Transforming C_{60} into graphene on Cu foils: procedure and characterization

High-quality PVD graphene growth by fullerene decomposition on Cu foils, *Carbon* 119, 535 (2017)

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A new strategy to grow large-area high-quality graphene from C_{60} is presented. Following a multitechnique characterization (μ-LEED, AFM, Raman, XPS, ARPES, SEM, EBSD) the quality of these layers is evaluated.

C_{60} molecules were used as carbon source to grow large-area high-quality graphene layers on polycrystalline Cu foils. The graphene growth process was performed in UHV conditions and was thermally promoted by annealing the substrate at 800 ºC during evaporation of C_{60} molecules. Several surface characterization techniques were applied to evaluate the quality of the graphene layer. *In-situ* low-energy electron diffraction (LEED) images show spots corresponding to a polycrystalline Cu surface with predominance of (110) faces and the typical LEED graphene ring. *Ex-situ* atomic force microscopy (AFM) and Raman spectroscopy were used to determine the quality and thickness of the graphene layer. This confirmed the existence of a graphene layer that extends over large areas. Angle-resolved photoemission spectroscopy (ARPES) measurements were performed to unveil the linear behaviour of electrons near the Dirac point. Additionally, the X-ray photoelectron spectroscopy (XPS) experiments showed the C1s XPS core level signature of clean graphene layers. Raman spectra show lower intensity signal just after graphene growth than after ageing, probably due to the decoupling induced by oxygen intercalation. It could be also verified that the present new protocol is a self-limiting process leading exclusively to one single graphene layer.

Graphene was prepared by evaporating C_{60} on polycrystalline copper at 800 ºC in UHV. Fig. 47a represents the μ-LEED pattern acquired at 40 eV after graphene growth on Cu foil showing a ring and multiple spots mainly with rectangular crystallographic order. The ring is the fingerprint of polycrystalline graphene while the multiple spots correspond mainly to the substrate (110) grains. Electron backscattered scattering diffraction (EBSD) measurements (see Fig. 47b) corroborate this preferred (110) orientation.

XPS and Raman spectroscopy were performed to evaluate the graphene quality. Fig. 48a shows the XPS C-1s spectrum of the graphene/Cu foil, acquired after exposing the sample to air, without any cleaning treatment. The spectrum was fitted with five subspectra assigned to C-sp2, C-OH, C-O, C=O, and C-C=O together with O-C=O species (284.4, 285.4, 286.7, 288.5 and 290.5 eV, respectively). The strong intensity of the C-sp2 component with respect to the oxide components evidences, even after air exposure, the high quality of the graphene layer. The combination of UHV conditions and low temperatures involved in the growth process ensures a more controlled and cleaner procedure than other methods.

Fig. 48b exhibits the Raman spectra of the graphene layer in the case of a freshly prepared graphene sample (red curve) and two months after growth (black curve). The red spectrum exhibits the G, 2D and D peaks that are distinctive of graphene although with very low intensity. Interestingly, the black curve exhibits those peaks but with a larger intensity. It is important to remark that no differences were observed by AFM in the morphology of the sample after ageing two months, suggesting that the increase in the signal is related to the evolution of the graphene/Cu interface. This suggests the formation of copper oxide in the interface by oxygen intercalation from the atmosphere. The calculated integrated I_{2D}/I_G ratio gives a value of 5.2, which supports the presence of a monolayer of graphene.

The authors present a new protocol to grow high-quality graphene on Cu foils using C_{60} as precursor molecules in UHV conditions. The growth mechanism involves the thermally activated decomposition of the C_{60} molecules on the Cu surface. The present approach introduces some advantages with respect to the use of hydrocarbons. From one side, it is a self-limiting process that gives rise only to one single graphene layer. On the other hand, it requires lower substrate temperatures than other conventional methods, as CVD, and therefore results in a clean graphene-copper interface. A multitechnique characterization was performed to evaluate the quality of the graphene layer grown by this protocol. Thus, all the results show that our protocol leads to a large-area high-quality graphene layer.

ACKNOWLEDGEMENTS

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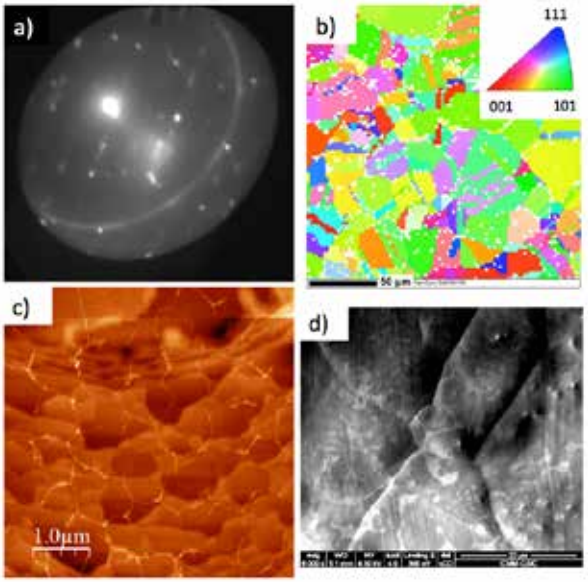

Figure 47: a) μ-LEED pattern, b) EBSD map (inset showing the color code) and c) AFM image of the graphene/Cu sample after growth. d) SEM image of an incomplete graphene layer.
Figure 47c shows an AFM image revealing the presence of different atomic steps delimiting terraces within a Cu grain and the graphene wrinkles. Fig. 46d exhibits the special case of a partial graphene layer on Cu as depicted by scanning electron microscopy (SEM), which reveals that graphene crosses the boundaries between neighboring Cu crystallographic domains, extending over different Cu grains. The uncovered Cu areas appear lighter than those from graphene.

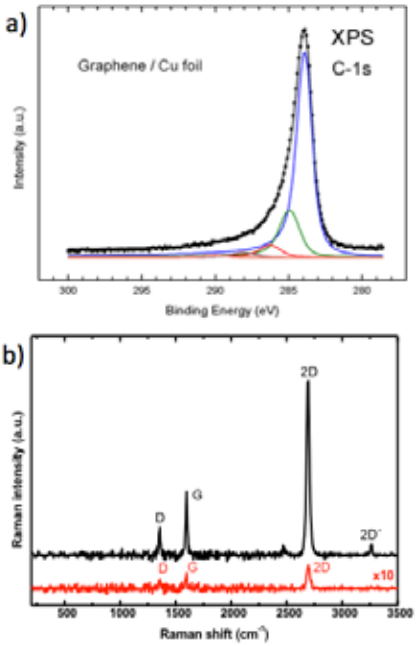

Figure 48: a) XPS C-1s core level spectrum of the graphene layer on the Cu foil, b) Raman spectra of a freshly prepared (red) and aged (black) graphene layer.

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