Selecting a single orientation for millimeter sized graphene sheets

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We have used Low Energy Electron Microscopy (LEEM) and Photo Emission Electron Microscopy (PEEM) to study and improve the quality of graphene films grown on Ir(111) using chemical vapor deposition (CVD). CVD at elevated temperature already yields graphene sheets that are uniform and of monatomic thickness. Besides domains that are aligned with respect to the substrate, other rotational variants grow. Cyclic growth exploiting the faster growth and etch rates of the rotational variants, yields films that are 99% composed of aligned domains. Precoating the substrate with a high density of graphene nuclei prior to CVD yields pure films of aligned domains extending over millimeters. Such films can be used to prepare cluster-graphene hybrid materials for catalysis or nanomagnetism and can potentially be combined with lift-off techniques to yield high-quality, graphene based electronic devices.

Graphene potentially constitutes a new material for electronic circuitry with vastly improved transport properties over traditional silicon[1]. A large scale application of graphene crucially hinges on a fabrication method that yields perfect graphene sheets, that is low-cost and reliable. CVD growth of graphene on metals has recently been demonstrated to yield large graphene sheets of uniform monatomic thickness[2,3,4,5,6]. This form of epitaxial CVD, which occurs through ethylene decomposition on the uncovered parts of the metal substrate, is self-limiting since the nature of the process limits the thickness of the graphene sheets to a single atomic layer, in contrast to e.g. graphene formed on heated SiC substrates[7,8]. Metal CVD thus appears to be the route of choice for fabrication of large graphene sheets. In situ growth studies with LEEM and PEEM have however, highlighted a new problem. The orientation of the domains that make up the graphene sheet is not always in registry with the substrate. For the case of e.g. Ir(111), four different orientations have been observed[9]. The electronic properties of graphene sheets depend sensitively on the relative orientation with respect to the substrate[10,11,12]. Also, applications of cluster superlattices of magnetically or catalytically active materials grown on the graphene sheets[13] require full control over the orientation of the domains. Here, we address this problem by tailoring the epitaxial process to grow a millimeter sized, monatomic thickness graphene sheet of single, aligned orientation.

An Ir(111) single crystal was heated to 1123 K and exposed to a 1·10⁻⁷ mbar partial pressure of O₂ to remove residual carbon contamination. CVD growth of graphene sheets was performed by exposing the surface to ethylene at elevated temperatures. Growth of the graphene ceases when the fractional surface coverage of graphene approaches 1 ML. Threshold PEEM images using a Hg discharge lamp yield a high intensity from the graphene flakes and very low intensity from the bare Ir(111) surface. Contrast between the different rotational domains is achieved in LEEM mode at various electron energies.

First, growth of a graphene sheet was studied at a temperature of 1411 K by exposing to an ethylene partial pressure of 1·10⁻⁷ mbar. The formation of the graphene is shown in Fig. 1. Initially, only a single phase forms that has its lattice vectors parallel to the substrate lattice. Later, graphene domains that are rotated with respect to the substrate lattice are observed to form at the edges of the original nuclei and grow at a rate that is substantially faster. In what follows, we shall refer to these as aligned and rotated domains, respectively. The structure of the graphene sheet after it has completed is shown in Fig. 1(b). From the simple observation that contrast between different domains is observed in these threshold PEEM images, we conclude that there is a significant variation of the electronic structure of the film between different domains. Even though the sheet thickness is very uniform and could already be characterized as a high quality graphene film, further control over the rotational orientation of the domains is desired.

One way to produce a high quality graphene film of a single rotational phase is done by exploiting the higher reactivity of the edges of the rotated domains. Not only do the three types of rotated domains grow at a rate that is higher than that of aligned domains, they are also etched away by oxygen at an increased rate[14]. Fig. 2 highlights this experimental approach. The Ir(111) surface was alternately exposed to ethylene and O₂ at partial pressures of 5·10⁻⁸ mbar. Exposure to ethylene leads to the formation of new nuclei and continued growth of aligned domains. It also gives rapid growth of any rotated domains that have formed. Exposure to O₂, shown in Fig. 2(b), then preferentially etches away the rotated
Two different types of domains are observed to form. The brighter of the two is aligned with the substrate, whereas the other, darker, type of domain is rotated by approximately 30° with respect to the substrate. The film has fully closed to form a graphene sheet consisting of various rotational domains. The majority of the graphene sheet consists of rotated domains.

The nucleation of rotated domains occurs at the edges of parallel domains [9]. In our measurements, we also observe that growth of aligned domains and the nucleation of rotated domains occurs predominantly at those edges that do not run parallel to the substrate lattice vectors. This observation was exploited to further improve the quality of the films beyond what was demonstrated in Fig. 2 with the cyclic recipe. A monolayer of ethylene was preadsorbed on the surface at room temperature. Upon heating the substrate to the growth temperature this leads to the formation of a high density of small aligned graphene domains that have edges parallel to the substrate lattice [4]. This effectively forces any graphene domains that impinge on existing nuclei to maintain their aligned orientation. Fig. 3 highlights the subsequent growth when the substrate is exposed to an ethylene partial pressure of $1 \cdot 10^{-7}$ mbar. Figs. 3(b) and (c) illustrate that growth of aligned domains is observed only in those locations where domain edges are rough, having an orientation deviating from the dense packed substrate directions. Small domains with edges oriented
FIG. 3: 4 µm FOV LEEM images of graphene growth on Ir(111) at a temperature of 1113 K and recorded with an electron energy of 18.6 V. The dark spot in the top of the images is an MCP defect. (a, t = 0 s) Start of ethylene exposure of the surface. The Ir(111) surface has been precovered with many small graphene nuclei, appearing dark in the LEEM images. (b, t = 139 s) Several of the predeposited domains have started to grow. Those domains that have edges along the substrate crystallographic directions are not observed to grow. (c, t = 631 s) The graphene film has nearly evolved into a sheet. No rotated domains that would yield a higher intensity than the aligned domains, are observed. Several precovered domains still persist and do not grow. (d, t = 1279 s) The film has fully closed to form a perfectly aligned graphene sheet. (e) A 0.25 µm FOV STM image of the growth of the parallel phase taken after the graphene film was only partially completed. The smaller nuclei with straight edges running along substrate crystallographic directions have not grown significantly, whereas domains with edges of different orientation have (I = 0.5 nA, V = 0.5 V). (f) µLEED pattern obtained of the closed graphene film. The orientation of the graphene is unaltered when the beam is scanned over an area of several millimeters.

In conclusion, we have grown millimeter sized, graphene films of a single orientation. Cyclic growth of the graphene film exploiting the different growth and O₂ etching speeds of the domain variants yields films that are aligned to the substrate dense packed orientation up to a fraction of 99%. The final approach, using preadsorption of ethylene on the Ir(111) surface at room temperature, followed by CVD growth at elevated temperatures yields perfectly aligned sheets that are ready for application.

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