

In situ studies of graphene growth during realistic CVD conditions

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Scalable, economic growth is a key requirement to utilise the unique properties of mono- and few-layer graphene (FLG) for device applications. The most promising and versatile growth technique for graphene is catalytic chemical vapour deposition (CVD), in which catalyst surfaces are exposed to a gaseous carbon precursor at elevated temperatures.¹ This offers a low-cost method of producing graphene across large areas, but at present the growth mechanism(s) are not well understood. Elucidation of the growth processes is needed to enable the control and optimisation of CVD graphene growth beyond the empirical calibrations of C dose and the process temperature profile. In particular, improvements in the domain size and the control of layer number are needed before CVD graphene becomes suitable for a wide range of applications.

We compare (few-layer) graphene growth based on a solid C source to graphene CVD based on low hydrocarbon exposures on thick (>300 nm), poly-crystalline transition metal films. We investigate a range of different solid and gaseous carbon precursors to understand the effect of C source on the growth. We focus on graphene nucleation and graphene domain size in relation to the catalyst grain size distribution and the C chemical potential.

We perform in-situ high-pressure X-ray photoelectron spectroscopy (XPS) and in-situ X-ray diffraction (XRD) during graphene growth at temperatures between ~300-700C, and during subsequent cooling. In situ XPS is carried out at the BESSY II synchrotron at the ISS end station of the FHI-MPG and in-situ XRD at ESRF at the Rossendorf Beamline. Time- and depth- resolved, high-pressure XPS² is used to obtain a detailed record of transient C/metal core level signatures prior to and during graphene formation for the different experimental conditions. Whereas XPS provides compositional data for the catalyst surface and near-surface (<1nm) region, we complement this technique with in-situ XRD which allows characterisation of the bulk crystalline phases present during growth. This allows determination of the catalyst microstructure, phase composition, and how this evolves during graphene nucleation and growth. Based on this combination of in-situ techniques, we model the growth processes involved in catalytic graphene growth.

Ex-situ characterisation is used to assess the uniformity and domain sizes of as-grown and transferred graphitic layers by optical/scanning electron microscopy, Raman spectroscopy, and transmission electron microscopy (TEM). The graphene film properties are then compared with the in-situ data to aid and corroborate the interpretation of the in-situ XPS and XRD results.

References

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