Detailed studies of graphene grown on C-face SiC

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ABSTRACT

Graphene samples were grown on the C-face of SiC, at high temperature in a furnace and an Ar ambient, and were investigated using LEEM, XPEEM, LEED, XPS and ARPES. Formation of fairly large grains (crystallographic domains) of graphene exhibiting sharp (1x1) patterns in μ-LEED was revealed and that different grains showed different azimuthal orientations. Selective area constant initial energy photoelectron angular distribution patterns recorded showed the same results, ordered grains and no rotational disorder between adjacent layers. A grain size of up to a few μm was obtained on some samples

Keywords: graphene, C-face SiC, ordered grains, LEEM, XPEEM, μ-LEED and ARPES.

1 INTRODUCTION

Graphene based nano-electronic devices has attracted much attention due to its excellent properties such as high electron mobility and chemically inertness. Thanks to the SiC composition it is possible to heat the SiC crystal up to elevated temperature to sublimate the SiC atoms and leave a single or few layers of graphene/graphite on top of the substrate. However, the registry of adjacent graphene layers grown on the C-terminated SiC(000-1) surface has been reported to be dramatically different [1-7] compared to graphene grown on the Si-terminated SiC(0001) surface. Whereas Si-face graphene exhibits sharp spots in LEED and the Bernal (ABAB…) stacking, multilayer graphene on the C-face has been reported to stack in such a way that adjacent graphene layers are rotated with respect to each other. X-ray diffraction and LEED experiments show [1,2,4,5,7] broad peaks indicating preferred rotation angles in a band of ±5°around 0°. It has also been suggested that the rotated layers are interleaved, instead of forming distinct domains of different orientations. The rotational disorder produce moiré patterns in STM topographs [6], and have been suggested to explain why epitaxial graphene films, tens of layers thick, show single layer electronic properties [2, 5]. For Si–face graphene the structural quality was shown to improve dramatically upon furnace growth at a high temperature and in an argon [8,9] environment, compared to *in situ* preparation. Considerably larger graphene domains were obtained by furnace growth at high temperature. Although a recent study of C-face graphene did not show a similar improvement [7] after growth at 1600°C in a 1 atm argon environment we wanted to find out if a higher growth temperature would give large enough grains/domains so single grains could be directly investigated also for C-face graphene.

We found [10] formation of fairly large grains (crystallographic domains) of graphene exhibiting sharp 1x1 spots in μ-LEED while adjacent grains were found to show different azimuthal orientations. The macro-LEED patterns were found to mimic earlier recorded [2,4,5,7] LEED patterns and indicated contribution from several grains of different azimuthal orientations. Selective area constant initial energy photoelectron angular distribution patterns collected showed the same result. When utilizing a small aperture (probing area) the six Dirac cones at the K-points of the Brillouin zone could be clearly resolved while several Dirac cone replicas from differently oriented grains were detected when a large aperture was utilized. These findings show clearly the existence of ordered multilayer graphene grains with different azimuthal orientations and not that adjacent graphene layers are rotationally disorder as earlier reported for C-face graphene.

2 EXPERIMENTAL

Graphene samples were grown on nominally on-axis C-face SiC and both n-type 6H and 4H substrates were used. High temperature sublimation in an inert gas environment was applied [8] and the temperature range 1800-2000°C, pressure range 500-850 mbar and average growth time of 15 min was used. The thickness, morphology and electronic structure of these graphene samples were investigated using Low-Energy Electron Microscopy (LEEM), X-ray Photo Electron Emission Microscopy (XPEEM), Photo Electron Spectroscopy (PES) and LEED on beam line I311 at the MAX laboratory. In the LEEM instrument it was possible to switch between energy filtered images of the surface and energy filtered photoelectron emission angular distribution patterns. Angle Resolved Photo Electron Spectroscopy (ARPES) experiments were performed also at beam line I4.

3 RESULTS AND DISCUSSION

A LEEM image collected from a sample at a voltage of 2.7 eV and a field of view of 10 μm is shown in Fig. 1a). This sample was grown on an on-axis 4H-SiC substrate. Extracted reflectivity curves from the areas labeled 1 to 5,

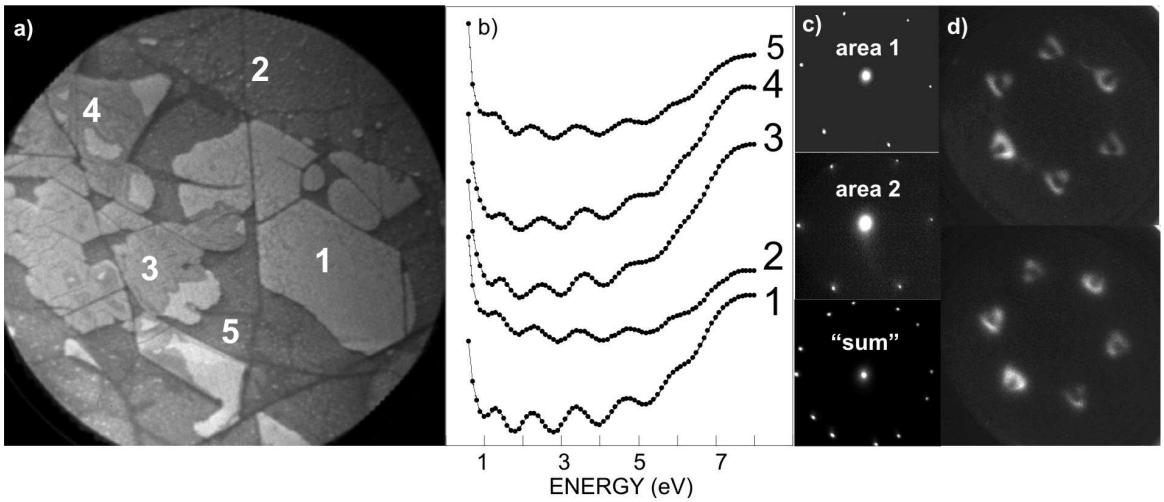

Fig. 1 a) LEEM image recorded from a sample at 2.7 eV and a field of view of 10 μm. b) Electron reflectivity curves extracted from the different areas labeled 1-5. c) The two upper panels show μ-LEED patterns collected at 45 eV using a probing area with a diameter of 400 nm from the positions labeled 1 and 2 in Fig. 1a). The lower panel shows the LEED pattern collected using a probing diameter of 5 μm at position 2. d) Shows two constant energy photoelectron angular distribution patterns (E_i,k_x,k_y) of the π-band collected using a probing area diameter of 800 nm, a photon energy of 45 eV and at an energy of about 2 eV below the Fermi. One Dirac cone centered at each of the six K-points in the Brillouin zone is clearly observed.

respectively, are plotted in Fig. 1b). Although clear domains appear in the LEEM image the reflectivity curves show that most have the same number of graphene layers. Six minima are clearly observed in curves 1, 2 and 5 while curves 3 and 4 appear to have only five minima. However, when looking in detail at these latter curves one finds that there actually appears a weak minimum at around 6.5 eV also in these. The coverage may thus actually be 6 ML (ML= monolayer) over the whole area in Fig. 1a). Whether the whole surface has a 6 ML coverage or some areas have 5 ML is however not important for the message we want to convey from this sample. The main message is contained in Figs. 1c) and d). Selected area LEED patterns collected using a probing area with a diameter of 400 nm from the positions labeled 1 and 2 in Fig. 1a) are shown in the two upper panels in Fig. 1c). It is obvious from these LEED patterns that a grain size larger than 400 nm has been achieved on this sample and that the stacking of the graphene layers in such that adjacent layers are not rotated with respect to each other. The third, bottom, panel in Fig. 1c) shows the LEED pattern collected using a 5 μm large probing area diameter at position 2. The sampled area then includes domains 2 and 1 and it is obvious that two grains of different azimuthal orientations are now probed since this LEED pattern just represents a superposition of the patterns shown in the upper two panels. To further emphasize that grains of multilayer graphene do form on the C-face and stack in such a way that no rotational disorder exists between adjacent layers, some constant energy photoelectron angular distribution patterns (E_i,k_x,k_y) of the π-band [11] were also recorded. Only six Dirac cones, which appear triangular at this initial energy, centered at the six K-points in the Brillouin zone are observed in these patterns, Fig. 1d). These confirm that adjacent graphene layers are not rotated relative to each other.

The XPEEM image in Fig. 2a) was recorded from a graphene sample grown on an on axis 6H substrate. The reflectivity curves show that 1-4 ML graphene have formed on the different areas. This XPEEM image also shows the variation in work function over the surface. The light grey areas correspond to regions where no graphene has formed while the darker gray areas indicate graphene formation. To further confirm this, C 1s spectra collected from areas 1 and 2 using 450 eV photons and a probing area of 1.5 μm are displayed in Fig. 2b). The G/SiC peak intensity ration is seen to be fairly high in the spectrum from area 1 and (1x1) pattern (see inset) demonstrates again that fairly large multilayer graphene grains, >5 μm, form that show no trace of rotational disorder between adjacent layers. It appears that the gray pattern on area 2 originates from graphene and that area 2 contains a mixture of graphene and silicate. No graphene component was detected in C 1s spectra collected from area 3 and the LEED pattern shows a ($\sqrt{3}$x$\sqrt{3}$) R30° reconstruction indicating silicate region.

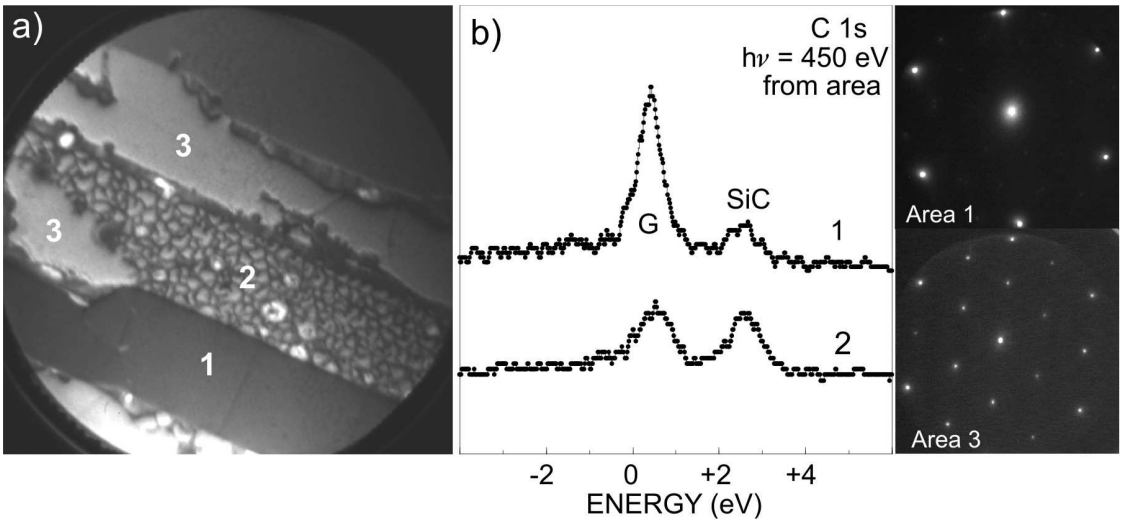

Fig. 2 a) XPEEM image recorded from a sample at 0.1 eV using 130 eV photon energy. b) C 1s spectra recorded, using 450 eV photon energy from the area labeled 1 and 2 in (a). μ-LEED patterns collected at 47 eV from the area labeled 1 and 3 using a probing area of 5 μm are also shown in the insets.

4 SUMMARY

The μ-LEED and constant energy photoelectron angular distribution patterns reported show unambiguously the same results, formation of ordered multilayer grains of graphene on the C-face of SiC with no rotational disorder between adjacent layers. It has earlier been claimed that adjacent graphene layers on the C-face are rotated with respect to each other, and may be interleaved. The reason we can observe ordered grains (crystallographic domains) of multilayer graphene we suggest is due to that larger grains form at the higher growth temperature we have utilized, compared to earlier efforts [1-7] where lower growth temperatures have been applied, resulting in smaller grain sizes.

5 ACKNOWLEDGEMENT

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