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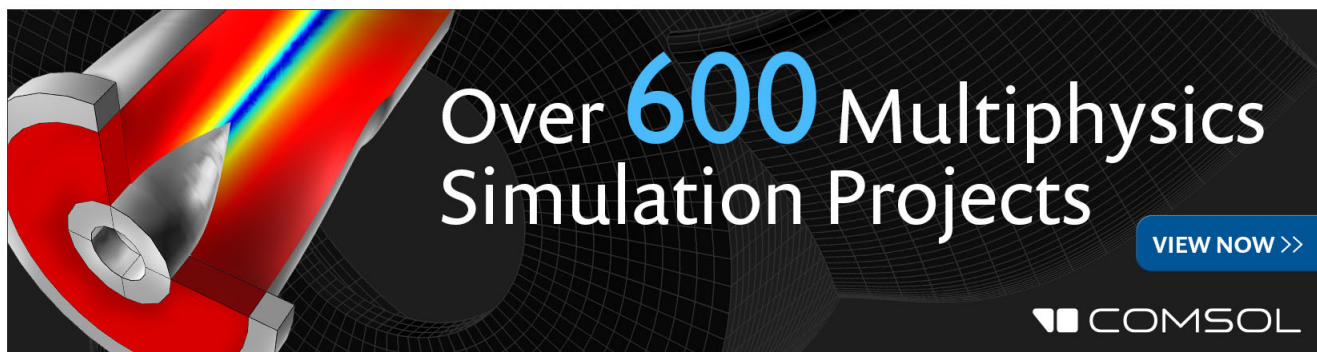
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Determination of the adhesion energy of graphene on SiC(0001) via measurement of pleat defects

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Pleat defects in graphene grown on SiC(0001) were studied and used to determine the adhesion energy between few-layer graphene (3 ± 1 monolayers) and the substrate. An adhesion energy of 3.0 ± 1.0 J/m² was determined using a continuum model describing the buckling of the film and delamination. The continuum model used can be applied to any graphene-substrate system in which pleat formation occurs due to differences in thermal expansion. The large value of adhesion energy observed for graphene on SiC, compared with that on materials such as Ni, Cu, and SiO₂, arises from delamination of the graphene film and buffer layer from the SiC substrate, which requires the breaking of covalent bonds. Preferential orientation of pleats at 120° with respect to each other was also observed; this is attributed to favorable formation of pleats along high symmetry directions of the graphene lattice. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4901941>]

The extremely high mechanical strength¹ and excellent electrical properties of graphene² make it the ideal candidate for future electronic devices. With significant recent interest in layered structures,^{3–5} a complete knowledge of graphene adhesion to different substrates is key, as the influence of the substrate has a large effect on mechanical properties at the nanoscale.⁶ Hence, a number of different methods have previously been used to measure the adhesion energy of graphene on different materials, such as pressurised blisters,^{7,8} deformation by atomic force microscope (AFM) tips,⁹ and intercalation with nanoparticles.¹⁰ However, experimental parameters are difficult to replicate and a simple method to determine the adhesion of graphene on any substrate is still required.

A common feature on both epitaxially grown and transferred graphene are pleat defects (also called wrinkles or folds), in which graphene layers delaminate from the substrate. Pleats have been observed on graphene grown on SiC,^{11,12} Cu,¹³ Ni,^{14,15} Pt¹⁶ as well as graphene transferred to SiO₂.¹⁷ This defect has been of interest due to the increased chemical reactivity along raised delaminated areas and has been proposed as a route to produce large arrays of graphene nanoribbons based on preferential etching along pleats.^{18,19} Pleat formation on epitaxially grown films is attributed to the difference in thermal expansion between the graphene and the substrate,¹¹ whereas on transferred graphene their formation is determined by the transfer to and surface morphology of the substrate.¹⁷ It has been concluded that pleat formation acts to reduce the strain on epitaxially grown graphitic films.²⁰ This strain and subsequent delamination is inherently linked to the interaction between the overlayer and substrate, and consequently the adhesion energy. A recent theoretical study by Zhang and Arroyo has described the formation of

large pleats from the merging of smaller wrinkles through the characterisation of pleats via the adhesion energy and frictional material parameters.²¹ The interplay between pleat formation and the adhesive properties of graphene allows the determination of an effective adhesion energy through the measurement of pleat heights and widths.

In this letter, we report the use of scanning tunnelling microscopy (STM) to observe pleat defects on graphene grown on SiC(0001). We demonstrate that easily measurable pleat heights and widths can be used, in conjunction with a simple continuum model adapted from the description of buckling of Cr films on polyimide,²² to obtain an effective value for the adhesion energy of graphene grown on the Si terminated face of SiC.

Few layer graphene samples (3 ± 1 monolayers (ML)) were grown on n-type zero off-cut angle 6H-SiC and 4H-SiC wafers (Tankeblue Semiconductor Co. Ltd. and Cree, Inc., respectively). The growth process was performed under high vacuum ($<5 \times 10^{-5}$ mbar at $T < 1900$ °C) in an upgraded commercial rapid thermal processor with a background pressure of $<3 \times 10^{-6}$ mbar, allowing fast controlled heating and cooling. Substrates were prepared *in-situ* by etching in 5% H₂/Ar forming gas at atmospheric pressure, followed by a 20 min heating step at 1200 °C before ramping to the growth temperature of 1775 °C. Full details of the growth procedure are reported elsewhere.¹²

Samples were transferred, through air, to an ultra-high vacuum (UHV) system (base pressure $< 5 \times 10^{-10}$ mbar) and annealed for 4 h at 200 °C to remove any atmospheric contamination from the surface that might have occurred between growth and transfer to the system. Low energy electron diffraction (LEED) patterns (Fig. 1(a)) showed the well known $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstruction,²³ indicating thin graphene films of high structural quality. Further characterisation was performed using Auger electron spectroscopy (AES) (Fig. 1(b)) from which a thickness of 3 ± 1 ML was

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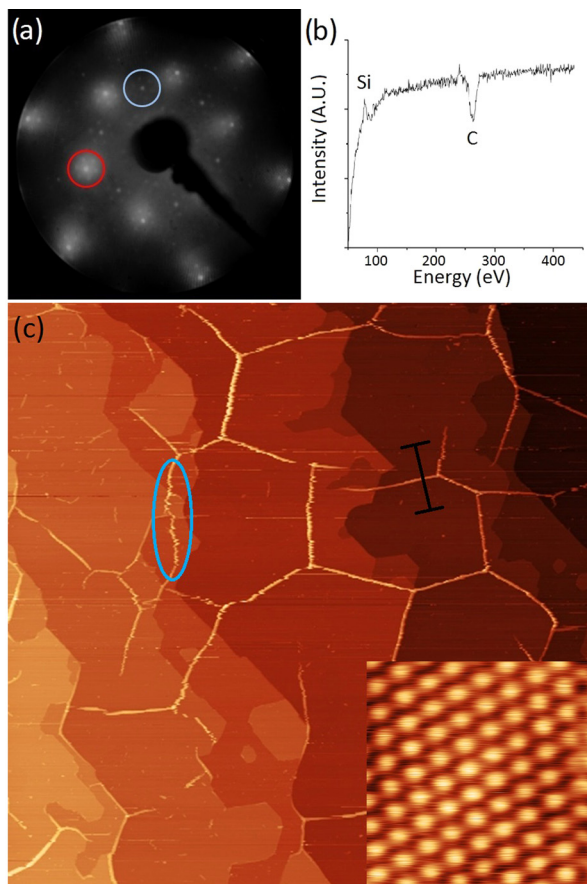


FIG. 1. (a) LEED image obtained at primary beam energy of $E_0 = 116.5$ eV showing graphene and SiC (1×1) spots (red and blue circles, respectively), and the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ buffer layer reconstruction. (b) Auger spectrum taken with a primary beam energy of 2.5 keV showing a strong silicon peak at 92 eV and a graphitic carbon peak at 271 eV. Film thickness is estimated to be 3 ± 1 ML. (c) $1 \mu\text{m}^2$ STM image taken at bias voltage $V_{\text{bias}} = 1.9$ V and tunnel current $I = 0.3$ nA, large graphene terraces are separated by SiC steps with pleat defects criss-crossing the surface in a roughly hexagonal shape meeting at 120° angles. Black line corresponds to height profile in Figure 2. The oval shows an area of pleat dragging. Inset: 2 nm^2 image taken at $V_{\text{bias}} = 0.2$ V and tunnel current $I = 1.9$ nA, showing graphene lattice at atomic resolution.

estimated based on the height ratio of the C *KLL* and Si *LMM* peaks; the calibration curve used is produced from the determination of C:Si sensitivity factors.^{24,25} This was supported by Raman spectroscopy measurements of the width of the 2D peak found at 2750 cm^{-1} . Raman measurements also indicated that the graphene is of a high quality due to the small size of the D peak observed at 1380 cm^{-1} (not shown). Raman Measurements were taken using a Horiba Jobin Yvon LabRAM HR system using a 514.5 nm laser. STM measurements were carried out using a commercial Omicron VT-SPM system; all images were taken in constant current mode.

STM images show high quality graphene forming large terraces over several hundred nanometers (Fig. 1(c)), the pristine hexagonal graphene lattice is visible at higher resolution (inset). Pleat defects are visible on the surface as pale lines intersecting to form an almost hexagonal network. The orientation of the pleats were found to be consistently at $\sim 120^\circ$ angles with respect to each other. This is the result of preferential formation along high symmetry directions, as verified by LEED patterns, indicating the

orientation of graphene on the surface. Consequently, the network of pleats reflects the hexagonal shape of the graphene lattice. Furthermore, junctions at which three pleats meet are prevalent as this allows full 360° stress release. This particular arrangement will also minimize the number of non-six membered rings required for pleats to merge, thus lowering the overall energy cost. Pleat heights and widths remained fairly consistent in range across different samples with average values of 1.0 ± 0.5 nm and 6.0 ± 2.0 nm, respectively, consistent with the previous observations by de Heer *et al.*¹¹ It is also apparent that pleats are not pinned on the surface and are often dragged by the STM tip (Figure 1(c) oval). This phenomenon has been observed before by Sun *et al.*,²⁶ in which pleats were manipulated and new ones even created. Dragged pleats often adhere preferentially at step edges, most likely due to the presence of an energy barrier that prevents further movement.

Our continuum model treats each pleat as a sinusoidal delamination of the graphene sheets from the surface, much like a one-dimensional blister described by Hutchinson and Suo.²⁷ The model form of these pleats is described by Eq. (1) and is shown schematically in Fig. 2 (dotted line). A close resemblance can be seen between the model pleat structure and the experimentally obtained height profile (black solid line). The model fits Eq. (1) by a non-linear least squares to the experimentally obtained pleat cross-section. A flat background is then applied outside the range of the pleat to ignore any small deformations of the surrounding film. This also negates the poor tracking of the surface by the STM tip at the edges of the pleat, visible as small negative excursions in the experimental data at the edges of the peak

$$Y = \frac{\delta}{2} \left(1 + \cos\left(\frac{\pi X}{b}\right) \right), -b \leq X \leq b. \quad (1)$$

The measurable parameters from such fits are the pleat height δ and width $2b$. The relation between these quantities and adhesion energy is given by

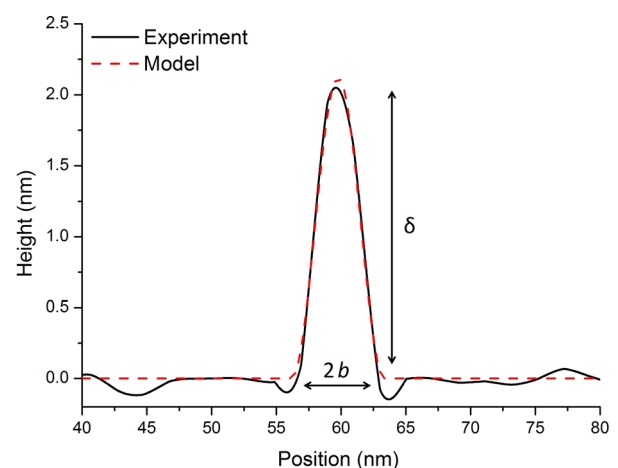


FIG. 2. Cross-section height profile of a pleat as measured in Figure 1(c) and the pleat treated by the continuum model, with pleat width $2b$ and height δ as seen in Eq. (1).

$$\sqrt{\frac{\delta}{h}} = (2\alpha)^{\frac{1}{4}} \frac{b}{h} \left(1 + \sqrt{1 + \frac{3}{4}\alpha \left(\frac{b}{h}\right)^4} \right)^{-\frac{1}{4}} \quad (2)$$

(derived in detail in Ref. 22) where h is the film thickness and the parameter α is related to the adhesion energy Γ by²⁸

$$\Gamma = \frac{hE'_f\alpha}{6} \left(\frac{\pi}{2}\right)^4, \quad (3)$$

where E'_f is the modified Young's modulus $E'_f = E_f/(1 - \nu_f^2)$, where E_f and ν_f are the unmodified Young's modulus and Poisson ratio of graphene. Values of $E_f = 1.00$ TPa and $\nu_f = 0.165$ were taken from the work of Lee *et al.*¹ and Scarpa *et al.*²⁹ to give $E'_f = 1.03$ TPa. Pleats observed at step edges were not used for further analysis due to the discontinuity on one side of the pleat, rendering the model unrealistic at these points; only pleats observed on terraces with flat areas either side were used with the continuum model.

Fig. 3 shows pleat data obtained plotted alongside curves for various adhesion energies at a trilayer thickness ($h = 6.7$ Å). These results indicate an average adhesion energy of 3.0 ± 1.6 J/m². This value is significantly larger than that previously determined on other substrates. The spread in data is assigned to differences from sample to sample, most likely due to differences in surface roughness, which has previously shown to significantly affect adhesion energy.³⁰ Previous work has found adhesion energies for monolayer graphene on copper,³¹ Polydimethylsiloxane (PDMS),⁹ and SiO₂ of 0.72 J/m², 0.176 J/m², and 0.45 J/m², respectively. These values indicate a significant variance in the adhesion energy due to the interaction between the graphene and the substrate. Koenig *et al.* attribute their value for graphene on SiO₂ to the high flexibility of graphene, allowing excellent conformation to the substrate.⁷ As a result, the interaction of graphene with the surface is a defining factor for the adhesion energy. At almost five times the adhesion energy of graphene on copper, a predominantly Van der Waals type of adhesion,³¹ we suggest a significantly different regime is in effect with graphene grown on SiC. We believe that the increased value obtained for the

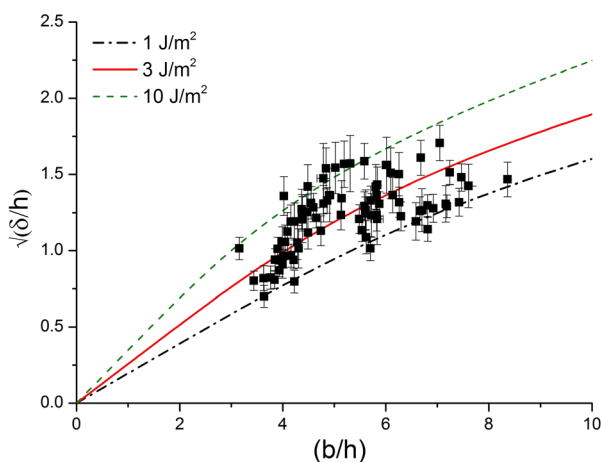


FIG. 3. Pleat height and width data as described by the model in Eq. (2) for a film thickness of 3 ML. Curves for adhesion energies of 1, 3, and 10 J/m² are shown to illustrate the average adhesion and upper and lower bounds.

adhesion is the result of the carbon rich buffer layer delaminating from the surface lifting all the graphene layers above. The formation of this intermediary layer, also known for producing the band gap splitting observed in this system,^{32,33} involves covalent bonds between the carbon atoms in the buffer and the Si atoms in the substrate below, resulting in a far stronger adhesion than is seen in other graphene substrate systems.^{20,34} Pleat formation therefore requires the breaking of these bonds in order to release the stress on the system via delamination of the graphene layers. A theoretical study by Mattausch and Pankratov indicating strong covalent bonding between the surface and the buffer layer, with weaker Van der Waals bonding for subsequent layers, calculated an adhesion energy of 2.3 J/m², supporting the larger value obtained here.³⁴ Furthermore, a study on graphene exfoliation from SiC via strain layers demonstrates that Cu, Pd, and Au are unable to remove graphene from the surface due to their smaller binding energies, whereas Ni is capable of exfoliating up 95% of the graphene layer.³⁵ The graphene-Ni adhesion energy has been reported to be as high as 3.65 J/m², suggesting that the graphene-SiC adhesion energy is similar in magnitude.³⁶

In conclusion, we have shown the adhesion energy of graphene on SiC(0001) can be obtained through the measurement of pleat defects. An orientational preference for pleat formation was observed, whereby formation occurs at $\sim 120^\circ$ angles with respect to other pleats. The orientational preference is assigned to preferable development along energetically favourable directions of the graphene lattice. A continuum model requiring only the easily measurable parameters of pleat height and width was used to determine a value for the adhesion energy of 3.0 ± 1.6 J/m². The significantly larger value obtained for this system, in comparison to earlier studies of graphene on other substrate materials,^{7,9,31} is attributed to the buckling of the buffer layer that forms upon graphene growth, requiring the breaking of covalent bonds between carbon atoms in the buffer layer and Si atoms on the substrate surface. Our model provides a simple method for determining the adhesion energy of graphene to a substrate that can be adapted to any system in which pleat formation occurs. Straightforward determination of graphene's adhesion energy on various substrates will allow for effective use of graphene layers in future electrical and mechanical devices.

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