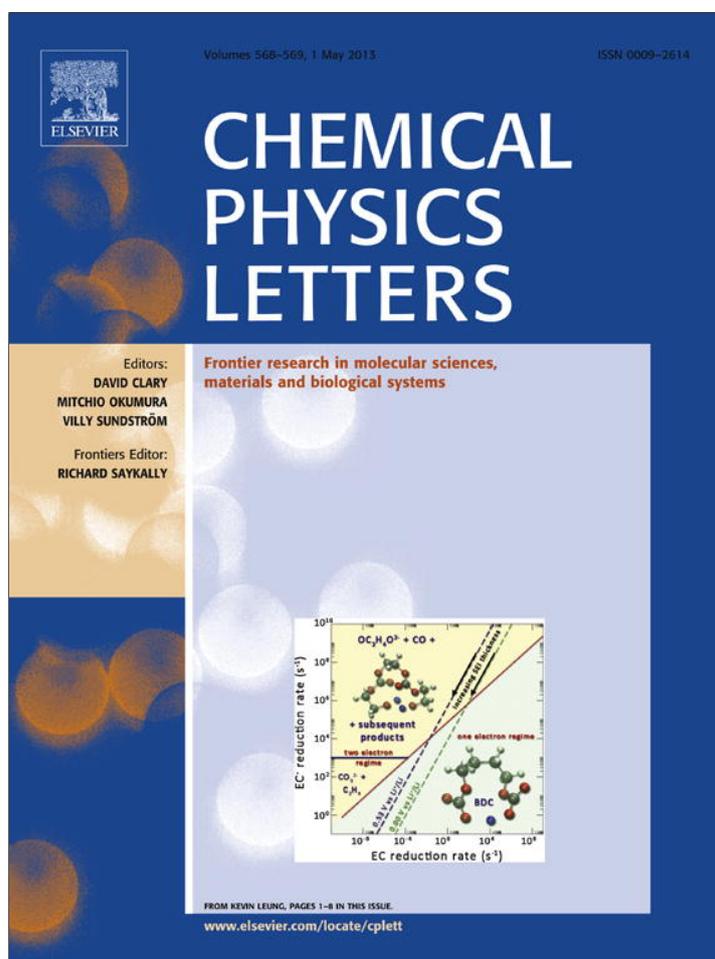


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Crystallographic orientation of early domains in CVD graphene studied by Raman spectroscopy

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ABSTRACT

Crystallographic orientations of early multi-lobe graphene domains in CVD-grown graphene are investigated. Partially grown graphene domains were transferred onto flexible substrates and uniaxial tensile strain was applied. From the polarization dependence of the Raman G band, split due to strain, the crystallographic orientation was determined. It was found that there are some single crystal domains. However, lobes have different orientations in some other multi-lobe domains. Within a given lobe, the orientation does not change as the domain grows, indicating that the orientations present in a graphene domain are determined at an early stage of growth.

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1. Introduction

Graphene is attracting much attention owing to its superior electrical, mechanical, thermal, and optical properties. For most applications, fabrication of high quality, large area graphene is essential, and chemical vapor deposition (CVD) on metal catalysts such as Ni or Cu is currently the most promising method [1–3]. Single-layer graphene sheets exceeding 30 inches in diagonal have been successfully grown [4]. Full coverage CVD-grown graphene films invariably have crystallographic grains because the growth is initiated at random nucleation sites on the metal surface. The grains usually have different crystallographic orientations, as measured by dark-field transmission electron microscopy (DF-TEM) [5,6]. Since grain boundaries are structural defects that may degrade the mechanical or electrical properties of graphene, it is important to develop growth techniques for large-grain or even single crystal graphene sheets. By controlling the nucleation density, large-grain single-layer graphene has been successfully grown [7]. One may suggest that aligning the crystallographic orientation of neighboring domains which finally merge to make a continuous film would reduce the detrimental effects of grain boundaries. Therefore, investigation of the distribution of domain orientations is necessary such as in partial coverage films where the domains are independent and have not yet merged into a continuous film.

In the early stages of CVD growth, graphene nuclei (also referred to as domains or islands) often have snowflake-like or petal-shaped forms with 4–6 lobes [7,8]. There have been suggestions that most graphene nuclei, or early graphene domains, are single crystals with all the lobes aligned in the same orientation [6–9]. However, the orientations of the lobes to date have been addressed by electron diffraction methods that are exceptionally time consuming, and so sufficient statistics have not been obtained. This motivates us to suggest that a much more rapid method of measuring crystal orientation is called for. In this Letter, we report on investigation of crystallographic orientations of the lobes of early graphene domains grown on Cu foil using polarized Raman spectroscopy combined with uniaxial tensile strain and suggest that further development of this method will mean that it will find use for rapid assessment of grain orientations in complete coverage graphene films.

Raman spectroscopy is one of the most widely used characterization tools in graphene research. It is used to determine the number of graphene layers [10–12], doping [13,14], mechanical properties [15–17], thermal properties [18–21], etc. When graphene is under uniaxial tensile strain, the G and 2D bands of the Raman spectrum red-shift and split. The split Raman bands exhibit a characteristic polarization dependence, which can be used to determine the crystallographic orientation relative to the strain axis [15,22,23]. Therefore, the orientations of different parts of isolated graphene domains at partial coverage can be probed by applying uniaxial tensile strain on the sample and measuring the polarization dependence of the Raman spectrum at each position.

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2. Experimental

The graphene samples were produced by low pressure CVD as reported in Ref. [2]. 25- μm thick Cu foil (Alfa Aesar, No. 13382) was loaded into a tube furnace and heated to 930 $^{\circ}\text{C}$. After a 10 min anneal in $\text{H}_2(\text{g})$ with a flow rate of 2 sccm and pressure ~ 30 mTorr, 1.0 sccm of CH_4 was then introduced for a total pressure of ~ 42 mTorr. The growth time was ~ 5 min to achieve isolated graphene domains on Cu. In order to apply uniaxial tensile strain, the graphene samples were transferred onto acrylic substrates using a micro-contact transfer printing technique as schematically shown in Figure 1 [24,25]. The transfer media and remover were replaced with fluoropolymer (CYTOP, Asahi glass Co.) and corresponding solvent (PF-5060, 3M Co.) because acrylic is easily damaged by organic solvents such as acetone or isopropanol. The detail of the transfer process is as follows: first, a CYTOP layer was spin coated on the Cu foil with graphene domains at 1800 rpm for 45 s and baked using a hotplate at 120 $^{\circ}\text{C}$ for 2 min. The CYTOP film with graphene was then separated by dissolving Cu foil in ammonium persulfate and transferred onto the center of an acrylic substrate. Finally, the CYTOP film was removed in PF-5060 (3M) for over 1 h [26].

The acrylic substrate was mechanically bent to apply uniaxial tensile strain on the graphene sample [15]. For polarized micro Raman spectroscopy, the 514.5-nm line of an Ar ion laser, with a power of 700 μW , was used as the excitation. A $50\times$ objective lens (0.8 N.A.) was used to focus the laser on the sample. The focus size was less than 1 μm in diameter. The scattered light was collected by the same objective and sent to a 0.55-m spectrometer (Jobin-Yvon Triax 550) with a liquid-nitrogen-cooled CCD detector array (SpectrumOne). The spectral resolution and the repeatability of the system were ~ 1 cm^{-1} each. The incident laser beam was linearly polarized along the direction of the uniaxial strain, and an analyzer was used to select the polarization of scattered photons. A half-wave plate was placed between the analyzer and the spectrometer and was adjusted to keep the polarization of the photons entering the spectrometer constant regardless of the analyzer direction. We measured a total of 7 samples, labeled S1 through S7.

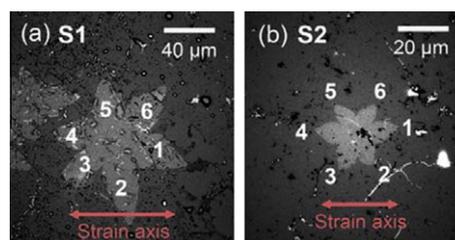


Figure 2. (a) and (b) Optical microscope images of two samples S1 and S2. Both have six lobes each.

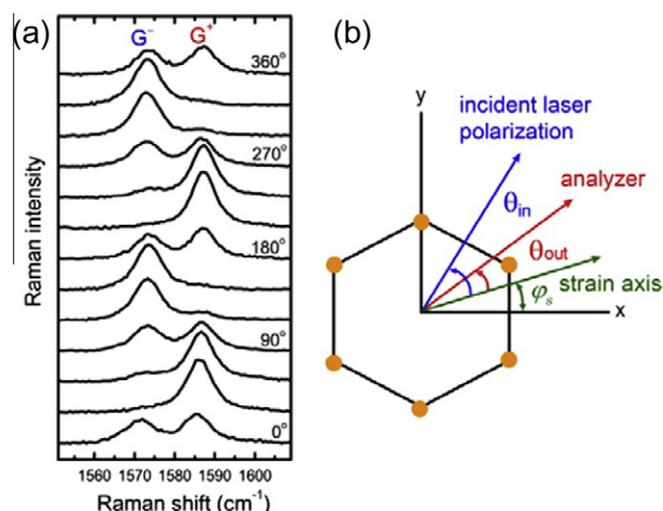


Figure 3. (a) Raman G band from lobe 5 of S1 subjected to $\sim 1\%$ of uniaxial tensile strain as a function of the analyzer angle θ_{out} . The incident polarization is fixed along the strain direction ($\theta_{\text{in}} = 0$). (b) Definition of the angles θ_{in} , θ_{out} , and ϕ_s with respect to the zigzag direction of the graphene lattice.

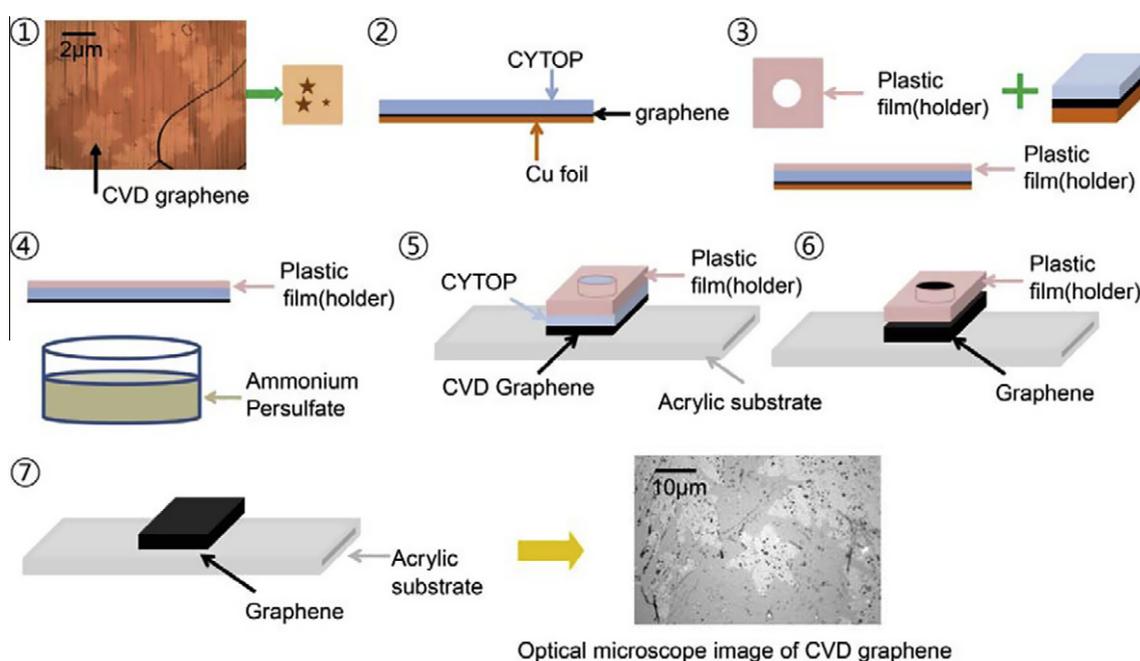


Figure 1. CVD graphene samples grown on Cu foil were transferred onto acrylic substrates using the micro-contact transfer printing technique [24,25].

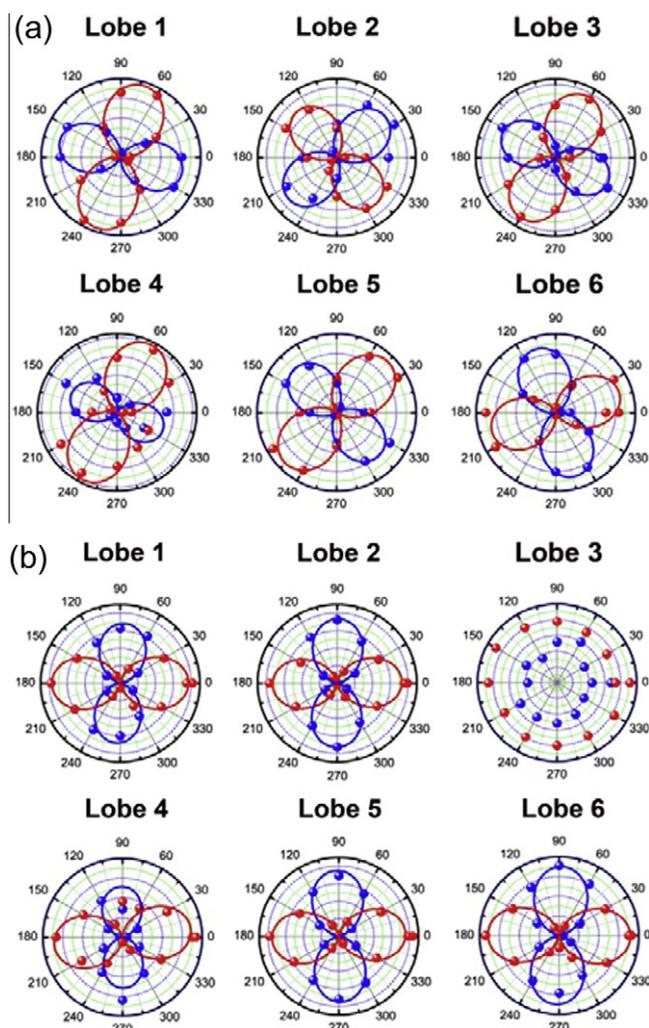


Figure 4. Polar plots of the intensities of G^+ (red curves) and G^- (blue curves) peaks for (a) S1 and (b) S2 at each lobe. The solid curves are fits to Eq. (1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

Figure 2 shows optical microscope images of S1 and S2, which were obtained from the same Cu foil. The petal-shaped early graphene domains have six lobes each. S1 is considerably larger than S2. The strain axis is indicated.

Figure 3a shows the polarization dependence of the G band from lobe 5 of S1 subject to $\sim 1\%$ of uniaxial tensile strain. When uniaxial tensile strain is applied, the G band split into two peaks since the double degeneracy of the E_{2g} vibrational mode at the zone center is broken [15,22,27]. The intensities of the two split peaks, designated G^+ and G^- , vary as a function of the analyzer

angle. The incident polarization was fixed along the strain direction. The intensities of the two peaks can be modeled to be [22,23]

$$I_{G^+} \propto \cos^2(\theta_{\text{in}} + \theta_{\text{out}} + 3\varphi_s) \text{ and } I_{G^-} \propto \sin^2(\theta_{\text{in}} + \theta_{\text{out}} + 3\varphi_s) \quad (1)$$

where the incident laser polarization θ_{in} , the analyzer angle θ_{out} , and the angle φ_s between the strain direction and the zigzag direction of the graphene lattice are defined in Figure 3b. Since the incident polarization is fixed at $\theta_{\text{in}} = 0$, we can obtain φ_s by fitting the intensities of the two peaks as a function of θ_{out} .

Figure 4 shows polar plots of the intensities of G^+ and G^- measured at each lobe of S1 and S2. The solid curves are fits to Eq. (1). Reasonable fits were obtained except for lobe 3 of S2. It seems that strain was not reliably applied to this lobe, although it is difficult to tell exactly what happened. Even though the G band from this lobe was red-shifted and split due to the applied tensile strain, the shift and the splitting was smaller than the other lobes and the relative intensities of the split G peaks did not change appreciably. For S1, the crystallographic orientation of each lobe is $\varphi_{1s} = 35.6 \pm 1.5^\circ$, $\varphi_{2s} = 16.5 \pm 2.0^\circ$, $\varphi_{3s} = 39.2 \pm 1.1^\circ$, $\varphi_{4s} = 38.3 \pm 2.5^\circ$, $\varphi_{5s} = 45.2 \pm 1.5^\circ$, and $\varphi_{6s} = 5.9 \pm 1.8^\circ$. Lobes 2 and 6 seem to have crystallographic orientations significantly different from the others. The other 4 lobes have more or less similar orientations within experimental uncertainties. For S2, the crystallographic orientation of each lobe is $\varphi_{1s} = 0.6 \pm 2.7^\circ$, $\varphi_{2s} = 0.1 \pm 2.0^\circ$, $\varphi_{4s} = 58.6 \pm 2.8^\circ$, $\varphi_{5s} = 59.3 \pm 2.0^\circ$, and $\varphi_{6s} = 0.6 \pm 2.5^\circ$. Except for lobe 3, where we could not obtain reliable data as explained above, the crystallographic orientations at all five lobes are similar, and so we conclude that this early graphene domain is a single crystal.

We repeated the measurements on samples S3 through S7, shown in Figure 5. The sizes of the early domains vary between 20 and 60 μm . The crystallographic orientation φ_s for each lobe is summarized in Table 1. For S5, all the lobes seem to have the same orientation within experimental error. On the other hand, S4, S6 and S7 have at least one lobe that has an orientation significantly different from those of the others. S3 is marginal: lobes 4 and 5 seem to have orientations somewhat different from the others, but the difference is just outside the experimental uncertainty. For some lobes where the orientation angle is missing in Table 1, reliable fits could not be obtained because strain was not properly applied. Based on these analyses, we can assign S2 and S5 to be single crystals whereas S1, S4, S6, and S7 are not.

In order to see if the crystallographic orientation evolves as an early domain grows laterally, we measured the orientations at several positions within lobes 5 and 6 of S1. The positions are indicated in Figure 6a. We chose three positions for each lobe radially moving from the center. As we already analyzed in the above, lobes 5 and 6 have different orientations. Figures 6b and c clearly show that although lobes 5 and 6 have different orientations, the orientation does not change within a lobe as the domain grows from the center nucleation point. Therefore, we can conclude that the orientation of each lobe within a domain is determined at an early stage of growth.

The crystallographic orientations in early graphene domains have been studied using DF-TEM [5,6], photoelectron emission

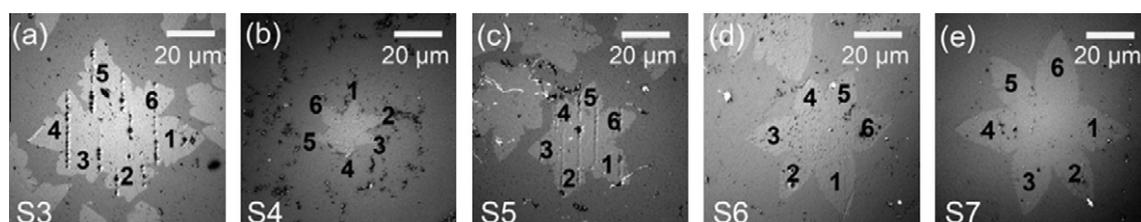


Figure 5. Optical microscope image of samples S3 through S7. The strain direction is horizontal in the image.

Table 1
Crystallographic orientation φ_s of each lobe for samples S1 through S7.

	Lobe 1	Lobe 2	Lobe 3	Lobe 4	Lobe 5	Lobe 6
S1	$35.6 \pm 1.5^\circ$	$16.5 \pm 2.0^\circ$	$39.2 \pm 1.1^\circ$	$38.3 \pm 2.5^\circ$	$45.2 \pm 1.5^\circ$	$5.9 \pm 1.8^\circ$
S2	$0.6 \pm 2.7^\circ$	$0.1 \pm 2.0^\circ$	–	$58.6 \pm 2.8^\circ$	$59.3 \pm 2.0^\circ$	$0.6 \pm 2.5^\circ$
S3	$45.7 \pm 1.5^\circ$	$44.5 \pm 2.5^\circ$	$45.5 \pm 2.5^\circ$	$35.6 \pm 3.8^\circ$	$53.6 \pm 4.4^\circ$	$46.7 \pm 3.5^\circ$
S4	$8.8 \pm 3.9^\circ$	$5.2 \pm 4.1^\circ$	$14.9 \pm 2.5^\circ$	$5.5 \pm 4.6^\circ$	$11.2 \pm 2.5^\circ$	$14.6 \pm 1.5^\circ$
S5	$15.8 \pm 2.2^\circ$	$13.8 \pm 1.8^\circ$	$16.6 \pm 1.8^\circ$	$15.4 \pm 2.2^\circ$	$18.1 \pm 1.7^\circ$	$19.4 \pm 2.1^\circ$
S6	$58.1 \pm 2.0^\circ$	$55.8 \pm 3.8^\circ$	–	$15.2 \pm 4.4^\circ$	$7.8 \pm 2.4^\circ$	$57.5 \pm 1.5^\circ$
S7	$16.2 \pm 4.6^\circ$	$10.9 \pm 1.5^\circ$	$10.2 \pm 1.5^\circ$	$5.3 \pm 2.5^\circ$	$9.8 \pm 2.5^\circ$	$9.9 \pm 1.5^\circ$

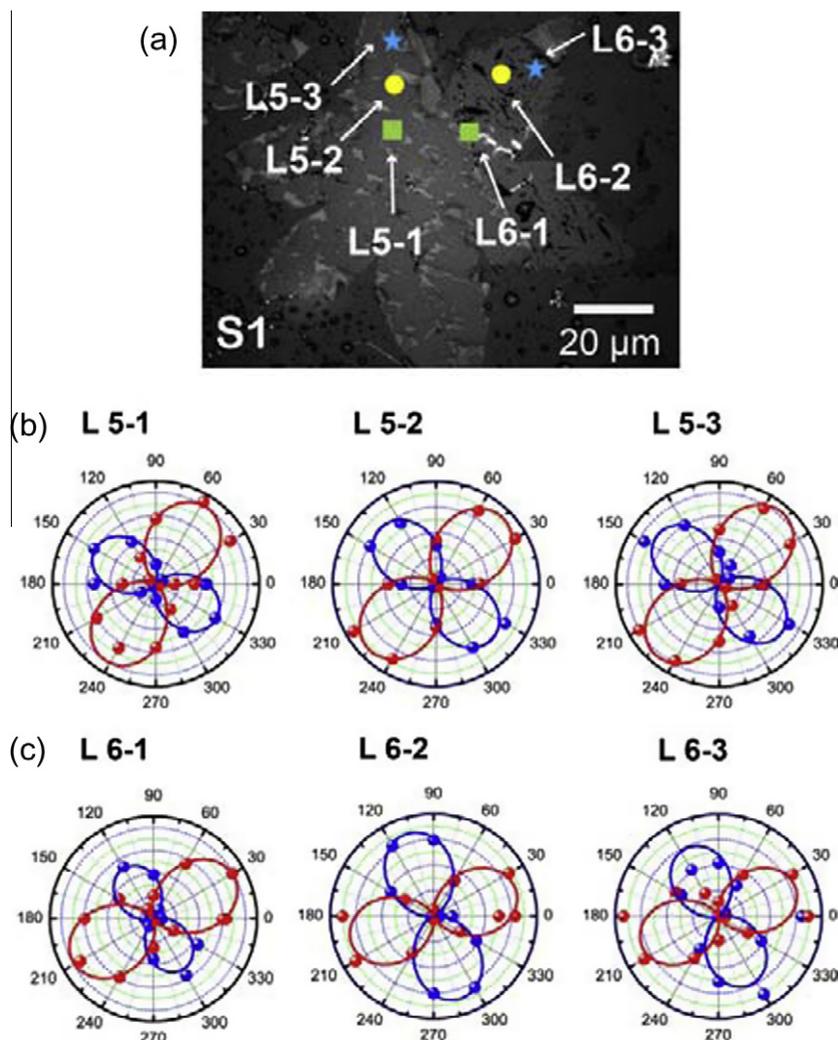


Figure 6. (a) Optical microscope image of S1, 3 points each for lobes 5 and 6 were measured. Polar plots of the intensities of G^+ (red curves) and G^- (blue curves) at each point of (b) lobe 5 and (c) lobe 6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

microscopy (PEEM) [7], high-resolution TEM [8], and low-energy electron microscopy (LEEM) [9,28]. Because these methods are very time-consuming, only a few samples were investigated in each study. Based on such data with limited statistics, conclusions were drawn as to whether early domains are single-crystalline [6–9,28] or polycrystalline [5,28]. Although our data set is not much larger than the previous studies, we found both single crystals and polycrystals among the early domains prepared in similar conditions. This suggests that it is possible to obtain large single-crystal domains, but more refinement or control of the growth parameters would be needed in order to increase the percentage of single-crystal domains. The current work does not address what

the critical parameters are that determine crystalline orientations. More refined studies would be necessary in order to correlate the growth parameters and the distribution of the crystallographic orientations in early domains.

4. Conclusion

We have used polarized Raman spectroscopy to find that the lobes in individual domains of partial coverage CVD graphene do not necessarily have the same crystallographic orientations. There are indeed some single crystal domains with all the lobes in the

same crystallographic orientation. However, in four out of seven multi-lobe domains investigated in this Letter, some of the lobes have orientations different from the others. Within a given lobe, the crystallographic orientation does not change as the domain grows, indicating that the orientation of a graphene domain is determined at an early stage of growth. This study also suggests that further effort is necessary to find out optimized parameter windows for single-crystal graphene domain growth. In the future, this approach can be further developed to provide a rapid screening method of grain orientation in full coverage graphene films.

Acknowledgements

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