

Large-scale Growth of Quasifreestanding Graphene by using a Single-step Process

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Various methods have been suggested to realize freestanding or suspended graphene, which is expected to exhibit the intrinsic properties of graphene. However, in previously reported methods, multiple-step processes have been applied to produce freestanding graphene on a substrate. Here, we demonstrate that quasifreestanding graphene on a substrate can be realized through a simple single-step process. In this experiment, self-etching of nano-scale SiC steps of 8° off-axis vicinal SiC contributed to the formation of quasifreestanding graphene on an Si-faced SiC wafer, which was confirmed using low-energy electron diffraction, Raman spectroscopy, scanning electron microscopy and two-probe resistance measurements. Such a single-step technique for the growth of quasifreestanding graphene could pave the way towards graphene-based silicon-carbide micro-electronics.

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I. INTRODUCTION

Graphene, a two-dimensional carbon material, possesses various unique features like ultrahigh carrier mobility [1], excellent mechanical strength and flexibility [2], superior thermal conductivity [3], high optical transparency [4], and potential chemical activity [5]. However, these intrinsic properties cannot be fully achieved in experiments, mainly owing to substrate effects. Various factors, such as surface structure, crystallinity, defects, and chemical compositions, govern the substrate effects [6–12]. For effective exploitation of the intrinsic properties of graphene, it has to be prepared and handled in such a way to minimize the influence of the aforementioned factors ignoring the surrounding environment. One of the possible ways to achieve this is through freestanding or suspended graphene, which comes very close to the ideal nature of graphene and, therefore, has attracted significant attention since its discovery owing to its unique properties [10,13,14]. Until now, various techniques such as chemical vapor deposition growth on a Ni/Cu foam [15], microwave plasma treatment [16], various treatments of epitaxial graphene on SiC like chemi-

cal etching [17], flash annealing at high temperature [18], and growth of three-dimensional freestanding graphene [19], have been developed to obtain large-area freestanding monolayer graphene. Similarly, the intercalation of graphene using H₂, F₂, O₂, Au, or Pb can decouple it from the substrate [20–24] and twisting a graphene layer can decouple it from the underlying graphene layers [25, 26], rendering quasifreestanding graphene. However, all these methods require multiple steps to fabricate the freestanding graphene.

Here, we demonstrate that quasifreestanding graphene can be grown on a substrate through a single-step process. In this experiment, a single-step thermal treatment was applied to a vicinal SiC(0001) wafer (8° off axis) without further processing. High densities of irregular nanoscale step-edges with very narrow step terraces act as a 3D nanoscale architecture on the SiC wafer [19]. Such irregular nanoscale step-edges enable graphene layers to decouple from the substrate. The nanoscale step-edges were self-etched at high temperatures, resulting in quasifreestanding graphene on the substrate, as shown in Fig. 1. The quasifreestanding graphene was grown on a millimeter scale with a spatial uniformity of a few tens of micrometers. The growth mechanism was also confirmed based on a comparative experiment between a flat SiC wafer and a vicinal SiC wafer. The surface

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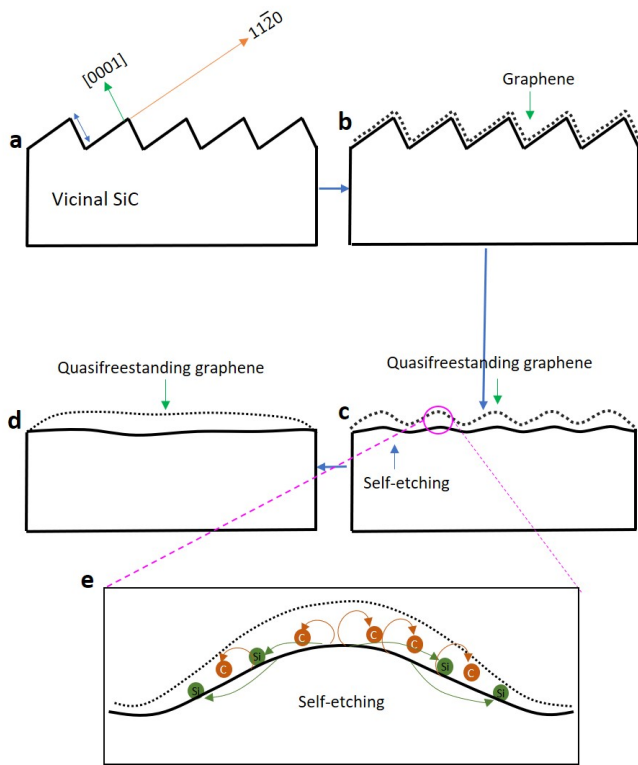


Fig. 1. Schematics of the single-step growth process of quasifreestanding graphene on a vicinal SiC(0001) wafer. (a) Schematic of nanoscale step-edge structures. (b) Typical growth of graphene on the nanoscale step-edge structure. (c) Self-etching of the nanoscale step-edge structures, which is shown in more detail in (e). (d) Quasifreestanding graphene on a self-etched surface. We note that the growth of graphene and the self-etching of nanometer-scale step-edge structures happen at the same elevated temperature.

morphology and the crystallinity were investigated using Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and low electron energy diffraction (LEED). The conductance of the quasifreestanding graphene on the vicinal SiC wafer was enhanced compared to that of typical epitaxial graphene on a flat SiC wafer, as inferred from the two-probe resistance measurements.

II. RESULTS AND DISCUSSION

Growth of quasifreestanding graphene was carried out using Si-faced vicinal 4H-SiC(0001) (8° off-axis) wafer in an Ar-chamber at 180 Torr. Samples were first chemically cleaned with acetone and isopropyl alcohol in an ultrasonic bath for 10 min total. After the samples were immediately introduced into the Ar gas chamber at a 180 Torr pressure and then annealed at a temperature in the range from 1700 to 1900 $^\circ\text{C}$ for a duration ranging

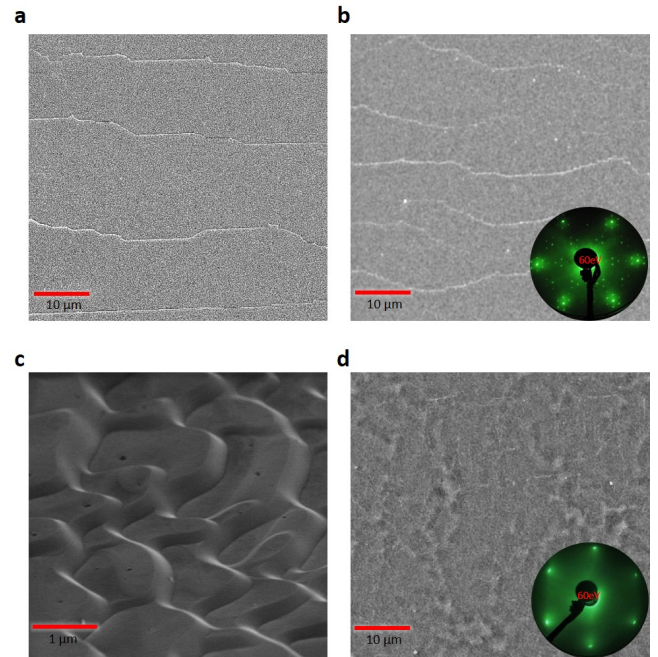


Fig. 2. SEM images of an on-axis SiC(0001) wafer (a) before and (b) after graphene growth at 1800 $^\circ\text{C}$. The inset of (b) is the LEED pattern of graphene grown on the on-axis SiC(0001) wafer. (c) SEM image of the vicinal SiC(0001) wafer before and (d) after graphene growth at the same temperature of 1800 $^\circ\text{C}$. The inset in (d) is the LEED pattern of graphene grown on the vicinal SiC(0001) wafer.

between 3 and 15 min. Raman mappings of the samples were carried out at a laser wavelength of 532 nm. For crystalline structure analysis, samples were loaded into an ultrahigh vacuum chamber, where we performed LEED measurements. For comparison, SEM images of the vicinal and the flat SiC wafers were taken before and after the growth.

For comparative experiments, graphene was grown both on on-axis and vicinal SiC (0001) wafers at the same temperature of 1800 $^\circ\text{C}$. Figures 2(a) and 2(b) show SEM images of the on-axis SiC(0001) wafer before and after graphene growth. Figure 2(a) shows an SEM image of the hydrogen-terminated SiC surface that was formed by etching an on-axis SiC(0001) wafer in a chamber filled with hydrogen gas at 1580 $^\circ\text{C}$. The edge structures shown in the SEM image are bunched steps due to the migrations of step edges at high temperatures [27]. When the hydrogen-terminated surface was heated at 1800 $^\circ\text{C}$, typical epitaxial graphene was grown on the on-axis SiC(0001) wafer, as observed in the LEED pattern in the inset of Fig. 2(b) [28]. We observed a typical LEED pattern of the buffer layer of the epitaxial graphene, $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ [29]. In addition, bunched step-edge structures similar to those before the high-temperature heating treatment were also observed in the SEM image (Fig. 2(b)). In comparison with the growth on a

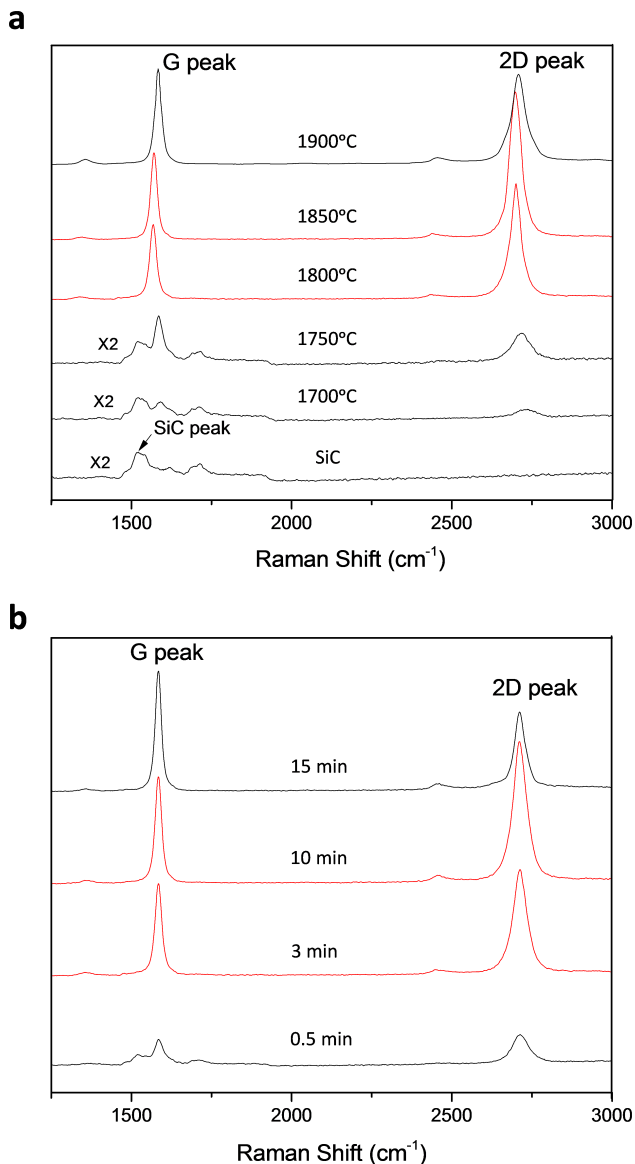


Fig. 3. (a) Raman spectra of graphene grown on a vicinal SiC(0001) wafer at different temperatures. (b) Raman spectra of graphene on a vicinal SiC(0001) wafer for growth at 1800 °C with different annealing times.

on-axis SiC(0001) wafer, graphene growth on a vicinal SiC(0001) wafer at high temperature was quite different. After a vicinal SiC(0001) wafer had been etched in a hydrogen chamber, high-density bunched step-edge structures with nanometer-scale heights were observed in an SEM image (Fig. 2(c)). After the hydrogen-terminated vicinal SiC(0001) wafer had been heated at 1800 °C, the bunched step-edge structures were no longer observed in the SEM image (Fig. 2(d)). This SEM image suggests that the step-edge structures were self-etched, as described in Fig. 1. The self-etching of the nanometer-scale SiC architecture was also reported in the formation of three-dimensional freestanding graphene [19]. After the

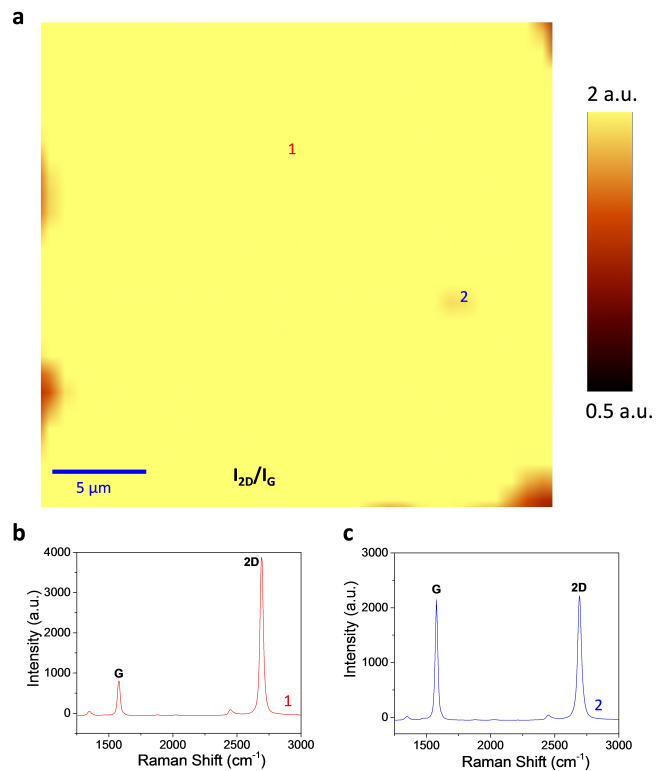


Fig. 4. (a) Raman mapping (I_{2D}/I_G) of quasifreestanding graphene grown on a vicinal SiC(0001) wafer. Raman spectra at (b) region 1 and (c) region 2 in (a).

bunched step-edge structures self-etched, the LEED pattern of only graphene was observed without the LEED pattern of the buffer layer (see the inset of Fig. 2(d)), as self-etching inhibits the formation of buffer layer.

To optimize the growth conditions of quasifreestanding graphene, we measured Raman spectra of graphene grown on a vicinal SiC(0001) wafer at different temperatures and annealing times. First, we varied the heating temperature and measured the Raman spectra of graphene grown on a vicinal SiC(0001) wafer (Fig. 3(a)). For a bare vicinal SiC(0001) wafer, a typical Raman peak at 1520 cm^{-1} , called the SiC peak, was observed (see Fig. 3(a)) [28]. The intensity of the SiC peak reduced upon increasing the heating temperature while the intensities of the typical Raman peaks of epitaxial graphene, called G (1597 cm^{-1}) and 2D (2736 cm^{-1}) peaks, were enhanced [30]. Here, the G and the 2D peaks originate from the doubly degenerate (i TO and LO) phonon mode at the Brillouin zone center and the second-order process (two i TO phonons near the K points), respectively [31]. Especially, when the heating temperature was more than 1800 °C, the SiC peak in the Raman spectrum could not be observed. These Raman spectra suggest that the nanometer-scale step-edge structures are completely self-etched at temperatures above 1800 °C, as reported in the formation of three-dimensional freestanding

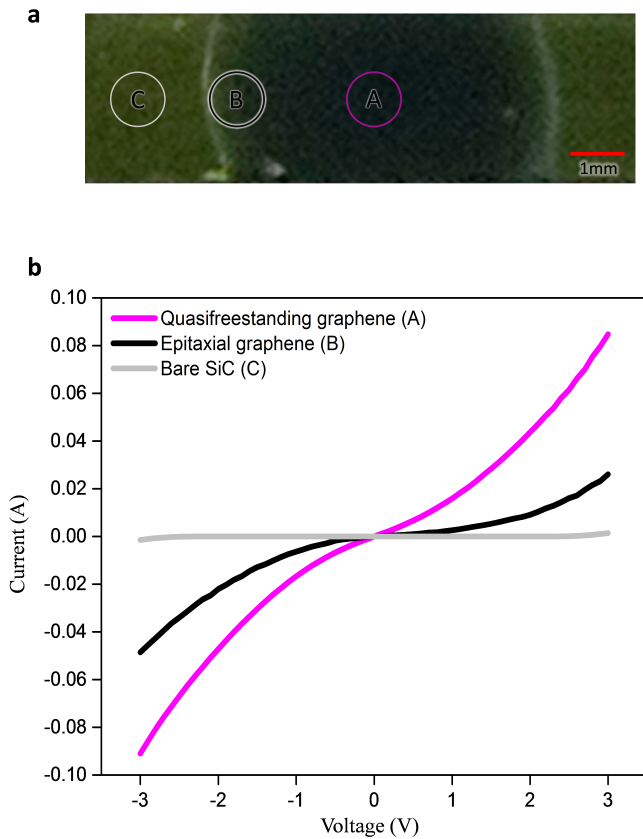


Fig. 5. (a) Optical image of graphene grown on a vicinal SiC(0001) wafer, where the wafer was heated with a thermal gradient. Quasifreestanding graphene, typical graphene, and bare SiC surfaces were observed in regions A, B, and C, respectively. (b) I-V curves in the different regions.

ing graphene [19]. We also measured the Raman spectra of graphene grown on a vicinal SiC(0001) wafer with different annealing time at the same heating temperature of 1800 °C (Fig. 3(b)). For a short annealing time below 1 min, the SiC peak was observed in the Raman spectrum (see Fig. 3(b)). The SiC peak disappeared for annealing times above 3 min, as shown in Fig. 3(b). These observations suggest that the nanometer-scale step-edge structures are completely self-etched for annealing times above 3 min, resulting in quasifreestanding graphene.

We also measured Raman maps of I_{2D}/I_G of the quasifreestanding graphene, where I_{2D} and I_G are the intensities of the 2D and the G peaks in the Raman spectrum, respectively. The blue shifts of the Raman peaks at high heating temperatures can be explained in terms of the compressive strain of epitaxial graphene grown on SiC [17, 32]. The quasifreestanding graphene can be grown up to a millimeter scale, as inferred from the LEED experiments. However, the spatial uniformity of quasifreestanding graphene was approximately $30 \mu\text{m}^2$, as shown in Fig. 4(a). In the greater part of the area, quasifreestanding graphene was in the form of a mono-

layer, as reflected by the Raman spectra in Fig. 4(b), where the I_{2D}/I_G is greater than 1.5 [33]. Quasifreestanding graphene was in the form of bilayers on the rest of the area as shown in Fig. 4(c), where the I_{2D}/I_G is approximately 1 [34].

The growth mechanism of the quasifreestanding graphene is described schematically in Fig. 1. A vicinal SiC wafer with 8° off axis contains a high density of terraces with randomly oriented facets. The 4H-SiC(0001) wafer used in this experiment was 8° off-axis along the [11-20] direction. Therefore, it contained a large number of facets preferentially oriented towards [11-20] and [1-100] in comparison with other orientation facets [27]. The Edges of the step terraces are the primary factors in the growth of typical epitaxial graphene on SiC wafer [35]. In our experiments, the step edges played an important role. The step edges are bunched in the preparation of a hydrogen-terminated SiC(0001) wafer (Fig. 2(c)), which is required in a high-quality SiC surface without defects, as shown in Fig. 2(c) [36]. The bunched steps became nanoscale three-dimensional SiC structures. As reported for the formation of three-dimensional freestanding graphene on a SiC wafer [19], three-dimensional nanoscale SiC structures can be self-etched at high temperatures when the structures are covered with graphene. The growth mechanism of the quasifreestanding graphene on a vicinal SiC wafer can be understood in terms of self-etching. When a vicinal SiC wafer is heated at a high temperature, the initial growth of the graphene is in the form of a stepped structure (Fig. 1(b)). Subsequently, the stepped structures are self-etched at the same temperature. In the process of self-etching, Si atoms evaporated thermally from the SiC bulk begin to etch C and Si atoms (Figs. 1(c) and 1(e)). Finally, the stepped SiC structures flatten, resulting in the formation of quasifreestanding graphene (Fig. 1(d)).

Graphene was grown on a vicinal SiC(0001) wafer with a temperature gradient, as shown in Fig. 5 to measure the changes in the resistance of graphene on a vicinal SiC(0001) wafer. While heating, the temperature at the center (A) of the sample was higher than that at the edge (C) of the sample. Figure 5(a) shows the sample in which quasifreestanding graphene and typical epitaxial graphene were grown in regions A and B, respectively, as confirmed by the LEED patterns (see the insets of Figs. 2(b) and 2(d)). In contrast, in region C, graphene was not grown. We measured the resistance in the three different regions with a two-probe measurement system. The I-V curves measured for the regions are plotted in Fig. 5(b). Region C is insulating because it is pure SiC, which is insulating in the bulk. The relative resistance in region B is higher than that in region A. This relative resistance is consistent with our experimental results. The freestanding or quasifreestanding graphene has higher conductance than typical graphene on a substrate [37].

III. CONCLUSION

We successfully fabricated quasifreestanding graphene on a large scale by using a single-step process. The bunched steps on a vicinal SiC wafer play a crucial role in the formation of quasifreestanding graphene. Graphene was grown on the stepped structures of a vicinal SiC wafer at a given temperature; subsequently, the underlying stepped SiC structures were self-etched, resulting in the formation of quasifreestanding graphene. The growth of the freestanding graphene was verified through SEM images, LEED patterns, Raman spectra, and I-V measurements.

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