# Growing graphene on polycrystalline copper foils by ultra-high vacuum chemical vapor deposition

**Niclas S. Mueller**[1], Anthony J. Morfa[1], Daniel Abou-Ras[2], Michael Giersig[1]

[1]Freie Universitaet Berlin, Department of Physics, Arnimallee 14, D-14195 Berlin, Germany
niclasm@physik.fu-berlin.de

[2]Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

## Abstract

The growth of graphene by chemical vapor deposition (CVD) on polycrystalline copper foils has become very popular owing to its scalability, high yield, inexpensiveness and suitability for industrial implementation [1, 2]. A detailed understanding of underlying growth mechanisms and the influence of growth parameters is crucial to obtain a quality of CVD graphene comparable to that of exfoliated graphene. The CVD growth process is usually performed at atmospheric pressure (APCVD), or at low pressures down to $10^{-3}$ mbar (LPCVD). Reports of graphene growth on copper in the high- and ultra-high vacuum regime (UHV-CVD) are rare [3-7] and often utilize difficult growth processes, such as thermal cycling [3, 7] or ion irradiation [4] to obtain sufficient graphene coverage (though these are currently limited to nanometer-scale domains). However the growth of graphene at UHV-pressures benefits from low contamination before and during the growth process. It is therefore of high interest for studying fundamental growth mechanisms. Furthermore it enables the investigation with in-situ techniques, such as low energy electron microscopy and diffraction, which have been successfully used for studying graphene growth on ruthenium [8] and platinum [9].

We show that monolayer graphene, with a low structural defect density, can be grown on polycrystalline copper foils with ultra-high vacuum chemical vapor deposition using acetylene as a carbon precursor. Our experimental results demonstrate that acetylene, compared to methane, is more suitable as a carbon precursor in this pressure regime, which we attribute to a higher adsorption energy on a copper surface. A simple one step growth process is demonstrated, in which the copper foil is exposed to acetylene isothermally at 900 °C. Partial pressures are monitored with in-situ quadrupole mass spectroscopy, while chamber pressures during growth are maintained below $10^{-6}$ mbar with controlled partial pressures of acetylene.
The controlled growth of graphene domains and continuous graphene film formation is demonstrated with representative data from Raman imaging, scanning electron microscopy and electron backscattering diffraction. A systematic study of the influence of growth parameters on the graphene growth, such as growth time, growth pressure, effects of additional hydrogen, is presented. Investigating the time dependence of the graphene area coverage at fixed temperature and pressure enables us to propose a kinetic growth model, which covers all stages of growth (Figure 1a-c). A dependency of the growth kinetics on the surface orientation of the copper grains is observed and attributed to the surface orientation dependent adsorption energy of acetylene on copper. Confocal Raman spectroscopy and mapping is used to characterize the properties of the as-grown graphene after transfer to an adequate substrate and proves that the graphene domains are monolayer with low structural defect density (Figure 1d-f). Furthermore we show that the graphene domains grow into a continuous film by increasing the partial pressure of acetylene during growth.

A manuscript is currently submitted for publication.

## References


[1] X. S. Li, et al., Science, **5932** (2009) 1312-1314.

[2] T. Kobayashi, et al., Applied Physics Letters, **2** (2013).

[3] L. Gao, et al., Nano Letters, **9** (2010) 3512-3516.

[4] A. J. Martinez-Galera, et al., Nano Letters, **9** (2011) 3576-3580.

[5] Z. R. Robinson, et al., Physical Review B, **23** (2012).

[6] L. Zhao, et al., Solid State Communications, **7** (2011) 509-513.

[7] T. Niu, et al., Journal of the American Chemical Society, **22** (2013) 8409-8414.

[8] P. W. Sutter, et al., Nat Mater, **5** (2008) 406-411.

[9] P. Sutter, et al., Physical Review B, **24** (2009) 245411.


## Figures

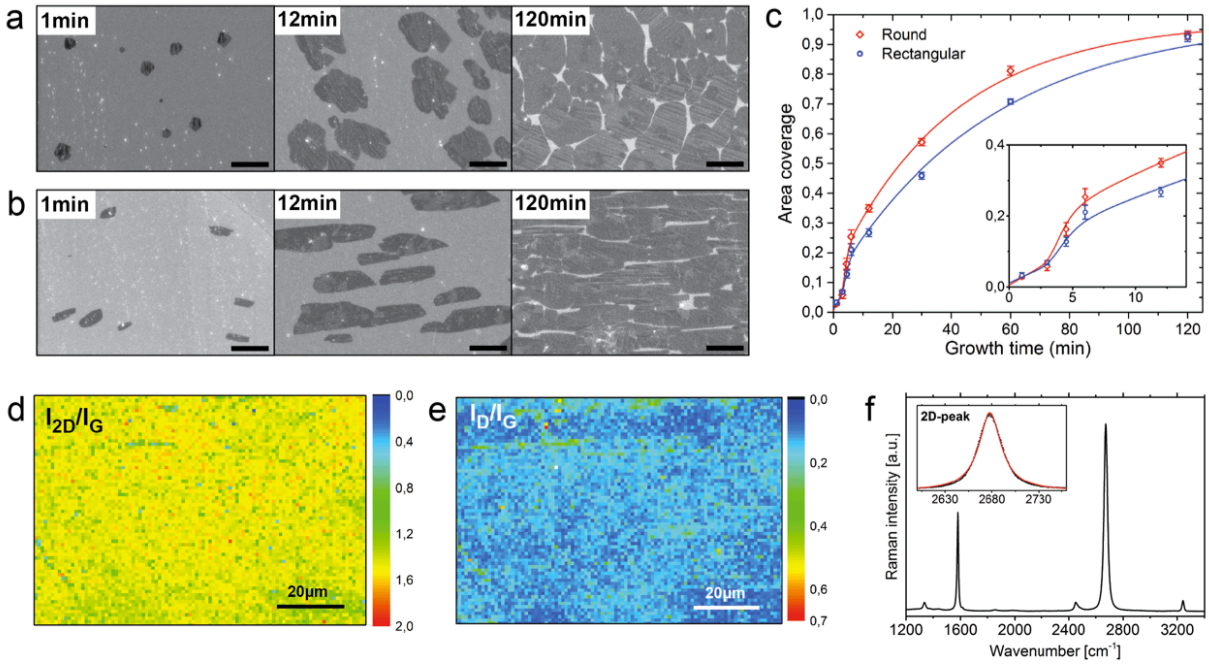


**Figure 1:** Characterization of UHV-CVD grown graphene by scanning electron microscopy (SEM) and Raman imaging. (a-c) SEM images of graphene domains of (a) round and (b) rectangular shapes for different growth durations and (c) evaluation of the time dependence of the area coverage (scale bars: 2µm). (d) Raman map of the 2D/G peak height ratio and (e) D/G height ratio of a transferred, continuous graphene film (excitation with 532 nm). (f) Typical Raman spectrum of a transferred graphene domain (inset shows 2D peak fit with a single-Lorentzian curve).