Extended Abstracts of the 2011 International Conference on Solid State Devices and Materials, Nagoya, 2011, pp1320-1321

KM-6-1(Invited)

Formation of graphene nanostructures on vicinal SiC surfaces

Satoru Tanaka, Takashi Kajiwara, Yusuke Kurisu, and Kouhei Morita

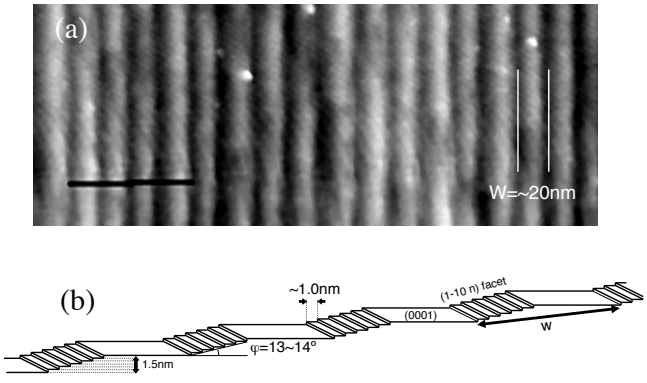
Department of Applied Quantum Physics, Kyushu University
744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
Phone: +81-92-802-3535 E-mail: stanaka@nucl.kyushu-u.ac.jp

1. Introduction

After the successful fabrication of graphene by the mechanical exfoliation method by Novoselov et al. [1], there have been many significant studies using graphene flakes. For future applications and further simplification of the experiments, it is essential to scale up the size and obtain high quality films. The surface decomposition of silicon carbide (SiC) in vacuum [2, 3] or inert gas environment [4] is one of the promising approaches for growth of epitaxial graphene. In the future, it will be possible to fabricate single layer graphene and a few layers of graphene (FLG) over the entire surface of the SiC substrate. Emtsev et al. demonstrated the fabrication of monolayer graphene with sufficiently large domain sizes on SiC substrates by high temperature annealing in an Ar atmosphere and nearly atmospheric pressure [4].

Graphene nanostructures such as nanoribbons (GNRs) and periodic ripples are of interest because of their electronic structures modified by quantization and potential fluctuations. Especially, GNRs gather interests due to the presence of edges, which are theoretically predicted to possess unique electronic characteristics [5]. However, it has been difficult to fabricate GNRs having very narrow widths below ~20nm, even with the use of the state-of-the-art lithographic techniques. Several ideas to realize GNRs are proposed: unzipping of carbon nanotubes (CNT) [6] and chemical synthesis [7].

In this study, we demonstrate a new approach, i.e. epitaxial growth of GNRs, by noticing 'SiC nanosurfaces' as a template and molecular beam epitaxy (MBE) [8].



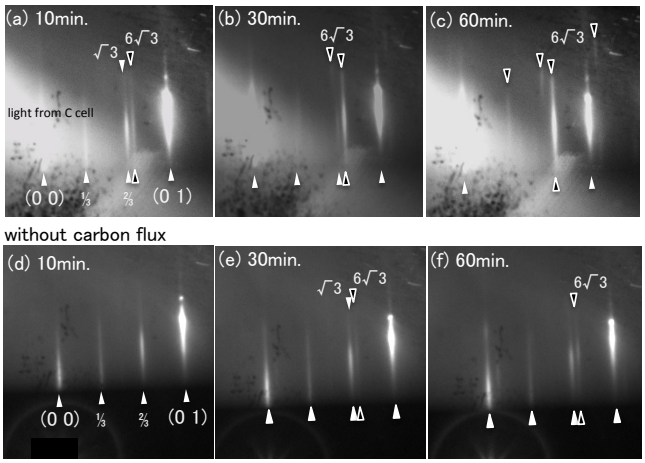
Figs. 1 (a) AFM image of SiC surface after H_2 etching and (b) the schematic model of the 'SiC nanosurface'. Note the surface consistst of the periodic surface morphology with the characteristic distance of ~20nm.

We found after H_2-gas etching the vicinal SiC surfaces exhibited self-ordered nanofacet structures consisting of pairs of a (0001) plane and a (1-10 n) nanofacet with a characteristic distance of 10/20 nm [9, 10], as shown in Figs. 1. Such unique vicinal SiC surfaces (SiC nanosurface) would play a significant role in obtaining self-ordered graphene nanostructures.

2. Experimental

Vicinal 6H-SiC(0001)-Si face (4° off toward [1-100]) substrates were used. H_2 gas etching was initially performed to obtain the periodic nanofacet structure as shown in Figs. 1. The typical width of (0001) terraces and (1-10 n) facets is both 10nm. The (1-10 n) facet consists of 6 bi-layer steps, which are corresponding to 1 unit-cell of 6H-SiC in c-direction, owing to quantized step bunching [10]. The SiC samples were then transferred to the UHV-MBE chamber ($<10^{-9}$ Torr) and annealed at 750°C for 180 min. and at 1050°C for 15 min. Carbon atoms were supplied by directly heating the graphite plate at ~2300°C. The SiC sample was heated to 1100°C with the carbon (C) flux, and hold for 30-120 min. to grow graphene. The similar process with the absence of the C-flux was also performed as a comparison. *In-situ* reflection high-energy diffraction analysis (RHEED) was conducted during graphene growth. The samples were *ex-situ* examined by low-energy electron diffraction (LEED), atomic force microscope (AFM), transmission electron microscope (TEM), angle-resolved photoemission spectroscope (ARPES) [11] and micro Raman spectroscope.

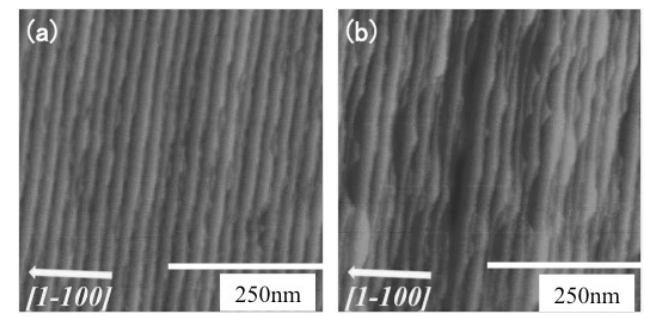
Figures 2 show *in-situ* RHEED images when the SiC substrate was heated at 1100°C for 60 minutes with and without the C-flux. A clear ×6 satellite streak owing to the $(6\sqrt{3}\times6\sqrt{3})R30°$ buffer layer was visible after 10min. with the C-flux (Fig. 3(b)), whereas the initial ×3 pattern, $(\sqrt{3}\times\sqrt{3})R30°$ due to Si adatoms, was kept without the C-flux (Fig. (d)). This implies the C-flux is effective to nucleate the $(6\sqrt{3}\times6\sqrt{3})R30°$ buffer layer. After 30 min. a faint streak next to the 2/3 streak due to the $(6\sqrt{3}\times6\sqrt{3})R30°$ buffer layer appeared in the sample without the C-flux (Fig. (e)) and was more clear after 60 min. in addition to the initial ×3 pattern. At this stage the surface without the C-flux was partially transformed to



Figs. 2 *In-situ* RHEED images of the samples with and without the C-flux after 10, 30, and 60 min. The bright area conceals a (00) rod is due to the reflected light of the carbon source.

the $(6\sqrt{3}\times6\sqrt{3})$R30° buffer layer, resulted from the surface decomposition at 1100°C. In contrast, the SiC(0001) surface with the C-flux was fully covered by the $(6\sqrt{3}\times6\sqrt{3})$R30° buffer layer, as indicated by the absence of the ×3 pattern shown in Fig. (c). Thus, it is believed that the GNRs may grow on (0001) terraces, whose width is ~10nm, after~60min. growth. Inclined streaks originated from graphene growth on (1-10 n) facets were evolved between 60~90 min. (not shown). The continued supply of the C-flux resulted in the growth of a continuous layer (like a carpet) over the whole surface area. This can be considered as a periodic ripple structure, in which ~10nm width of $(6\sqrt{3}\times6\sqrt{3})$R30° buffer layer on (0001) and ~10nm width of graphene on (1-10 n) facets are laterally connected.

Figures 3 show the AFM images after 60min. growth (a) with and (b) without the C-flux. Morphological evolutions such as step wandering and bunching are apparent in Fig. 3(b) without the C-flux, which is expected assuming SiC surface decomposition. The initial periodic feature of the SiC nanofacets is maintained with the presence of the C-flux, indicating the growth of the $(6\sqrt{3}\times6\sqrt{3})$R30° buffer layer directly on the SiC surface. This is evidenced by Raman spectra of this sample before and after hydrogen intercalation (hydrogenation). A G'(2D) peak is appeared after hydrogen intercalation because of the transformation of the $(6\sqrt{3}\times6\sqrt{3})$R30° buffer layer into a quasi-free-standing graphene monolayer [12].



Figs. 3 AFM images of the SiC surfaces after 60min. (a) with the C-flux and (b) without the C-flux.

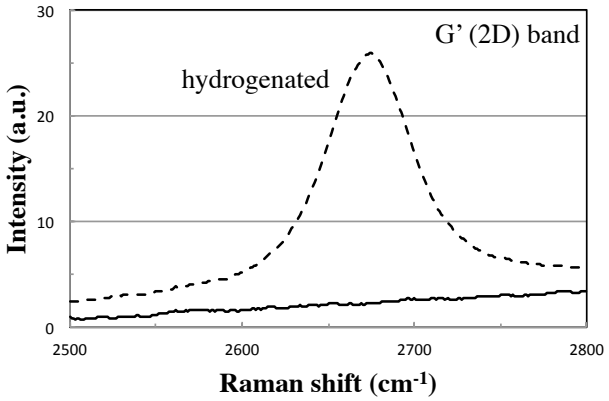


Fig. 4 Micro Raman spectra of the sample with the C-flux after 60 min. growth. A solid and dot curve is G'(2D) band spectrum before and after hydrogen intercalation (hydrogenation), respectively.

3. Summary

Graphene nanostructures, nanoribbons and periodic ripples, were fabricated on vicinal SiC surfaces, which consist of periodic nanofacet structures, by carbon source MBE at relatively low temperatures at 1100°C. In contrast to surface decomposition at high temperatures (>1500°C), the resulting surface morphologies after growth indicate similar features of 'SiC nanosurface', suggestive of the growth of the $(6\sqrt{3}\times6\sqrt{3})$R30° buffer layer on (0001) terraces. After hydrogen intercalation this layer can be transformed into monolayer graphene, probably indicating the GNR formation.

References

[1] K. S. Novoselov *et al*., Nature **438**, 197(2004).
[2] A. J. van Bommel *et al*., Surf. Sci. **48**, 463 (1975).
[3] S. Tanaka *et al*., Phys. Rev. B **81**, 041406(R)(2010).
[4] K. V. Emtsev *et al*., Nat. Mater. **8**, 203 (2009).
[5] M. Fujita *et al*., J. Phys. Soc. Jpn **65**, 1920 (1996).
[6] D. Kosynkin *et al*., Nature **458**, 872 (2009).
[7] X. Li *et al*., Science **319**, 1229 (2008).
[8] Al-Temimy *et al*., Appl. Phys. Lett. **95**, 231907 (2009).
[9] H. Nakagawa *et al*. , Phys. Rev. Lett. **91**, 226107 (2003).
[10] M. Fujii and S. Tanaka, Phys. Rev. Lett. **99**, 016102 (2007).
[11] K. Nakatsuji *et al*., Phys. Rev. B **84**, 045428 (2010).
[12] C. Riedl *et al*., Phys. Rev. Lett. **103**, 246804 (2009).