Unraveling the rotational disorder of graphene layers in graphite

H. S. Wong and C. Durkan*
Nanoscience Centre, University of Cambridge, 11 JJ Thomson Avenue, Cambridge CB3 0FF, United Kingdom
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We present a study on the dependence of atomic mismatch between graphene sheets in graphite and the misorientation of the resulting superlattice domains. We demonstrate, through measurements of the atomic orientation of the top sheet and the angular misorientation between superlattice domains, that it is possible to compute the actual degree of atomic mismatch on the underlying graphene sheet. We show that the odd-even transition is evident for superlattices with relatively small periodicity in the range 1–2 nm and less apparent for those with larger periodicity in the range 5–8 nm, and present a signature of the transition. We also demonstrate that the degree of interlayer coupling between graphene sheets depends on the extent of rotational mismatch in relation to interlayer spacing as has previously been predicted.

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I. INTRODUCTION

Observation of Moiré patterns or superlattices on the highly oriented pyrolytic graphite (HOPG) surface is commonplace using the scanning tunneling microscope (STM), and studies in understanding the origin of this phenomenon are abundant.[1–10] It is widely accepted that superlattices are a consequence of the relative rotation of graphene sheets at or near to the basal plane. This rotation induces a superperiodic modulation in the density of states, which manifests itself in STM images as a hexagonal pattern with periods ranging from less than 1 nm to tens of nanometers. Studies on superlattices are becoming increasingly relevant since by merely modifying the stacking of graphene sheets, a nanoscale long-range periodic enhancement of the surface density of states is introduced, which could act as a template for some additional process. The fact that the electronic properties of graphite can be locally engineered, based on the correlation between the electronic and atomic structure, could ultimately lead to applications in novel devices involving a few layers of graphene (FLG).[4,9–11]

From the periodicity of superlattices, the misorientation between the top and underlying graphene sheets can be calculated using the simple Moiré rotation-pattern assumption: The periodicity, D, of the resulting Moiré hexagonal structure is related to the misorientation angle, θ, between the two layers of the hexagonal lattice, with lattice constant d, as

$$D = d/[2\ \sin(\theta/2)]. \quad (1)$$

Additionally, the orientation of the Moiré pattern, Π, with respect to the atomic orientation of the top layer is related to the misorientation angle, θ, as

$$\Pi = 30\ ^\circ - (\theta/2). \quad (2)$$

The Moiré rotation-pattern assumption has been verified experimentally many times over the past 20 years and has attracted considerable interest among the modeling community.[2] However, in situations where two or more domains of superlattices having varying periodicities are observed, Eqs. (1) and (2) alone do not unveil the true atomic misorientation between layers. In this paper, we demonstrate, through measurements of the atomic orientation of the top sheet and the angular misorientation between superlattice domains, that it is possible to compute the actual degree of atomic mismatch on the underlying graphene sheet per se, and these measurements are all supported by a simple phenomenological model of the density of states of graphite.[6] We have also investigated the odd-even transition phenomenon and demonstrate its dependence on the superlattice periodicity.

Finally, it has been predicted that as the top layer of HOPG becomes increasingly misoriented with respect to the underlying layers, the interlayer spacing decreases (for misorientations between 0° and 30°),[7] suggesting that it becomes more strongly bound. The energy minimum for the system is of course for a rotation of 0°, with a sharp rise in energy as soon as any rotation is introduced, with the next minimum occurring at a rotation of 30°. Building on our recent work of tip-induced vertical displacement of the top layer,[8] our results indicate that this is indeed the case experimentally for misorientations below 11°.

II. EXPERIMENTAL, RESULTS, AND DISCUSSION

All STM images were acquired in constant-current mode using an Omicron UHV STM/AFM with a base pressure on the order of 10^{-10} mbar at room temperature and with mechanically cut Pt/Ir tips. HOPG substrates were cleaved with adhesive tape followed by treatment with 1,2,4-trichlorobenzene, which is known to induce the formation of superlattices, without any evidence of intercalation.[12] The density-of-states simulations were calculated using MATHEMATICA with the simple analytical model which we reported previously.[6] In this model, STM images are simulated by considering the top three layers with relative weightings of 1, −0.5, and 0.125, respectively, where the variation in weighting is simply due to the distance of the layers from the tip and the minus sign for the second layer represents the fact that the stacking is A-B. These weightings have been found to give the best agreement with experimental STM images and they apply when the distance between the layers is 0.335 nm. Modification in the interlayer distance through the tip-sample interaction results in a shift in these weightings and therefore a change in the image contrast, which is the essen-

tial finding reported in this paper. It is also a simple matter to introduce a lateral rotation between the layers and simulate a superlattice using this model. As this model is phenomenological, it is purely intended to act as a framework for describing our results, and as we will show, it can be successfully used to reproduce much of our experimental data, further strengthening the argument that superlattices are indeed due to rotational misorientation between graphene layers in graphite.

A. First-order misorientation between layers of graphene

In order to support the hypothesis that Moire interference is the origin of superlattices, in Fig. 1(a) we present a set of superlattices having two different periodicities of 5.29 nm in the upper region and 7.95 nm in the lower region [The different periodicities can be seen clearly in the inserted two-dimensional fast Fourier transform (2DFFT) of the image where the two sets of hexagonally arranged spots refer to the two superlattices.] These periodicities correspond to angular misorientations between the top two graphene sheets at the Basal plane of 2.63° and 1.75°, respectively, from Eq. (1). From the atomic-resolution image obtained at the boundary between the two superlattice domains as shown in Fig. 1(b), we ascertain that the top graphene sheet is a continuous layer, as is further indicated by the superimposed straight line stretching across the boundary without a trajectory change in the surface atomic rows. Hence, the atomic mismatch between this set of superlattices must come from the underlying layer(s), which is most probably due to a buried dislocation or grain boundary. This buried boundary is revealed as a chain of bright spots with an enhanced density of states, as is typically the case.[2] To validate that the atomic mismatch comes from the underlying layer, we compare the hexagonal orientation between the two sets of superlattices as observed experimentally in Figs. 1(a) and 1(b), and through modeling, as presented in Fig. 1(c), and see that both are in agreement. The simulated images are calculated assuming the rotational misorientations measured above and consequently result in superlattices with the same periodicities as are observed experimentally. An additional observation we make here is in relation to the odd-even transition phenomenon, which is characterized by the shifting of the apparent (i.e., as observed by STM) atomic rows by half a row period as they traverse a superlattice corrugation maximum.[5,13,14] For the superlattices in Fig. 1, this transition is absent both in the experimental images [see Fig. 1(b)] and in the simulated ones [Fig. 1(c)], suggesting that the transition is absent in superlattices that arise due to small misorientations between the respective graphene layers, in agreement with previous works.[6,13,14] The significance of this finding is that, like the superlattice itself, the odd-even transition is an electronic interference phenomenon, simply at a fine scale.

The above analysis is typical where there is a first-order misorientation between two regions on the surface and where the Moiré model is simple to implement. We now turn our attention to the more complex and rare case where there is a second-order misorientation (involving several layers) and where more care must be taken in the interpretation of STM images.

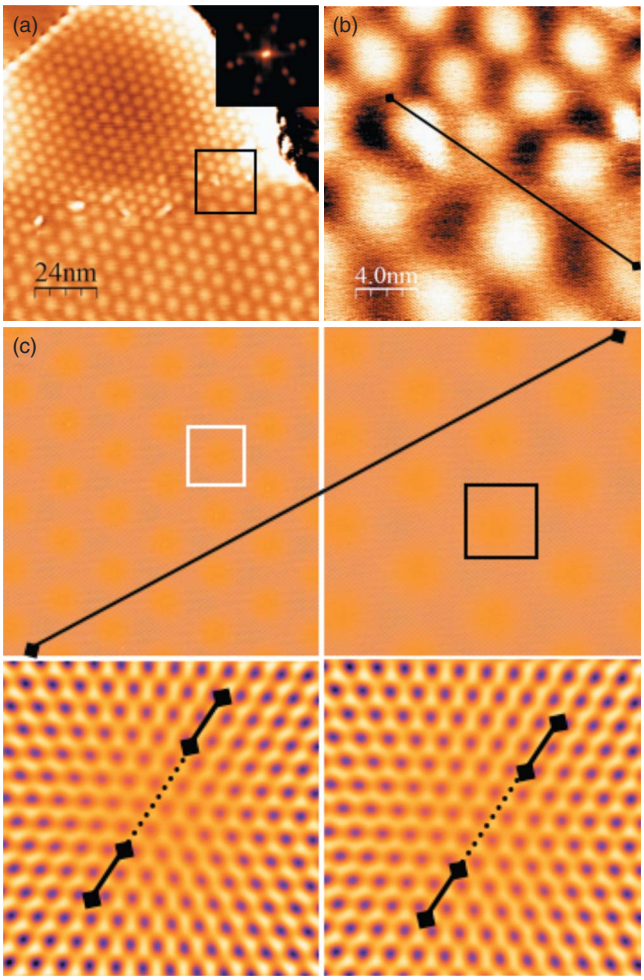

FIG. 1. (Color online) (a) A set of superlattices having periodicities 5.29 nm (upper region) and 7.95 nm (lower region). (0.2 V, 0.2 nA) (Inset: FFT showing two hexagonal patterns. The orientational mismatch between both superlattices is negligible.) (b) A closeup of the boundary region indicated by the box in (a) showing the atomic resolution of graphite lattice in both superlattice regions. (0.08 V, 0.2 nA) The straight line indicates a continuous surface graphene layer. The odd-even transition is not discernible for this set of superlattices which have large periodicities; (c) a model of the two superlattice regions having the same respective periodicities as (a)/(b). The model assumes either the top or underlying layer is continuous and agrees well with the experimentally measured mismatch in (a). Size of simulation: 30×30 nm^2 for top two, and 2.5×2.5 nm^2 and 3×3 nm^2 for the bottom left and right, respectively, as indicated by the white and black boxes in the top two images. The bottom images indicate that the odd-even transition is absent, consistent with the observation in (b).

B. Second-order misorientation between layers of graphene

Figure 2(a) presents another two sets of superlattices with the superlattice on the right having a lower corrugation than the one on the left and also having a different periodicity and orientation. This is further highlighted in Fig. 2(b), which

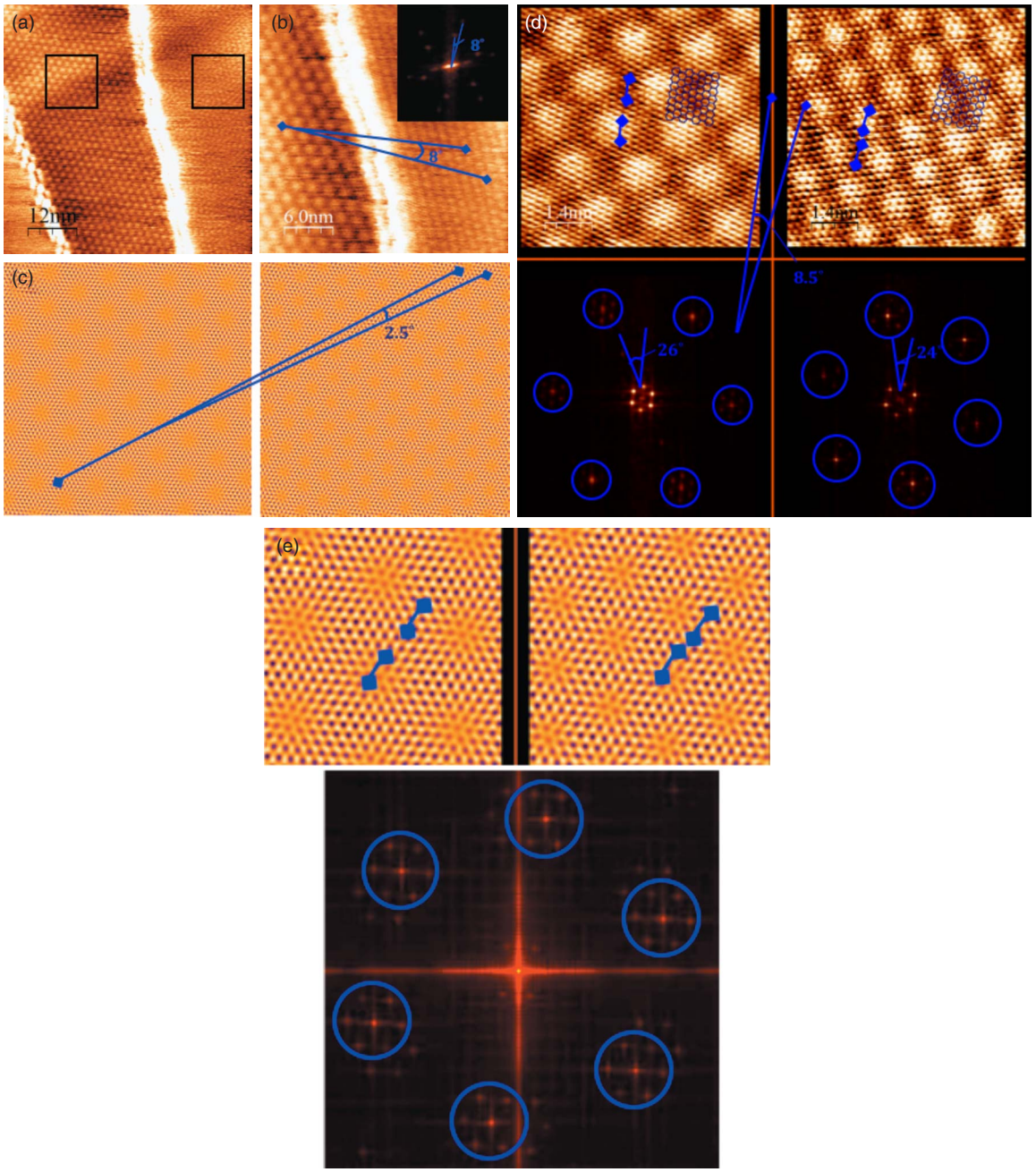

FIG. 2. (Color online) (a) A set of superlattices whose periodicities (1.97 nm on the left and 1.36 nm on the right) are smaller than those in Fig. 1 (i.e., a larger rotational mismatch). (−0.2 V, 0.2 nA) (b) The measured superlattice orientation mismatch is about 8°. (0.15 V, 0.2 nA); (c) density of state (DOS) simulation of the two superlattice regions having the same respective periodicities as (b), assuming the underlying layers in both regions have the same atomic orientation (simulation size: 15×15 nm^2). The measured superlattice mismatch from simulation is 2.5°. The discrepancy of 5.5° will be accounted for in the next figure; (d) the superlattice on the left and right regions with atomic resolution indicated by the boxes in (a) (left: 0.1 V, 0.2 nA; right: 0.15 V, 0.2 nA). The atomic-orientation difference between the two regions is about 8.5°. The odd-even transition phenomenon is evident for both regions. This atomic-row shifting is mapped out on the corresponding FFT (underneath each image) that shows a hexagonal pattern around each atomic site indicated by the rings; (e) DOS simulation of (d) clearly showing the presence of the odd-even transition and similar characteristics of the FFT as those observed experimentally (simulation size: 5×5 nm^2).

shows a zoom-in of the boundary region, from which we see that the angle between the superlattices is 8°. This is at odds with the simulation in Fig. 2(c), which shows that the misorientation between superlattices should be 2.5°. In Fig. 2(d), which shows zoom-ins in the vicinity of the boundary region, we observe the typical atomic resolution image of HOPG, displaying triangular symmetry. A 2DFFT on each region reveals two misoriented hexagonal patterns, the outer and inner ones corresponding to the atomic lattice and the superlattice, respectively. The boundary separating the two

regions has strong contrast, and appears to be a result of a split in the top layer, causing a change in the atomic orientation as we traverse the surface between the two regions. The superlattices have periodicities of 1.97 and 1.36 nm, respectively. The misorientation between the superlattice and atomic lattice orientation for the left and right regions as derived from their periodicities are 26.4° and 24.8°, respectively, using Eq. (1), corresponding to rotational misorientations of 7.2° and 10.4°. These calculated values based on the periodicities agree well with the measured misorientation of 26° and 24°, respectively, from the 2DFFT images (the difference between both sets of values is due to nonlinearity of the STM scanner). The consistency between these values further verifies the origin of the superlattices observed here as Moiré patterns. This is illustrated in Fig. 2(e), which presents density of states and 2DFFT simulations based on the Moire rotation model for superlattices, for misorientations of 7.2° and 10.4°, respectively, showing excellent agreement with experiment.

The difference in atomic orientation between the two superlattice regions, measured from Fig. 2 is 8.5°. Assuming that the atomic orientation of the underlying graphite layer is continuous, the calculated atomic mismatch should be $10.4°\,(\text{right}) - 7.2°\,(\text{left}) = 3.2°$. We therefore suggest that the excess mismatch of 5.3° is due to a misorientation within the underlying layer so it is in fact not continuous at the boundary either. We refer to this as a second-order misorientation.

As these superlattices have arisen due to a relatively large misorientation, we expect the odd-even transition to be apparent. This is highlighted in Fig. 2(d) and it is seen that the atomic rows indeed do shift by half a row spacing at the superlattice peaks. This is further apparent in the 2DFFTs of the images where there is a series of hexagonally arranged satellite peaks around each spot associated with the atomic lattice. The same is seen in the simulation of Fig. 2(e) and should be taken as a characteristic signature of the odd-even transition.

It has been shown theoretically in Ref. 7 that there is a strong interdependence between the coupling and the rotational misorientation between the graphene layers in graphite. We have verified this experimentally using a technique we have recently reported for locally displacing the top graphene layer using the STM tip.[8] The principle of the technique is that, during scanning, the tip-sample distance and therefore, the interaction between the two can be varied (either by changing the bias voltage, the tunneling current, or the lateral scan speed of the tip over the surface). We have already demonstrated that it is possible to decouple the layers sufficiently to observe the true honeycomb lattice of graphene layers, and that, with our technique, the displacement can be vertical rather than lateral as is generally assumed (i.e., the transition from a triangular to a honeycomb lattice is not necessarily due to a change in the layer stacking from A-B to A-A but can be due to the top layer being sufficiently displaced vertically that it behaves as a single layer).

Figures 3(a) and 3(b) show the same region of the superlattice on the left but with a triangular and honeycomb atomic lattice, respectively, as imaged during separate scans with different experimental conditions. In Fig. 3(b), the top

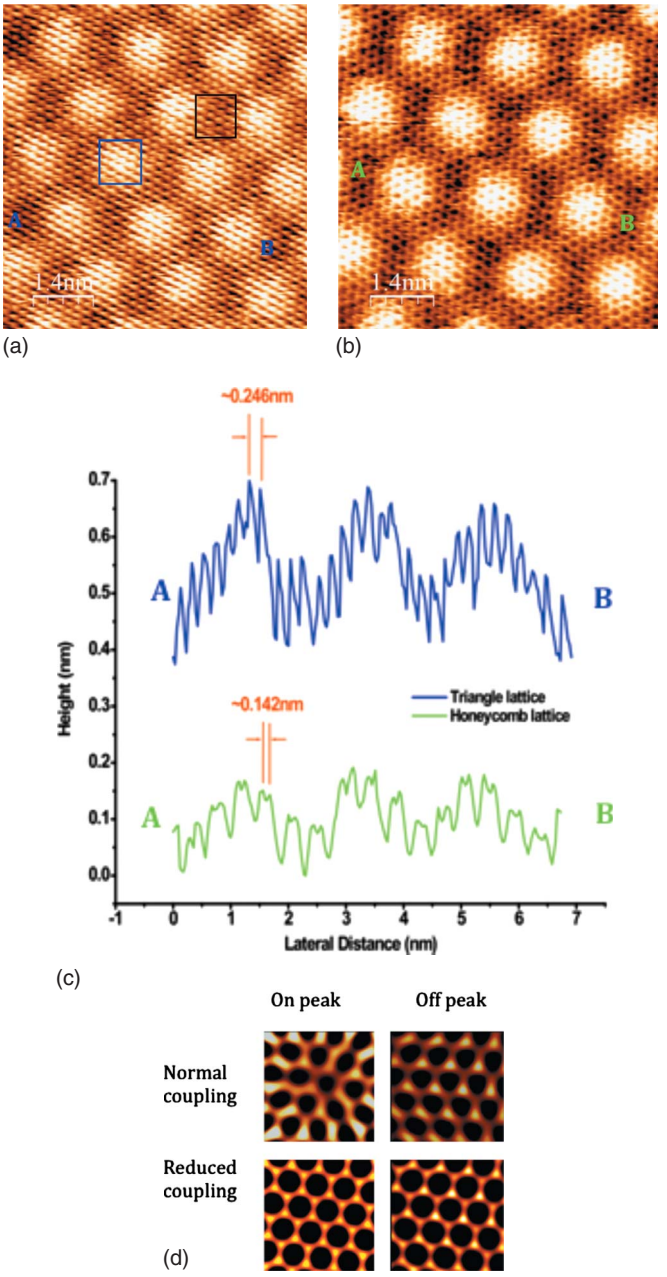

FIG. 3. (Color online) [(a) and (b)] The same region indicated by a black box in Fig. 1(a), showing (a), respectively, triangular atomic structure (0.1 V, 0.2 nA) and (b) honeycomb atomic structure (0.2 V, 0.2 nA). For both, the superlattice is observed superimposed onto the atomic lattice. (c) The line profiles following the atomic corrugation from point A to point B as indicated in (a) and (b). The lower curve shows the honeycomb atomic lattice while the surface graphene layer is being decoupled due to the tip-surface interaction. The superlattice periodicity is preserved before and after the transition; (d) DOS simulation of the superlattice peak and trough indicated by the blue and black boxes, respectively, in (a), showing the influence of atomic structure on the coupling between graphene sheets (simulation size: 1×1 nm^2). In normal coupling, both peaks and trough shows a triangular atomic structure. In reduced coupling due to displacement, the honeycomb atomic structure which reveals the true sixfold rotational symmetry of graphene is observed.

layer has been vertically displaced by the STM tip by around 3.3 Å during scanning, effectively decoupling it from the layers underneath. Figure 3(c) presents the line profiles as indicated on Figs. 3(a) and 3(b). The line profile for Fig. 3(a) shows a periodic atomic modulation of approximately 0.246 nm corresponding to the distance between every second atom in the triangular atomic structure, whereas the line profile for Fig. 3(b) resolves the individual atomic modulation of 0.142 nm, which is the true distance between adjacent carbon atoms in the honeycomb structure. Due to the odd-even transition phenomenon, which is present in both circumstances, the line section that follows the atomic rows strictly is not a straight line. Nevertheless, the periodicities of the atomic peaks for both line profiles are still well defined and the periodicity of the superlattice corrugation, superimposed onto the atomic corrugation, remains unchanged in both instances. Figure 3(d) shows the results of a simulation of the density of states both for the case of normal coupling between graphene layers, where the triangular lattice is observed everywhere; and for the case of reduced coupling after the vertical displacement, where a honeycomb lattice is seen on the superlattice peaks and a hybrid triangular/honeycomb lattice is seen between the superlattice peaks. The lateral resolution of our instrument is not capable of verifying the latter point although it appears that not every atomic site in between the superlattice peaks is equivalent, in general agreement with our model.

This vertical displacement of the top graphene layer was relatively simple to achieve and highly reproducible in the region where the misorientation is 7.2°, as well as in the superlattices presented in Fig. 1, where the misorientations are 2.63° and 1.75°. However for the superlattice region where the misorientation was 10.5°, we have been unable to displace the top layer, indicating that it is more strongly bound to the underlying layers, in agreement with the simulation of Ref. 7.

III. CONCLUSION

To conclude, we have revealed the atomic misorientation between adjacent lateral regions of the surface layer as well as the underlying layer through the misorientation between superlattice domains in graphite. This serves as a convenient way to identify the presence and compute the degree of underlying atomic misorientation. The odd-even transition is evident to be present only in superlattices with relatively smaller periodicity. We also demonstrated the ease of surface displacement especially in superlattices with relatively small misorientation, in agreement with recent predictions. Knowledge of these is particularly consequential and relevant in both experimental and theoretical framework regarding FLG, which have attracted considerable attention in recent years, as well as the tailoring of graphene sheets in novel FLG devices.

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*Corresponding author; cd229@eng.cam.ac.uk

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