75, 233404 (2007).

27) P. Stoyanov, S. Akhter, and J. M. White, Surf. Interface Anal. 15, 509 (1990).

28) Y. Takata et al., Appl. Phys. Lett. 84, 4310 (2004).

29) Y. Tateno, T. Yonemura, Y. Kubo, F. Mitsuhashi, M. Okada, M. Ueno, H. Fukidome, M. Suemitsu, and T. Nakabayashi, Graphene Week, 2018.