

# Formation of Graphene on Diamond C(111) Surfaces by Vacuum Annealing

Shuichi Ogawa<sup>1</sup>, Takatoshi Yamada<sup>2</sup>, Shinji Ishizuka<sup>3</sup>, Akitaka Yoshigoe<sup>4</sup>, Toshiteru Kaga<sup>1</sup>, Hideaki Hozumi<sup>1</sup>, Masataka Hasegawa<sup>2</sup>, Yuden Teraoka<sup>4</sup>, and Yuji Takakuwa<sup>1</sup>

<sup>1</sup> Institute of Multidisciplinary Research for Advanced Materials(IMRAM), Tohoku University  
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

Phone: +81-22-217-5367, E-mail: ogasyu@tagen.tohoku.ac.jp

<sup>2</sup> National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba 305-8568, Japan

<sup>3</sup> Akita National College of Technology, 1-1 Iijimabunkyo-cho, Akita, Akita 011-8511, Japan

<sup>4</sup> Japan Atomic Energy Agency, 1-1-1 Koto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

## 1. Introduction

Graphene on diamond (GOD) structures have been attracted much attention as a substrate for the high-speed and high-power semiconductor devices in communication industries [1]. By using a diamond C(111) surface as a GOD substrate, the epitaxial growth of graphene can be expected. It has been reported that the graphitization of the diamond C(111) surfaces by annealing in vacuum [2], but the detail of graphitization process has not been clarified yet. The aim of this study is to identify the  $sp^2$ -bonded carbon layer and to clarify the formation mechanism of a graphene layer on the diamond C(111) surfaces. In order to achieve the aim, real-time photoemission spectroscopy using synchrotron radiation was employed for investigation of the vacuum annealing process of the Hydrogen-terminated diamond C(111) surface.

## 2. Experimental methods

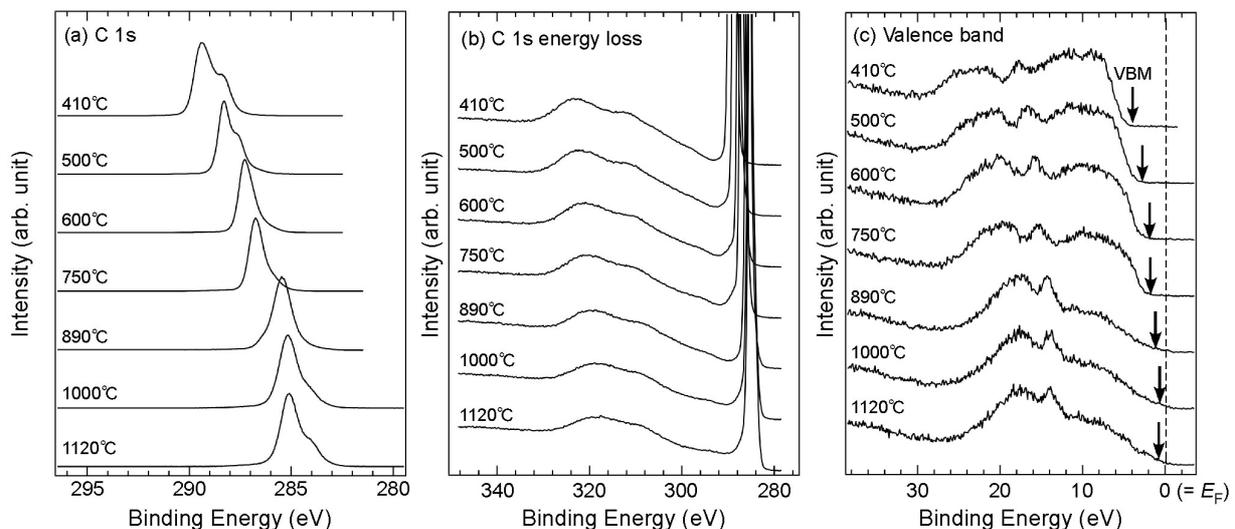
Photoelectron spectroscopy observations were performed using a surface reaction analysis apparatus placed at BL23SU of SPring-8. Diamond C(111) surfaces were treated by  $H_2$  plasma irradiation for H termination. This sample was introduced to the measurement chamber without any wet cleaning. The H-terminated diamond C(111) substrates were heated indirectly using a Ta ribbon heater,

and its temperatures measured by a K-thermocouple. The energy of synchrotron radiation and polar angle of photoelectrons was 710 eV and  $70^\circ$ , respectively. The C 1s photoelectron spectra, the energy loss spectra of C 1s, and the valence band (VB) spectra were measured *in situ* during the annealing.

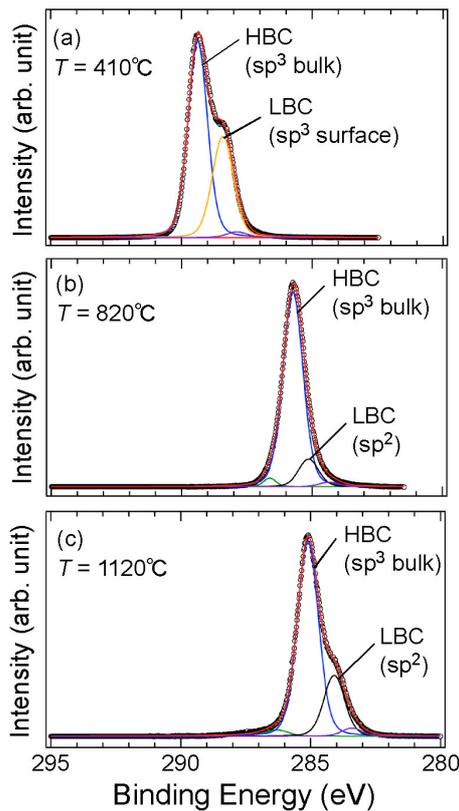
## 3. Results and discussion

In Fig. 1, C 1s and valence band spectra show a energy shift toward the low binding energy side with increasing temperature. This peak shift is due to the band bending. Furthermore, the shape of C 1s photoelectron spectra is also changed with increasing temperature.

In order to clarify the changes of chemical bonding states, the peak decomposition analysis of C 1s spectra was performed. The results of peak decomposition are summarized in Fig. 2. There are mainly two peaks, which are low and high binding energy component (LBC and HBC), in the C 1s spectra of the diamond C(111) surfaces. The HBC is derived from the bulk diamond ( $sp^3$ -bulk). On the other hand, LBC corresponds to the surface component derived from a diamond C(111)- $2\times 1$  structure in low temperature. The temperature dependence of LBC/HBC intensity ratio is shown in Fig. 3(a). The LBC intensity decreases with the temperature, and this is due to the structural transition from



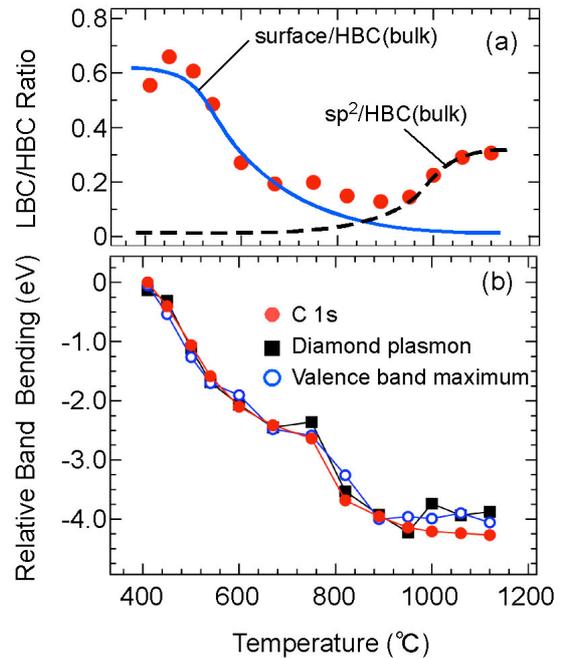
**Fig.1.** Temperature dependence of (a) C 1s photoelectron spectra, (b) C 1s photoelectron energy loss spectra, and (c) valence band spectra of the Diamond(111) surface during annealing. Arrows indicate the position of the valence band maximum (VBM).



**Fig. 2.** Temperature dependence of C 1s peak deconvolution analysis at (a) 410°C, (b) 820°C, and (c) 1120°C, respectively.

2×1 to 1×1[3]. However, the LBC increases above ~900°C. It is thought that the increase of LBC at high temperature does not indicate the increase of the surface component but increase of  $sp^2$  component, because the binding energies of surface and  $sp^2$  components are too close to distinguish each other. The  $sp^2$  component comes out as surface component goes in by annealing. Based on this suggestion, it is found that the  $sp^2$  carbon layer forms above ~800°C on diamond C(111) surfaces as shown by broken line in Fig. 3(a), and its thickness is less than 1 ML.

In order to clarify the structure of  $sp^2$  bonded carbon on the diamond C(111) surfaces, the peak deconvolution analysis of energy loss spectra of C 1s photoelectron is also performed. In the low temperature region under ~950°C, only plasmon loss peaks derived from diamond appear. When the temperature increases above ~950°C, the plasmon loss peaks from graphite also can be observed. This is indicated that the graphite layer is not formed under ~950°C but  $sp^2$ -bonded carbons are generated above ~800°C on the diamond C(111) surface. Here, it is noteworthy that the width of plasmon loss spectra is broad, so that even the plasmon loss spectra of high temperature can be fitted without the graphite plasmon. However, the relative band bending obtained from the plasmon loss spectra using both diamond and graphite peaks agree with the that from C 1s photoelectron spectra and VB position as shown in Fig. 3(b). If the plasmon loss spectra was fitted using only diamond plasmon, the value of relative band bending



**Fig. 3** (a) Temperature dependence of the intensity ratio between LBC and HBC ( $sp^3$ -bulk). LBC corresponds to a surface component in the low temperature and  $sp^2$  component in the high temperature region, respectively. (b) Temperature dependence of the relative band bending to the value of 410°C. The values obtained from three different spectra (peak position of C 1s spectra, peak position of the diamond plasmon loss peak, and position of the VBM) show good agreements.

obtained from the plasmon peaks did not agree with that from C 1s and VB spectra. This result indicates the adequacy of the peak deconvolution analysis of plasmon loss spectra. From these results, it is found that  $sp^2$ -bonded carbon is generated at 800°C, and graphene forms on diamond C(111) surfaces above ~950°C.

#### 4. Conclusions

Synchrotron radiation photoelectron spectroscopy was used to investigate the graphene growth process on diamond C(111) surfaces by annealing in vacuum. It is found that  $sp^2$ -bonded amorphous carbon layer generated at ~800°C. By further annealing above ~950°C, the amorphous  $sp^2$  carbons graphitize, leading to the graphene formation on the diamond C(111) surfaces.

#### Acknowledgements

This study was partly supported by the Cooperative Research Program of "Network Joint Research Center for Materials and Devices" and Nano-net Support Project of JAEA. (Proposal No.2010B3873)

#### References

- [1] T. Yamada, C. E. Nebel, K. Somu, H. Uetsuka, H. Yamaguchi, Y. Kudo, K. Okano, and S. Shikata, *Phys. Stat. Sol. (a)* **204** (2007) 2957.
- [2] T. Yamada, K. Somua, C. E. Nebela, and S. Shikata, *Diam. Relat. Mater.* **17** (2008) 745.
- [3] C. Su, and J. C. Lin, *J. Chem. Phys.* **109** (1998) 9549.