Most promising approaches for industrial scale production of graphene are based on metal catalysed chemical vapour deposition (CVD). Although improvements in graphene quality and yield have been achieved, there remains a lack in the mechanistic understanding of graphene formation. This lack of understanding is due to the fact that most insights on graphene growth have been derived from post growth characterizations, which are in principle incapable of capturing the dynamics of a CVD process. As we have learned from heterogeneous catalysis, a mechanistic insight can (in most cases) only be obtained on the basis of in-situ techniques that are capable of capturing the interaction of the catalyst with the environment while the product is formed. Here we report on in-situ graphene growth on nickel, copper and platinum catalysts inside a modified environmental scanning electron microscope. Using this method, we are able to visually follow the complete CVD process involving substrate annealing, graphene nucleation and growth and finally, substrate cooling. Due to the high sensitivity of the secondary electron signal to changes at the surface, we are able to visualize the formation and growth of single atom thick graphene sheets.

The in-situ experiments presented here reveal the dynamic nature of the process in an unparalleled way and provide important insights on the growth kinetics and the substrate-film interactions at the micron to nanometer scale (Figure 1). In the case of growth on nickel, temperature and atmosphere induced dissolution and precipitation dynamics can be observed. For the case of copper, it is found that graphene growth above 850°C occurs on a pre-melted, highly mobile surface.

The nucleation and growth behaviour will be discussed and the influence of grain dependent surface dynamics presented. Furthermore, we show that graphene induced copper surface reconstructions occur during cooling.
Fig. 1: a) shows colorized snapshots taken during low-pressure CVD growth of graphene on copper at 1000°C. The growth and nucleation behaviour can directly be abstracted from the recorded images as shown in b).