Structure and electronic properties of closed-ring defects in epitaxial graphene

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Abstract
A number of past studies have focused on point and line defects in graphene epitaxially grown on SiC substrates. However, few studies have investigated closed-ring defects formed within grain boundary loops. The present study addresses this issue by applying low-temperature scanning tunneling microscopy/spectroscopy to investigate the atomic structures of closed-ring defects in graphene epitaxially grown on 4H-SiC, and to evaluate their effects on the electron state density. The results indicate that the orientations of the graphene lattice inside and outside of grain boundary loop structures are rotated uniformly by an angle of 30° relative to each other, suggesting that closed-ring defects are highly ordered and are mainly composed of clusters of pentagon-heptagon carbon rings and highly ordered pentagon-heptagon chains. In addition, the spectroscopy results reveal for the first time that the density of electron states inside a closed-ring defect is strongly localized and position-dependent. Moreover, these closed-ring defects can eliminate intervalley scattering while maintaining intravalley scattering. These findings are not only helpful for contributing to a deeper understanding of the effects of closed-ring defects in graphene, but also present a potentially useful valley-filtering mechanism for charge carriers that can be applied to the practical development of all-electric valley-based devices.

1. Introduction
Graphene is a two-dimensional material with extensive application potential due to its excellent energy band structure and ultra-high charge carrier mobility [1, 2]. Commercial applications of graphene depend on the growth of large-area highly crystalline graphene layers with excellent properties. These are typically grown by chemical vapor deposition (CVD) [3] or epitaxially grown on single-crystal SiC by high-vacuum graphitization [4, 5]. However, these graphene layers inevitably include various defects that affect their conductivity [6] and mechanical strength [7]. Grain boundary defects, which are the most common defects in graphene, disrupt the periodicity of the graphene lattice, and thereby detract from its charge carrier transmission performance. The existence of grain boundaries in graphite was first observed by Albrecht et al [8] in 1988 using scanning tunneling microscopy (STM). Subsequently, typically grown graphene was found to include both ordered and disordered grain boundary defects [9–11]. Huang et al [9] observed by means of transmission electron microscopy (TEM) that some grain boundary defects in graphene are aperiodic. The effects of these defects on the density of states (DOS) of electrons in graphene have been studied systematically using scanning tunneling spectroscopy (STS), and the analyses have demonstrated that disordered grain boundary defects act as scattering centers, leading to decreased conductivity [12], whereas ordered defects can enhance the DOS of electrons near the Dirac points of...
the electronic band structure [13]. Therefore, disordered grain boundaries should be avoided as much as possible during the growth of graphene, while the deliberate introduction of ordered grain boundaries can be applied effectively for tuning the electronic band structure of graphene. Tison et al [14] found that graphene epitaxially grown on SiC hosts a high proportion of ordered grain boundary defects. These defects were associated with highly ordered grain boundaries comprising continuous chains of edge-sharing alternating pentagonal and heptagonal carbon ring defects, which have been shown to represent the lowest formation energy structural motif, and therefore the most stable grain boundary structure in graphene [15, 16]. The individual pentagon-heptagon units within these chains are commonly denoted as pentagon-heptagon disinclination dipoles. It is also well-demonstrated that pentagon-heptagon disinclination dipoles can be rotated in sequence to form closed loops, which are commonly denoted as pentagon-heptagon grain boundary loops. However, while a number of past studies have focused on the point and line defects formed by pentagon-heptagon disinclination dipoles [17–24], few studies have investigated the closed-ring defects formed by pentagon-heptagon grain boundary loops. We also note that, while Guisinger et al [25] first reported on closed-ring defects in SiC-grown epitaxial graphene, their effects on charge carrier transport in graphene have not been investigated.

The present study addresses this issue by applying low-temperature STM/STS to investigate the atomic structures of closed-ring defects in graphene grown on the (0001) surfaces of silicon-terminated 4H-SiC wafers by the thermal desorption of Si atoms from the wafer surfaces at high temperature [26], and the effects of these defects on the electron state density of graphene are analyzed in detail. Different types of defects, including flower defects and closed-ring defects, are observed directly by STM. The DOS of electrons inside and outside of closed-ring defects, as well as on the grain boundary are evaluated by STS. The results show that ordered closed-ring defects have a significant effect on the DOS of electrons inside the grain boundary loop, and that this internal DOS exhibits obvious localization and position-dependence. Moreover, the results indicate that closed-ring defects can eliminate the scattering of charge carriers between the valleys of the graphene energy band structure (i.e., intervalley scattering), while maintaining scattering within the valleys (i.e., intravalley scattering). These findings are helpful for contributing to a deeper understanding of the effects of closed-ring defects on the charge carrier transport characteristics of graphene, and provides guidance for the practical development of high-performance graphene-based devices.

2. Experimental

The SiC wafers were first washed with alcohol to remove grease and other contaminants from the surface prior to transferring the wafers into a vacuum chamber, and evacuating the chamber to a pressure of $1 \times 10^{-10}$ Torr. The wafers were then heated to a temperature of 500 °C by a direct-current heating unit and held at that temperature for 10 h for degassing. The wafers were subjected to a final high-temperature degassing stage by heating to 900 °C and holding for 15 min and then heating to 1300 °C and holding for 15 min to ensure the desorption of all Si atoms from the surface, yielding graphene layers on the surface of the SiC wafers. Other researchers have also obtained graphene films under degassing conditions of 1300 °C to 2000 °C [27, 28]. Finally, the wafers were slowly annealed at decreasing temperature down to room temperature over a period of 4 h. The samples were transferred to the STM sample-stage and cooled to liquid nitrogen temperature (77 K) under ultra-high vacuum conditions ($5 \times 10^{-10}$ Torr). Subsequently, STM topography images of the graphene surfaces were captured in constant-current mode. The STM images were analyzed using WSxM software [29]. In addition, tunneling conductance (dI/dV) spectra were collected from the graphene surfaces via STS using the standard lock-in technique with a modulation frequency $f = 973$ Hz. The obtained samples were also subjected to Raman spectroscopy using a Renishaw inVia confocal Raman microscope with an excitation wavelength of 532 nm, laser power of 2.5 mW, and an acquisition time of 10 s.

3. Results and discussion

Figure 1 presents STM topographic images of various types of defects observed on representative surfaces of graphene, which are marked by the arrows in the images. These defects vary from a single flower defect marked by the yellow arrow in figure 1(a) to a composite flower defect marked by the blue arrow in figure 1(a), as well as an irregularly-shaped closed-ring defect marked by the pink arrow in figure 1(b). We also note that $(\sqrt{3} \times \sqrt{3})$ R30° superstructures are clearly observed in the range of about 1 nm around the three types of defects. Such superstructures are formed by charge carrier scattering and interference at the grain boundaries, and the short range of the superstructures around the defects indicates that these superstructures are caused by short-range scattering [22]. Figure 1(c) presents a typical graphene morphology obtained by STM. The structure shown here differs entirely from the $(6, \sqrt{3} \times 6, \sqrt{3})$ R30° structure of the buffer layer. Accordingly, we can conclude that this film is graphene [30]. This is clarified in figure 1(d), where the black and green curves are the
The raw Raman spectra of the bare SiC substrate and graphene grown on SiC, respectively. The spectra are shifted vertically for clarity. The inset of the figure presents the Raman spectrum of graphene after subtracting the SiC background, and the red line is the fitted curve.

Figure 1. (a), (b) Scanning tunneling microscopy (STM) topographic images of various types of defects observed on the surface of graphene epitaxially grown on semi-insulating 4H-SiC (0001) wafers. (c) A partially enlarged view of (a). The scanning parameters employed were a sample bias $V_s = 650$ mV and a tunneling current $I_t = 40$ pA. All STM/STS analyses were conducted at a temperature of $T = 77$ K. (d) Raman spectra of the bare SiC substrate (black) and graphene grown on SiC (green). The spectra are shifted vertically for clarity. The inset presents the Raman spectrum of graphene after subtracting the SiC background, and the red line is the fitted curve.
was conducted for only 15 min at 1300 °C in the present work, while this stage was conducted for 120 min in the work of Cui et al. Nonetheless, composite flower defects were observed in the present study as well. This indicates that the duration of high-temperature degassing may have no effect on the formation of these composite defects, but may be related solely to the lower formation energy of these defects than single flower defects.

The sizes of irregularly-shaped closed-ring defects, like that marked by the pink arrow in figure 1(b), ranged from 2 to 10 nm, and these were observed to be surrounded by prevalent superstructures. A relatively bright spot can be observed on the grain boundary of the closed-ring defect shown in figure 1(b), which is of the same size as that of the conjoined-twin flower defect marked in figure 1(a). This suggests that the observed closed-ring defects may be the result of merging between single or incomplete flower defects. These defects were still observed when the growth temperature was increased to 1600 °C. However, the samples could not be heated in excess of 1600 °C due to equipment limitations, so the presence of these defects at higher temperatures could not be verified.

The effects of these flower defects on the electronic structure of graphene was investigated by evaluating the DOS of electrons in and around various flower defects on the graphene surface by STS and tunneling conductance mapping. Figure 2(a) presents an STM topographic image of five isolated flower defects, around which obvious \((\sqrt{3} \times \sqrt{3}) R30^\circ\) superstructures are also observed. Figure 2(b) presents \(dI/dV\) spectra acquired for both a defect-free region and at the center of a single flower defect, which are respectively marked as positions A and B in the atomic resolution image presented in the inset of figure 2(b). The global minima of both spectra appear at a negative bias slightly less than 0 V rather than at precisely 0 V, which is consistent with previously reported results [26, 30]. In addition, the second-lowest energy points, which correspond to the Dirac points of the graphene sample, appear at a bias voltage of \(-0.3\) V (i.e., the Dirac points are 0.3 eV below the Fermi level). This, in conjunction with the fact that the Dirac points of graphene approach the Fermi energy with an increasing number of epitaxial layers, indicates that the graphene sample is an n-type bilayer [38]. This is further

![Figure 2](image-url)
substantiated by the electron doping characteristics revealed by the Raman spectroscopy results (figure 1(d)). Moreover, the number of graphene layers has been clearly demonstrated to increase with increasing temperature [27, 28, 36]. Therefore, the low graphitization temperature of 1300 °C adopted for only 15 min ensures a bilayer configuration. We also note that the effective electron–donor doping of graphene is induced by the difference between the work functions of graphene and the SiC substrate, which drives electrons at the SiC/graphene interface from the SiC substrate into the graphene. The difference between the DOS of electrons in the defect-free region and at the center of the flower defect is mainly manifested in the form of defect states. The DOS at the center of the flower defect exhibits a peak at a bias voltage of 0.16 V, while the intensity attenuates rapidly from the defect center out to the defect-free region, and vanishes completely at a distance of 3 nm from the center. These results indicate that the density of electron states is strongly localized.

These results are clarified by the dI/dV mapping shown in figure 2(c) for the same area as that shown in figure 2(a). It can be seen that the tunneling conductance of the flower defects is much less than that of the defect-free regions of the graphene sheet. This can be attributed to the localized DOS surrounding the flower defects resulting from the disruption of the graphene lattice [21]. We also note that the quasi–particle scattering diameter of the flower defects is around 2.5 nm, as indicated by figure 2(c), which is greater than the size of the defects themselves. This indicates that some portions of the (√3 × √3)R30° superstructures adjacent to the defects are also part of the quasi-particle scattering centers, and can contribute to the decreased tunneling conductance. This represents a kind of short–wave scattering caused mainly by intravalley scattering, which is consistent with previously reported experimental results [21, 26, 39]. Moreover, obvious light–and–dark stripes are observed in the dI/dV mapping results around the flower defects, and the contrast between these stripes is observed to decrease from the scattering center outward. Therefore, these stripes represent interference patterns resulting from the scattering of charge carriers by the flower defects. However, these are longer–wave scattering patterns than the short–wave intravalley scattering patterns caused by the (√3 × √3)R30° superstructure.

The scattering patterns shown in figure 2(c) are further examined as wave vectors in reciprocal space by applying the fast Fourier transform (FFT), as presented in figure 2(d). The long wave scattering caused by the flower defects and the intravalley scattering caused by the superstructures can be inferred from the bright points highlighted by the green and yellow hexagons, respectively. In addition, the bright blue spot at the center of the yellow hexagon is representative of intervalley scattering, which can be attributed to the spin and chiral electrons of graphene [40]. We see that the magnitude of the wave vector caused by the flower defect in the first Brillouin zone is smaller than that of the graphene lattice, but larger than the magnitude of the wave vector of intravalley scattering caused by the superstructures. This indicates that the flower defects can generate sufficiently strong scattering potentials to mix two adjacent Dirac cones in the graphene Brillouin zone. The fact that these atomic-scale flower defects can destroy the symmetry of the Hamiltonian in the Dirac equation offers a convenient and effective means of modulating the unique Dirac cone band structures of graphene that have a linear energy dispersion relationship near the Fermi level, which has been long sought by researchers in related fields.

Figure 3(a) presents an atomic–resolution STM image of two closed–ring defects on the surface of an epitaxial graphene sample. Here, an area containing no nearby flower defects was selected to exclude any interference arising from them, and the irregularly–shaped grain boundaries were selected to avoid preferential orientations. Interference patterns associated with (√3 × √3)R30° superstructures are visible both inside and outside of these grain boundaries. Here, the superstructures extend outward as far as ∼4 nm from the outer edges of the grain boundaries, while they extend ~4 nm inward from the inner edges. We propose that the greater extension of superstructures inside the grain boundaries arises as a result of the enhanced scattering intensity induced by the relatively heavy interference among charge carriers from the different sides of the grain boundaries. This division of superstructures inside and outside of the grain boundaries represents separated single-crystal domains with different lattice vectors and orientations. This is illustrated very clearly in the FFT image shown in the inset of figure 3(a), which denotes the reciprocal lattice vectors inside and outside of the grain boundaries by the red and yellow circles, respectively. The misorientation angle obtained from the STM image in figure 3(a) and the corresponding FFT results is about 30°, which is consistent with the value calculated by Yazyev and Louie [15] based on the hypothesis that these grain boundaries are composed of pentagon-heptagon disinclination dipole chains.

Figure 3(b) presents the dI/dV spectra obtained by STS at several locations on both sides of a single grain boundary loop shown in figure 3(a). These locations include three equidistant points 0.8 nm apart inside the grain boundary loop, a single point lying directly on the grain boundary, and one point lying outside of the grain boundary loop. The spectrum obtained on the grain boundary exhibits an evident defect state energy of 0.2 V, which is 0.04 eV greater than the defect state energy observed for flower defects. The intensity of this defect state initially decreases with increasing distance inward from the grain boundary, but then increases and obtains a maximum value at the center of the closed–ring defect. This point of maximum intensity may be induced by the maximum charge carrier interference intensity at the center of the closed–ring defect. The position of the defect
state also changes among the measured locations inside the grain boundary loop, which may be related to the extreme variations in the directions of the scattering and interference arising from the tortuousness of the grain boundary. Another feature observed in the spectra is evident Van Hove singularity (VHS) points. In the domain on the left, the VHS in curve C is a peak at 0.3 V in the defect state, while the VHS points are observed at valleys in curves D and E. In contrast, the VHS is always a peak measured at the F, G, and H points shown infigure 3(a). This difference in the VHS behavior indicates that the density of electron states inside a closed-ring defect is strongly localized and position-dependent. Therefore, we can attribute this VHS behavior to interference with scattering due to scattering resonances arising from the random arrangement of defects found within the coherence length.

The spatial distribution of these electronic states is further illustrated by the $dI/dV$ map in figure 3(c) for the same region shown in figure 3(a). Here, the greater magnitude of the tunneling conductance of the grain boundaries is indicated by the brighter color. The non-uniform density of electron states shown by the color variation near the grain boundaries is indicative of strong localization and position dependence for the electronic states near the grain boundaries. The scattering caused by the grain boundaries is illustrated by the reciprocal lattice vector of graphene in its Brillouin zone shown in the FFT image presented in figure 3(d) of the $dI/dV$ map presented in figure 3(c). We note that no intervalley scattering between adjacent Dirac cones resulting from quasi-particle scattering by the defects because the dimensions of the scattering potentials here exceed the C–C bond length, which prohibits intervalley scattering [21]. Conversely, intravalley scattering is evident in the figure 3(d). These results indicate that introducing closed-ring defects into graphene can directionally eliminate intervalley scattering while maintaining intravalley scattering.

Figure 4(a) presents an STM image of an irregular closed-ring defect accompanied with two adjacent flower defects on the surface of an epitaxial graphene sample with the corresponding FFT image presented in the inset. The grain boundary of the closed-ring defect exhibits two relatively bright spots in close proximity to the flower defects, and the point with the closest distance from its corresponding flower defect is larger and brighter. These
results suggest that the flower defects interact with the grain boundary of the closed-ring defect. Superstructures are observed around the grain boundary of the closed-ring defect in figure 4(a), and the orientations of the graphene lattice inside and outside of the grain boundary loop are again rotated by an angle of 30° relative to each other. This misorientation introduces protrusions and other irregularities in the shape of the grain boundary, and may also induce corrugations as an effective means of reducing the stress induced by the misorientation \[11\]. We also note that the structure of the grain boundary is blurred in the STM image due to the complicated DOS induced by the VHS there.

The height profile along the white line shown in figure 4(a) is presented in figure 4(b), which includes a flower defect and a bright spot on the grain boundary of the closed-ring defect. These results indicate that the superstructures inside and outside of the closed-ring defect lie essentially on the same plane, while the heights of the grain boundary and the flower defect are approximately the same, and are both about half of the height of the bright spot on the right along the white line in figure 4(a). The diameters of the flower defects and this bright spot are approximately equivalent, and are both greater than the width of the grain boundary. These results suggest that the grain boundary may be formed of incomplete flower defects.

The calculation results of Yazyev and Louie \[15\] provide good evidence to speculate that the grain boundaries of closed-ring defects are formed from pentagon-heptagon chain loops. Accordingly, we propose the atomistic model presented in figure 4(c), where the bright spot on the left in figure 4(b) is modeled as a single flower defect while that on the right in figure 4(b) is modeled as a cluster of several pentagonal and heptagonal carbon rings, and the remainder of the grain boundary is modeled as highly ordered pentagon-heptagon chains. This model represents a good starting point for conducting large-scale numerical investigations of epitaxial graphene with realistic defect structures. However, this task lies beyond the scope of the present study, and is left as a suggestion for future study.

4. Conclusion

The present study investigated closed-ring defects formed within grain boundary loops in graphene epitaxially grown on 4H-SiC and evaluated their effects on the electron state density by means of STM and STS. The results demonstrated that the orientations of the superstructures inside and outside of the grain boundary loops are rotated uniformly by an angle of 30° relative to each other. This was demonstrated to indicate that closed-ring defects are highly ordered and are mainly composed of clusters of pentagon-heptagon carbon rings and highly ordered pentagon-heptagon chains. The graphene growth conditions employed in this study also suggest that the low formation energy of pentagon-heptagon disinclination dipoles plays the most important role in the formation of grain boundary loops rather than the duration of high-temperature degassing. In addition, the spectroscopy results reveal for the first time that the density of electron states inside a closed-ring defect is strongly localized and position-dependent. Moreover, our results have demonstrated that closed-ring defects can eliminate intervalley scattering in graphene while maintaining intravalley scattering. Accordingly, the introduction of highly ordered closed-ring defects provides an effective means for tuning the electronic band structure and charge carrier transport properties of graphene.
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