Formation of wide and atomically flat graphene layers on ultraprecision-figured 4H-SiC(0001) surfaces

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1. Introduction

Perfect surfaces are expected to upgrade the quality of films grown on them. As discussed in this paper, graphene layers of excellent quality can be grown upon an atomically flat and defect-free SiC surface. In other words, imperfect surfaces degrade the property of the surfaces themselves and the performance of the integrated materials upon them. In general, wafers (or substrates) are bought, then “clean” surfaces are prepared on them by annealing, sputtering, wet etching, and so on. In standard wafer manufacturing, surface-figuring processes are introduced to obtain a flat surface after slicing a wafer from an ingot. As a figuring process of wafers, chemical mechanical polishing (CMP) with a SiO2 or diamond abrasive is generally used [1]. CMP techniques have been modified and are now well established, particularly for Si wafers [2]; however, it was reported that damaged layers result from the abrasion, the thickness of which is commonly about one-fourth of the abrasive particle size (typically 50–70 nm in manufacturing processes) [3]. Surface cleaning procedures are useful for removing native oxides and surfactants on a Si surface for improving the surface flatness, but they cannot remove damaged layers completely. CMP techniques have also been used for other materials under certain modifications based on the conditions used for Si wafers. For SiC wafers, a lot of micro scratches and considerable subsurface damage, which deteriorate surface integrity, are inevitably generated on their surface, due to the physical hardness and chemical inertness of SiC [4,5]. Therefore, it is difficult to obtain sufficient surface integrity for the growth of epitaxial films on commercial SiC wafers.

In order to obtain ideal SiC surfaces, CMP-alternative and novel surface-figuring techniques are desired. Commercial SiC wafers contain many scratches with an average depth of a few nm even after CMP, as shown in the typical atomic force microscope (AFM) image in Fig. 1(a). Recently, we have developed a catalyst-referred etching (CARE) method as a novel damage-free technique for the planarization of SiC substrates [6], which was used to obtain an atomically flat SiC surface on an entire 2-inch wafer [7–10]. Fig. 1(b) shows a typical AFM image of a CARE-treated SiC(0001) on-axis surface without subsequent annealing in UHV. The AFM image shows a step-terrace structure without inhomogeneous structures such as scratches.

SiC has been focused on for its use in next-generation semiconductor power devices because of its excellent properties, for instance, wide band-gap energy, high thermal conductivity, high saturated electron-drift velocities, and high breakdown electric fields. It is well known that graphene films can be grown on SiC surfaces [11–21].
Graphene has attracted considerable attention and interest owing to its unconventional two-dimensional electron gas and electron transport properties [11,21–23]. Epitaxial graphene layers can be grown on SiC(0001) surfaces by solid-state graphitization during the sublimation of decomposed Si atoms, where the number of graphene layers is controlled by the annealing temperature and duration under ultrahigh vacuum (UHV) condition [11–20] or atmosphere condition [21]. A technique for forming monolayer graphene on SiC(0001) has been searched, and the structure and physical properties of graphene layers have been actively studied.

One of the general preparation methods to obtain graphene under UHV condition is the Si-flux method: the thermal etching of SiC with the deposition of Si atoms to reduce Si sublimation at areas with damage due to surface polishing [11–17,19,20]. Recently, Emtsev et al. proposed the atmospheric-pressure graphitization of SiC and succeeded in forming high-quality graphene [21]; the ex-situ graphitization of SiC(0001) without Si flux but in an argon atmosphere produces monolayer graphene films with considerably higher quality and larger domain size compared with the graphene films prepared by vacuum annealing. However, the growth of a specific number of large well-ordered graphene layers on SiC(0001) in UHV was not achieved in previous studies. At present, graphene layers grown on SiC(0001) surfaces in UHV have a domain size of at most 100 nm, and the graphene domains exist on only part of the substrate rather than the entire substrate [11–17,19,20,24,25], because the decomposition of SiC is not a self-limiting process and, as a result, regions of different film thicknesses coexist. Roughness on SiC surfaces, which increases as a result of scratches [26], defects [27], inhomogeneity [13,14], and so on reduces the quality of graphene films. Therefore, we expect that graphene layer of excellent quality can be formed upon an atomically flat and defect-free SiC surface even by vacuum annealing.

In this paper, we report the formation and quality of graphene layers on CARE-SiC and wet-treated CMP-SiC surfaces subsequently annealed in UHV. We found that the graphene layers grown on CARE-SiC was markedly high, while the quality of the graphene on wet CMP-SiC was considerably degraded. We also found that the Si desorption started at almost the same temperature for both CARE-SiC and wet CMP-SiC surfaces, however, the graphitization temperature for wet CMP-SiC surfaces was approximately 200 °C higher than that for CARE-SiC. On graphitized CARE-SiC surfaces, step terraces of ~500 nm width exhibited erosion at step edges and hexagonal pits on terraces, while step terraces of ~300 nm width exhibited hardly any erosion and pit. Here, we emphasize that CARE should become one of widely-used surface-figuring techniques in the wafer manufacturing process, as CMP, in future.

2. Experimental

Two-inch wafers of commercial CMP 4H-SiC(0001) with a 0°-off (± 0.5°, on-axis oriented) Si face (N-doped, 0.02 Ω · cm) were used. The wafers were planarized by the CARE technique [6,8–10], where a Pt plate was used as a catalyst in HF solutions. Each SiC substrate was dipped in a sulfuric peroxide mixture (SPM) solution [28] for 10 min, dipped in HF for 10 min, planarized in HF for 5–10 h, dipped in SPM solution for 10 min, dipped in aqua regia for 20 min, and dipped in HF for 10 min. After every process, the substrate was rinsed with flowing
ultrapurue water [29]. To confirm the advantageous effect of surface planarization on the graphene quality, we prepared a reference CMP-SiC sample without CARE planarization; another 2-inch wafer was kept in HF for 6 h instead of being subjected to the planarization process but was subjected to all the other processes. Here, we denote samples treated with and without the CARE planarization process as CARE-SiC and wet-treated CMP-SiC, respectively. After the wet procedures, samples of 2 × 7 mm² area were cut from the wafers and introduced into a UHV chamber with a base pressure of less than 1 × 10⁻⁶ Pa. [J30–32]. The graphitization of SiC(0001) was performed in UHV by annealing; the SiC samples were degassed at ~300 °C for 3–5 h and annealed at 900–1300 °C for 5 s–10 min at a pressure below ∼2 × 10⁻⁷ Pa. In-situ low-energy electron diffraction (LEED), in-situ reflection high-energy electron diffraction (RHEED), in-situ scanning tunneling microscopy (STM), ex-situ X-ray photoelectron spectroscopy (XPS), ex-situ Raman spectroscopy (HORIBA, LabRAM HR-800), ex-situ Temperature Programmed Desorption (TPD), and ex-situ AFM (Digital Instruments, D3110) were used for the surface characterization. All experiments except the TPD were performed at room temperature (RT), and all experiments except the RHEED and Raman spectroscopy were performed in a class 1 clean room. AFM and Raman spectroscopy were performed under atmosphere pressure. Almost all the obtained STM images were topographic except Fig. 5(a), which is a current image. All the obtained AFM images were in non contact mode. Raman spectroscopy was performed using an excitation laser with a photon energy of 2.37 eV.

3. Results and discussions

3.1. Surface structures of CARE-SiC

Fig. 1 shows typical AFM images, and LEED, and RHEED patterns of SiC(0001) 0°-off surfaces of as-received commercial (CMP), CARE-treated, and wet-treated CMP wafers. The AFM image of the as-received commercial wafer [Fig. 1(a)] showed many scratches on the surface with an average depth of a few nm, as mentioned before. The LEED and RHEED patterns (the insets in Fig. 1(a) and (d), respectively) of the as-received SiC exhibited diffused 1 × 1 patterns with a high background, arising from a native oxide layer of 0.2–0.4 nm thickness [33], implying poor surface crystallinity after surface-figure treatment (for example, CMP, etc.) [34]. For the CARE-SiC(0001) surfaces without subsequent annealing in UHV [Fig. 1(b), (e), and (h)], the AFM image showed a step-terrace structure with a terrace width of ~300–500 nm, and the LEED and RHEED patterns exhibited sharp and intense 1 × 1 spots. The spot profiles of the RHEED patterns (Fig. 1(g)–(i)) show obvious differences in spot intensities among the differently treated SiC surfaces [35]. The RHEED pattern in Fig. 1(e) with sharp and intense Kikuchi lines demonstrates that the CARE-SiC surface is ideally flat. This surface has an inert property due to surface termination [33], that is, surface oxidation does not progress even in air. The CARE technique is highly reproducible, which makes it possible to repeatedly obtain atomically flat terraces with uniform and straight steps on the surfaces [6,8–10]. On the other hand, for the wet CMP-SiC surface [Fig. 1(c), (f), and (i)], LEED and RHEED patterns exhibited sharper and more intense 1 × 1 spots than those for the as-received surface [Fig. 1(a), (d), and (g)] but more diffuse and weaker spots than those for the CARE surface [Fig. 1(b), (e), and (h)], while the AFM image showed similar features to those observed for the as-received SiC. This suggests that surface damage including scratches was not removed, although the native oxide layer (SiO₂) was dissolved and the surface was terminated by dipping in HF solution [36].

After the CARE treatment, an entire wafer surface has a terrace-step structure without scratches [6–10,37]. Fig. 2 shows typical AFM images of a CARE-treated SiC(0001) 0°-off wafer. All AFM images show terrace-step structures without scratches, and we can see the different step densities depending on the area of the wafer. This is caused by the poor slicing accuracy within the error range (±0.5°) in the manufacturing process [10,34,37]. In this case, the average terrace width was ~140 nm, corresponding to the average off-angle ~0.10°. It was confirmed that the CARE technique can lead to atomically flat terrace-step surfaces independent of the off-angle and the quality of the initial wafer [8,10,37]. In the CARE process, the surface conditions of the initial SiC wafer, such as surface crystallinity, morphology, the thickness of the damaged layer, scratches, carrier densities, and so on, do not affect the final surface condition, but affect the etching speed and total etched volume of SiC.

Usually in order to prepare SiC flat surfaces, H₂ annealing treatment (H₂ etching), which can produce the terrace-step SiC surfaces without scratches, has been used for CMP treated SiC surfaces [38–40]. The H₂ etching is an etching without arbitrary reference planes, which is different from CMP or CARE figuring method. The reaction (etching) area and depth are not self-limited and the etching controllability is lower than CARE method. Indeed, the SiC surfaces prepared by the H₂ etching contained facet boundaries at the step edges [38], tilted (not straight) steps [40], and remained (screw) dislocations [40]. Anisotropic step bunching is also induced by H₂ etching [40]. These factors which decline the total surface smoothness on SiC surfaces, were not observed on the CARE surface [7,8,10,37]. We consider CARE treatment as a final figuring technique alternative to CMP treatment, and emphasize that the substrate surfaces with CARE treatment require no more complex surface treatment, such as H₂ etching and Si flux, to obtain clean and flat SiC surfaces and graphene films, as shown in a following section.

As mentioned before, damaged layers and polishing haze exist on commercial wafer surfaces resulting from the abrasion during the figuring processes. The CARE reaction automatically stops after removing a certain amount (about 50–100 nm) of the surface layers [7,8]. Since the CARE reaction is truly a chemical and autonomous reaction, CARE treatment can remove damaged layers completely, resulting in perfect surfaces. Harathe et al. studied the crystallographic properties of 4H-SiC(0001) surfaces before/after CARE treatment using cross-section transmission electron microscopy (TEM) [7]. Their TEM images show disordered arrangements due to the damaged layers in the surface region of an as-received commercial (CMP) sample. On a CARE-SiC sample, however, such disordered arrangements were removed and well-ordered arrangements remained. Although the mechanism of the CARE reaction is not clear yet, the CARE technique can reproduce damage-free terrace-step surface structures. Moreover, this method has generally; it has been successfully applied to not only SiC but also GaN surfaces [41–43].

3.2. Graphene layers grown on SiC surfaces

Fig. 3(a) shows a typical LEED pattern for a CARE-SiC(0001) surface annealed at 900 °C for 5 min in UHV without Si flux, which clearly displays a (6 √3 × 6 √3)R30° (hereafter 6 √3) reconstruction pattern. The 6 √3 reconstruction has been pointed out to be a prerequisite but not a sufficient condition for the formation of a uniform graphene film [12]. Considering the periodicities of both graphite and SiC, 13 times the graphite lattice constant (a graphite = 0.246 nm) coincides with 6 √3 times the SiC lattice constant (a SiC = 0.308 nm) ≈ 3.20 nm. The initial stage of graphitization on SiC surface is the 6 √3 reconstruction and graphene layers are grown on the buffer layer at higher annealing temperatures and/or longer annealing times, keeping a 6 √3 periodicity. It is known that the specific properties of graphene develop from only the first graphene layer on the 6 √3 buffer layer [44]. We found that the 6 √3 sample in Fig. 3 is monolayer graphene by analyzing the results of LEED, XPS (not shown), and Raman spectroscopy, as discussed below.

The surface structure on the CARE-SiC(0001) changed from 1 × 1 to √3 × √3 with increasing annealing temperature, and the 6 √3
structure appeared at 900 °C [33]. On non-CARE-SiC(0001) surfaces prepared using Si flux, 3 × 3, √3 × √3, 6 × 6, or 6√3 × 6√3 structures appear depending on the preparation conditions [11–21,25]. The LEED pattern of the 900 °C-annealed CARE-SiC (Fig. 3(a)) showed only the 6√3 reconstruction without the other phases. The pure 6√3 phase was confirmed by the chemical shifts and the areal ratio of Si 2p and C 1s in XPS spectra for the 1×1, √3 × √3, and 6√3 × 6√3 phases [45]. The RHEED pattern also showed clear 6√3 reconstruction (Fig. 4(a)). An STM image of the annealed CARE-SiC(0001) surface (Fig. 3(c)) showed a rhombic unit with a length of ~1.8 nm (note that the distortion observed here is due to thermal drift). Although the atomic crystallographic structure was not completely resolved, the periodicity of ~1.8 nm can be attributed to the 6×6 reconstruction. In STM, the 6√3 × 6√3 structure is often imaged with an apparent 6×6 periodicity, particularly at a high tunneling bias [12], as shown in Fig. 3(c) and (e). Depending on the bias voltage, this ‘quasi’-6×6 corrugation appears as rings in a honeycomb pattern (Fig. 3(c)) and as a hillock structure (Fig. 3(e)). So far, at least four types of 6√3 structure, the buffer layer underneath mono-, bi-, and tri-layer graphene, and the buffer layer without the graphene layer [12], have been confirmed on SiC(0001) surfaces through the graphitization. Recently, Starke and Riedl estimated the thickness of graphene layers on SiC from dispersion curves obtained by angular-resolved photoelectron spectroscopy, and suggested a strong correlation between the thickness and the intensities of some LEED spots [12]. This suggestion enables us to determine the number of layers approximately by comparing the relative intensity of the “graphite spot” with that of the satellite spots in the 6√3 pattern at 126 eV, as shown in Fig. 3(b). From the LEED fingerprints in Ref. [12], we estimated that the graphene in Fig. 3 had roughly monolayer thickness [30].

This method of thickness estimation based on the LEED pattern is easy to use under in-situ conditions; however, it is not a quantitative method. Therefore, we also confirmed the monolayer thickness of graphene from XPS [30] and Raman spectroscopy for the same CARE-SiC sample annealed at 900 °C for 5 min. The chemical shifts in the C 1s core-level spectra [30] showed that the surface region includes three inequivalent types of carbon atoms; those in the graphene layer (graphic peak), those in the underneath 6√3 buffer layer (buffer peak), and those in the SiC substrate (bulk peak) [12,15]. We estimated the overlayer thickness from the intensity ratio of the surface and bulk components [15,30] to be 0.33 ± 0.06 nm, assuming a simple layer attenuation model. This value is close to the interlayer distance in graphite (0.335 nm). The graphene thickness estimated from the results of XPS is consistent with the thickness determined from the LEED intensity profile. We found that the thickness of graphene layers grown on CARE-SiC can be easily controlled by tuning the annealing temperature and duration. For further-annealed samples at 1000 °C for 2 min, we also estimated a bilayer graphene film by XPS and LEED [30]. Moreover, these methods also showed the formation of monolayer graphene on 8°-off CARE-SiC surfaces by annealing at 900 °C for 2 min [30].

Fig. 4(b) shows the Raman spectra of D, G, and G′ bands [46–55] for the 6√3 sample of Fig. 3. The G band around 1580 cm−1 (1598 cm−1 in Fig. 4(b)) is first-order Raman scattering and the Raman active mode of graphene or graphite, corresponding to the doubly degenerate phonon mode at the Brillouin zone (BZ) center [46]. The graphene film thickness [53,55] can be estimated by the Raman shifts of the G band. The G′ band around 2700 cm−1 (2691 cm−1 in Fig. 4(b)) and the D band around 1350 cm−1 (1368 cm−1 in Fig. 4(b)) correspond to the double resonance of the incident laser excitation energy around K points in BZ; the G’ band is allowed in graphene without any kind of
disorder or defects [47], and the D band appears due to some structural disorder in a graphene sample [48,49]. We can see the intense and sharp G band appearing at 1598 cm$^{-1}$. Since the SiC bulk contributed peak appears at around 1570 cm$^{-1}$ [55], we consider that the tail of the peak D around 1570 cm$^{-1}$ would correspond to the SiC elements, and the G peak could be fitted by single-Lorentzian with a full width at half maximum (FWHM) of 18 cm$^{-1}$. The G band was observed at 1586 cm$^{-1}$ for the exfoliated monolayer graphene [53], at 1608 cm$^{-1}$ for a 1.5 monolayer graphene film grown on a SiC(0001) surface [55], and at 1578 cm$^{-1}$ for highly oriented pyrolytic graphite (HOPG) [55]. Röhrl et al. [55] reported that the scattered Raman peak shift of the G and G$'$ bands happened even among samples with the same graphene thickness. They suggested that strains in film samples fabricated by different methods mainly cause the Raman shift. The observed G peak frequency is consistent with that in previous reports on monolayer graphene on SiC substrates within the expected range of the shift due to the strain.

The identification of the number of graphene layers by Raman spectroscopy is also established using the G$'$ bands [50,52]. For monolayer graphene, a symmetric G$'$ band is observed and fitted by one Lorentzian. For bi-, tri-, and quad-layer graphenes, and HOPG samples, the G$'$ peaks become broader and asymmetric, and are fitted

**Fig. 3.** (a) A typical LEED pattern at 135 eV displaying the (6√3×6√3)R30° reconstruction for a CARE-SiC(0001) surface after annealing at 900 °C for 5 min in UHV. First-order fundamental diffraction spots from the SiC(0001) substrate and graphene are indicated by yellow and green circles, respectively. The satellite spots around the fundamental spot of the graphene at 126 eV are shown in (b), which enable us to determine the graphene-layer thickness [12]. (c)-(e) Topographic STM images of graphene on the same CARE-SiC surface; the sample bias voltage is +2.8 V and the tunneling current is 0.5 nA. (c) Typical (6×6) (cyan) rhombic unit with ~1.8 nm unit length but hardly any atomic-scale protrusions due to the poor tip condition in this case. (d) Atomically flat and homogeneous surface with wide flat terraces with a width of over 250 nm, an arm chair (ac) edge at the upper left, and a zig-zag (zz) edge at the upper right. (e) A magnified image of (d) with zig-zag edge. Note that the curved feature of the arm chair step in the upper part of (d) is caused by thermal or piezotube-response drift.

**Fig. 4.** (a) Typical RHEED pattern for the (6√3×6√3)R30° reconstruction for a CARE-SiC(0001) surface after annealing at 900 °C for 5 min in UHV. The incident 15 keV beam was in the [1100] direction. (b) Raman spectrum with 2.37 eV laser excitation for the CARE-SiC in Fig. 3. The spectrum shows a G band at ~1598 cm$^{-1}$ and a G$'$ band at ~2691 cm$^{-1}$. The G and G$'$ peaks were almost symmetric and described by one Lorentzian (red lines) with an FWHM of 18 cm$^{-1}$ and 45 cm$^{-1}$, respectively. The small D band is shown around 1370 cm$^{-1}$. 

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by four, six, three, and two Lorentzians, respectively. The observed G’ band (Fig. 4(b)) is almost symmetric and fitted by one Lorentzian (red line) at 2691 cm$^{-1}$ with an FWHM of 45 cm$^{-1}$; this is a characteristic feature of monolayer graphene. Therefore, we can conclude that the observed 6×3 sample was almost monolayer graphene, which is consistent with the LEED and XPS results as mentioned before. Note that there is still a possibility that bi- and tri-layer graphene partially exist in the graphene, since LEED, XPS, and Raman results showed the average information, and no microscopically resolved measurements have been conducted in this study.

We can also see a small D band (1368 cm$^{-1}$) at about half the frequency of the G’ band. In general, a D band appears in samples with structural disorders that break the translational symmetry (e.g., impurities, edges, finite size effects, etc.) [48,49,51,52]. The intensity of the D band in CARE-SiC is quite smaller than that in the previous samples [25,51,52], implying the high crystallinity of graphene on the CARE-SiC surfaces, probably because the graphitization temperature for the CARE-SiC samples (900 °C) was considerably lower than temperatures for non-CARE-SiC surfaces (1100–2700 °C) [18,25].

From the Raman spectrum (Fig. 4(b)), Refs. [25] and [51] suggested that the estimation of the grain size, $L_g$ of “nanographite” films using the $I_D/I_G$ ratio in the empirical formulas. Here, $I_D$ and $I_G$ are the integral intensities of the D and G bands, respectively. The obtained values of $I_D/I_G$ were 0.10–0.11 for the monolayer graphene, corresponding to the in-plane domain size of ~160–200 nm and ~390–440 nm, by the formulas in Refs. [25] and [51], respectively. Here, we should notice the width of the G band peak; less quality graphene has wider width due to stress by imperfection, multiple layers, and so on. In particular, the multiple layers leading to multiple peaks, similar to the G’ band, would result in the increase of $I_D$ extraneously. The observed G band (Fig. 4(b)), indeed, is quite narrower (18 cm$^{-1}$ in FWHM) than those in Fig. 2 in Ref. [25] and Fig. 3 in Ref. [51]. Moreover, the observed D band is small as noise level, which indicates a high-quality graphene. Therefore, we doubt the generality of the proposed empirical formulas for $L_g$ at present, though only one laser-energy was used in our study.

The monolayer graphene formed on CARE-SiC was remarkably uniform and consisted of wide terraces and steps. Fig. 3(d) shows a wide-scale STM image of the 6×3 phase on the CARE-SiC of Fig. 3(a)–(c). The STM image exhibits a wide uniform surface; the ordered 6×3 terrace has an area of at least 250×250 nm$^2$, and there are no defects or inhomogeneous structures except for dust from the STM tip. Moreover, the STM images showed that the 6×3 protrusion arrangement was maintained in entire terraces (≥250 nm in size), that is, no domain boundaries appeared on the terraces. The step in the upper left of Fig. 3(d) is straight but partially rounded near the bottom. This straight edge is parallel to [T20]$_{SiC}$, which corresponds to an arm chair (ac) edge [54]. Fig. 3(e) shows a typical STM image including a zig-zag (zz) step edge, where the straight edge is parallel to [T10]$_{SiC}$. The step heights in Fig. 3(d) and (e) were ~0.25 nm, which corresponds to the height of a bilayer of 4H-SiC(0001) (0.251 nm).

Fig. 5(a) and (b) shows STM images around the domain boundaries for the 6×3 phase on the same CARE-SiC. We can confirm that these are domain boundaries but not steps from Fig. 5(c), which shows that the terrace height is the same on both sides of each boundary. We did not observe a domain enclosed by boundaries or steps in the area of 330×330 nm$^2$, that is the maximum scan area in our STM system, at over ten different positions on the surface. This indicates that the domain size of the monolayer graphene on CARE-SiC exceeded 300 nm. The diffraction spot profiles in LEED and RHEED supported the estimation of the domain size roughly, though the fine incident-beam size prevented the accurate estimation. The sharper LEED, RHEED spots and Raman peaks, however, indicate that the CARE-SiC can be produced the high-quality graphene films.

AFM images also showed a uniform graphene layer grown on CARE-SiC. Moreover, the images revealed the considerable erosion of
regions for two monolayer graphene samples (900 °C for 5 min) by AFM. Roughly, two types of the regions could be classified. Majority was narrow terrace (11 regions) and minority was wide terrace (6 regions), as follows. The graphene surfaces in Fig. 6(a) and (b) have average terrace widths of ~300 nm and ~500 nm, corresponding to local off-angles of 0.05° and 0.03°, respectively, both of which are the direction of [1010]_{SiC}. Although a uniform monolayer graphene formed on both narrow (Fig. 6(a)) and wide (Fig. 6(b)) terraces, different features of the graphene can be observed depending on the terrace width. Fig. 6(a) shows that most of the steps in the narrow terrace area have zig-zag edges along the [1010]_{SiC} direction, while the minority of steps have arm chair edges along the [1210]_{SiC} directions. The inset of Fig. 6(a) displays few small pits (defects) in a 10×10 μm² region on the narrow (~300 nm) terrace. The average step height was ~0.25 nm, which is consistent with the STM results within the margin of error. Since the STM results (Figs. 3 and 5) indicate that the 6√3 domain covers entire terraces without domain boundaries over an area of ~300×300 nm², the wide-scan AFM image in Fig. 6(a) should also display the growth of an atomically flat monolayer graphene over a domain size of ~300 nm with few defects. On the other hand, on the wide (~500 nm) terrace in Fig. 6(b), we can see dominant arm chair edge and roundish (finger-like) step edges and also many characteristic hexagonal pits, the edge directions of which are those of the arm chair edges. We found that the depths of the pits had discrete values, ~0.50 nm, ~0.75 nm, and ~1.00 nm, corresponding to the heights of two, three, and four bilayers of 4H-SiC(0001), respectively, within the margin of error. Similar hexagonal pits on the terraces of a graphene layer on SiC surfaces have been reported [57,58]; Bolten et al. suggested that the creation of pits supplies the carbon atoms to form graphene on SiC [57].

The quality of the graphene layers on wet-treated CMP-SiC surfaces was considerably lower than that of layers on CARE-SiC surfaces. Annealing temperatures above 1100 °C were required to obtain 6√3 LEED patterns on wet-CMP-SiC surfaces. Fig. 7(a) and (b) show a typical LEED pattern and an AFM image of graphene on a wet-CMP-SiC surface after annealing at 1100 °C for 5 min, respectively. Weak and diffused 6√3 spots with a higher background than that in the case of a CARE-SiC surface, appeared in the LEED pattern, for instance, the satellite spots in the green square in Fig. 7(a) are much weaker and diffused than those on CARE-SiC. The AFM image shows an inhomogeneous surface with many pits. Some pits have characteristic hexagonal shapes.
weaker than those in Fig. 3(a). The corresponding AFM image shows a nonuniform layer with many hexagonal pits (Fig. 7(b) inset); step and terrace structures are hardly seen. These results imply that it is difficult to grow well-ordered graphene with a specific number of layers on wet CMP-SiC surfaces, in contrast to growth on CARE-SiC surfaces. Though the formation mechanism of graphene on SiC surfaces is still unclear, the processes of SiC decomposition, Si sublimation, C diffusion, and graphene formation have been suggested [13,18,24,57,59,62]. To obtain a monolayer graphene on SiC surfaces, diffusion, and graphene formation have been suggested surfaces. The surface roughing factors, such as, scratches, dislocations and so on, induce much excess Si desorption from SiC, and would prevent the nucleation growth of graphene, resulting in the facet boundaries at step edges and that from the defects on the terraces. On the wide terraces, the sufficient size of the pits would be grown before the graphitization from the step edges. More stable arm chair step edges would be formed by the release of many carbon atoms from the edges before the graphitization of the terraces. In contrast, on the narrow terraces, sufficient number of carbon atoms should be supplied before the terrace graphitization. The surface roughing factors, such as, scratches, dislocations and so on, induce much excess Si desorption from SiC, and would prevent the nucleation growth of graphene, resulting in the facet boundaries at step edges [38], tilted (not straight) steps [40], and remained (screw) dislocations, anisotropic step and so on. So far, Si flux have been required for the graphitization process in UHV condition on the SiC surfaces prepared by H2 etching [11–17,19,20]; the role of Si flux is to compensate for the excess desorbed Si. However, the Si flux is not needed on CARE-SiC even for the graphene prepared by vacuum annealing. We consider that substrate uniformity and flatness is one of the key factors in achieving uniform, wide, and thickness-controlled graphene layers on SiC substrates.

4. Conclusion

Damage-free and atomically flat 4H-SiC(0001) surfaces with terrace-step structures were prepared by a novel planarization method, catalyst-referred etching. We demonstrated the formation of graphene films on ultraprecision-figured 4H-SiC(0001) surfaces (CARE-SiC); almost monolayer graphene films were successfully formed with wide and atomically flat terraces and few defects on entire CARE-treated 4H-SiC(0001) surfaces by annealing in UHV. We could control the number of graphene layers on CARE-SiC by changing the annealing temperature and duration. The graphene on CARE-SiC surfaces displayed clear step and terrace structures with an average domain size of over 300 nm in almost entire area, while that on non-CARE-SiC (wet CMP-SiC) surfaces hardly showed the structures. In the graphene on CARE-SiC, the narrow terraces of ~300 nm width mainly had zig-zag step edges and few pits, while the wide terraces of ~500 nm had a significant number of arm chair step edges and many hexagonal pits. We emphasize that the surface uniformity and flatness
of the SiC substrate, in other words, the perfection of the SiC surface, strongly affect the graphene quality.

Wide and flat graphene domains with few defects are expected to be important and useful for studies on the fundamental properties and applications of graphene films. For instance, a domain wider than the electron coherent length in LEED (30 nm) makes detailed structure analyses possible. Such a domain can reduce the uncertainty of momentum in photoelectron spectroscopy. In conductivity measurements, it can reduce extrinsic scattering factors. Of course, wide and high-quality graphene is required for applications such as metallic transistors. We can fabricate a higher-quality monolayer graphene on CARE-SiC surfaces in UHV by the simple method of annealing without any Si flux. This study demonstrates one of the advantages of ultraprecision-figured 4H-SiC(0001) surfaces. The CARE technique can remove the damaged layers on substrate surfaces independent of the initial surface conditions. We consider that damage-free samples can be used to produce higher-quality epitaxial grown films, which have excellent properties. We believe that the CARE technique will become an indispensable basic technique to support future nano-scale technologies.

Acknowledgements

This study was partly supported by a grant of the Global COE Program, “Center of Excellence for Atomically Controlled Fabrication Technology” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, the Industrial Technology Research Grant Program in 2005 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan, and Kyoto-Advanced Nanotechnology Network under sponsorship from MEXT, Japan. One of the authors (ANH) was supported in part by Special Coordination Funds for Promoting Science and Technology from MEXT for the Osaka University Program for the Support of Networking among Present and Future Women Researchers.

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