Graphene Growth Kinetics Under Purified Conditions

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Abstract
Chemical vapor deposition (CVD) is one of the most promising route towards the mass production of graphene sheets for industrial applications requiring large surfaces and pristine quality. To reach the necessary standardization of the resulting material and to further model and engineer the growth, a fundamental understanding of the growth kinetics, including a reliable database of the associated parameters, is still lacking. Our group has recently shown the important role of oxidizing impurities [1, 2], even at trace level, under graphene CVD growth conditions. Using a severe control over these impurities from both the furnace and gas feedstock, we were able to identify two growth regimes: Oxidizing impurity limited growth and precursor dissociation limited growth. According to our findings, most kinetic studies in the literature using standard ultra-high purity (UHP) gases are in the oxidizing impurity limited growth regime. In order to better discretize growth parameters effects and extract fundamental kinetics values, we devised a set of experiments where purity conditions are minimized in order to set the growth conditions in the precursor dissociation limited regime. We conducted LP-CVD growth experiments with varying growth conditions: pressure, temperature and time. The samples were characterized using microscopic methods (scanning electron microscopy (SEM) and Low energy electron microscopy (LEEM)) to study the surface morphology, crystallinity, nucleation density and coverage. RAMAN spectroscopy was used to assess the graphene quality and thickness. In route toward the full model, we found out that in purified condition the growth is greatly accelerated by a factor of x50 compared to UHP condition without affecting the graphene quality. For instance, we reached >85% coverage in 10min @ 800 °C and full coverage in 20 s @ 1000 °C. We also determined that the total dose of methane is the main parameter controlling the graphene coverage (see figure below) and that the H_2 has only minor effect when O_2 is minimized. Effects of growth parameters on nucleation density and crystallite size will be further commented within the presentation. This study will allow retrieving the fundamental kinetic constants and activation energies that are essential to later model and engineer graphene for future applications and also give new fundamental insight on the catalytic activity of copper for dissociating methane.

References
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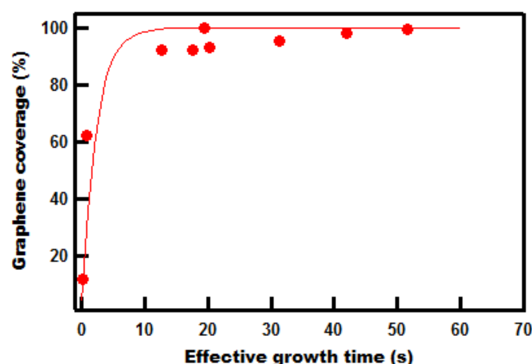

Figure: Effective growth time influences graphene coverage. These growths were obtained with varying total methane doses.