Growth and Characterization of Graphene / Hexagonal Boron Nitride Heterostack on Cu(111)

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Abstract

Graphene offers great potential for applications in electronic devices [1], but in order to transfer this potential to the industrial scale, production methods for high quality material are vigorously investigated, as well as suitable substrate materials. Hexagonal boron nitride (h-BN) has appeared as a natural candidate substrate due to its closely related structure, its flatness and its wide band gap. It could be shown, by building devices using standard exfoliation techniques, that h-BN supported graphene exhibits superior electronic properties [2], and that few layers of h-BN can be used as a barrier in a field-effect tunneling transistor [3]. Several groups have reported direct growth of graphene on h-BN on metal surfaces in a two-step chemical vapor deposition (CVD) process: on Ni(111) [4,5], Ru(0001) [6], polycrystallinge Cu foils [7], as well as on Ni(111) films on W(110), and with Au intercalated between the h-BN and the Ni(111) [8].

Building on our long-term experience in the growth of epitaxial single-layer h-BN [9,10] and graphene [11-13] films on metal surfaces, we have investigated the sequential CVD growth of a single graphene layer on a predeposited single h-BN layer on Cu(111). Borazine (HBNH)₃ [4] and 3-pentanone ($C_2H_5COC_2H_5$) [13] were used as precursors for h-BN and graphene growth, respectively. Substrate temperatures were of the order of 1000 K, and borazine dosing was done at a pressure in the 10⁻⁶ mbar range, leading to the self-saturating growth of a single h-BN layer on the Cu(111) surface. Low-energy electron diffraction (LEED), x-ray photoelectron diffraction (XPD) and angle-resolved photoemission (ARPES) data (Fig. 1a) testify for the presence of a well ordered boron nitride single layer. The LEED data show the h-BN lattice with a slightly smaller lattice constant and a small spread in crystal orientations of not more than 3°, which is consistent with the observation of moiré patterns observed for this system in a recent low-temperature scanning tunneling microscopy (STM) study [14].

The growth of graphene on top of the h-BN layer required much higher precursor pressures and exposure times. X-ray photoelectron spectroscopy (XPS) data confirm the presence of a single graphene layer with the desired stacking sequence of graphene/h-BN/Cu(111). In the ARPES data the graphene π band is observed with the characteristic linear dispersion up to the Fermi energy (Fig. 1b), leading to a six-fold arrangement of maxima in the Fermi surface map displayed in Fig. 1c. No indication of a band gap is observed in these data.

In this talk, a detailed structural characterisation of this graphene/boron nitride heterostack will be presented, showing that the largely predominant phase on the surface features a graphene layer that matches the orientation of the h-BN lattice but exhibits a lattice mismatch of the order of 1.4-1.6%, similar to the mismatch between graphite and bulk h-BN. This presence of this phase is confirmed by the observation of the characteristic moiré pattern in STM images. A weak electronic coupling between the two layers arises due to this incommensurate growth, which can rationalize the absence of a band gap in the graphene layer.

References

- [1] A. Geim, K. Novoselov, Nature Materials, 6 (2007) 183.
- [2] C. R. Dean et al., Nature Nanotechnol., **5** (2010) 722.
- [3] L. Britnell et al., Science, **335** (2012) 947.
- [4] A. Nagashima et al., Phys. Rev. B, 54 (1996) 13491.
- [5] C. Oshima et al., Solid State Commun., **116** (2000) 37.
- [6] C. Bjelkevig et al., J. Phys.: Condens. Matter, 22 (2010) 302002.
- [7] Z. Liu et al., Nano Letters, 11 (2011) 2032.
- [8] D. Usachov et al., Phys. Rev. B, 82 (2010) 075415.

- [9] W. Auwärter et al., Surf. Sci., **429** (1999) 229.
- [10] M. Corso et al., Science, **303** (2004) 217.
- [11] D. Martoccia et al., Phys. Rev. Lett., 101 (2008) 126102.
- [12] T. Brugger et al., Phys. Rev. B 79 (2009) 045407.
- [13] S. Roth et al., Surf. Sci., **60** (2011) L17.
- [14] S. Joshi et al., Nano Letters 12 (2012) 5821.

Figures



Fig. 1: He II α (40.8 eV) excited ARPES data from (a) a single layer h-BN on Cu(111) and from (b) a graphene/h-BN/Cu(111) stack, both measured along the $\overline{\Gamma K}$ direction of the two-dimensional Brillouin zone. In (c), a Fermi surface map of the graphene/h-BN/Cu (111) stack is displayed, showing six dominant spots associated with Dirac cones. (d) Intensity distributions along a circular path in (c), crossing all six Dirac points. In (a), the sharp feature appearing between 2 eV binding energy and the Fermi energy is from the fast dispersing sp band of the Cu(111) substrate.