Surface Modification of SiC by Plasma Oxidation to Form Graphene/SiC Structure with Low Pit Density

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The sublimation of Si atoms from a SiC surface by annealing in UHV is a familiar method for the epitaxial growth of graphene. However, a problem is the pitted morphology of the graphene/SiC(0001) structure after simple annealing above 1100°C in UHV as shown in Fig. 1. It is well known that, prior to graphene growth above 1100°C, a buffer layer is formed at around 1000°C. The pitted morphology in Fig. 1(b) is probably caused by the insufficient amount of liberated carbon atoms on the SiC surface to form a uniform buffer layer because the rapid sublimation of Si atoms occurs on an area not covered by a buffer layer, causing the formation of pits. Thus, the control of the carbon concentration at the monolayer level on an initial SiC surface is important.

We have found a new chemical route to achieve this, which is the plasma oxidation of a SiC surface near room temperature followed by HF etching. This is referred to as the plasma-assisted process hereafter. Figure 2 shows the change in O1s XPS spectra caused by the plasma-assisted process. Figure 2(a) indicates that the initial untreated SiC surface is terminated by OH species, which are the origin of the hydrophilic property of the surface as shown in the inset in Fig. 2(a). In contrast, after the plasma-assisted process, a shoulder peak corresponding to C-O bonds appears in the O1s spectrum in Fig. 2(b). Taken together with the C1s spectrum, we consider that a mixture of C-C and C-O bonds exists, which agrees with the slightly hydrophobic property of the treated SiC surface as shown in the inset in Fig. 2(b). We speculate that carbon species composed of C-C and C-O bonds accumulated at the SiO_2/SiC interface during plasma oxidation near room temperature. When the SiO_2 layer was stripped off by subsequent HF etching, additional carbon species with a thickness of 1-2 monolayers appeared on the SiC surface as shown in Fig. 3(a). When the surface in Fig. 3(a) was annealed at 1100°C for 30 min in UHV, a graphene/SiC structure with a low pit density was obtained as shown in Fig. 3(b), which is completely different from the structure in Fig. 1(b). This is probably because the additional carbon species produced by the plasma-assisted process contribute to the formation of a uniform buffer layer, which suppresses random Si sublimation at elevated temperatures of above 1000°C.

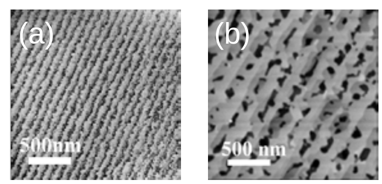

Figure 1. AFM images (a) before and (b) after graphene growth on untreated 4H-SiC(0001).

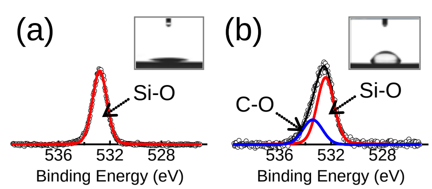

Figure 2. O1s spectra of (a) untreated and (b) plasma-assisted processed SiC surfaces.

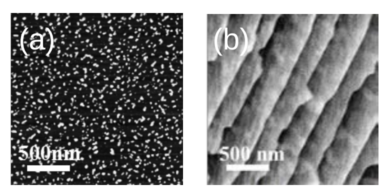

Figure 3. (a) AFM images (a) before and (b) after graphene growth on a plasma-assisted processed SiC surface.

[1] N. Saito, K. Arima et al., Carbon **80**, 440 (2014).
[2] K. Arima et al., Meeting Abstracts of 230th ECS Meeting, 2062 (2016).

Suplementary information:

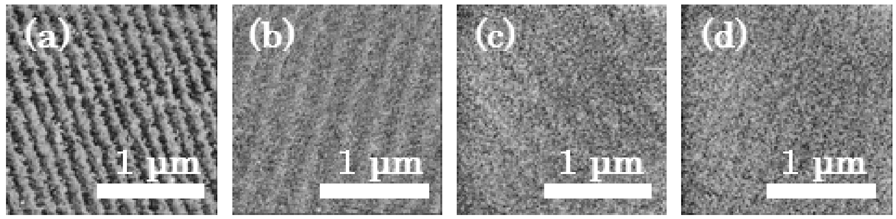

Figure 4. Change in surface morphologies of SiC caused by the plasma-assisted process. (a) Untreated SiC. The SiC surface in (a) was then treated by plasma oxidation for (b) 1 min, (c) 5 min and (d) 10 min. The images in (b-d) were obtained after the removal of the SiO_2 layer by HF etching.

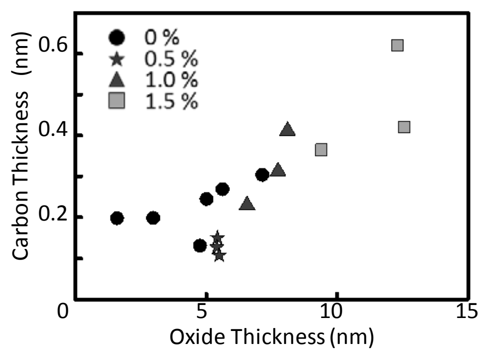

Figure 5. O_2 gas in plasma promotes the oxidation of a SiC surface even near room temperature. After removing the surface SiO_2 layer by HF etching, a thin film composed of carbon species was formed. This graph shows the thickness of the additional carbon layer as a function of the oxide thickness on SiC. Different symbols indicate different concentrations of O_2 gas intentionally introduced to the chamber.

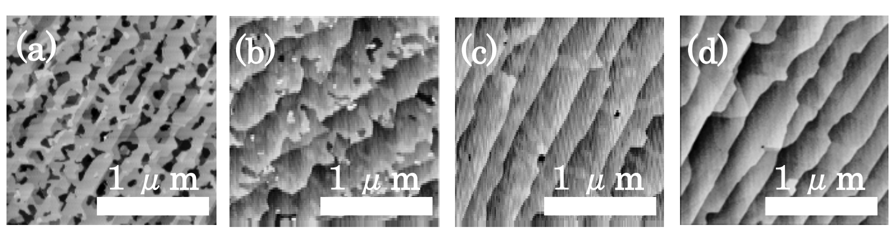

Figure 6. Surface morphologies of graphene/SiC structures after annealing at 1100°C for 30 min in UHV. (a) Without and (b-d) with the plasma-assisted process prior to annealing. More specifically, in (b), (c) and (d), the initial SiC surface was treated by plasma oxidation for 1 min, 5 min and 10 min, respectively.