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IN SITU EXPERIMENTS IN SEM/TEM

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Dr. Miroslav Kolibal has been involved in various research projects dealing with hybrid top-down/bottom-up lithographic approaches for preparation of nanostructures and electron microscopy. He was a visiting scientist at FEI R&D in Hillsboro, Oregon (U.S.A.) and at IBM Zurich Research Laboratory (Switzerland), developing in-situ electron microscopy for observation of CVD processes and high-*k* dielectric templates for directed III-V nanowire growth, respectively. His current research interests include low-dimensional materials, wide-bandgap semiconductors and gas-phase catalytic reactions. A common link in between these research areas is in-situ and in-operando microscopy, which is the main workhorse in his group. He has published 46 publications indexed in WoS.

Microscope is commonly understood as a tool to observe small things. One can learn how e.g., an eye of a spider looks like; one can see individual nanoparticles within car-exhaust catalyst system or that graphene is made of hexagonal array of carbon atoms. This is how many people use microscope – as a tool for static imaging of stationary samples. However, how does the insect eye work? What happens on the catalyst surface during the catalytic reaction? How graphene is formed from precursor molecules? The answers to these questions could possibly be inferred from static images; however, that usually requires enormous effort and is extremely challenging, if possible at all in many cases. On the other hand, observing these processes "*in situ*" or "*in operando*" [1] is advantageous and often crucial regarding our understanding of the involved processes and mechanisms behind.

In this contribution, I will focus on several demonstrations of such in situ approach to electron microscopy. For a material scientist, there are two prominent cases where in situ microscopy is of great use: growth of low dimensional materials and catalysis. These processes commonly pose two requirements onto the microscope in use: Ability to heat the sample to elevated temperature and imaging at elevated pressure.

There are interesting exceptions. Chemical vapour deposition (CVD) of graphene does not require high pressures. Instead, a very high vacuum turns out to be advantageous because the effect of different molecules within the residual gas in the growth chamber can be recognised and, potentially, suppressed. Figure 1a shows the growth evolution of graphene flake on Pt polycrystal. Automated image recognition makes it easy to plot different growth characteristics (e.g., area/growth rate versus time, etc.) and to model them with conventional growth models [2]. Comparison with experimental data allows for the fitting of input model parameters and thus a deeper understanding of growth mechanisms. It is obvious that in situ experimental data are critically important as model inputs. Specifically, while the classical growth model predicts a steadily decreasing growth rate as a result of the shrinking catalyst substrate surface, our data show a deviation from this behaviour in the early growth stage. Initially, the growth rate increases over time. This behaviour suggests that in the early stages, the growth is fed by the direct decomposition of the precursor and another source of carbon. It is plausible that the carbon dissolved in the bulk platinum is considered as the additional carbon source. Such conclusions allow us to build more realistic growth models and lead to customised and optimised growth recipes.

In situ observation of chemical reactions is irreplaceable in identifying effects that are hidden from common *ex situ* analyses. For example, Fig. 1c shows the etching of multilayers of graphene (again on a platinum polycrystal) by oxygen. The graphene was prepared in an "inverted wedding cake" configuration, which is schematically shown in the figure as well. As a matter of fact, one would expect the outer graphene layer to etch first, followed by the layers below, until the first graphene layer on top of the platinum is etched away. The image sequence reveals a surprising fact: The bottom layers start to etch even before the etching front of the top graphene layer reaches them! This observation implies an exciting conclusion. The oxygen

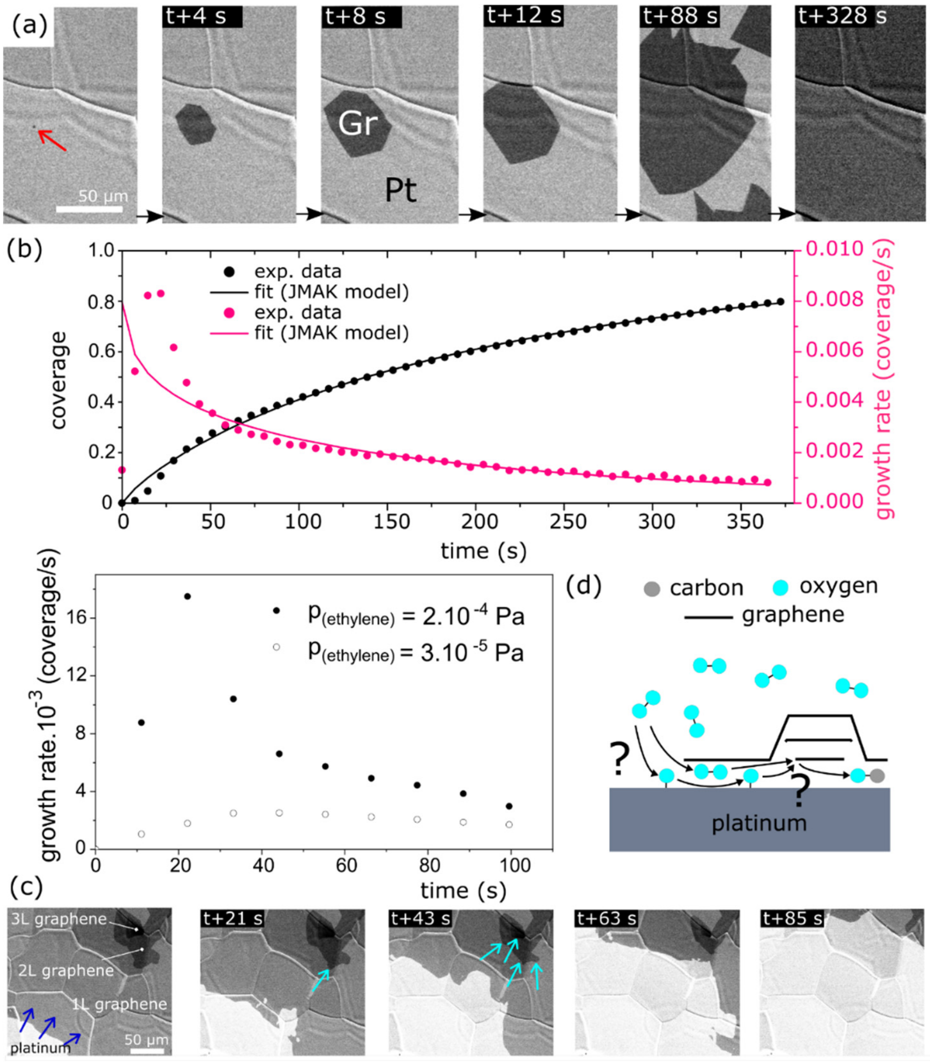

Figure 1. Utilising a very high vacuum to study the CVD growth of graphene and its etching. a) Image sequence depicting the growth of graphene on a Pt polycrystal. Carbon is supplied by dissociating ethylene molecules; the base pressure in the chamber is 6×10^{-7} Pa. Therefore, the hydrogen and oxygen fractions in the residual gas are very low. The red arrow marks the nucleation site. b) Dependence of coverage and growth rate on time (taken on a different grain than in a). c) Image sequence demonstrating etching of graphene within the van der Waals gap. Graphene is prepared in the "inverted wedding cake" geometry (see the schematic in d). The etching rate of the first layer of graphene by oxygen is constant, and the etching front (dark blue arrows) of the top graphene layer propagates from the left bottom corner up and to the right. Surprisingly, the graphene layers beneath the top one start to etch even before the etching front reaches its edges (cyan arrows). d) The schematic shows just a few possible etching scenarios: Dissociative oxygen adsorption, diffusion of atomic or molecular oxygen, and one of the possible etching products, the CO molecule.

molecules (or atoms) diffuse below the outer graphene layer, within the so-called van der Waals gap, and etch layers below the cover of the outer graphene layer. On the basis of *in situ* imaging, the etch rates could be quantified and compared between the different layers. Theoretical modelling predicts an enhanced reaction rate within the gap [3], which would be a promising approach towards, e.g., rate enhancement of catalytic reactions. *In situ* real-time imaging is the most relevant and reliable way to prove or disprove this hypothesis.

Ultra-high-vacuum experiments are extremely valuable, but their relevance to realistic process conditions remain limited. One of the most striking examples is the question concerning the existence of platinium oxide [4], which has been bothering the catalysis community for decades. According to current understanding, platinium oxide forms on the surface at high oxygen pressures in oxygen-rich atmosphere (above several millibars), whereas at lower pressures, oxygen is only dissociatively adsorbed. Thus, the reaction mechanisms deduced from many high-vacuum studies cannot be projected to real catalytic conditions. Our current knowledge of this essential industrial catalyst is still incomplete. More examples of surface structures that exist only under high pressure conditions could be found.

Furthermore, it is not only the presence of such intermediate structures, but also their activity within the process studied and the overall reaction kinetics that profoundly affect the reaction output. Intensive exchange of species between the solid surface and the gas phase is limited in high-vacuum experiments. Thus, these studies offer just a glimpse of the complex mechanisms involved in most reactions. This gap between the working conditions of available analytical techniques (with particular emphasis on electron microscopy) and the reaction conditions of realistic processes is depicted in Fig. 2. Low-energy electron microscopy (LEEM) is extremely surface-sensitive due to the low landing energy of primary electrons (0 - 40 eV). That is achieved via a cathode-lens effect – a high voltage applied to the sample. The risk of sparking between the sample and the objective lens increases at elevated pressure, possibly resulting in irreversible sample damage. As a result, this effect limits the maximum pressure in the chamber during measurement. Other electron microscopes (EMs) can cover higher pressure range. Equipped with sets of pressure-limiting apertures, the modified microscopes can operate up to relatively high pressures. These solutions, however, come at the cost of deteriorating resolution, since various other detection schemes are required. The situation is more complicated for SEMs, as compared to TEMs. TEM has the advantage of having a very small sample and related sample volume within the microscope. SEM is more versatile; however, the large chamber, potentially filled with a gas, represents a significant challenge, especially for safety reasons. Hence, with TEM offering atomic resolution and simpler adaptation to high pressures, why bother with SEM? The small sample size in TEM is its Achilles heel. Imaging technologically relevant processes often requires large fields of view. A complete picture of the process is not provided by atomic resolution. Imagine a pocket watch – what would the movement of a single cogwheel tell the engineer about the working principle of the watch? From this perspective, SEMs are an indispensable tool in material research, providing variable view fields of bulk samples. Figure 2 shows some technological processes relevant to in situ electron microscopy studies. Catalysis is a domain of surface science; however, the techniques with the best surface sensitivity require a very high vacuum. Therefore, the pressure gap in catalysis research is the subject of intensive and continuous instrumental development. Chemical vapour deposition and chemical vapour transport (CVT) are conducted at high pressures as well. Performing these processes in EM is often considered challenging, especially because of the possible contamination by process species. However, in the following paragraphs, I will show that these experiments are very rewarding once performed.

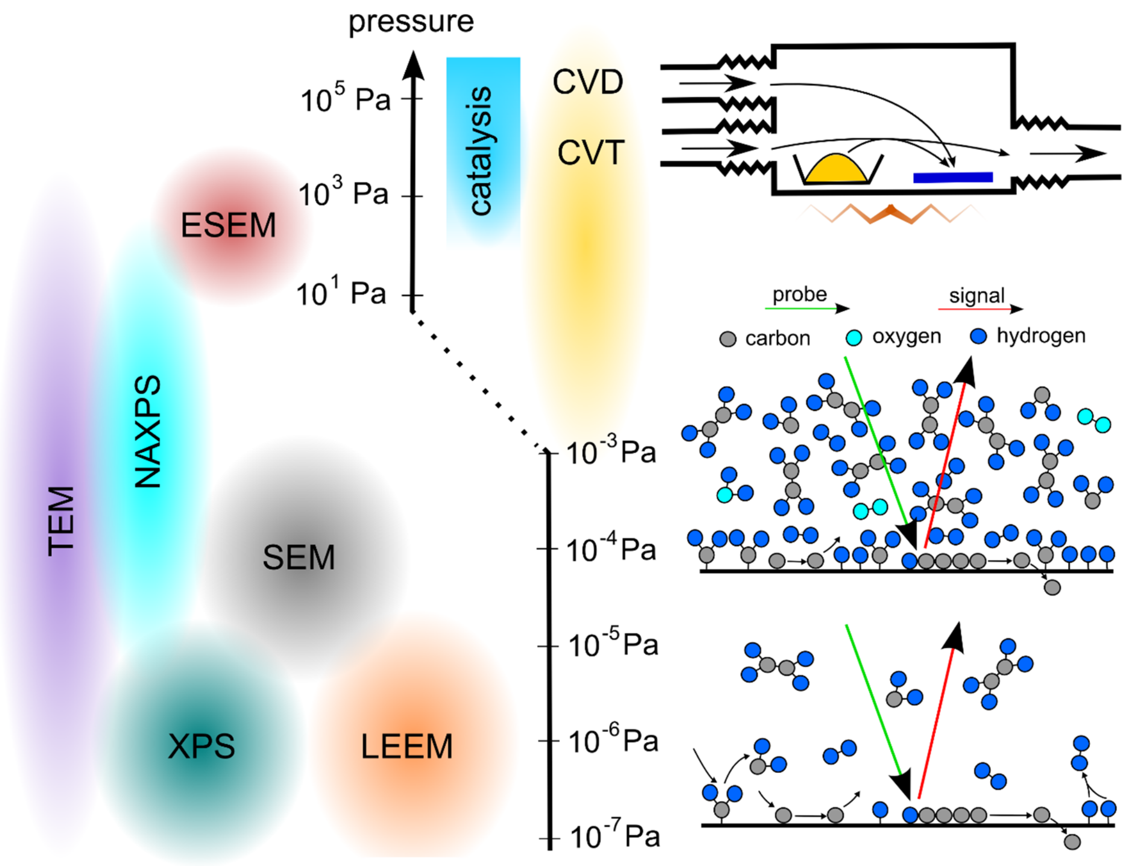

Figure 2. Pressure gap(s). On the left, operational pressure ranges of standard scanning electron microscopy (SEM) and low-energy electron microscopy (LEEM), including X-ray photoelectron spectroscopy (XPS) as a representative of the surface sensitive spectroscopic technique, are shown. Environmental SEM (ESEM) and near-ambient XPS (NAXPS) are ‘high pressure’ versions of these techniques. Catalysis and chemical vapour deposition (CVD) and chemical vapour transport (CVT) are examples of processes working at higher pressures (on the right). Pressure gaps between analytical techniques and real processes are apparent. On the other hand, thanks to the recently employed MEMS-based approach (Fig. 3d), the TEMs operate over a wide pressure window. The sketches on the right illustrate two main issues emerging with increasing pressure. First, the probe or signal (or both) is significantly attenuated at higher pressures. Next, the signal is compromised by many ‘parasitic’ processes, which cannot be easily separated from each other, as in the case of a very high vacuum. However, the pressure gap arises primarily because of the inability of the techniques to work at elevated pressures. This is limited mainly by some parts of the analytical system that require high vacuum for operation.

There are many lessons to be learned from the workhorse of surface science, X-ray photoelectron spectroscopy (XPS). The most pursued approach is to design a differentially pumped analyser and a high-pressure sample-containing cell (Fig. 3a). Pressures can reach up to 130 mbar [5] and even higher these days. The application of similar principles to SEM is known as environmental SEM (e.g., ESEM), where a series of pressure-limiting apertures lower the pressure gradient across the electron column. In connection with a dedicated pressure cell [6], such a system can offer high-pressure imaging at a slightly deteriorated resolution. Compared to XPS, the detection system is placed inside the cell (Fig. 3b). We have demonstrated the successful use of such a setup for gallium oxidation reactions [7]. These experiments identified a number of significant pitfalls in this design. Reaction products easily and quickly contaminate the detector, resulting in its failure. Therefore, a distinct detector design or a conceptually different solution that places the detection system outside the pressure cell, preferably in the high-vacuum environment of the microscope chamber, must be sought. The latter concept has the advantage that the pressure cell (from now on called a reactor) can be integrated into an existing SEM without significant hardware changes. One of the approaches is to use an inverted pressure cell (Fig. 3c), where the rear side of the sample is exposed to the probe beam. The reaction proceeds on the front side. Indeed, the sample has to be relatively thin for the ejecting signal to be detected above its rear side – usually, the graphene membrane support for reactive nanoparticles is used [8]. In transmission electron microscopy, similar approaches have been commercialised using encapsulated MEMS chips (Fig. 3d). Once again, the sample has to be very thin. Hence, even though almost realistic process conditions can be reached within these solutions, the sample is ill-defined, rarely reflecting real-world bulk samples and their surfaces. Unlike TEMs, SEMs permit using bulk samples on MEMS chips enclosed within a small volume that can be pressurised (Fig. 4e). This technology was developed e.g., by Thermo Fisher Scientific. The manufacturer and our group have been working closely on its applications. One of the experiments currently being conducted in our laboratory is the growth of 2D materials on liquid substrates.

The seamless stitching of domains is crucial to the formation of monocrystalline 2D materials on large scales. The emergence of electronically detrimental domain boundaries can be mitigated by tailoring the crystallographic orientation of the substrate to match the symmetry of the 2D material (see Figs. 4a to 4d). This is possible for graphene, which exhibits six-fold symmetry, but is increasingly difficult for other materials of interest. Therefore, a universal approach is being sought. Rheotaxy (growth on a liquid substrate) was proposed as a viable method to achieve domain ordering and self-assembly in 2012 for graphene [9]. However, it remains poorly explored due to a lack of in situ experimental techniques that confirm or disprove hypotheses about the formation and stitching mechanisms [10]. On a solid substrate, the most straightforward strategy is to suppress subsequent nucleation events after the initial one, which avoids any stitching at all. That is, however, very challenging to follow experimentally (see, e.g., Fig. 1a, where multiple nucleation events are observed), as there are too many knobs to turn. As stated at the beginning of this chapter, the growth modelling suffers due to the lack of reasonable quantitative inputs. Diffusion coefficients of atomic building blocks,

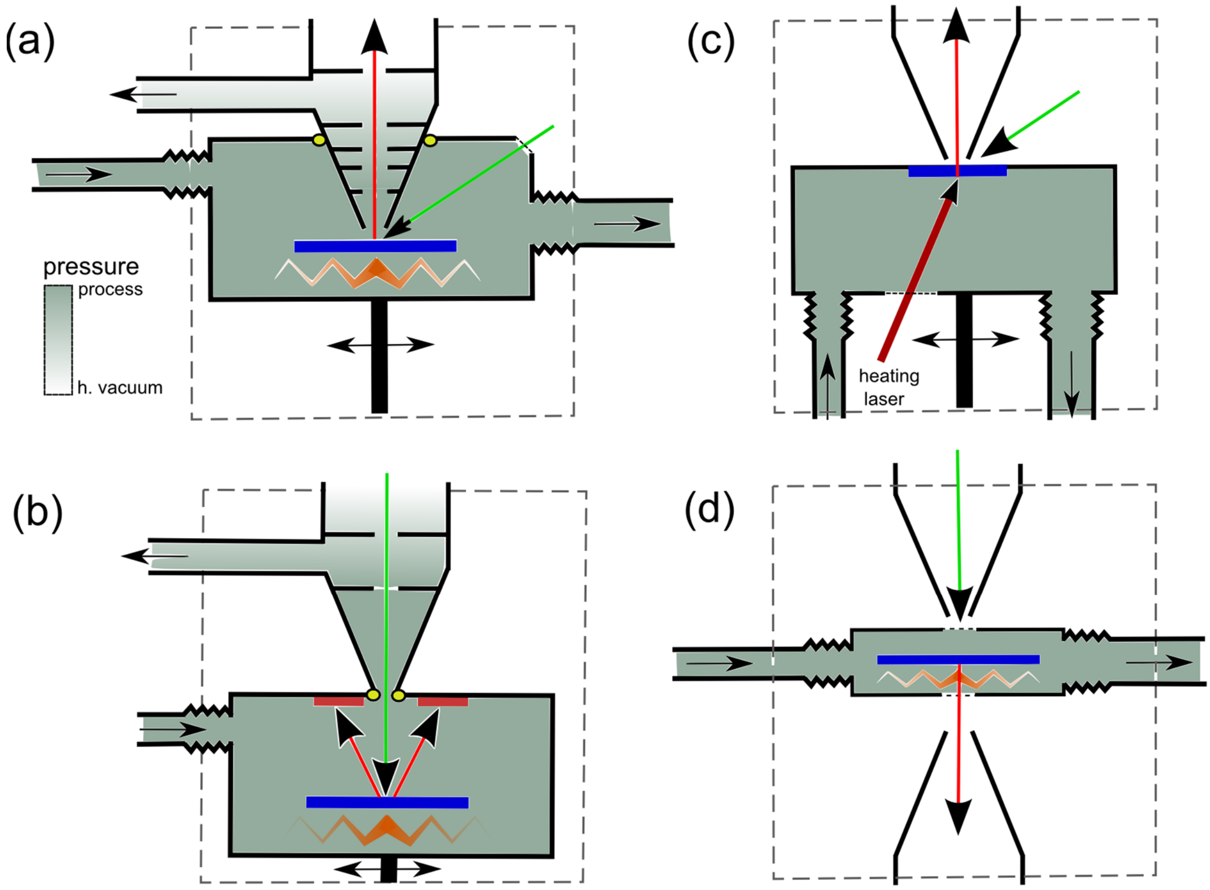

Figure 3. How to bridge the pressure gap. a) A differentially pumped analyser is used in NAXPS, similar to ESEM. b) The concept of an inverted cell allows the use of a standard XPS analyser. c) Reactor-in-SEM, where the detection system is placed inside the reactor (utilised by our group in) [7]. d) Miniaturisation of the reactor to the extreme: A sandwich made of two atomically thin membranes with the reaction volume in between, including a MEMS sample heater. This universal approach is commonly used in TEM and can also be used in XPS and SEM. The pros and cons of these solutions are discussed in the text.

attachment/detachment rates, and nucleation barriers need to be quantified experimentally to make the growth simulations quantitative. However, these data are unknown; their absence is the biggest obstacle to modelling real systems. Hence, a lack-of-data-based gap exists between growth experiments and growth modelling [11]. I have already shown in Fig. 1 that such data can be obtained from in situ microscopic experiments.

The MEMS chip enclosed in a microreactor (Fig. 4e) allows the melting of any piece of material with a melting point of up to 1,100 °C. We have chosen gold (T_m = 1,064 °C) as the growth substrate, as it has a very low vapour pressure, ensuring its stability in the liquid phase during the experiment (Figs. 4f and 4g). The individual graphene domains grown on the surface of

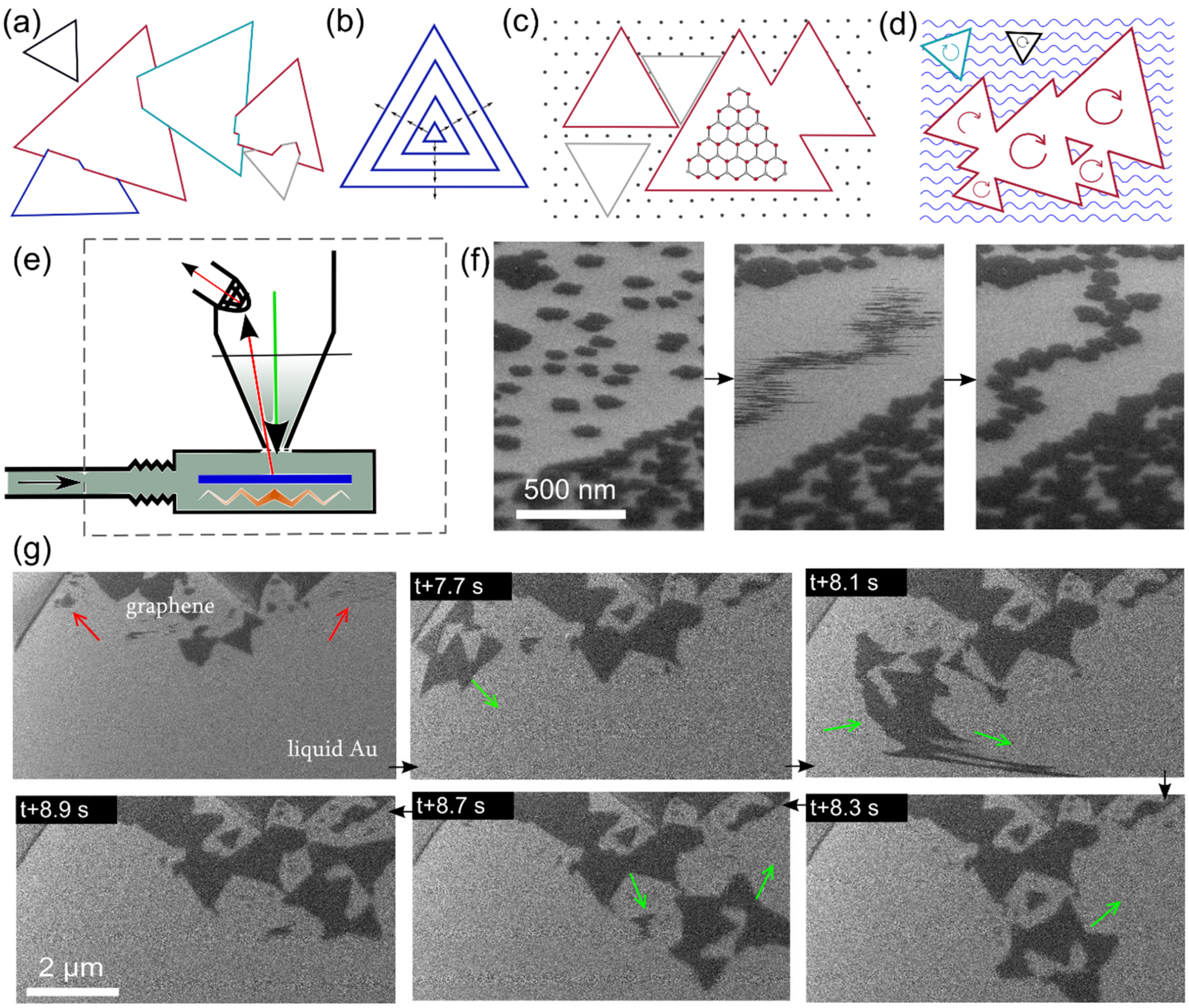

Figure 4. Toward CVD rheotaxy in a scanning electron microscope. a) Multiple random nucleation events result in the formation of a polycrystalline layer, where the grain boundaries separate different oriented domains as they meet during growth. This is the most significant issue for the scalability of the 2D-materials growth process. The solutions include b) nucleation of a single nucleus while suppressing other nucleation events, and c) growth of oriented domains, which requires, e.g., single-crystal substrate. It works for graphene, but for 2D materials with lower surface symmetry, this approach cannot prevent, e.g., twin GB formation (see panel c), where red and grey edges meet). If a liquid substrate is used, the domains are hypothesized to rotate freely and align d). A schematic of a MEMS-based microreactor is shown in e). f) Image sequence showing the transition of a gold substrate from solid (left) to liquid (middle) at 1,050 °C. The phase change is fast (the scan time is 0.18 s) and the graphene grains float on the liquid surface until they are anchored (right). g) Graphene can nucleate even on the liquid surface (red arrows) at 1,085 °C, and the growing grains are again very mobile (green arrows in the images). The movement stops immediately if the domains are attached to a stable large-domain cluster. Interestingly, no assembly is observed, compared to other reports [9].

liquid gold partially exhibit expected behaviour; they are very mobile on the surface. Contrary to theoretical predictions, they are rarely seen to align and seamlessly coalesce (Fig. 4f). Instead, they behave as though they are stitched together without any evidence of regular assembly. Our further research into this phenomenon will focus on the effect of the surrounding atmosphere on the floating grains (specifically hydrogen, which can potentially terminate graphene edges), as well as nucleation probabilities on solid and liquid surfaces (although it is claimed difficult to see nucleation events on a liquid surface, Fig. 4g). Such data are of general interest, even beyond the community of 2D materials.

MEMS reactors offer close-to-real process conditions, but sample preparation is time-consuming and challenging. Hence, our latest activities aim to develop a macroscale reactor that permits the use of real bulk samples (e.g., pieces of silicon wafer), thus mimicking CVD and CVT tubes. Such an approach also offers other advantages over microscale reactors. Most importantly, the precursor for growth can be vaporised close to the sample, similar to conventional CVD and CVT tubes (see schematic in Fig. 2, top right). Complicated precursor delivery systems are thus avoided; however, it poses new challenges to reactor design.

Nevertheless, we have managed to build such a system (Fig. 5c) and demonstrate its use within the real-time in situ experiment of ZnSe nanowire growth (Figs. 5d and 5e). ZnSe powder is vaporised by the precursor heater. A carrier gas transports the vapour toward the sapphire substrate, which is held at a different temperature by a separate heater (usually at a lower temperature than the precursor). The sapphire substrate is covered with gold nanoparticles, which serve as collectors for both Se and Zn atoms, making their condensation site specific at the droplet location due to the vapour-liquid-solid process [12]. The droplets are pushed within the predefined trenches on the substrate by the growing ZnSe crystal behind, and thus in-plane nanowires are formed on the substrate. This technology has been envisioned to become one of the approaches towards nanowire-based electronics (Fig. 5a) [13]. However, nanowire-based architecture requires a thorough understanding of growth mechanisms, especially those that govern the growth direction of nanowires. Because of the in situ microscopic approach, we were able to watch the nanowires grow in real time and reveal the causes of their misalignment with the predefined trenches on the substrate. These include structural defects within the trench structure, surface contamination, and non-catalysed deposition of ZnSe on the surface (Fig. 5d). Therefore, this study presents a clear picture of the requirements for substrate and process cleanliness in the (possible) future. In addition, we were able to track individual nanowires and quantify their growth rate dependence on nanowire radius (Fig. 5e). Such data are possible to fit with appropriate growth model [14] and provide valuable insight into the growth process. In this particular case, the slope of the dependence in Fig. 5e gives information on the dimensionality of surface diffusion. Similar data are impossible to extract from the ex-situ growth experiments, because the nucleation delay significantly affects the resulting nanowire length. As a result, *ex-situ* analysis often leads to erroneous conclusions.

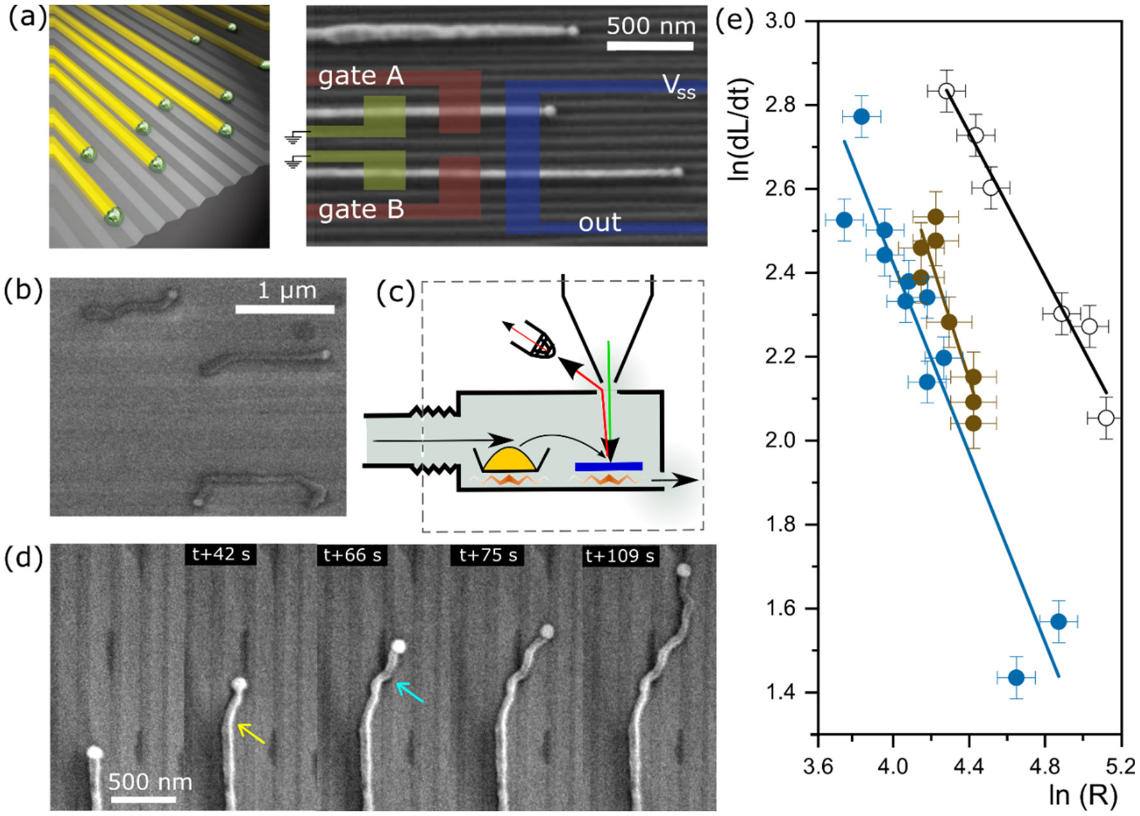

Figure 5. Mimicking CVT reactions. a) Electronics based on in-plane nanowires is envisioned as a promising technology, especially due to the integration of other materials on a silicon platform. The requirement is absolute control of the growth direction (reprinted with permission, © Ernesto Joselevich). Ideally, one can build simple logic gates based on these nanowires (the image on the right shows a PMOS NAND gate). b) In reality, it is often not the case, as the in-plane growing wires are found outside the predefined trenches on the substrate surface. c) A schematic of a macroscale reactor designed to mimic CVT growth of these nanowires in an SEM. The detection system is placed outside the reactor (contrary to the design shown in Fig. 3b), significantly improving the resistance to contamination. The colour coding and symbols are identical to those used in Fig. 3. d) An image sequence showing the growth of a ZnSe nanowire, guided by a gold droplet, on a surface of sapphire. Several events can divert the nanowire from its original straight growth trajectory – unseen contamination on the surface (yellow arrow), carbon contamination (cyan arrow), and possibly also corrugation of the surface trench geometry (not shown, see [14]). e) Nanowire growth rate dependence on radius (both in logarithmic scale). Each point represents a single nanowire, different colours mark different experimental runs.

In conclusion, I have focussed on our work in the field of in situ microscopy. By taking advantage of the fertile soil of microscopy research in Brno, and collaborating with other industrial entities, we are able to visualise things not seen before. Applying the above principles allows us to perform curiosity-driven research due to the development of novel instrumentation. Within these studies, we collected valuable data on processes envisioned as future directions in the preparation of nanoscale materials. I have also demonstrated that there are ways to mitigate the pressure gap between the operational conditions of an electron microscope and a real process environment. However, it is far from resolved. Bridging this gap will require unrelenting effort in the coming years, and it is a very promising field of research and development.

It is very tempting to draw conclusions based solely on unique microscopic observations. However, the microscopic experiments must be corroborated by other techniques and analyses. The choice of experiments presented here was made with respect to this fact; the obvious example of incomplete description is the etching of graphene within the van der Waals gap shown in Fig. 1c. To perceive the world around us, we also need other senses (e.g., the microscope, see Fig. 6). Consequently, implementing novel in situ techniques within an electron microscope is another promising way to increase the impact of these studies. We are currently conducting research in this area. Indeed, the development of working solutions is challenging; however, it is very rewarding when it is successful.

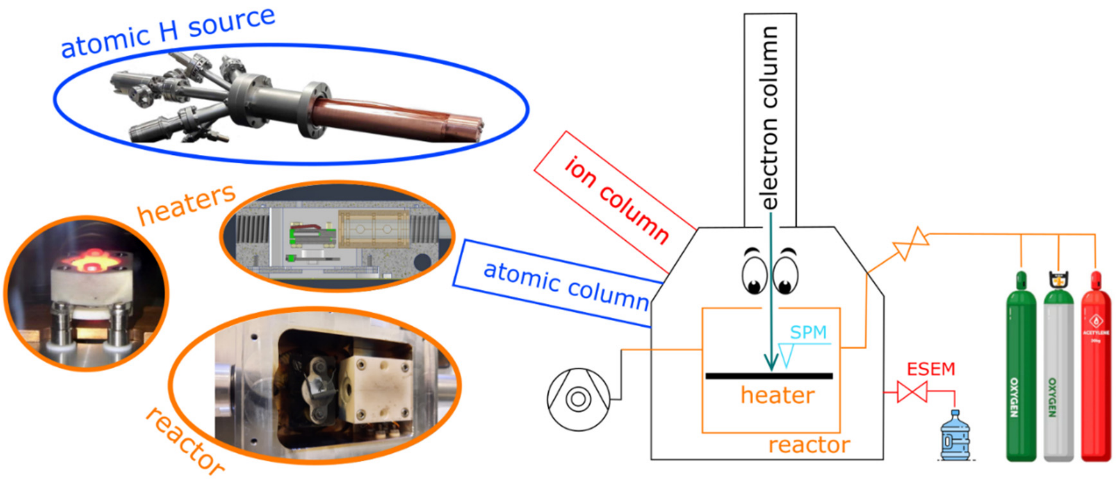

Figure 6. Electron microscope as a laboratory for research on quantum materials. A conventional scanning electron microscope (black) is a dedicated tool for observing bulk samples, utilising an electron beam as a probe and various detection schemes for detecting distinct signals (electrons, X-rays, and light). These two principal components are continuously improved over time. Disruptive events in microscope development were the introduction of the focussed-ion beam (FIB) and ESEM (red). Our work focusses on utilising SEM for complex experiments dealing with (quantum) materials. Such an aim requires modifications of the microscope, including the development of unique instrumentation. This includes, e.g., a column for the generation of atomic beams (blue), reactor-in-SEM including a hot stage and a gas injection system for in-situ microscopy (orange), etc. These activities would not be possible without the support of an industrial partner (Thermo Fisher Scientific). Image formation is not necessarily limited to electron-beam-induced signal; in collaboration with NenoVision, we pursued the pathway towards correlative imaging utilising scanning probe microscopy. We develop methodologies for advanced modes of SPM (e.g., Kelvin probe force microscopy) in conjunction with the electron beam. The know-how on surface science and related processes (and characterisation techniques) we carry allows us to get a deep insight into the formation of quantum materials, their interaction with the electron beam, and behaviour under reactive atmosphere and under real process conditions.

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