**Structural and Electronic Features of Epi-graphene on Silicon Carbide**

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**Abstract.** Epi-graphene is graphene grown by thermal decomposition of SiC. It is suitable for electronic applications, because wafer-scale single-orientation graphene can be directly grown on the semi-insulating substrate. The interface between graphene and the SiC substrate is characterized by the presence of the buffer layer. The electronic states of graphene are strongly affected by the atomic-scale interface modification, such as the rapid-cooling technique, twisting graphene layers, and hydrogen intercalation.

# INTRODUCTION

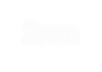
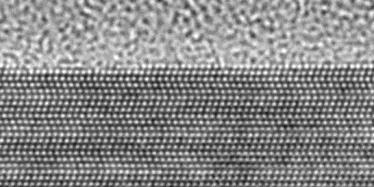
Graphene is a one-atom-thin carbon material, having a hexagonal honeycomb lattice. It has been attracting a lot of researchers due to its fascinating electronic, thermal, and mechanical properties from the pioneering work by Geim et al. in 2004 [1]. In the same year, de Heer et al. reported graphene epitaxially grown on the single crystal SiC substrate exhibited the two-dimensional electronic features [2]. It should be noted here that the patent by de Heer et al. on the application of epitaxial graphene on SiC was applied in 2003 [3]. Epitaxial graphene on SiC is now called epi-graphene, in order to distinguish it from epitaxially grown graphene on other substrates. SiC is now widely used in so-called power electronic devices [4]. The SiC wafer technology has been rapidly developed in these 20 years. A wide-bandgap semiconductor SiC can be used as a semi-insulating substrate for graphene electronics. Thus, epi-graphene is a material suitable for various electronic device applications.

Epi-graphene can be grown by thermal decomposition of SiC. Figure 1 illustrates the schematic diagram of growth and surface features of epi-graphene [5,6]. As shown in the high-resolution transmission electron microscope (HRTEM) image in Fig. 1(a), when we heat the SiC substrate at more than 1600 C in atmospheric pressure of Ar, only the silicon atoms leave the surface and the remaining carbon atoms form graphene. One of the characteristic features of epi-graphene is the presence of the buffer layer in the interface. The buffer layer is also composed of carbon atoms, and it is illustrated as a broken line in Fig. 1(a) [7]. In the buffer layer, the in-plane atomic arrangement is almost the same as that of graphene, but some of the carbon atoms form strong covalent bond with the silicon atoms beneath them. Due to this strong bond, the buffer layer does not have the electronic states like graphene.

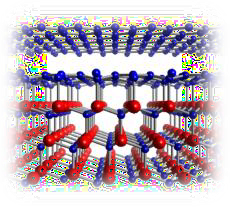
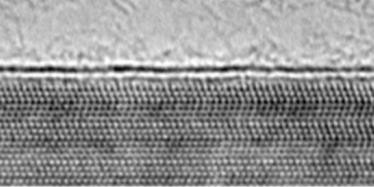
Now, epi-graphene can be grown epitaxially on a wafer-scale SiC substrate with the atomically flat surface. Figure 1(b) shows the atomic-force microscope (AFM) images before and after graphene growth. Before graphene growth, the surface of the SiC wafer is typically etched by annealing under hydrogen atmosphere at more than 1200 °C. By this hydrogen etching treatment, the surface becomes clean and composed of the perfectly periodic steps. After graphene growth, the perfect periodicity disappears, but it keeps atomically flat surface. The AFM phase image reflects the uniformity of the surface composition, and we can find that almost 100 % of the surface can be

covered by monolayer graphene. In this review article, I will introduce the structural and electronic features of epi- graphene, particularly focusing on the interface modification.

(a)



2nm

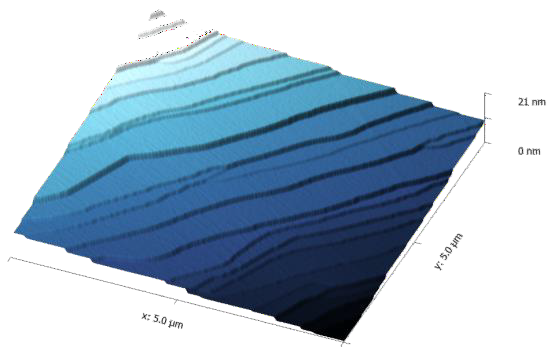
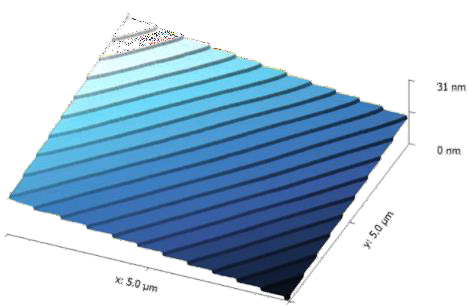
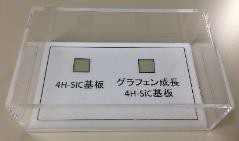
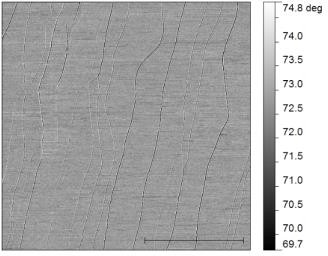


Graphene

1600℃~ in Ar

SiC

Si



(b)

Monolayer coverage:

1nm ~100%

Phase image

2m

*10x10mm2*

SiC

~1200℃

**FIGURE 1.** (a) HRTEM image and schematic diagram of epi-graphene growth by thermal decomposition of SiC. (b) Three- dimensional AFM topography before and after graphene growth, together with an AFM phase image and a photograph of the substrate. Reproduced from [5,6] with permission.

# STRUCTURE AND ELECTRONIC STATES MODIFIED BY THE INTERFACE ENGINEERING

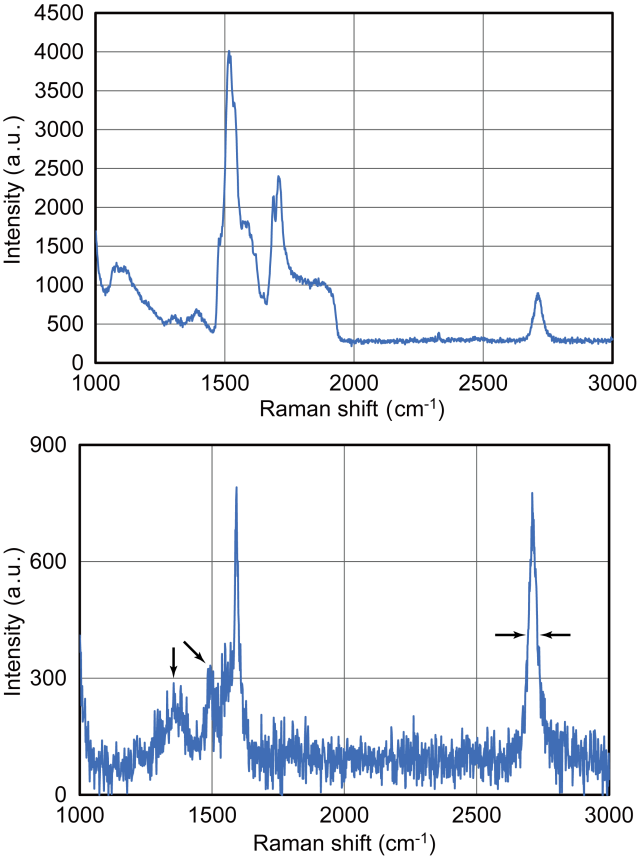
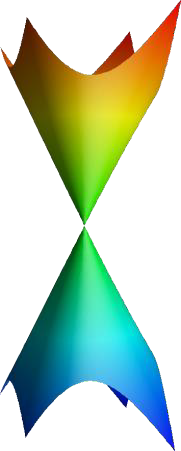
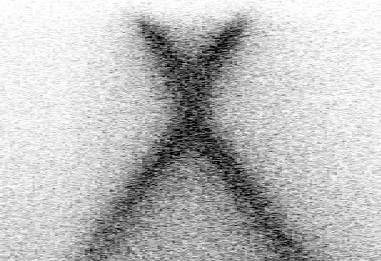
Before describing about the interface modification, I'd like to show the basic features of epi-graphene, which is shown in Figure 2 [6]. The electronic structure of graphene is characterized by the linear band dispersion, which is called the Dirac cone shown in the inset in Figure 2(a). The electronic structure can be experimentally observed by angle-resolved photoemission spectroscopy (ARPES). Typical ARPES *E*-*k* image of epi-graphene is shown in Figure 2(a). The cross section of the Dirac cone can be clearly seen. We can find that the Dirac point is present about 0.4 eV below the Fermi energy *E*F. This means that epi-graphene is electron-doped. This electron doping is due to the presence of the buffer layer and the spontaneous polarization of the hexagonal SiC substrate [8]. In order to measure the electron concentration, we can perform Hall-effect measurements using epi-graphene grown on the semi-insulating SiC substrate. Figure 2(b) is the results of Hall-effect measurements. The Hall coefficient is negative, indicating that the dominant carriers are electrons. The blue circles and the red squares are plots of the mobility and the electron concentration, respectively. The electron concentration is about 1.1 x 1013 cm-2, and it does not depend on temperature. The mobility is about 900 cm2/Vs at room temperature, and it increases by decreasing temperature, reaching about 1,800 cm2/Vs at 20 K. The mobility decrease with increasing temperature is due to the carrier scattering by phonon of the buffer layer. The sheet resistance at RT and 20 K are about 600 and 300 Ohm/sq., respectively. It is widely known that the mobility increases with decreasing the carrier concentration, and the highest mobility of epi-graphene up to now is about 70,000 cm2/Vs at the carrier concentration of about 0.6 x 1010 cm-2 [9]. On the other hand, the highest mobility of about 140000 cm2/Vs was reported in graphene sandwiched by hexagonal boron nitride at the carrier concentration of about 2.0 x 1011 cm-2 [10]. Difference of these values can be attributed to the substrate polar phonon [11].

Presence of epi-graphene and some structural information can be detected most easily by Raman spectroscopy. Typical Raman spectrum of epi-graphene is shown in Fig. 2(c). Strong peaks present around 1000-1900 cm-1 are from the SiC substrate. By subtracting the SiC component, we can obtain the graphene Raman spectrum, which is

shown in Fig. 2(d). Sharp peaks at about 1600 and 2700 cm-1, which are called the G and 2D band, respectively. These are characteristic peaks of graphene, and in particular, the sharp 2D band with the full width at half maximum less than about 40 cm-1 is the signature of monolayer graphene. If the width of the 2D band was more than 50 cm-1 and the peak became asymmetric, it can be recognized as bilayer graphene. We can also see several broad peaks around 1300-1600 cm-1. These are due to the buffer layer which is present between graphene and the SiC substrate. In other words, when we modify the interface including the presence of the buffer layer, these features can be also modified.

(a)

0.0



(c)

(d)

G

2D

buffer

-0.2

-0.4

-0.6

E-EF [eV]

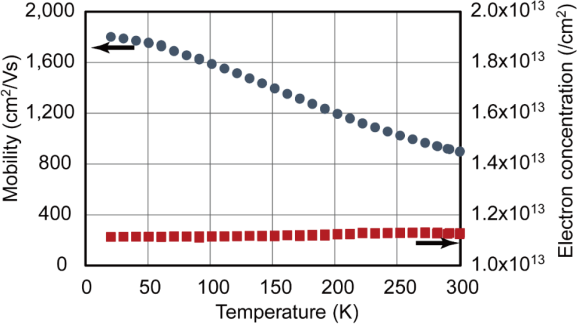
-0.8

-1.0

-1.2

-0.2 -0.1 0.0 0.1 0.2

*kx* [Å-1]



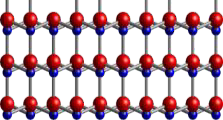
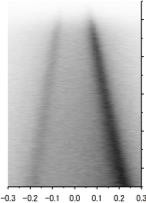
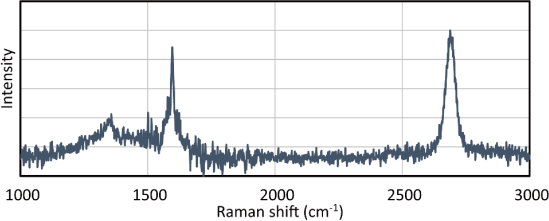
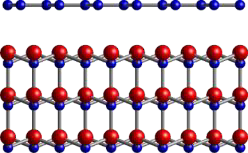
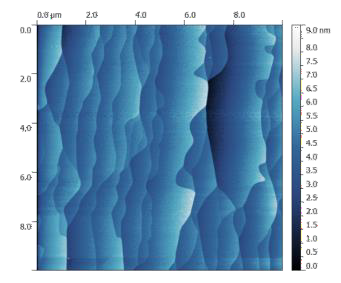
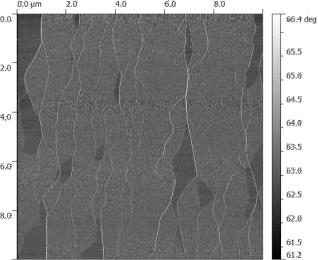
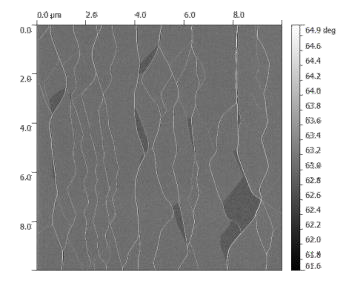
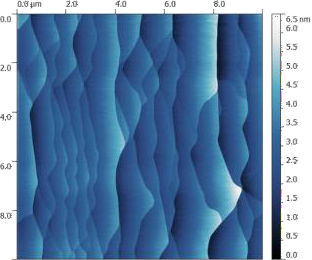
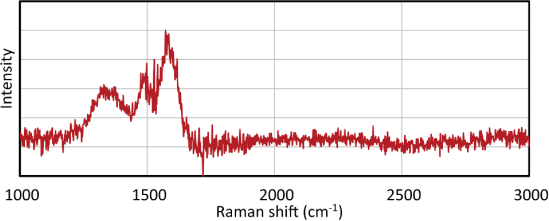
(b)

**FIGURE 2.** (a) ARPES *E-k* image of monolayer epi-graphene on SiC, together with the band structure of graphene. (b) Carrier mobility and carrier concentration of epi-graphene measured by Hall-effect measurement. (c) Raman spectrum of epi-graphene on SiC. (d) Raman spectrum of epi-graphene after subtracting the SiC substrate component. Reproduced from [6] with permission.

The first example of the interface modification is the graphenization of the buffer layer by rapid-cooling [12]. Interestingly, graphene is known to have a negative thermal expansion coefficient [13]. It is then suggested that when we rapidly cool the buffer layer sample on SiC, the buffer layer with the graphene-like structure expands, while SiC shrinks. Due to this mismatch, the chemical bond between the carbon atom in the buffer layer and the topmost silicon atom in SiC can be physically broken. In other words, we expected that the buffer layer could be converted into graphene by rapid cooling (RC) treatment. Figure 3 is the experimental results. The AFM topography and phase images before RC shown in (a) and (b), indicated that the surface was very flat and about 95 % of the surface was covered by the buffer layer, and the remaining 5 % was bare SiC surface. Presence of the buffer layer was evidenced by the Raman spectrum in (c), showing the broad peaks around 1300-1600 cm-1. In the ARPES image shown in (d), no band dispersion was observed. On the other hand, after RC, the situation completely changed. In the AFM images, the surface features were quite similar to the one before RC. However, in the Raman spectrum, the sharp peak at 2688 cm-1 appeared, which is known as the 2D band. The width of the 2D band was about 42 cm-1, indicating the presence of monolayer graphene. In the ARPES image in (h), very clear linear band dispersion was

found, which is the evidence of high-quality graphene. In contrast to monolayer graphene on SiC with the buffer layer, the Dirac energy was estimated to be about 0.5 eV above the Fermi energy, indicating heavy hole doping. These results demonstrate that the buffer layer could be converted into quasi-freestanding monolayer graphene, which is an alternative method to make graphene.

k (Å-1), ⊥Γ-M k (Å-1), ⊥Γ-M



Before

(a)

(b)

After

(e)

(f)

**0L 1L**

**SiC**

**SiC**

(c)

Buffer layer

(g)

1L graphene

2D-Peak @2687.71 (cm-1) FWHM:42.1(cm-1)

(d)

0.0

(h)

0.0

-0.2

-0.2

-0.4

-0.4

-0.6

-0.6

ARPES

-0.8

ARPES

-0.8

E-EF (eV)

E-EF (eV)

**FIGURE 3.** (a) and (b) AFM topography and phase images, (c) Raman spectrum, and (d) ARPES *E*-*k* image before RC treatment.

(e) and (f) AFM topography and phase images, (g) Raman spectrum, and (h) ARPES *E*-*k* image after RC treatment. Schematic diagram of the conversion from the buffer layer into quasi-freestanding monolayer graphene is also inserted. Reproduced from

[12] with permission.

In the graphene research community in these several years, the most exciting topic is twisted bilayer graphene (TBG). TBG is two graphene layers stacked with a certain angle *θ*, as shown in Fig. 4(a). Although TBG has been widely investigated in this decade [14], it became hot again due to the discovery of superconductivity in so-called magic-angle twisted bilayer graphene (MATBG). At the magic-angle 1.1°, superconductivity was observed below TC=1.7 K [15]. If we understood the origin of superconductivity, we would get the pathway to raise the transition temperature. For example, higher transition temperature 2.1 K was reported in the magic-angle 1.5° twisted trilayer graphene [16]. The origin of the superconductivity in MATBG could be attributed to the large density of states at the Fermi energy due to the flat band. The direct observation of the flat band was achieved by two groups in 2021 [17,18]. In these cases, TBG samples are basically fabricated by the standard tear and stack technique, which limits the sample size to be about several or several tens of micrometers. On the other hand, we can grow millimeter-scale monolayer epi-graphene with the single orientation. If we can exfoliate large-area graphene and transfer to another graphene, millimeter-scale TBG can be obtained. Figure 4(b) illustrates the sample preparation procedure [19].

**FIGURE 4.** (a) Schematic diagram of twisted bilayer graphene with the twist angle of *θ*. (b) Fabrication procedure of large-area TBG sample. (c) Experimental (Exp.) and theoretical calculation (calc.) of the ARPES *E-k* images of MATBG sample. The intensity line profiles along the *kx*=0.02 Å-1 are also shown. Reproduced from [19] with permission.

First, we grow monolayer graphene on SiC with the substrate size of 5 x 5 mm2. Gold thin film with the thickness of about 200 nm was deposited on graphene and then, graphene was exfoliated together with gold, using thermal release tape. It was put on another graphene on SiC with some twist angle *θ*. Finally, tape and gold were removed. In this technique, we confirmed that more than 3 x 5 mm2 sized TBG sample was successfully fabricated. In the MATBG sample, we observed its band structure using ARPES measurement. Figure 4(c) is the *E*-*k* dispersion image of the MATBG sample. As denoted by red and blue arrows, a few bands can be clearly observed. In the intensity profile along the *kx*=0.02 Å-1 line, we can see three intensity maxima as shown by broken lines. As shown on the right, we also calculated the spectral function of MATBG from the band structure of 1.08° TBG sample based on the tight-binding framework. The flat band is obvious as shown by a green arrow. Its intensity profile is shown in its left, indicating the similar behavior to the experimental results with respect to the peak positions. In other words, the flat band was directly observed in the millimeter-scale magic-angle twisted bilayer graphene. Not only just the success of the observation of flat band, but also some interesting features were found. In the present case, the energy of the flat band lies at about -0.37 eV below the Fermi energy. It means that the TBG was electron doped, which is due to effect of the buffer layer [8].

The final example of the interface modification is the hydrogen intercalation in the interface between the buffer layer and SiC. It was known that the buffer layer could be converted into quasi-freestanding monolayer graphene by hydrogen intercalation [20]. In this technique, hydrogen penetrates the buffer layer, breaks the Si-C bond, and then saturates silicon dangling bond. As stated previously, epi-graphene on SiC with the buffer layer has the low- temperature mobility of about 1,800 cm2/Vs, and it decreases with increasing temperature. This mobility decrease is due to the phonon scattering by the buffer layer. Since hydrogen intercalation converts the buffer layer into graphene, this phonon scattering disappears, and then the mobility does not have the temperature dependence [21]. So,

hydrogen intercalation is a good technique to obtain high mobility in the epi-graphene system. However, if the unsaturated silicon dangling bonds exist, it acts as the carrier scattering center, which degrades mobility. So, the 100 % hydrogen termination is necessary for electronics application, and then understanding the mechanism of intercalation is important.

**Raman shift [cm-1]**

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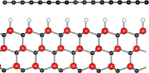
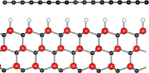
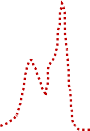
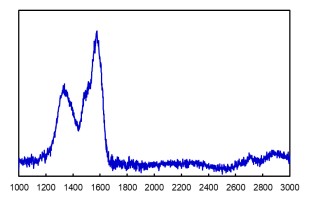
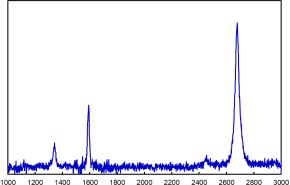
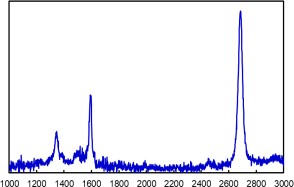
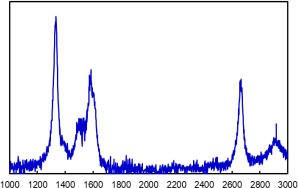
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**Buffer layer**

**600℃300 sec.**

**330 sec.**

**2400 sec.**

(a)

**D**

(c) **2D**

(d) **2D**

**G**

(b)

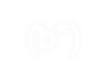
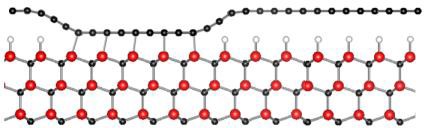
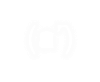
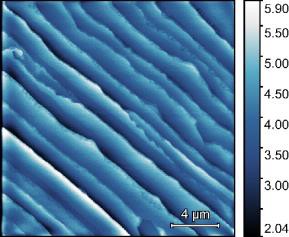
**2D**

**D**

**G**

**G**

**D**



(a’)

nm

(b’)

nm

(c’)

nm

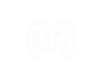
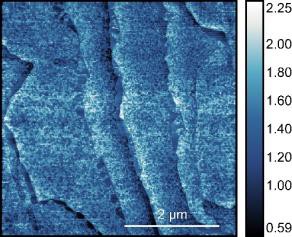
(d’)

2 μm

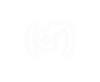
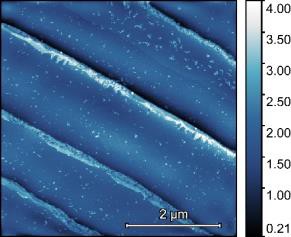
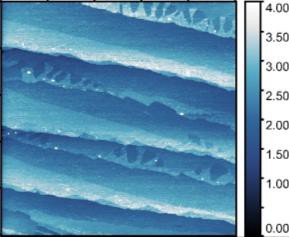
(b’’)

**Intensity [a.u.]**

**Raman shift [cm-1]**



**Raman shift [cm-1] Raman shift [cm-1]**



nm

**FIGURE 5.** Raman spectra of (a) the buffer layer, (b) the sample annealed at 600 °C for 300 seconds, (c) 330 seconds, and (d) 2400 seconds. (a'-d') Corresponding AFM topography images. (b'') HRTEM image of the sample shown in (b). Reproduced from

[21] with permission.

Although it was known that hydrogen can intercalate in the interface between the buffer layer and SiC, from where and how hydrogen can enter the interface has not been revealed. We investigated the atomic-scale intercalation mechanism by observing surface and the interface. Figure 5 is the experimental results [22]. Figure 5(a) and (a') are the Raman spectrum and AFM topography of the buffer layer sample. The Raman spectrum is quite similar to that shown in Fig. 3(c). In the AFM image, very flat terrace was observed with the width of about a few micrometers. After annealing this buffer layer sample at 600 °C under the hydrogen gas flow at the atmospheric pressure for 2400 seconds, the Raman spectrum was completely converted into the one of monolayer graphene as shown Fig. 5(d). Similar spectrum was obtained by annealing at 600 °C for 330 seconds as shown in (c), which has a little stronger D peak. In these cases, the surface was also atomically flat as shown in (c') and (d'). On the other hand, the features are completely different when the samples were annealed for 300 seconds. The Raman spectrum in (b) has the mixed features of (a) and (c), and in addition, significantly strong D band was observed. In the AFM image of this sample shown in (b'), the surface on the terrace was atomically rough. In the HRTEM of this sample shown in (b''), there are convex and concave regions as shown by blue and red arrows, respectively. If the hydrogen atoms intercalate, the surface becomes high by the size of hydrogen atom. In other words, the convex and concave regions correspond to the hydrogen intercalated and non-intercalated regions, respectively. The boundary between these regions can be regarded as the edge of graphene, which could give rise to the strong D band found in the Raman spectrum in (b). These results suggest that hydrogen penetrated through the buffer layer randomly and simultaneously at many places on the terrace, and diffused in the interface. This is an important fact, because of the recent development of the hydrogen energy technology.

# CONCLUSIONS

In this paper, structural and electronic features of epi-graphene are reviewed particularly focusing on the interface modification. The interface can be characterized by the presence of the buffer layer. The buffer layer can be converted into quasi-freestanding monolayer graphene by the rapid-cooling and hydrogen intercalation techniques. Fabrication of the millimeter-scale twisted bilayer graphene was possible using epi-graphene, and its electronic states were strongly affected by the interface. Epi-graphene is strongly expected in the electronics applications, due to the wafer-scale production and controllability of its electronic states.

# ACKNOWLEDGMENTS

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