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Experimental study of nucleation and growth mechanisms of graphene synthesized by Low Pressure Chemical Vapor Deposition on copper foil

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During the past 40 years, the fields of micro-electronic, energy and communication devices have experienced an unbelievable evolution. To continue these progresses, the development of multi-functional materials presenting a broad range of properties such as high electronic and thermal conductivities, high transparency and good mechanical properties is needed. Graphene, a hexagonal arrangement of carbon atoms forming a one-atom thick planar sheet could match these demands.

Several methods can be used for graphene synthesis, even though Chemical Vapor Deposition (CVD) on catalytic surfaces is foreseen to be the most compatible one with industrial requirements. Indeed, CVD graphene with an electronic conductivity of $7350 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, an electrical resistance of $30 \text{ }\Omega/\text{sq}$ and a transparency of 90% has already been obtained.¹ However, these values are still far from the theoretical ones announced by physicists, because graphene grows as randomly oriented domains in which scattering at the boundaries leads to lower physical properties. The CVD formation of graphene on Cu substrates has long been considered to be surface-mediated and self-limiting due to the very low carbon solubility in Cu, thus leading to single layers formation. However, numerous studies in 2011 have shown that this is true only in a small window of deposition conditions, especially for methane partial pressure². As a consequence, the control of graphene thickness and crystalline uniformity on large surface areas still remains elusive and needs a better understanding of the mechanisms of graphene nucleation and growth.

In this framework, the present study consists in synthesizing graphene on copper foils (25 μm thick, 99,999% Alfa Aesar) by CVD from methane diluted in hydrogen and argon at 0.5 Torr of total pressure. The operating temperature was fixed at 1000°C. Scanning electron microscopy (SEM), optical microscopy and Raman spectroscopy measurements were carried out to investigate the quality and extend of graphene sheets.

First, the influence of the methane partial pressure P_{CH_4} was investigated. During these experiments, as shown in Fig.1, for all tested P_{CH_4} , gradients in size, shape and density of graphene flakes were evidenced on the parts of the samples placed in the substrate holder slot.

For the two lowest positions in the slot, graphene nucleation increases with the methane partial pressure, as found by Wu et al.²; the preferential growth of multi lobes flakes observed at the lowest methane pressure is lost at higher values. The Raman spectra (not shown) indicated that lowering the CH_4 partial pressure allows to decrease the defects in the graphene (D band), but the partial pressures tested were too high to obtain single layer graphene (I_{2D}/I_G ratios always lower than two).

These observed gradients in size, shape and density of graphene flakes led to think to a mechanism of graphene nucleation and growth based on unsaturated species C_xH_y . These radicalar

species are probably formed by the catalytic cracking of methane and hydrogen on copper, as proposed by Vlasiouk et al.³ To confirm our assumption, we set an enclosure in order to confine the Cu foil; this enclosure could act as a trap for the radicals present near the Cu surface. We performed several runs with two Cu foils (with and without confinement) in the isothermal zone of the reactor. The presence of the enclosure clearly led to less and smaller graphene flakes on the whole surface of the Cu foils. Moreover, Raman spectra (not shown) indicated that using the confinement allowed to decrease the I_D/I_G ratios, thus the number of defects in graphene, as obtained for lower methane partial pressures.

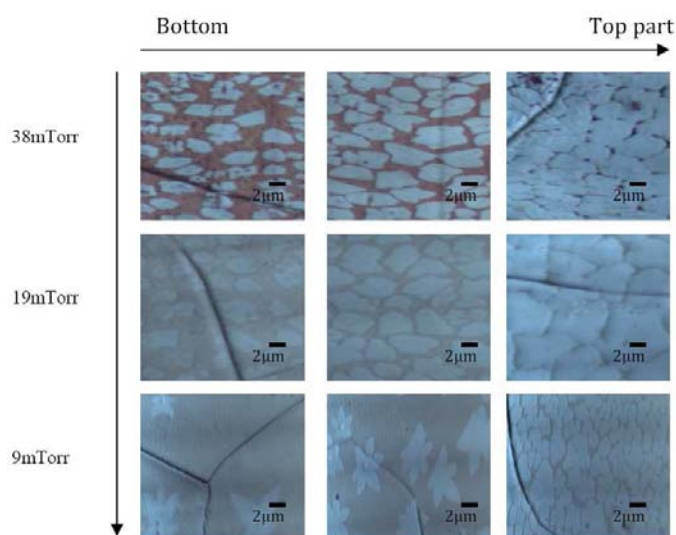


Figure 1: Optical micrographies of the evolution of graphene flakes density, size and shape for various positions on the samples and methane partial pressures.

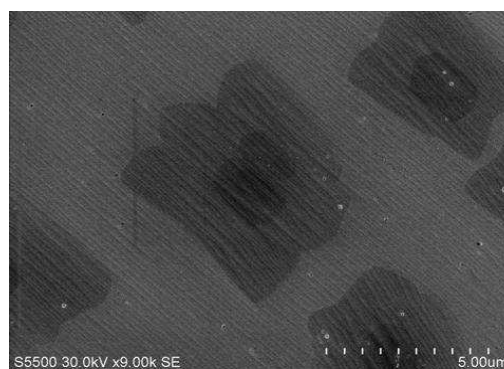


Figure 2: SEM image of multi-layers graphene flakes

For graphene flakes obtained on enclosed copper foils, and only in this case, the presence of additional layers is observed in the middle of the flakes, as shown in Fig.2. According to Vlasiouk et al.³, these additional top layers are formed at the beginning of the growth, when the nuclei perimeter is small. Therefore, the consumption of active surface-bound carbon is lower than the supplying, leading to multi-layers. When flakes grow, the amount of produced active carbon decreases due to a smaller area of open catalytic copper, and is mostly consumed by the first layers. In our case, without confinement of the copper foil, the amount of active surface-bound carbon formed is probably so high that complete multi-layers graphene flakes are formed.

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