Conductive-probe atomic force microscopy and Kelvin-probe force microscopy characterization of OH-terminated diamond (111) surfaces with step-terrace structures

Masatsugu Nagai¹, Ryo Yoshida¹, Tatsuki Yamada¹, Taira Tabakoya¹, Christoph E. Nebel²,4, Satoshi Yamasaki²,3, Toshiharu Makino⁵, TsuBASE Matsumoto¹,², Takao Inokuma¹, and Norio Tokuda¹,²,³

¹Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan
²Nanomaterials Research Institute, Kanazawa University, Kanazawa Ishikawa 920-1192, Japan
³Advanced Power Electronics Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan
⁴Fraunhofer-Institute for Applied Solid State Physics (IAF), Tullastraße 72, Freiburg 79108, Germany
⁵E-mail: tokuda@ec.t.kanazawa-u.ac.jp

Received December 15, 2018; accepted March 25, 2019; published online June 18, 2019

We characterized OH-terminated diamond (111) surfaces which show step-terrace (ST) and bunching-step (BS) regions from contact potential difference (CPD) and current measurements conducted by conductive-probe AFM and Kelvin-probe force microscopy. The CPD and current were highly correlated with the surface topography. Hereby, we found that the contact potential difference (CPD) and current were highly correlated with the surface topography and concluded that the interface states were generated around steps on the OH-terminated diamond (111) surfaces.

1. Introduction

Diamond has a high breakdown field, high carrier mobilities and the highest thermal conductivity.¹–⁵ That is why diamond is a promising material for next generation high-power devices such as field effect transistors, which are vigorously studied. Actually, junction field effect transistors,⁶–⁸ metal semiconductor field effect transistors (MOSFETs)¹²–¹⁸ have been already reported in the literature. Furthermore, we recently realized the world’s first inversion channel diamond MOSFET with normally off characteristics by using an atomic layer deposition Al₂O₃ film as its gate oxide, which was deposited on an OH-terminated diamond (111) surface.¹⁹ The OH-termination was performed by water vapor annealing.²⁰ However, the field effect mobility was much lower than expected, which was attributed to the high interface state density at the oxide/diamond interface.¹⁹,²¹ To reduce such interface state densities, origins of the interface states need to be known. Based on the fact that interface states exist around steps on Si surfaces in case of SiO₂/Si interfaces,²² there is a strong possibility that interface states generate around steps also on OH-terminated diamond (111) surfaces. However, this thesis is up to now not supported by any experimental results.

In this paper, we report about a detailed characterization of OH-terminated diamond (111) surfaces with step-terrace (ST) and bunching-step (BS) regions. In order to obtain the OH-terminated diamond (111) surfaces, we combined three techniques: anisotropic diamond etching by thermochemical reaction between Ni and diamond in high-temperature water vapor,²³ hydrogen plasma treatment²⁴ and water vapor annealing.²⁰ For characterization of the topography as well as electronic surface properties, atomic force microscopy (AFM), Kelvin-probe force microscopy (KPFM) and conductive-probe AFM (CPAFM) were applied.²⁵–²⁸ Hereby, we found that the contact potential difference (CPD) and current were highly correlated with the surface topography and concluded that the interface states were generated around steps on the OH-terminated diamond (111) surfaces.

2. Experimental methods

A high-pressure and high-temperature p-type (111)-oriented diamond substrate was used for these experiments. The boron concentration and the typical misorientation angle of the substrate were 10¹⁷ atoms cm⁻³ and 2°, respectively. Firstly, a p⁺ layer was grown on the back side of the substrate for ohmic contact formation by microwave plasma enhanced chemical vapor deposition (MPCVD), using a MPCVD system made by Arios Inc. We used CH₄ in combination with (CH₃)₃B, diluted in H₂. The total pressure, microwave power, substrate temperature, methane concentration in the gas phase and ratio of boron to carbon (B/C) were 30 kPa, 1000 W, 900 °C, 0.2% and 10000 ppm, respectively. The thickness of the p⁺ layer was 900 nm after the growth. Secondly, the anisotropic diamond etching by thermochemical reaction between Ni and diamond in high-temperature water vapor was applied to expose (111) basal planes.²³ The basal planes had slightly rough surfaces. The diamond etching was conducted in three steps: (1) deposition of Ni to diamond, (2) annealing in water vapor and (3) removal of Ni and Ni oxide. Ni was thermally evaporated using shadow masks to form well organized square Ni films of 50 μm × 50 μm size and ~150 nm thickness. The annealing was conducted at 900°C for 1.5 h with an electric furnace using wet N₂ gas as an annealing gas. For the removal of Ni
and Ni oxide, the sample was immersed in a hot mixed acid of H₂SO₄/HNO₃ (3:1) at 220 °C for 45 min. Then, the (111) basal planes were exposed to a hydrogen plasma to obtain an atomically well-defined diamond (111) surfaces with ST and BS regions. The hydrogen plasma treatment was applied for 3 h using 600 W. Figure 1 shows cross sectional schematic diagrams as well as 3D laser microscopic images of the sample surface after the treatments. Finally, the sample was annealed in water vapor to terminate the diamond (111) surfaces with OH groups. The annealing was conducted at 500 °C for 1 h with an electric furnace using wet N₂ gas. The CPD maps of the OH-terminated diamond (111) surfaces were obtained by the KPFM measurements, using PtSi probes (NANO SENSORS Inc.). The current maps and
I–V characteristics of the OH-terminated diamond (111) surfaces were obtained by the CPAFM measurements using Pt-coated probes.

3. Results and discussion

Figure 2(a) shows the topographic image and the CPD map of the OH-terminated diamond (111) surface with ST and BS regions. Figure 2(b) shows the cross sectional image and current profile corresponding to the line B–B’ in the Fig. 2(a). The forward voltage of 0.6 V was applied to measure the current. The upper detection limit of current was 10 nA. The average current detected in the BS region surrounded by the black broken line was smaller than that in the ST region surrounded by the white broken line by 3 nA or more, taking the upper detection limit into consideration.

The height and width of the BS regions were 140 nm and 2 μm, respectively. Taking 2.1 Å as the distance between carbon atoms in ⟨111⟩ direction into account, the number of atomic steps in the BS region was 700. Therefore, the step density in the BS region was calculated to be 350 steps μm⁻¹. On the ST region, we detect the typical step density of 16 steps μm⁻¹. That means step density in the BS region is one order of magnitude higher than that in the ST region.

Figure 2(b) shows the CPD results indicating correlations with the surface topology. The absolute value of the CPD in the BS region was about 60 mV smaller than that in the ST region [see Fig. 2(b)]. This indicates that the Fermi level at the interface was shifted for ca. 60 meV due to the formation of non-OH-terminations in the BS region, and that the termination structures in the BS region are differed from that in the ST region.

Figure 3(a) shows the AFM topographic image and current map of the OH-terminated diamond (111) surface with ST and BS regions. Figure 3(b) shows the cross sectional image and current profile corresponding to the line B–B’ in the Fig. 3(a). The forward voltage of 0.6 V was applied for the current measurement. On the line B–B’, the current detected in the BS region decreased to about 2 nA while that in the ST region were above the upper detection limit of 10 nA. The average current detected in the BS region surrounded by the black broken line was smaller than that in the ST region surrounded by the white broken line by 3 nA or more, taking the upper detection limit into consideration. These results show a strong correlation between the local current and surface topology.

Fig. 3. (Color online) (a) The AFM topographic image and current map of the OH-terminated diamond (111) surface with ST and BS regions. (b) The cross sectional image and current profile corresponding to the line A–A’ in the Fig. 3(a). The upper detection limit of current was 10 nA. The average current detected in the BS region surrounded by the black broken line was smaller than that in the ST region surrounded by the white broken line by 3 nA or more, taking the upper detection limit into consideration.

Fig. 4. (Color online) The typical I–V characteristics detected on the ST region (blue) and on the BS region (red) of the OH-terminated diamond (111) surfaces. The upper detection limit of current was 10 nA. The straight lines are the fitting curves based on the thermionic emission expressed by the following formula: \( I = I_0 \exp \left( \frac{qV}{nkt} \right) - 1 \) where \( I \), \( I_0 \), \( q \), \( V \), \( n \), \( k \) and \( T \) are the forward current, the reverse saturation current, the elementary charge, the forward voltage, the ideality factor, the Boltzmann constant and the absolute temperature, respectively.

local I–V characteristics of the OH-terminated diamond (111) surfaces were obtained by the CPAFM measurements using Pt-coated probes.

3. Results and discussion

Figure 2(a) shows the topographic image and the CPD map of the OH-terminated diamond (111) surface with ST and BS regions. Figure 2(b) shows the cross sectional image and CPD profile corresponding to the line A–A’ in the Fig. 2(a). The height and width of the BS regions were 140 nm and 2 μm, respectively. Taking 2.1 Å as the distance between carbon atoms in ⟨111⟩ direction into account, the number of atomic steps in the BS region was 700. Therefore, the step density in the BS region was calculated to be 350 steps μm⁻¹. On the ST region, we detect the typical step density of 16 steps μm⁻¹. That means step density in the BS region is one order of magnitude higher than that in the ST region. Figure 2(b) shows the CPD results indicating correlations with the surface topology. The absolute value of the CPD in the BS region was about 60 mV smaller than that in the ST region [see Fig. 2(b)]. This indicates that the Fermi level at the interface was shifted for ca. 60 meV due to the formation of non-OH-terminations in the BS region, and that the termination structures in the BS region are differed from that in the ST region.

Figure 3(a) shows the AFM topographic image and current map of the OH-terminated diamond (111) surface with ST and BS regions. Figure 3(b) shows the cross sectional image and current profile corresponding to the line B–B’ in the Fig. 3(a). The forward voltage of 0.6 V was applied for the current measurement. On the line B–B’, the current detected in the BS region decreased to about 2 nA while that in the ST region were above the upper detection limit of 10 nA. The average current detected in the BS region surrounded by the black broken line was smaller than that in the ST region surrounded by the white broken line by 3 nA or more, taking the upper detection limit into consideration. These results show a strong correlation between the local current and surface topology.
Figure 4 shows the typical $I$–$V$ characteristics detected on the ST region (blue) and on the BS region (red) of the OH-terminated diamond (111) surfaces. Curve fitting was carried out based on the thermionic emission expressed by the following formula:

$$I = I_0 \exp \left( \frac{qV}{nkT} \right) - 1, \quad (1)$$

where $I$, $I_0$, $q$, $V$, $n$, $k$ and $T$ are the forward current, the reverse saturation current, the absolute temperature, respectively. The ideality factors ($n$) obtained by the fitting curves were 1.5 on the ST region and 2.0 on the BS region. As the $n$ were much higher than that of an ideal Schottky contact ($n = 1.0$), we concluded that a metal–insulator–semiconductor (MIS) diode structure was formed by the Pt probe, some sort of interfacial layer and the OH-terminated diamond (111) surface. The interface layer presumed to be a hydrocarbon (soft carbon) layer. For the reason that a MIS tunnel diode generally have a negligibly small interface state density at the metal/insulator interface, the $n$ of the MIS tunnel diode increases as the interface state density at the insulator/semiconductor interface increases according to:

$$n = 1 + \left( \frac{\delta}{\varepsilon_i \varepsilon_0} \right) \left( \frac{\varepsilon_s \varepsilon_0}{W_A} + qD_n \right), \quad (2)$$

where $\delta$ is the thickness of the interface layer, $\varepsilon_i$ is the relative dielectric constant of the interface layer, $\varepsilon_s$ is the dielectric constant of vacuum, $W_A$ is the width of the depletion layer, $q$ is the elementary charge and $D_n$ the interface state density at the insulator/semiconductor interface. Considering that the step density in the BS region was over 20 times higher than that in the ST region, the steps should have generated the interface states in some way.

Figure 5 summarizes our proposed model of formation of termination structural defects at steps. Atomically flat terraces are seemingly terminated by OH in a perfect way. However, termination structural defects, i.e. non-OH-terminations such as dangling bonds, O-terminations or carbon-reconstructions can be formed at steps. We therefore concluded that the termination structural defects at steps generated the interface states. To fabricate perfect diamond MOS structures with minimized interface state densities and realize high performance diamond MOSFETs, the step densities need to be minimized by fully preventing BS regions. Further experiments are currently prepared like deep level transient spectroscopy to reveal termination structural defects (non-OH-termination) as well as their energy levels in the band-gap of diamond in detail.

4. Conclusions

In this paper we introduced the CPD and current map and local $I$–$V$ measurements on the OH-terminated diamond (111) surfaces with ST and BS regions. We detected the CPD shift of ca. 60 mV in the BS region. The CPD shift was correlated to the termination structural defects at the steps. In addition, the increase of the $n$ from 1.5 on the ST region to 2.0 in the BS region supports the formation of interface states around the steps. We discussed the surface topography in combination with the electronic properties and introduce the model of formation of termination structural defects at steps. The results indicate that atomically flat diamond surfaces with minimal step densities are required to form ideal MOS structures with minimized interface state densities.

Acknowledgments

This work was partially supported by Kanazawa University SAKIGAKE Project 2018 and JSPS KAKENHI Grant Number JP17H02786.
10) M. Kasu, K. Ueda, H. Kageshima, and Y. Yamauchi, Diam. Relat. Mater. 17, 741 (2008).
11) G. Conte, E. Giovine, A. Bolshakov, V. Ralchenko, and V. Konov, Nanotechnology 23, 025201 (2012).
12) T. T. Pham, N. Rouger, C. Masante, G. Chicot, F. Udrea, D. Eon, E. Gheeraert, and J. Pernot, Appl. Phys. Lett. 111, 173503 (2017).
13) K. Hizama, H. Sato, Y. Harada, H. Yamanoto, and M. Kasu, Jpn. J. Appl. Phys. 51, 090112 (2012).
14) H. Kawarada, T. Yamada1, D. Xu, H. Tsuboi, Y. Kitabayashi, D. Matsumura, M. Shibata, T. Kudo, M. Inaba, and A. Hiraiwa, Sci. Rep. 7, 42368 (2017).
15) M. Kasu, Jpn. J. Appl. Phys. 56, 01AA01 (2017).
16) J. W. Liu, H. Oosato, M. Y. Liao, M. Imura, E. Watanabe, and Y. Koide, Appl. Phys. Lett. 112, 153501 (2018).
17) N. Oi, M. Inaba, S. Okubo, I. Tsuyuzaki, T. Kageura, S. Onoda, A. Hiraiwa, and H. Kawarada, Sci. Rep. 8, 10660 (2018).
18) J. Zhang, Z. Ren, J. Zhang, C. Zhang, D. Chen, S. Xu, Y. Li, and Y. Hao, Jpn. J. Appl. Phys. 56, 100301 (2017).
19) T. Matsumoto, H. Kato, K. Ohaya, T. Makino, M. Ogura, D. Takeuchi, T. Inokuma, N. Tokuda, and S. Yamasaki, Sci. Rep. 6, 31585 (2016).
20) R. Yoshida, D. Miyata, T. Makino, S. Yamasaki, T. Matsumoto, T. Inokuma, and N. Tokuda, Appl. Surf. Sci. 458, 222 (2018).
21) T. Matsumoto, H. Kato, T. Makino, M. Ogura, D. Takeuchi, S. Yamasaki, M. Imura, A. Ueda, T. Inokuma, and N. Tokuda, Jpn. J. Appl. Phys. 57, 04FR01 (2018).
22) R. Hasumura, A. Ando, K. Miki, and Y. Nishioka, Appl. Surf. Sci. 159–160, 83 (2000).
23) M. Nagai, K. Nakamishi, H. Takahashi, H. Kato, T. Makino, A. Yamasaki, T. Matsumoto, T. Inokuma, and N. Tokuda, Sci. Rep. 8, 6687 (2018).
24) H. Kuroshima, T. Makino, S. Yamasaki, T. Matsumoto, T. Takao, and N. Tokuda, Appl. Surf. Sci. 422, 452 (2017).
25) M. Tachiki, Y. Kaibara, Y. Sumikawa, M. Shigeno, H. Kanzawa, T. Banno, K. S. Song, H. Umezawa, and H. Kawarada, Surf. Sci. 581, 207 (2005).
26) B. Rezek and C. E. Nabel, Diam. Relat. Mater. 14, 466 (2005).
27) J. Alvarez1, M. Boutchich, J. P. Kleider, T. Teraji, and Y. Koide, J. Phys. 47, 355102 (2014).
28) E. Tranvouez et al., J. Appl. Phys. 106, 054301 (2009).
29) B. Rezek and C. E. Nabel, Diam. Relat. Mater. 15, 1374 (2006).
30) S. M. Sze and K. K. NG, Physics of Semiconductor Devices (Wiley, New York, 2006) 3rd ed., p. 110.