

Growth Dynamics, Stacking Sequence and Interlayer Coupling in Few-Layer Graphene Revealed by *in Situ* SEM

Z.J. Wang¹, Gyula Eres², Ding Feng³, Robert Schloegl¹ and Marc Georg Willinger^{1,4}

¹ Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin, Germany.

² Materials Science and Technology Division, Oak Ridge National Laboratory, Tennessee, USA

³ Institute of Textiles and Clothing, Hong Kong Polytechnic University, Hong Kong, China

⁴ Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

We have modified the set-up of a conventional scanning electron microscope (SEM) in order to enable the observation of catalyst surface dynamics under controlled atmosphere and temperature. Using this instrument, we perform *in situ* investigations on chemical vapor deposition (CVD) growth of graphene on different metal catalysts. Since the experiments are performed in the chamber of a microscope, it is possible to observe complete CVD processes starting from substrate annealing through graphene nucleation and growth and, finally, substrate cooling in real time at nanometer-scale resolution without the need of sample transfer. The nucleation and growth of single layer graphene can be investigated at temperatures of up to 1000°C, while at the same time, surface dynamics of the active metal catalyst can be studied. Growth on polycrystalline substrates reveals grain orientation dependent growth dynamics and catalytic activity [1]. Due to the high sensitivity of the secondary electron signal to changes in the work function and charge transfer at the surface, we are able to visualize different degrees of graphene-substrate coupling [2].

In the case of graphene growth on copper substrates, we present detailed investigations on the growth dynamics during different stages of growth as well as the effects of grain dependent substrate dynamics. In the case of graphene growth on platinum substrates, we will discuss growth kinetics of different layers in few-layer graphene. Real-time imaging under well-controlled atmosphere enables the observation of the response of in-plane dynamics in few-layer graphene to changes in the chemical potential of the atmosphere. By switching between graphene growth and hydrogen etching we were able to distinguish between graphene layers that are inserted underneath or forming on top of the initial layer. It is thus possible to abstract information about the stacking behavior of 2D materials directly from the observation of in-plane dynamics [3].

It will be shown how layer dependent etching rates can be used to determine the relative strength of the graphene-graphene and graphene-substrate interaction. Using anisotropic etching rates extracted from the evolution of the shape of islands and vacancy islands (holes) we were able to judge the strength of the interaction between graphene edges and steps at the Pt surface.

Finally, it will be highlighted that *in situ* scanning electron microscopy completes the spectroscopic data that is provided by complementary *in situ* techniques that provide spectroscopic information, such as ambient pressure X-ray and Raman spectroscopy. It adds the visual information and provides unprecedented and direct insights about the complex interplay between environment, catalyst and formed product.

References:

- [1] Z.-J. Wang *et al.*, ACS Nano **9** (2015), p. 1506.
 [2] P. R. Kidambi *et al.*, Nano Lett. **13** (2013), p. 4769
 [3] Z.-J. Wang *et al.*, Nature Communications **7** (2016), Article number: 13256.

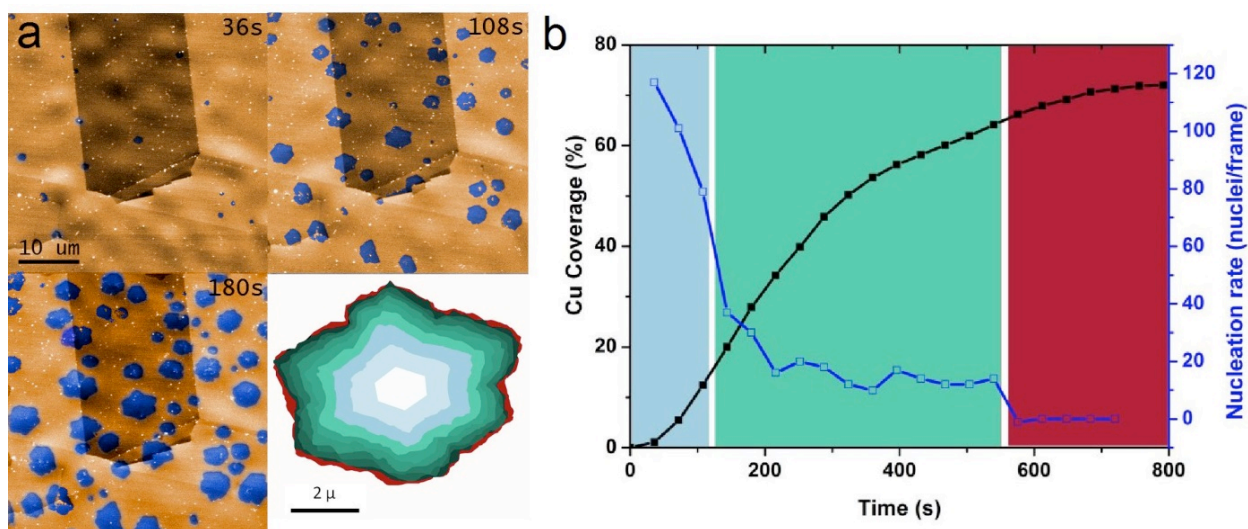


Figure 1. (a) Colorized snapshots taken during low-pressure CVD growth of graphene on copper at 1000°C. The growth and nucleation behavior can directly be abstracted from the recorded images as shown in (b).

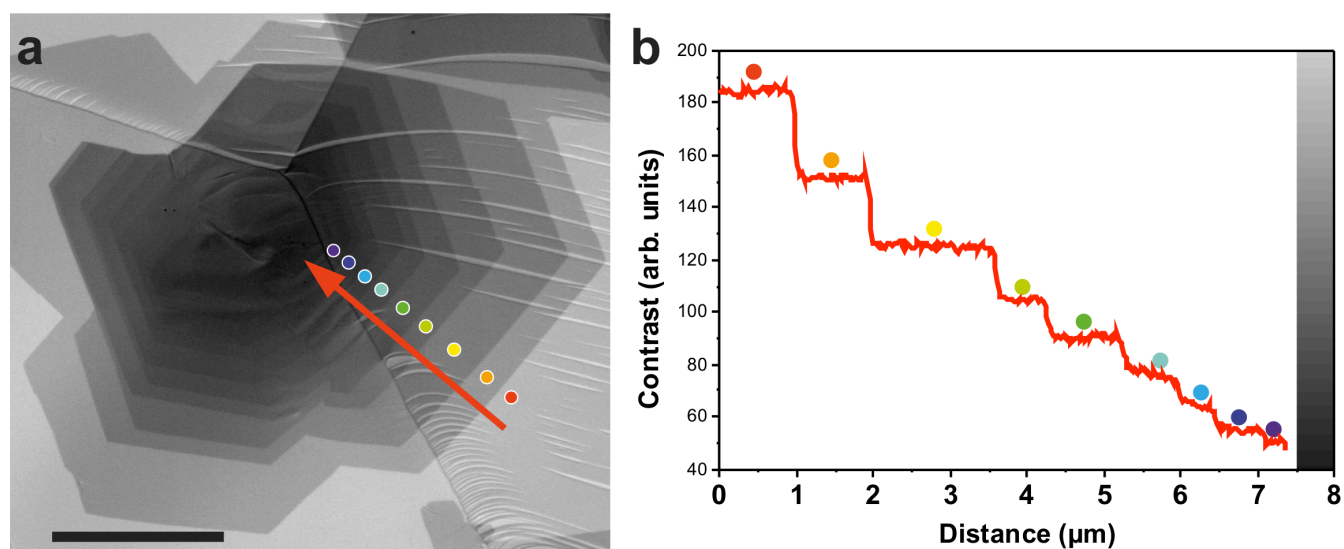


Figure 2. (a) Images of a few-layer graphene stack recorded during CVD growth. Up to 9 individual layers can be differentiated by their contrast (b). It is thus possible to study layer dependent growth kinetics.