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Flat-band Electronic Structure and Interlayer Spacing Influence in Rhombohedral Four-layer Graphene

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ABSTRACT: The stacking order of multilayer graphene significantly influences its electronic properties. The rhombohedral stacking sequence is predicted to introduce a flat band, which has high density of states and the enhanced Coulomb interaction between charge carriers, thus possibly resulting in superconductivity, fractional quantum Hall effect and many other exotic phases of matter. In this work, we comprehensively study the effect of the stacking sequence and interlayer spacing on the electronic structure of four-layer graphene, which was grown on a high crystalline quality 3C-SiC(111) crystal. The number of graphene layers and coverage were determined by low energy electron microscopy. First principles density functional theory calculations show distinctively different band structures for ABAB (Bernal), ABCA (rhombohedral) and ABCB (turbostratic) stacking sequences. By comparing with angle resolved photoelectron spectroscopy data, we can verify the existence of a rhombohedral stacking sequence and a nearly dispersionless electronic band (flat band) near the Fermi level. Moreover, we find that the momentum width, bandgap, and curvature of the flat-band region can be tuned by the interlayer spacing, which plays an important role in superconductivity and many other exotic phases of matter.

KEYWORDS: Graphene, Rhombohedral stacking, flat-band, interlayer spacing, superconductor

Recently, multilayer graphene has attracted much interest due to its stacking-dependent electronic properties.¹⁻⁴ In particular, the rhombohedral stacking sequence is predicted to introduce a nearly dispersionless electronic band (flat band) near the Fermi level (E_F).¹ The flatness of this band depends on the number of layers in the rhombohedral multilayer graphene (RMG).^{1, 4} Such a flat band would possibly result in superconductivity.³ For conventional superconductors, the critical temperature depends exponentially on the electronic density of states (DOS) at E_F . In an extreme case, the dispersionless band leads to a diverging DOS at E_F in RMG.⁴⁻⁶ Furthermore, the Coulomb interaction between electrons is increased in the flat-band.^{3, 7} It is well known that Coulomb interaction plays a crucial role for the exotic properties of two-dimensional materials, such as the quantum spin Hall effect.⁸⁻⁹ Hence, the flat-band of RMG could also support new exotic electronic states.

Different methods have been developed to fabricate graphene. Exfoliation from graphite can generate graphene flakes with a maximum size of $\approx 10 \mu\text{m}^2$, but this size is not sufficiently large for industrial device processing. Chemical vapor deposition of graphene has been achieved on metal surfaces,¹⁰ but it has compatibility problems with industrial semiconductor processes due to need of transfer to other substrates while maintaining large area as well as is challenged by domain sizes being limited by metal grain sizes. Sublimation growth of epitaxial graphene on SiC has been developed to become a reliable method for fabricating large-area, low-defect-density single layer graphene on a semiconducting substrate.¹¹⁻¹³ It has the largest application potential in electronics, gas storage, high performance sensors etc.¹⁴⁻¹⁸ Pioneering work has been done to grow graphene on various polytypes of silicon carbide (4H-, 6H-, and 3C-SiC).^{13, 19-21}

The preparation of large-area homogeneous multilayer graphene is still a great challenge.²¹ The formation of a particular stacking order is strongly influenced by the substrate.²² Considering all

substrates that have been used to support graphene growth, the 3C-SiC substrate is the most suitable one for growth of rhombohedral multilayer graphene due to its ABC stacking along the [111] direction. Coletti *et al.* reported angle resolved photoelectron spectroscopy (ARPES) data on tri-layer graphene on 3C-SiC, exhibiting the tendency toward large-area RMG,²³ as tri-layer is just a beginning of an “ABC” stacking.¹ Later, Pierucci *et al.* presented results of five-layer RMG on a thin (12 μm) 3C-SiC crystal on 2° off-axis 6H-SiC.⁴ However, the small domains (40 – 50 nm) of RMG made the ARPES data fuzzy and the determination of stacking sequences was not conclusive.

In this letter, we report a successful synthesis of four-layer RMG on 4° off-axis 3C-SiC(111). We address the issue of the structural influence on the electronic structure of RMGs and propose a possible method to manipulate the width of the flat-band at E_F . Direct characterizations of quality, coverage and number of layers were done via low energy electron microscopy (LEEM). The band structure of four-layer graphene measured by ARPES allows a direct comparison to the first principles density functional theory (DFT) calculation in order to determine the stacking sequence and interlayer spacing.

Figure 1. LEEM measurements of graphene grown on 3C-SiC(111). (a-c) LEEM images of graphene samples grown at 1800 °C for (a) 15 min, (b) 30 min and (c) at 2000 °C for 30 min, measured with an electron energy of 5.48 eV, 5.88 eV and 2.89 eV at a field of view of 10 μm, 15 μm and 10 μm, respectively. (d-f) Electron reflectivity curves extracted from the labeled areas in (a-c). The number of minima in an electron reflectivity curve indicates the number of graphene layers.

The LEEM measurements were performed to characterize the thickness distribution of graphene grown on 3C-SiC(111) at different conditions. Figure 1a-c are the results measured on the samples aimed for different number of layers. Based on the electron reflectivity curves (Figure 1d-e), one can determine the thickness of graphene in the field of view (FOV) labeled by colored arrows.²⁴ The LEEM results show that the samples grown at 1800 °C for 15 and 30 minutes are covered to 91% by monolayer graphene and to 87% by bilayer graphene, respectively. Most importantly, the sample grown at 2000 °C for 30 min is dominated by 4 ML graphene with a

coverage of 70%. The large domain size of about ten micrometers enable the feasibility to experimentally determine stacking sequence and the electronic structure of the 4 ML graphene.

Figure 2. π band dispersion and constant energy contours obtained by ARPES. (a) Band structure of a 1 ML graphene sample showing the linear dispersion. The Dirac point is located at a binding energy of 0.42 eV below E_F . (b) Band structure of a 2 ML graphene sample indicating an AB stacking sequence. The Dirac point, E_D , is located at a binding energy of 0.34 eV below E_F . The energy difference between the top of the lowest π band and the Dirac point is 0.36 eV. (c) Band structure of a 4 ML graphene sample showing a flat-band at E_F with a momentum width of $\sim 0.07 \text{ \AA}^{-1}$. All constant energy contours were plotted at the binding energy of -1.0 eV. The number of bands and contours agree with the number of layers. (d) A second derivation of (c) shows the band dispersion clearer, which facilitates a comparison with DFT calculations shown in Figure 3. Note that the π band dispersion is symmetric in (a) and (b) along $k_{//x}$, but asymmetric along $k_{//y}$ in (c).

Figure 2a shows the typical linear π band dispersion and three-fold symmetric constant energy contour of 1 ML graphene around the $\bar{K}$ point of surface Brillouin zone (SBZ). Due to the charge transfer from the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ carbon rich buffer layer,²⁵ the Dirac point is shifted below E_F by 0.42 eV. The ARPES data of 2 ML graphene shows two π bands and two concentric contours.

The position of the bands indicates an AB stacking (Figure 2b). The Dirac point is shifted by 0.08 eV towards E_F compared to 1 ML graphene. The top of the lower π band and the Dirac point have an energy difference of 0.36 eV. These values are consistent with the ARPES results measured on graphene grown on 6H- and 4H-SiC substrates,^{4, 25-27} and can be explained by the model proposed by Kopylov *et al.*²⁸ The electron transfer originates from the bulk SiC or interface states between buffer layer and graphene. In Figure 2a, b, π bands were mapped along the direction perpendicular to $\bar{\Gamma}\bar{K}\bar{M}$ direction, which makes the bands symmetric at $\bar{K}$. From the constant energy contour in Figure 2c, one can see that π bands along $k_{//y}$ are better resolved than along $k_{//x}$. Hence, for the four-layer graphene sample, π bands were mapped along the $k_{//y}$ direction. The width of the flat-band at E_F is measured to be $\sim 0.07 \text{ \AA}^{-1}$, which is quite close to the reported value of the flat band region of $0.08 \text{ \AA}^{-1}$ in five-layer graphene by Pierucci *et al.*⁴ To compare experimental results with DFT calculations to determine the stacking sequences, second derivation of the data in Figure 2c was implemented (Figure 2d). It shows that one band crosses E_F and the other three bands coincide at a binding energy (E_C) of -0.45 eV.

We performed band structure calculations of three possible stacking sequences after full relaxation, i.e., ABCA (rhombohedral), ABCB (turbostratic) and ABAB (Bernal) stacking shown in Figure 3. The major difference between Figure 3a, b, and c is that Bernal and turbostratic stacking have no band degeneracy at the $\bar{K}$ point below E_F . Moreover, there is no observable flat-band at E_F for Bernal stacking. Hence, we can conclude that the experimental data are consistent with the presence of four-layer RMG. Since Pierucci *et al.* measured ARPES with a probe area of approximately $50 \times 100 \text{ \mu m}^2$, the quality of the data was not satisfying due to small domains of RMG (40 - 50 nm). The size of the light spot in our experimental setup is about 1 mm^2 , and four

π bands are clearly observed in Figure 2c, indicating large domains and high coverage of four-layer graphene on 3C-SiC(111), as confirmed by the LEEM results in Figure 1.

Figure 3. Calculated band structure of four-layer graphene. (a) Calculated band structure of ABCA stacking showing one flat valence band near E_F and the other three valence bands coincide at a binding energy of -0.30 eV. The flat-band width is about $0.06 \text{ \AA}^{-1}$. (b, c) Calculated band structure of ABCB and ABAB stacking, respectively, showing two valence bands joined at E_F and there are no other degenerate band at the $\bar{K}$ point. The insets are atomic models of the corresponding stacking sequences. The bands were plotted along the $\bar{\Gamma}\bar{K}$ direction of the SBZ. The red dashed line indicates the position of the $\bar{K}$ point.

The electronic structure of four-layer RMG is illustrated in Figure 3a. The average interlayer spacing (D_s) was found to be $3.40 \text{ \AA}$ after full relaxation of all atomic positions. Yoo *et al.* reported an average D_s of $3.85 \text{ \AA}$ for four-layer graphene obtained by mechanical graphite cleavage.²⁹ Agrinskaya *et al.* reported an average D_s of $3.39 \text{ \AA}$ for eight-layer graphene.³⁰ Pierucci *et al.* reported $3.44 \text{ \AA}$ for five-layer graphene using scanning transmission electron microscopy.⁴ Kasper *et al.* have discussed the relationship between D_s and number of bands.³¹ However, the influence of D_s on the band structure of multilayer graphene has not been explored yet in the literature.

Figure 4. Band structure calculation of four-layer RMG as a function of interlayer spacing. (a) The blue axis and triangles are the flat-band widths extracted from band structure calculations. The red axis and spots are the binding energy positions where the three lower π bands coincide (E_C). The dashed lines are guides to the eye showing the tendency of the change as a function of interlayer spacing. (b-e) Calculated band structure of four-layer RMG with interlayer spacings of 3.20, 3.40, 3.60 and 3.80 Å, respectively. The $k_{||}$ range is same as in Figure 3. (f-i) Zoom-in plots of flat-bands close to E_F from (b) to (e) respectively. The $k_{||}$ range is ± 0.75 Å⁻¹ centered at the $\bar{K}$ point, indicated by the red dashed lines.

In Figure 3a, the position of E_C and flat-band width do not agree with experimental results, which leads to further investigation. There are four structural parameters for four-layer graphene: lattice constant (2.46 Å), atomic structure of each layer (honeycomb), stacking sequence (ABCA) and interlayer spacing (D_s). Since the former three parameters are well defined, we thus performed band structure calculations of four-layer RMG as a function of D_s . The changes in the flat-band width (blue triangles) and position of E_C (red spots) are two characteristic features displayed in Figure 4a. The dashed lines are guides to the eye, suggesting that E_C moves towards E_F and that the width of the flat-band decreases with increasing D_s . Figure 4b-e show the results with interlayer spacings of 3.20, 3.40, 3.60, and 3.80 Å, respectively. A detailed analysis of the calculated flat-band is presented in Figure 4f-i. It shows clearly that the flat-band becomes narrower but flatter

when D_S increases. In order to achieve a high critical temperature superconductor, the possibility of increasing the DOS near E_F is essential. Based on our theoretical results, we propose a possible way to increase the DOS through tuning the interlayer spacing. Noticeably, a phase transition from semimetal to semiconductor occurs when increasing the interlayer spacing. A band gap of ~ 4.5 meV is induced when D_S equals $3.60 \text{ \AA}$. This indicates that the interlayer spacing also plays an important role for the electronic properties of graphene such as flat-band width and band gaps.

In conclusion, we report promising epitaxial growth of graphene on 3C-SiC(111) with different number of layers related to growth parameters. The high quality and large coverage of graphene with different thicknesses allowed reliable characterization by LEEM. We observed a flat-band with a width of $\sim 0.07 \text{ \AA}^{-1}$ close to E_F . The PBE + DFT calculations, including vdW interaction, permit us to verify the existence of a rhombohedral stacking. Finally, we present detailed theoretical studies of the flat-band as a function of interlayer spacing that could shed light on the progress of superconductivity in rhombohedral multilayer graphene.

Experimental methods.

Bulk-like off-axis 3C-SiC(111) samples with a thickness of ~ 1 mm were grown on 4° off-axis 4H-SiC substrates (SiCrystal) by the sublimation process.³²⁻³³ Then $300\sim 400 \text{ }\mu\text{m}$ thick freestanding 3C-SiC layers were obtained by polishing away the 4H-SiC substrates and the transition interface between 4H and 3C-SiC.. To remove surface contaminations and oxides, the 3C-SiC substrates were chemically cleaned by acetone, ethanol, $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{O}_2$ (5:1:1), $\text{H}_2\text{O}:\text{HCl}:\text{H}_2\text{O}_2$ (6:1:1) and hydrofluoric acid (HF). Before growth of graphene on 3C-SiC, we studied the as-grown substrates by atomic force microscopy (AFM) in order to select samples free from macroscopic defects and with a regular step structure corresponding to the off-cut angle of 4H-SiC substrate. For the growth of monolayer and bilayer graphene, the samples were annealed during

15 and 30 min, respectively, in an inductively heated furnace at 1800 °C with a ramping rate of 25 °C/min in an 850 mbar argon atmosphere. For the growth of four-layer graphene, the sample was annealed at 2000 °C during 30 min. The number of graphene layers was determined by LEEM measurements at beamline I311 at the MAX-lab synchrotron radiation laboratory, Lund, Sweden. The ARPES data were acquired at room temperature at Linköping University using a Phoibos 100 analyzer from Specs with a two-dimensional detector. The energy and angular resolutions were 50 meV and 0.3°, respectively. A helium discharge lamp was used as light source, providing photons with an energy of 21.22 eV. Both LEEM and ARPES measurements were carried out in ultrahigh vacuum (UHV). Clean samples were prepared *in-situ* by annealing at 600 °C to remove contaminations from them prior exposure to air. First-principles DFT calculations were used to investigate the band structure as a function of the stacking sequence of graphene. The structure was modelled by a periodic slab, which was built by ABCA, ABCB or ABAB stacking sequences of four-layer graphene with a theoretical lattice constant of 2.46 Å. A vacuum spacing of 19 Å was included to avoid interaction between repeated slabs. The DFT calculations were performed using the functional of Perdew, Burke and Ernzerhof (PBE) and the projector augmented wave (PAW) method Vienna ab initio simulation package code (VASP).³⁴ Structural relaxation was carried out using a k-point mesh of (24 × 24 × 1). The Tkatchenko-Scheffler method is used to describe van der Waals (vdW) interactions.³⁵ The energy cut-off of the plane wave basis set was 1000 eV. The fully relaxed four-layer models were optimized until all residual forces were less than 10 meV/Å. The momentum width of the calculated flat-band was measured within the energy range of ±10 meV.

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