Electronic structure of polycrystalline CVD-graphene revealed by Nano-ARPES

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Abstract. The ability to explore electronic structure and their role in determining material’s macroscopic behaviour is essential to explain and engineer functions of material and device. Since its debut in 2004, graphene has attracted global research interest due to its unique properties. Chemical vapor deposition (CVD) has emerged as an important method for the massive preparation and production of graphene for various applications. Here by employing angle-resolved photoemission spectroscopy with nanoscale spatial resolution ∼100 nm (Nano-ARPES), we describe the approach to measure the electronic structure of polycrystalline graphene on copper foils, demonstrating the power of Nano-ARPES to detect the electronic structure of microscopic single crystalline domains, being fully compatible with conventional ARPES. Similar analysis could be employed to other microscopic materials.

1. Introduction

Graphene has attracted intensive research attentions in the past decade due to its excellent structural and electronic properties as well as great potentials in applications[1, 2, 3, 4, 5]. CVD[6, 7, 8, 9, 10] is, among others to date, the dominant technology that yields to scale and performance for graphene growth on metals[11, 12]. Recently, commercially available cooper foils have become an efficient and inexpensive substrate for scalable CVD growth of large-area graphene films[12, 13]. However, in most cases the CVD-grown graphene films on Cu foils are polycrystalline with microscopic single crystal domains. This naturally lowers the possibility for traditional ARPES to characterise the detailed electronic structure of graphene. The recent conceptional and technical progress represented by Nano-ARPES[14, 15, 16] has opened a new path to characterise the electronic structure of microscopic crystal. Here we will discuss the general approach for ARPES and Nano-ARPES to measure the comprehensive band structure and Fermi surface of CVD-grown graphene on Cu foils. We observe clear features for the Fermi surface of both graphene and Cu, with that the relative orientation between graphene and Cu surface can be discussed. We then analyse in detail the approach for Nano-ARPES to study the electronic structure of microscopic graphene grains. These comprehensive electronic structures of polycrystalline graphene/Cu provides valuable information to understand and further to optimise the properties of CVD-graphene. We also expect that these general approaches combining ARPES and Nano-ARPES techniques would be employed to many other different types of nanomaterials.
2. General Fermi surface and orientation of graphene/Cu revealed by ARPES

![Figure 1. General ARPES measurement geometry and Fermi surface of polycrystalline graphene/Cu. a, Schematic for Fermi surface mapping by ARPES. b, Fermi surface of polycrystalline graphene on Cu. The schematic orientations of graphene and Cu terraces are shown, Red dashed circle indicates the Fermi surface of graphene.](image)

Fig. 1a shows the experimental geometry for conventional ARPES measurements. $\mathbf{A}_\mathbf{H}$ ($\mathbf{A}_\mathbf{V}$) is the vector potential of the incident light with linear horizontal (vertical) polarisation, $\theta$ and $\omega$ denote the polar and azimuthal degree of freedom and $\theta_i$ is the polar angle of incidence. The analyser slit horizontally oriented permits photoelectron detection from one cut in angular (momentum) space along the $x$ axis. For all different $\theta$, the incident photon momentum, the photoelectron momentum and the surface normal lie on the same plane ($\mathbf{e}$). The Fermi surface of the sample is mapped by rotating the sample $\omega$ axis while taking spectra along $x$ axis for each $\omega$ angle. Fig. 1b shows the examplary Fermi surface mapping of polycrystalline graphene/Cu. First we rotate the sample to the right polar angle $\theta$, in order to cover the Dirac cone at $K$ points. Then we rotate the azimuthal angle $\omega$ to make individual spectra and integrate them into Fermi surface.

As analysed in detail in Fig. 1b, the Fermi surface for graphene consists of a circle with radius being $\sim 1.7 \ \text{Å}^{-1}$, which corresponds to the Brillouin zone corner $\mathbf{K}$ point. This circle, rather than isolated points for the Brillouin zone corner of single crystalline graphene, results from the polycrystalline nature of graphene. As for traditional ARPES, the beam size on the sample is around 100 $\ \mu$m, this continuous circle means that single crystalline microscopic domains of graphene take their orientations randomly. This is in complete contrast with graphene grown on nickel, iridium and cobalt[7], in which cases graphene can only have single or few orientations respect to the substrate surface lattice.

It is quite interesting to note that, the substrate surface is dominated by the (111) crystal plane of Cu single crystal, which can be judged by the Fermi surface shape of Cu $sp$ bands. However, the (111) orientation is not normal to the substrate surface. As shown in Fig. 1b, the Brillouin zone centres of both graphene and Cu (111) locate at $(k_x, k_y) = (0.46\pm0.01, 0.86\pm0.01) \ \text{Å}^{-1}$. This coordinate corresponds in angular space an offset of $11.4\pm0.1^\circ$ for the (111) crystal plane, indicating that graphene grows along the (111) plane terraces of Cu single crystal, which is not the normal direction of Cu substrate surface. As analysed in detail in
Fig. 1b, the normal surface of Cu substrate actually represents the (223) crystal plane of Cu single crystal. Also in Fig. 2b, the crystal orientations [-1,-1,2] and [110] are indicated by black arrows, with the former corresponding to the $\Gamma - M$ direction for Cu (111) hexagonal lattice.

Figure 2. Nano-ARPES working principle and its study on the electronic structure of microscopic graphene grains. a, Graphene Dirac one measured by ARPES. White dashed frame indicates the energy-momentum window integrated to generate the valence band intensity distribution image (measured by Nano-ARPES) shown in d. b, Schematic for working principle of Nano-ARPES. c, Optical image of CVD-grown graphene grains on Cu. d, Valence band intensity distribution image mapped by Nano-ARPES. e, typical Dirac cone electronic structure from one single graphene domain measured by Nano-ARPES.

3. Microscopic characterisation of graphene grains by Nano-ARPES
Having established the polycrystalline nature with random orientation of graphene, we now use Nano-ARPES to study the electronics structure for single crystalline domains. Fig. 2b shows the schematic of our Nano-ARPES system. Synchrotron radiation (beam) is focused by Zone Plate (ZP). The focused spot size on sample is around 100 nm. The manipulation of sample is realised by a XY scanning controller with interferometric feedback to avoid thermal perturbation. Fig. 2a shows one spectra of Dirac cone measured by ARPES as discussed in Fig. 1. The broad bandwidth and not well-defined band gap result from the fact that many graphene grains with different orientation are measured for this spectra. By integrating the spectral intensity within one particular energy-momentum window while scanning the sample in real space along $x$ and...
y directions, the angle-resolved spectral intensity distribution image can be obtained, as shown in Fig. 2d.

It is clear that in this area the CVD-graphene actually consists of many grains no larger than few tens of micrometers, with some of them merging together. The optical image shown in Fig. 2e proves the existence of these graphene grains. The perfect match between the Nano-ARPES spectral intensity image and optical image undoubtedly proves the ability of Nano-ARPES to locate the microscopic sample by photoemission spectral weight.

Fig. 2e shows one typical Nano-ARPES spectra of graphene Dirac cone from one single graphene grain. Compared with ARPES spectra in Fig. 2a, the bandwidth of Dirac cone is much less and the Dirac gap is better resolved. This is naturally due to the single crystalline nature of the studied graphene grain. Together with the perfect match between Nano-ARPES image and optical image, these results demonstrated the full capability of Nano-ARPES to study the electronic structure of microscopic materials.

4. Discussion
Taking polycrystalline CVD-graphene/Cu as an example, we have fully shown the capability of Nano-ARPES to study the electronic structure of microscopic materials. Electronic structure, which describes the distribution of electronic states in reciprocal space, is one of the most fundamental concepts in condensed matter physics, since it determines the electrical, optical and magnetic behaviours of materials. The rapid development of nanotechnology and nanomaterial requires electronic structure probes with nanometer resolution. In this context, Nano-ARPES, although still being at its very early stage, has a promising future for the electronic structure study of various nanomaterials.

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6. References
[1] Castro Neto, A. H. et al. 2009. Reviews of Modern Physics 81 109-162
[2] Geim, A. K. & Novoselov, K. S. 2007 Nature Materials 6 183-191
[3] Geim, A. K. 2009 Science 324, 1530-1534
[4] Han, W., Kawakami, R. K., Gmitra, M. & Fabian, J. 2014 Nat Nanotechnol 9 794-807
[5] Bonaccorso, F., Sun, Z., Hasan, T. & Ferrari, A. C. 2010 Nat. Photonics 4 611-622
[6] Voloshina, E. & Dedkov, Y. 2012 Physical chemistry chemical physics : PCCP 14 13502-13514
[7] Batzill, M. 2012 Surface Science Reports 67, 83-115
[8] Wintterlin, J. & Bocquet, M. L. 2009 Surface Science 603 1841-1852
[9] Zhang, Y., Zhang, L. & Zhou, C. 2013 Accounts of Chemical Research 46 2329-2339
[10] Mattevi, C., Kim, H. & Chhowalla, M. 2011 J. Mater. Chem. 21, 3324-3334
[11] Kim, K. S. et al. 2009 Nature 457 706-710
[12] Li, X. et al. 2009 Science 324 1312-1314
[13] Bae, S. et al. 2010 Nat Nanotechnol 5 574-578
[14] Avila J and Asensio M C. 2014 Synchrotron Radiation News 27 24-30
[15] Bostwick, A. et al. 2012 Synchrotron Radiation News 25 19-25
[16] Jose, A. et al. 2013 Journal of Physics: Conference Series 425 192023