

## Applications of Environmental SEM as In Situ Surface Science Tool with Atomic Layer Sensitivity

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Methodological developments and the availability of commercial tools for in-situ electron microscopy have extended our possibilities substantially. Besides imaging of static atomic arrangements in vacuum, it is now possible to observe materials in an interactive, dynamic state and to study their behaviour under conditions far beyond thermodynamic equilibrium.

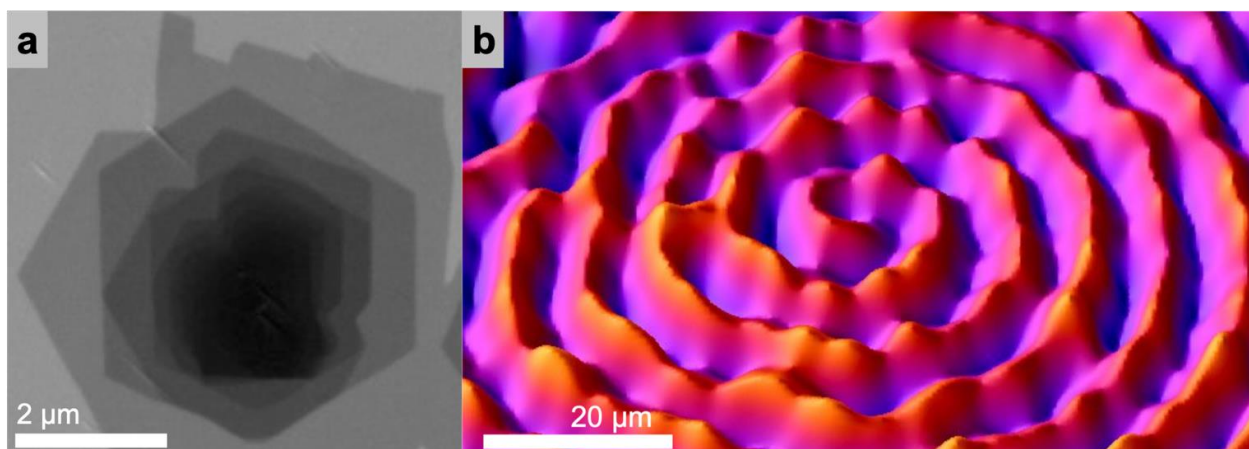
Indeed, everything that functions, interacts or lives, is dynamic. Direct insights into how (functional) materials react and interact with a defined (chemical) environment at high resolution and across various length and timescales is thus key for our understanding of processes that are relevant for material science, chemistry and biology.

Fascinated by the ability to resolve structures at the most fundamental, atomic scale, the electron microscopy community was largely focusing on the development and application of in-situ TEM. However, as a very local method, it should be complemented by methods that are capable of delivering information about processes that dominate at larger-scale. Indeed, context embedded studies require the consideration of dynamics that involve collective motion of many atoms, such as effects related to heat- and mass-transfer. Over the last years, we have thus complemented in-situ TEM with experiments performed inside the chamber of an environmental scanning electron microscope (ESEM). We thereby realized the fascinating potential of in-situ and operando SEM, which seems to have been partially overlooked by the growing in-situ TEM community.

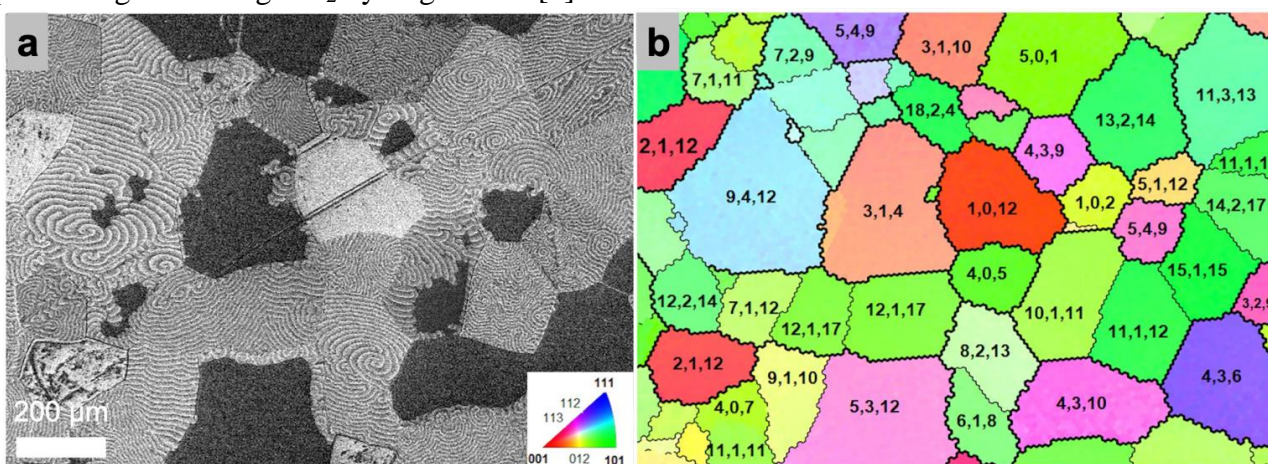
The aim of my presentation is to highlight some of the capabilities of in-situ SEM, especially with respect to the achievable surface sensitivity. By equipping a commercial environmental SEM with a laser heating stage and a gas-feeding and analysis station, we were able to study the dynamic interplay between catalytically active materials and well-controlled reactive atmospheres. We realized the important role that in-situ SEM plays in bridging gaps between fundamental UHV-based surface science investigations of model systems on one hand, and studies on complex-structured functional materials under application relevant conditions on the other hand. The possibility to directly visualize the growth of single and few-layer graphene at temperatures of around 1000 °C during CVD growth experiments showed that the secondary electron signal is sensitive enough to detect changes in surface coverage on the atomic level even under CVD growth conditions (see Figure 1a). This allows real-time control of the graphene growth and etching behaviour [1, 2].

Building on this, we started to investigate catalysed surface reactions, such as the hydrogenation of NO<sub>2</sub> (Figure 1b, Figure 2). Here, we could resolve, in real-time, how grain orientation and surface structure of a polycrystalline platinum foil is linked to catalytic activity [3]. The experiments showed how cross-talk and spill-over effects, combined with excitability and refractory behaviour, finally lead to formation of complex dissipative structures that are formed by propagating reaction fronts. Meanwhile we have extended the studies to other systems where we observed similar complex and oscillatory dynamics [4,5].

Overall, our studies demonstrate that consideration of non-locality and effects related to collective processes is important, and that local atomic scale observations alone are not sufficient to capture multi-scale phenomena. SEM is, compared to in-situ TEM, relatively easy to implement. It imposes far less restrictions concerning sample dimensions and, due to the large chamber size, offers the possibility to install complementary analytical tools, such as in-situ atomic force microscopy or microcalorimetry.



**Figure 1.** **a)** Spiral growth of multi-layer graphene imaged during CVD growth on a platinum substrate inside the SEM chamber at  $\sim 1000\text{ }^{\circ}\text{C}$  [1, 2]. **b)** false-coloured image showing secondary electron intensity as height profile. The spiral pattern is caused by propagating reaction fronts on the surface of a platinum grain during  $\text{NO}_2$  hydrogenation [3].



**Figure 2.** **a)** Propagating chemical waves on a polycrystalline platinum foil during  $\text{NO}_2$  hydrogenation ( $T = 164\text{ }^{\circ}\text{C}$ ;  $p_{\text{NO}_2} : p_{\text{H}_2} \approx 1:10$ ;  $p_{\text{tot}} = 3.6 \times 10^{-2}\text{ Pa}$ ). **b)** EBSD grain orientation map.

#### References:

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