In-situ TEM study of hexagonal holes in graphene growing from defects in oxygen atmosphere

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Abstract

The recent improvements in the quality of the graphene growth [1-2] have narrowed down the differences in terms of performances between artificially produced and mechanically exfoliated graphene. In particular, Chemical Vapor Deposition (CVD) seems to represent the most suitable technique for the implementation of graphene films as components in standard cleanroom fabrication processes. In order to preserve and exploit the outstanding properties of graphene, great care has to be spent in preserving the structure and smoothness of the edges, crucial parameters for the performances of most of the graphene-based devices [3]. For this reason, a large scale patterning technique able to preserve the crystallographic orientation and quality of the graphene edges would be ideal. Catalytic oxidation of graphene by metal nanoparticles [4-5] appears to be an interesting candidate for such a purpose. The intrinsic stochastic nature of the motion of the particles [5] poses fundamental limitations on the control and reproducibility of the etched channels and fabricated devices. The anisotropic oxidation of graphene can overcome these limitations. Defects in graphene develop into hexagonal shapes at high temperatures (around 800 °C) in oxygen rich atmosphere [6] or in presence of hydrogen plasma [7-8]. The edges of these hexagons are parallel to the <100> crystallographic direction in the graphene lattice, the so-called zigzag (ZZ) direction [6-8]. All the previous reports on this phenomenon were performed *ex-situ* and on a support, typically silicon oxide [6-8]. In this work we report, for the first time, the *in-situ* observation of oxidation of suspended graphene inside a FEI Titan Environmental Transmission Electron Microscope (E-TEM). The evolution of the defects in the graphene flake is studied in a large temperature range (room temperature – 1000 °C) and with different oxygen pressures. This results in a wide ensemble of behaviors of the holes, which grow as hexagons only in a specific temperature range (400 °C – 700 °C), while presenting a more isotropic dynamics at higher temperatures. The measure of the velocity of the receding edges is carefully evaluated with a statistical approach of the discrete removal of carbon atoms. The resulting energy barrier is compared with Density Functional Theory (DFT) calculations, which help to explain the cause of the exclusively ZZ edges of the hexagons. High resolution (HR) TEM images makes possible to estimate the roughness of the produced holes, which results to smaller than 1 nm.

References

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Figures

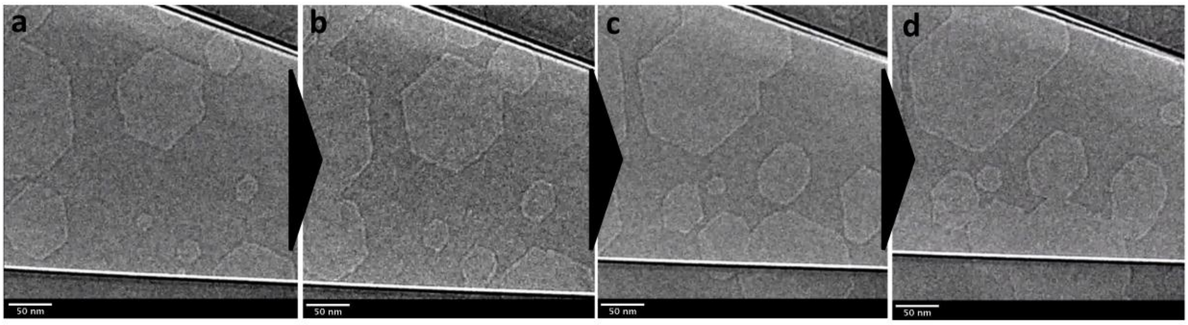

Fig. 1 – a-d TEM images of the evolution of beam-induced defects in suspended graphene at 600 °C and 10^{-2} mbar oxygen atmosphere. The scale bar is 50nm and the time between two consecutive frames is 30s.