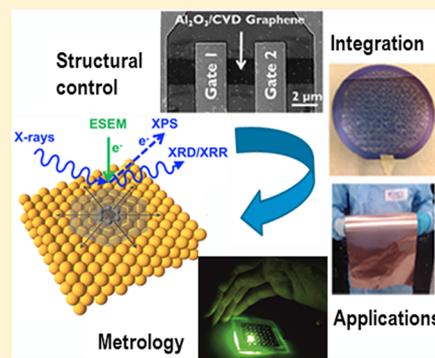


## CVD-Enabled Graphene Manufacture and Technology

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**ABSTRACT:** Integrated manufacturing is arguably the most challenging task in the development of technology based on graphene and other 2D materials, particularly with regard to the industrial demand for “electronic-grade” large-area films. In order to control the structure and properties of these materials at the monolayer level, their nucleation, growth and interfacing needs to be understood to a level of unprecedented detail compared to existing thin film or bulk materials. Chemical vapor deposition (CVD) has emerged as the most versatile and promising technique to develop graphene and 2D material films into industrial device materials and this Perspective outlines recent progress, trends, and emerging CVD processing pathways. A key focus is the emerging understanding of the underlying growth mechanisms, in particular on the role of the required catalytic growth substrate, which brings together the latest progress in the fields of heterogeneous catalysis and classic crystal/thin-film growth.



Graphene, with its characteristic hexagonal  $sp^2$  bonding, is the archetypal 2D material and one of the thinnest materials with which one can engineer. Although many of the key attributes of graphitic layers have been known for a long time,<sup>1–3</sup> the isolation of monolayers has brought graphene into the limelight over the past decade, following the heightened interest in fullerenes and carbon nanotubes (CNTs).<sup>4</sup> Mechanical exfoliation, in its simplest form via Scotch tape, provides easy access to graphene flakes and has been widely used experimentally to reveal extraordinary electronic, optical, mechanical, and thermal properties for single-crystalline graphene on the nano- to micrometer scale.<sup>5</sup> Many of these properties are strongly dependent on the environment, and hence interfacing of graphene is crucial, and typically dictates device behavior.<sup>6</sup> Graphene is under consideration for a wide range of applications and emerging technologies, and as with many emergent nanomaterials, the foremost challenge is to develop manufacturing and processing techniques that fulfill the industrial demands for quality, quantity, reliability, and low cost.<sup>7</sup> A plethora of diverse fabrication methods have emerged to produce different types of graphene material. Various forms of exfoliation of bulk graphite have been commercially adopted to give isolated small (typically  $<1 \mu\text{m}$ ) graphene flakes, suited as functional additives or for the formulation of inks.<sup>7</sup> For the manufacturing of continuous graphene films that in particular serve the industrial demand for “electronic-grade” material, chemical vapor deposition (CVD) has emerged as the most versatile and commercially viable technique. CVD is already the dominant manufacturing route for many other nanomaterials, as it enables not only bulk production but importantly also direct device integration and interfacing, that is, CVD enables integrated manufacturing. Practically all commercial CNT production<sup>8</sup> is now based on CVD and this offers an especially insightful comparison to the ongoing industrial materials development for graphene and other 2D materials.

Here, we offer a perspective on recent progress in graphene CVD, in particular the efforts toward integrated manufacturing of “electronic-grade” 2D materials. Instrumental to the graphene CVD process is a catalyst or suitable substrate surface to effectively dissociate the gaseous carbon precursor and to aid crystallization, that is, to promote the  $sp^2$  bonding arrangement. Hence, an understanding of the underlying growth mechanisms is essential to quality and interface control for 2D material CVD. Such understanding remains incomplete, especially for those conditions most relevant to scalable manufacturing. However, numerous detailed studies across the literature allow some first-order growth model generalizations to be made that provide important insights and that we wish to focus on here. Single-crystal graphene domains currently up to centimeter dimensions have been demonstrated by CVD,<sup>9–11</sup> and the quality and properties of such flakes are emerging as equivalent to those of mechanically exfoliated material,<sup>12</sup> that is, representing the “best” material available. However, given the present lack of standardization and that high-throughput large-area characterization remains a significant challenge, the attributes of “best” or “high-quality” are poorly defined and inconsistently applied. Commonly used metrics for “high-quality” are high carrier mobility as measured by electronic transport measurements or a negligible defect (D) peak in Raman spectroscopy. Larger-area graphene CVD films are continuous but typically polycrystalline, and hence, macroscopic film properties depend to varying degrees on the domain size, connectivity, and the domain-boundary structure including related defects.<sup>13,14</sup> This polycrystallinity can be engineered via control over nucleation density and domain shape evolution during the graphene CVD process. At present,

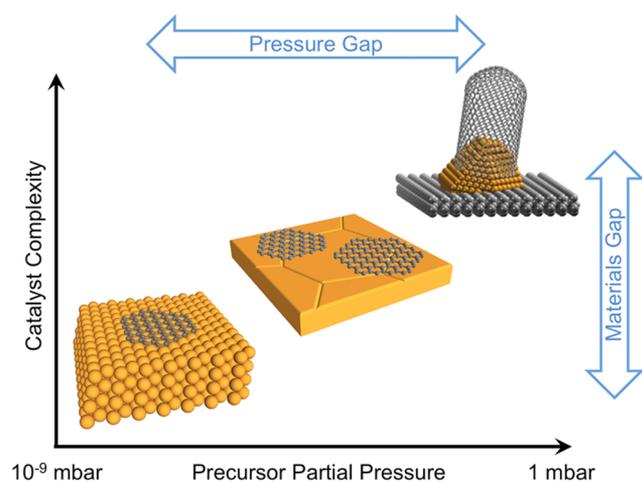
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industrial integration of CVD graphene often relies on transfer of the as-grown graphene films away from the catalyst support onto a desired target substrate. Although a range of transfer techniques have been developed,<sup>15</sup> including roll-to-roll processes, large-area transfer remains highly challenging and typically degrades quality and contaminates the graphene films with process chemicals and residues. CVD allows a more direct integration route for applications where the catalyst or growth substrate forms part of the device structure. Such direct device integration and interfacing has been a particular strength of CNT CVD and has been successfully implemented already for graphene applications where a metallic catalyst film is part of the device structure, such as in spintronics.<sup>16,17</sup> This drives an increasing effort to explore alternative graphene catalysts, including dielectric or semiconducting growth substrates,<sup>10</sup> as well as efforts involving removal/conversion of the catalyst after growth and the direct encapsulation and protection of the graphene device layer at the point of growth.<sup>18–22</sup> Commercially produced graphene is currently based on CVD batch processing, but depending on integration route, semicontinuous or continuous CVD production processes are under development.<sup>7,23</sup> Most other application-relevant 2D materials have more complex crystal layer structures or are compounds, such as h-BN, which means that their controlled CVD is inherently more complex, as two elements need to be fed. In this context, the insights gained from graphene CVD offer a framework to drive the manufacturing of these more complex compound nanomaterials.

Figure 1 outlines the basic graphene CVD growth process and highlights that, due to its catalytic nature, the parameter space spans not only that of classic crystal growth and thin film deposition techniques but also includes that of heterogeneous catalysis. A planar catalyst, such as a film or foil, is exposed to a gaseous precursor at temperatures/conditions for which it dissociates and upon the carbon species at the catalyst surface

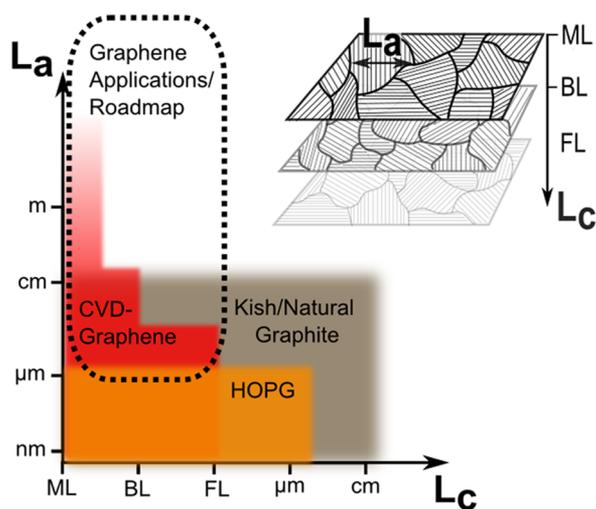


**Figure 1.** Pressure and materials gap for the catalytic CVD of carbon nanomaterials. Ultrahigh vacuum studies on single crystal surfaces suffer from lack of applicability to “real-world” conditions, that is, less well-defined atmospheres at higher pressures (pressure gap) and more complex surface structures (materials gap), relevant to cost-effective manufacturing. The growth of CNTs thereby represents a highly complex scenario, for which graphene CVD can serve as a planar model system. The historic development of CNT production offers an insightful comparison to the ongoing industrial materials development for graphene and other 2D materials.

reaching a critical concentration, a graphitic layer nucleates and grows. Although there is a lot of data on how to prevent such formation of graphitic deposits (coking) in catalysis and there are numerous surface science studies on the atomic structure of graphene layers on metal surfaces,<sup>24,25</sup> it should be emphasized that the conditions and challenges for scalable graphene CVD are notably distinct. Results from idealized model systems based on for instance well-prepared, single-crystal surfaces at well-defined ultrahigh vacuum conditions cannot straightforwardly be extrapolated to “real-world” conditions relevant to cost-effective manufacturing. In analogy to the well-known challenges in heterogeneous catalysis termed “pressure” and “materials gaps”,<sup>26</sup> Figure 1 highlights this situation for the CVD of carbon nanomaterials. Bearing in mind that graphene corresponds to a surface coverage of only a monolayer, the fact that CVD of “high-quality” graphene can be achieved on (often only partly cleaned) polycrystalline catalyst templates and under vacuum/CVD process conditions that are not particularly stringent is a key advantage for its commercial exploitation. Yet developing an understanding of graphene formation under such relevant conditions is highly challenging, even when just first-order approximations are considered as a rationale to optimize growth. To address this challenge substantial progress has been made recently in developing in situ metrology that provides atomic-scale insights into reaction processes under industrially relevant conditions.<sup>26–28</sup> In the following, we will outline major results from this approach for graphene CVD. Figure 1 further highlights the direct link between catalytic CVD of graphene and CNTs. CNT nucleation requires the catalyst to be in (supported) nanoparticle form and typically requires higher precursor exposure pressures than for graphene.<sup>29</sup> CNT growth is based on the formation of graphene layers on a multifaceted catalyst particle and a single-walled CNT nucleates by lift-off of a carbon cap. Cap stabilization, which determines the so-called chirality, and CNT growth involve the dynamic reshaping of the catalyst nanocrystal itself.<sup>29</sup> This reshaping effect is in turn related to the carbon concentration in the catalyst.<sup>30</sup> Hence, in terms of materials and pressure gap, CNT growth is most complex and graphene CVD can serve as a planar model system to study carbon/graphene-catalyst interactions in this case.<sup>31</sup> The structural reciprocity apparent in CNT growth is also highly relevant to graphene CVD. In particular for graphene CVD conditions where the catalyst is close to its melting point and its surface is highly mobile, the formation of a graphene layer can lead to catalyst recrystallization at the graphene interface and studies on this are ongoing and important to interpret any epitaxial or pseudoeptitaxial graphene–catalyst relationships.<sup>32</sup>

CVD uniquely fulfils an ever-increasing application-driven demand for continuous, large-area mono- or few-layer graphene films.

It is instructive from a fundamental as well as application point of view to consider the structure of CVD graphene films in the context of the historically well-explored crystallinity of natural and synthetic graphite, which is the parent material of all exfoliated graphene. Figure 2 adopts the widely used structural parametrization in terms of the crystalline domain

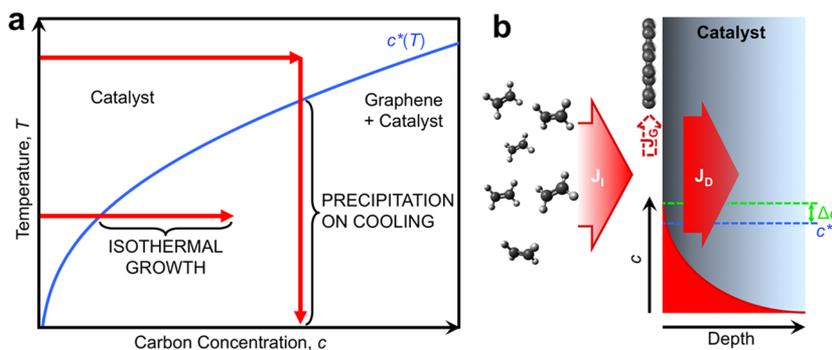


**Figure 2.** Structure of CVD graphene films in the context of natural and synthetic graphite. The crystal size is expressed in terms of the crystalline domain size within the basal plane,  $L_a$ , and interplanar crystal dimension  $L_c$ . Maximum known crystal dimensions are indicated for commercially available graphite, which present limits for any form of exfoliation. The single crystal sheet size for CVD graphene, on the other hand, can be orders of magnitude larger. The inset highlights the often rather complex structure of few-layer CVD graphene films, where each constituent layer has its own polycrystalline microstructure. ML, BL, and FL denote mono-, bi-, and few-layer graphene.

size within the basal plane,  $L_a$ , and interplanar crystal dimension  $L_c$ .<sup>33</sup> The natural graphite of highest known crystallinity is vein or lump graphite, believed to form pyrolytically from subterranean fluid, and flake graphite formed in metamorphic or calcareous sedimentary rocks. Although average values for  $L_a$  and  $L_c$  for such natural graphite are of the order of tens of micrometers, typically characterized by X-ray diffraction (XRD), isolated flakes can reach crystal dimensions ( $L_a$ ) in the cm range. Such maximum sizes, however, are rarely reported because they fall outside the range of current industrial graphite screening/characterization. Although synthetic kish graphite, formed upon cooling of molten steel,<sup>34</sup> can have similar  $L_a$  and  $L_c$  to natural graphite, synthetic highly

oriented pyrolytic graphite (HOPG) is characterized by the highest purity and degree of three-dimensional ordering, but the dimensions of individual constituent crystals are usually limited to the micrometer range.<sup>35</sup> Figure 2 highlights that CVD can uniquely fill the increasing application driven demand for continuous, large-area mono- or few-layer graphene films. CVD allows direct layer control in terms of  $L_c$ , and lateral domain sizes,  $L_a$ , of centimeter dimensions have already been demonstrated,<sup>9–11</sup> larger than that of any natural or other synthetic graphite. On the basis of improving the understanding of the crystal growth mechanisms, as discussed below,  $L_a$  can further be increased for the CVD process and the average defect density of the film can be significantly decreased. There is also an increasing effort to understand the origin of specific layer stacking (e.g., Bernal, rhombohedral, or turbostratic configurations)<sup>36</sup> in order to tailor the properties of bi- or trilayer graphene CVD films and to enable the direct, controlled CVD of out-of-plane 2D heterostructures. Currently, the crystallography of large area, few-layer graphene CVD films can be rather complex, as shown in Figure 2, with each layer possessing a different in-plane microstructure, and hence, many different misorientation angles can exist vertically in such a sample; that is,  $L_c$  typically corresponds to just the thickness of a graphene monolayer.

The process of graphitization is complex and not well understood.<sup>37</sup> The formation of pyrolytic graphite by the decomposition of hydrocarbons or crystallization of solid carbon precursors typically requires temperatures in excess of 1500 °C to form a graphitic lattice of high crystallinity. Therefore, critical to the CVD process is the use of a catalyst that enables low activation energy pathways for precursor dissociation, graphene nucleation, crystal growth, and domain merging. Transition metals are thereby the most catalytically active, as is well known from heterogeneous catalysis and surface science.<sup>25,38</sup> The atomic structure of graphene monolayers on various low-index metal surfaces has been studied in detail, including the potential forms of epitaxy and the resulting impact on the graphene morphology, for example, corrugations.<sup>32,39,40</sup> On the basis of the resulting changes to the electronic structure of the graphene, the interaction with the metal can generally be categorized as either weak, typical for simple sp metals or metals with closed d-shells such as Cu, or



**Figure 3.** (a) Generic catalyst–carbon phase diagram illustrating that carbon supersaturation and hence graphene nucleation and growth can occur isothermally via continued carbon precursor exposure or the solvus can be crossed vertically at a given carbon concentration via catalyst cooling due to the associated reduction in carbon solubility. (b) Schematic illustration of balance between the carbon flux due to precursor impingement and dissociation,  $J_i$ , and that related to carbon diffusion into the catalyst,  $J_D$ , with the difference in fluxes,  $J_C$ , feeding the growing graphene layer at the catalyst surface. Higher precursor pressures can result in a local carbon supersaturation  $\Delta c$  near the catalyst surface that leads to graphene monolayer formation, whereas the diffusion of carbon into the catalyst bulk remains limited as indicated by the carbon concentration depth profile in red. Such kinetic considerations can serve as a basis for a general first-order growth model framework for any elemental or alloy catalyst system.

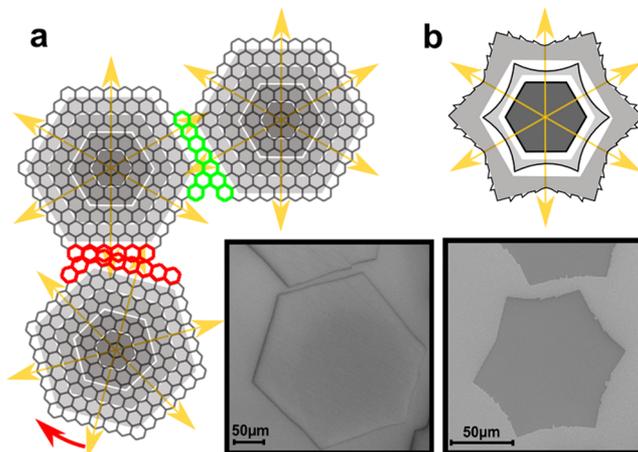
strong, for metals with an open d-shell structure such as Ni.<sup>41</sup> For the latter, the overlap between the graphene  $\pi$  and metal d valence band states completely destroys the linear graphene band dispersion around the Fermi level, whereas for the weakly interacting metals the linear band structure of free-standing graphene is preserved but charge transfer typically shifts the Fermi level. Although the study of such metal–graphene interactions has historically been limited to single-crystal surfaces at ultrahigh vacuum conditions, recent work clearly shows that the interactions can significantly change in the presence of for instance oxygen, high carbon precursor pressures and high concentrations of dissolved carbon in the catalyst,<sup>28,31</sup> which represent prime examples of the pressure gap highlighted in Figure 1.

When it comes to the choice of catalyst, a widely used rationale is to consider the equilibrium carbon solubility. Graphene nucleation and subsequent growth requires the carbon concentration near the catalyst surface,  $c$ , to exceed the equilibrium solubility,  $c^*$ , and for a carbon supersaturation,  $\Delta c = c - c^*$ , to thereby develop. As indicated in the generic phase diagram of Figure 3a, such supersaturation can result from the solvus being crossed horizontally via continued hydrocarbon exposure and dissociation at the catalyst surface at constant temperature, which is referred to as *isothermal growth*. The solvus can also be crossed vertically at a given carbon concentration via catalyst cooling due to the associated reduction in carbon solubility, which is referred to as *precipitation on cooling*.

For a basic CVD process, consisting of heating up and pretreatment of a catalyst, exposure to a hydrocarbon at constant temperature, and cooling down in an inert atmosphere, graphene formation will proceed via isothermal growth but additional layers may grow during cooling.<sup>27,42</sup> Hence, it is often argued that for monolayer graphene CVD a catalyst with low carbon solubility is essential and that for high carbon solubility metals, graphene growth occurs via precipitation upon cooling, leading to multilayer formation.<sup>11,43–45</sup> Figure 3b shows why such simple thermodynamic considerations of carbon solubility are insufficient to capture even basic growth behavior. The central point is that although the catalyst's carbon solubility presents a potential reservoir, depending on CVD conditions, this reservoir may never be filled, and thus the kinetics of the CVD process are critical to the growth behavior.<sup>46</sup> A basic balance can be considered between the carbon flux due to precursor impingement and dissociation,  $J_p$ , and that related to carbon diffusion into the catalyst,  $J_D$ , with the difference in fluxes,  $J_G$ , feeding the growing graphene layer (Figure 3b). High precursor pressures, thus, can result in a local carbon supersaturation at the catalyst surface that leads to graphene monolayer formation, whereas the diffusion of carbon into the catalyst bulk remains limited. Hence, a complete graphene monolayer can form on a thick, high carbon solubility catalyst without it becoming saturated throughout with carbon.<sup>46</sup> In this case, the CVD mechanism is purely isothermal with negligible precipitation upon cooling, and this has been directly experimentally verified by in situ metrology.<sup>31,42,47–49</sup> Such kinetic considerations can serve as basis for a general first-order growth model framework useful for any elemental or alloy catalyst system.

The microstructure of a graphene CVD film (Figure 2) is directly linked to how graphene domains nucleate and how the domain shapes evolve and merge to form a continuous film, as schematically outlined in Figure 4. There are two basic

For most graphene applications, ranging from electronics, photonics to biomedical and electrochemical devices, it can in fact be the material interfaces that dictate properties and overall functionality.



**Figure 4.** (a) Origin of the microstructure of a CVD graphene film:  $L_a$  relates to nucleation density of graphene domains as well as how they eventually merge. A misorientation between different graphene domains, as highlighted in red, leads to grain-boundaries and polycrystalline film structure (see inset Figure 2), whereas collective alignment or epitaxy can give large monocrystalline graphene, highlighted in green. (b) Graphene domain shape evolution can be generally either limited by the incorporation kinetics of the constituent species at the growth fronts or by the diffusion of constituent species. However, for industrially relevant CVD conditions an often complex balance between carbon incorporation and competing etching processes has to be considered. The insets show plan-view scanning electron microscope (SEM) images of CVD graphene domains grown on Cu surfaces. This can be recorded in situ, at high temperatures (1000 °C) during hydrocarbon exposure (mbar levels), to develop a detailed understanding of the growth mechanisms.<sup>28</sup>

approaches to achieve large  $L_a$  for monolayer graphene (Figure 4a). The first is to lower the graphene nucleation density. The diffusion length or capture radius of growth species on the catalyst surface provides a minimum estimate of the graphene nucleation density. In general, higher exposure temperature and lower precursor pressure, theoretically typically expressed as a lower carbon chemical potential,<sup>31</sup> result in lower nucleation densities. Catalyst surface imperfections, such as step edges, defects, and impurities, can be active sites for graphene nucleation. To obtain low nucleation densities, these active sites may be passivated to reduce their density, by catalyst surface pretreatments such as oxidation<sup>9</sup> or catalyst alloying.<sup>27</sup> Alternatively, more preferential nucleation sites can be created, again using pretreatment techniques such as admixtures<sup>50</sup> or through lithographic patterning of seed nuclei,<sup>51</sup> the density of which now defines the nucleation density. A second approach to achieve large  $L_a$  is to minimize the misorientation between different graphene domains, so that in an ideal case, these multiple domains would all merge into a seamless graphene crystal rather than creating grain boundaries. Although this allows higher growth rates compared with the first approach,

this typically necessitates well-defined, highly crystalline catalyst surfaces with a minimum lattice mismatch to graphene.<sup>10,11,25,47</sup> A central question that is often neglected in this context is how the graphene domain anchors on the catalyst surface, as this can dictate the domain orientation. It has been shown that even for low-index model surfaces such as Ni(111), there can be a number of different growth mechanisms, and epitaxial relationships, depending on the CVD conditions with graphene either growing on top of the metal surface or embedded in the topmost metal plane.<sup>47</sup> For all approaches, it should be emphasized that the catalyst surface can be highly dynamic and liquid-like under the conditions typically used for CVD, that is, temperatures close to the catalyst melting point and at high gas exposures. Hence, again with reference to Figure 1, it is crucial to understand the highly dynamic interactions at the catalyst surface at realistic conditions rather than assuming idealized surfaces.

Following nucleation, the graphene domain evolution at the catalyst surface can be generally either limited by the incorporation kinetics of the constituent species at the growth fronts or by the diffusion of constituent species (Figure 4b). The latter results in dendritic domain growth due to instabilities arising from growth front protrusions, whereas for the former the domain evolution can be described via kinematic Wulff constructions.<sup>52</sup> However, rather than focusing only on the carbon addition, competing etching processes such as by hydrogen, water, or oxygen species and their balance also must be taken into account for realistic CVD conditions. The mode of domain evolution will in turn dictate how and to what level the overall graphene film will merge. Many applications do not require monocrystalline graphene films, but a minimum requirement for most applications of large area CVD graphene is homogeneity and reproducible film properties. This requires an understanding of the grain boundary formation and structure for the different growth modes. In contrast to other materials, such as metals, where postdeposition treatments such as annealing allow a significant evolution of the microstructure, a postgrowth improvement of the graphene crystallinity such as an increase in domain size is practically limited to the case where the graphene layer is still in contact with the catalyst. Such catalytic graphene recrystallization has been considered,<sup>53</sup> and analogous to the growth scenario, the underlying mechanisms and, for example, required temperatures closely depend on the graphene-catalyst interactions.

In situ metrology allows an increasingly detailed understanding of the catalytic growth mechanisms, which translates into increasing control of the microstructure of these CVD films.

Catalytic graphene CVD is often described as inherently being self-limited because a monolayer coverage will cutoff the precursor supply to the catalyst surface and, hence, prevent formation of a second layer. However, this only refers to conditions of low carbon chemical potential, that is, low precursor pressures. For typical catalyst metals including Cu, it can be shown that at higher precursor pressures additional graphene layers nucleate at the interface between the catalyst and the initial graphene layer fed via precursor leakage through

intrinsic defects (including grain boundaries) in the initial graphene monolayer.<sup>54</sup> This presents a pathway for the controlled CVD of bi- and trilayer graphene films.<sup>46</sup> Because of the different nucleation and growth conditions, each of the resulting additional graphene layers typically, however, has a different basal microstructure, as indicated in Figure 2. A number of different approaches, including feeding carbon through the catalyst bulk<sup>55</sup> or looking at epitaxial growth regimes with CVD conditions tuned to nucleate a second epitaxial layer, are currently being pursued as means for the possible control of layer stacking during CVD of bi- or trilayer graphene films.<sup>31,56–58</sup> In principle, the same pathway allows the direct CVD of out-of-plane 2D heterostructures, such as alternating graphene and h-BN layer stacks.<sup>22</sup> The growth mechanisms for compound 2D materials such as h-BN are inherently more complex, as two elements need to be fed and incorporated into the growing nanostructure and bond polarity can affect the structural formation.<sup>50,59</sup> Similar to graphene CVD, growth control for monolayer h-BN films requires an understanding of nucleation and domain evolution and subsequent merging.<sup>50</sup> However, now the interaction of two elements with the catalyst or catalyst alloy, that is, more complex ternary phase diagrams, and the kinetic balance of an increasing number of fluxes have to be considered even for the simplest of growth models. For example, for a polycrystalline Cu catalyst, it has been shown that boron dissolves into the catalyst bulk, whereas nitrogen does not and this can lead to a situation where the h-BN growth is limited by the nitrogen supply.<sup>59</sup> This is reminiscent of the situation for catalytic III–V nanowire growth, where the group V constituent typically has a low solubility in the conventionally used Au catalyst and, despite a high bulk solubility of the group III element, atomically sharp heterostructures can be obtained.<sup>60</sup> Further complexity arises when attempting to form heterostructures of materials with completely different elemental compositions (e.g., graphene and h-BN) where the compatibility of all constituents must be taken into account.

Overall, tremendous progress has been made in the CVD manufacture of graphene and other 2D materials. As highlighted, CVD uniquely fulfils an ever-increasing application-driven demand for continuous, large-area mono- or few-layer graphene films. At the same time, novel in situ metrology allows an increasingly detailed understanding of the catalytic growth mechanisms, which translates into increasing control of the microstructure of these CVD films. In particular, the ability to monitor CVD under conditions directly relevant to cost-effective manufacturing, that is, bridging the so-called pressure- and materials-gaps, makes this feedback loop extremely powerful, and this will allow an ever increasing control over the film properties. Fostering an understanding of the underlying growth mechanisms will have to be a major future focus. Emerging technology and commercialization is currently developing based on two major distinctive forms of graphene: small graphene (or graphene oxide) flakes and continuous graphene films. For the latter, CVD is bound to become the industrial standard process technique, enabling integrated manufacturing of 2D materials of “electronic-grade”, that is, of the highest quality available. Efforts on industrial standardization of these materials are already underway, but with monocrystallites going beyond centimeter dimensions and atomically thin films being grown on the meter scale, there is clearly a need to apply and develop new methods for high-throughput large-area characterization. A deeper understanding

is not only required for nucleation and growth, but crucially also for interfacing and device integration of these new materials. For most graphene applications, ranging from electronics, photonics to biomedical and electrochemical devices, it can in fact be the material interfaces that dictate properties and overall functionality. At present, CVD on metal foils mostly relies on transfer, and although some current transfer methods might be acceptable for centimeter areas, such transfer is not appropriate for technological implementation in the long term. Hence, the future requires integrated manufacturing of these nanomaterials. Direct device integration and interfacing has been a particular strength of CNT CVD, and has been successfully implemented already for graphene applications where a metallic catalyst film is part of the device structure. For future technology, the direct encapsulation and protection of the 2D device layer and its interface is required at the point of growth. Current directions for this include the removal/conversion of the catalyst after growth, the combination of 2D material CVD and atomic layer deposition (ALD) of dielectrics for the growth<sup>61</sup> (and subsequent transfer) of heterostructures (e.g., graphene sandwiched between dielectric layers) and the direct growth on dielectric or semiconducting substrates. Hybrid layer structures will help to controllably define and protect the properties of atomically thin 2D films, such as doping, carrier mobility, and electronic band structure, which is crucial to their development as “electronic-grade” device materials. Equally, CVD allows the direct growth of unique novel layer materials, that have no “top-down” equivalent via exfoliation, including in-plane heterostructures with covalently bonded, atomically thin interfaces and foam- or aerogel-like structures via 3D catalyst templates. This offers exciting future pathways to engineer novel nanomaterial structures and interface them with the existing material portfolio and processing platforms of for instance microelectronics, CMOS technology and flexible electronics.<sup>62</sup> This is central to the near term technology roadmap<sup>7</sup> and opens the route to new functionalities using graphene in applications ranging from electronics and photonics, including terahertz and RF components, photodetectors, light emitting diodes, spintronics, liquid crystal devices, to energy generation, storage and conversion, including photovoltaics, thermoelectric devices, supercapacitors, and batteries, and biomedical applications such as sensors, tissue engineering, and membranes for microscopy, filtration, and DNA sequencing. Many of the challenges outlined for 2D materials are common to other nanomaterials, such as CNTs, and as history shows the development of new device materials to industrial maturity can take significantly longer than a decade. The timeline for 2D materials will crucially depend on the progress in industrial materials development and as highlighted in this perspective, CVD will be a key technology to enable this.

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## REFERENCES

- (1) Morgan, A.; Somorjai, G. Low Energy Electron Diffraction Studies of Gas Adsorption on the Platinum (100) Single Crystal Surface. *Surf. Sci.* **1968**, *12*, 405–425.
- (2) Eizenberg, M.; Blakely, J. M. Carbon Interaction with Nickel Surfaces: Monolayer Formation and Structural Stability. *J. Chem. Phys.* **1979**, *71*, 3467–3477.
- (3) Wallace, P. R. The Band Theory of Graphite. *Phys. Rev.* **1947**, *71*, 622.
- (4) Noorden, B. R. Van. The Trials of New Carbon. *Nature* **2011**, *469*, 14–16.
- (5) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nature* **2005**, *438*, 197–200.
- (6) Dean, C. R.; Young, A. F.; Meric, I.; Lee, C.; Wang, L.; Sorgenfrei, S.; Watanabe, K.; Taniguchi, T.; Kim, P.; Shepard, K. L.; et al. Boron Nitride Substrates for High-Quality Graphene Electronics. *Nat. Nanotechnol.* **2010**, *5*, 722–726.
- (7) Ten Years in Two Dimensions. *Nat. Nanotechnol.* **2014**, *9*, 725.
- (8) De Volder, M. F. L.; Tawfik, S. H.; Baughman, R. H.; Hart, A. J. Carbon Nanotubes: Present and Future Commercial Applications. *Science* **2013**, *339*, 535–539.
- (9) Hao, Y.; Bharathi, M. S.; Wang, L.; Liu, Y.; Chen, H.; Nie, S.; Wang, X.; Chou, H.; Tan, C.; Fallahzad, B.; et al. The Role of Surface Oxygen in the Growth of Large Single-Crystal Graphene on Copper. *Science* **2013**, *342*, 720.
- (10) Lee, J.-H.; Lee, E. K.; Joo, W.-J.; Jang, Y.; Kim, B.-S.; Lim, J. Y.; Choi, S.-H.; Ahn, S. J.; Ahn, J. R.; Park, M.-H.; et al. Wafer-Scale Growth of Single-Crystal Monolayer Graphene on Reusable Hydrogen-Terminated Germanium. *Science* **2014**, *344*, 286–289.
- (11) Nguyen, V. L.; Lee, Y. H. Towards Wafer-Scale Monocrystalline Graphene Growth and Characterization. *Small* **2015**, DOI: 10.1002/sml.201500147.
- (12) Petrone, N.; Dean, C. R.; Meric, I.; Van Der Zande, A. M.; Huang, P. Y.; Wang, L.; Muller, D.; Shepard, K. L.; Hone, J. Chemical Vapor Deposition-Derived Graphene with Electrical Performance of Exfoliated Graphene. *Nano Lett.* **2012**, *12*, 2751.
- (13) Tsen, A. W.; Brown, L.; Levendorf, M. P.; Ghahari, F.; Huang, P. Y.; Havener, R. W.; Ruiz-Vargas, C. S.; Muller, D. A.; Kim, P.; Park, J. Tailoring Electrical Transport Across Grain Boundaries in Polycrystalline Graphene. *Science* **2012**, *336*, 1143–1146.
- (14) Zayzev, O. V.; Chen, Y. P. Polycrystalline Graphene and Other Two-Dimensional Materials. *Nat. Nanotechnol.* **2014**, *9*, 1–13.
- (15) Kang, J.; Shin, D.; Bae, S.; Hong, B. H. Graphene Transfer: Key for Applications. *Nanoscale* **2012**, *4*, 5527.

- (16) Dlubak, B.; Martin, M.-B.; Weatherup, R. S.; Yang, H.; Deranlot, C.; Blume, R.; Schloegl, R.; Fert, A.; Anane, A.; Hofmann, S.; et al. Graphene-Passivated Nickel as an Oxidation-Resistant Electrode for Spintronics. *ACS Nano* **2012**, *6*, 10930.
- (17) Martin, M.-B.; Dlubak, B.; Weatherup, R. S.; Yang, H.; Deranlot, C.; Bouzehouane, K.; Petroff, F.; Anane, A.; Hofmann, S.; Robertson, J.; et al. Sub-Nanometer Atomic Layer Deposition for Spintronics in Magnetic Tunnel Junctions Based on Graphene Spin-Filtering Membranes. *ACS Nano* **2014**, *8*, 7890.
- (18) Omiciuolo, L.; Hernández, E. R.; Miniussi, E.; Orlando, F.; Lacovig, P.; Lizzit, S.; Menteş, T. O.; Locatelli, A.; Larciprete, R.; Bianchi, M.; et al. Bottom-up Approach for the Low-Cost Synthesis of Graphene-Alumina Nanosheet Interfaces Using Bimetallic Alloys. *Nat. Commun.* **2014**, *5*, 5062.
- (19) Sutter, P.; Sadowski, J. T.; Sutter, E. A. Chemistry under Cover: Tuning Metal-Graphene Interaction by Reactive Intercalation. *J. Am. Chem. Soc.* **2010**, *132*, 8175–8179.
- (20) Shin, H. J.; Choi, W. M.; Yoon, S. M.; Han, G. H.; Woo, Y. S.; Kim, E. S.; Chae, S. J.; Li, X. S.; Benayad, A.; Loc, D. D.; et al. Transfer-Free Growth of Few-Layer Graphene by Self-Assembled Monolayers. *Adv. Mater.* **2011**, *23*, 4392–4397.
- (21) Kosaka, M.; Takano, S.; Noda, S. Direct Synthesis of Graphene on Dielectric Substrates by “Etching-Precipitation” Method. *Carbon N. Y.* **2013**, *82*, 254.
- (22) Oshima, C.; Itoh, A.; Rokuta, E.; Tanaka, T.; Yamashita, K.; Sakurai, T. Hetero-Epitaxial-Double-Atomic-Layer System of Monolayer Graphene/Monolayer H-BN on Ni(111). *Solid State Commun.* **2000**, *116*, 37–40.
- (23) Kobayashi, T.; Bando, M.; Kimura, N.; Shimizu, K.; Kadono, K.; Umezu, N.; Miyahara, K.; Hayazaki, S.; Nagai, S.; Mizuguchi, Y.; et al. Production of a 100-M-Long High-Quality Graphene Transparent Conductive Film by Roll-to-Roll Chemical Vapor Deposition and Transfer Process. *Appl. Phys. Lett.* **2013**, *102*, 023112.
- (24) Baker, R. T. K.; Barber, M. A.; Harris, P. S.; Feates, F. S.; Waite, R. J. Nucleation and Growth of Carbon Deposits from the Nickel Catalyzed Decomposition of Acetylene. *J. Catal.* **1972**, *26*, 51–62.
- (25) Batzill, M. The Surface Science of Graphene: Metal Interfaces, CVD Synthesis, Nanoribbons, Chemical Modifications, and Defects. *Surf. Sci. Rep.* **2012**, *67*, 83.
- (26) Stierle, A.; Molenbroek, A. Novel in Situ Probes for Nanocatalysis. *MRS Bull.* **2007**, *32* (December), 1001–1009.
- (27) Weatherup, R. S.; Bayer, B. C.; Blume, R.; Ducati, C.; Baetz, C.; Schlögl, R.; Hofmann, S. In Situ Characterization of Alloy Catalysts for Low-Temperature Graphene Growth. *Nano Lett.* **2011**, *11*, 4154–4160.
- (28) Kidambi, P. R.; Bayer, B. C.; Blume, R.; Wang, Z. J.; Baetz, C.; Weatherup, R. S.; Willinger, M. G.; Schloegl, R.; Hofmann, S. Observing Graphene Grow: Catalyst-Graphene Interactions during Scalable Graphene Growth on Polycrystalline Copper. *Nano Lett.* **2013**, *13*, 4769–4778.
- (29) Hofmann, S.; Sharma, R.; Ducati, C.; Du, G.; Mattevi, C.; Cepek, C.; Cantoro, M.; Pisana, S.; Parvez, A.; Cervantes-Sodi, F.; et al. In Situ Observations of Catalyst Dynamics during Surface-Bound Carbon Nanotube Nucleation. *Nano Lett.* **2007**, *7*, 602–608.
- (30) Diarra, M.; Zappelli, A.; Amara, H.; Ducastelle, F.; Bichara, C. Importance of Carbon Solubility and Wetting Properties of Nickel Nanoparticles for Single Wall Nanotube Growth. *Phys. Rev. Lett.* **2012**, *109*, 1–5.
- (31) Weatherup, R. S.; Amara, H.; Blume, R.; Dlubak, B.; Bayer, B. C.; Diarra, M.; Bahri, M.; Cabrero-vilatela, A.; Caneva, S.; Kidambi, P. R.; et al. Interdependency of Subsurface Carbon Distribution and Graphene–Catalyst Interactions. *J. Am. Chem. Soc.* **2014**, *136*, 13698–13708.
- (32) Wilson, N. R.; Marsden, A. J.; Saghir, M.; Bromley, C. J.; Schaub, R.; Costantini, G.; White, T. W.; Partridge, C.; Barinov, A.; Dudin, P.; et al. Weak Mismatch Epitaxy and Structural Feedback in Graphene Growth on Copper Foil. *Nano Res.* **2013**, *6*, 99–112.
- (33) Kelly, B. T. *Physics of Graphite*; Applied Science Publishers: California, 1981.
- (34) Liu, S.; Loper, C. R. The Formation of Kish Graphite. *Carbon N. Y.* **1991**, *29*, 547–555.
- (35) Brownson, D. A. C.; Kampouris, D. K.; Banks, C. E. Graphene Electrochemistry: Fundamental Concepts through to Prominent Applications. *Chem. Soc. Rev.* **2012**, *41*, 6944.
- (36) Freise, E. J. Structure of Graphite. *Nature* **1962**, *193*, 671–672.
- (37) Franklin, R. E. Crystallite Growth in Graphitizing and Non-Graphitizing Carbons. *Proc. R. Soc. A* **1951**, *209*, 196–218.
- (38) Norskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. Towards the Computational Design of Solid Catalysts. *Nat. Chem.* **2009**, *1*, 37–46.
- (39) Oshima, C.; Nagashima, A. Ultra-Thin Epitaxial Films of Graphite and Hexagonal Boron Nitride on Solid Surfaces. *J. Phys. Condens. Mater.* **1997**, *9*, 1–20.
- (40) Corso, M.; Auwärter, W.; Muntwiler, M.; Tamai, A.; Greber, T.; Osterwalder, J. Boron Nitride Nanomesh. *Science* **2004**, *303*, 217–220.
- (41) Voloshina, E. N.; Dedkov, Y. S. General Approach to the Understanding the Electronic Structure of Graphene on Metals. *Mater. Res. Express* **2014**, *1*, 035603.
- (42) Weatherup, R. S.; Bayer, B. C.; Blume, R.; Baetz, C.; Kidambi, P. R.; Fouquet, M.; Wirth, C. T.; Schlögl, R.; Hofmann, S. On the Mechanisms of Ni-Catalysed Graphene Chemical Vapour Deposition. *ChemPhysChem* **2012**, *13*, 2544–2549.
- (43) Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; et al. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* **2009**, *324*, 1312.
- (44) Reina, A.; Jia, X.; Ho, J.; Nezich, D.; Son, H.; Bulovic, V.; Dresselhaus, M. S.; Kong, J. Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Lett.* **2009**, *9*, 30.
- (45) Mattevi, C.; Kim, H.; Chhowalla, M. A Review of Chemical Vapour Deposition of Graphene on Copper. *J. Mater. Chem.* **2011**, *21*, 3324.
- (46) Weatherup, R. S.; Dlubak, B.; Hofmann, S. Kinetic Control of Catalytic CVD for High Quality Graphene at Low Temperatures. *ACS Nano* **2012**, *6*, 9996–10003.
- (47) Patera, L. L.; Africh, C.; Weatherup, R. S.; Blume, R.; Bhardwaj, S.; Castellarin-Cudia, C.; Knop-Gericke, A.; Schloegl, R.; Comelli, G.; Hofmann, S.; et al. In Situ Observations of the Atomistic Mechanisms of Ni Catalyzed Low Temperature Graphene Growth. *ACS Nano* **2013**, *7*, 7901–7912.
- (48) Addou, R.; Dahal, A.; Sutter, P.; Batzill, M. Monolayer Graphene Growth on Ni(111) by Low Temperature Chemical Vapor Deposition. *Appl. Phys. Lett.* **2012**, *100*, 021601.
- (49) Grüneis, A.; Kummer, K.; Vyalikh, D. V. Dynamics of Graphene Growth on a Metal Surface: A Time-Dependent Photoemission Study. *New J. Phys.* **2009**, *11*, 073050.
- (50) Caneva, S.; Weatherup, R. S.; Bayer, B.; Brennan, B.; Spencer, S. J.; Mingard, K.; Cabrero-Vilatela, A.; Baetz, C.; Pollard, A. J.; Hofmann, S. Nucleation Control for Large, Single Crystalline Domains of Monolayer Hexagonal Boron Nitride via Si-Doped Fe Catalysts. *Nano Lett.* **2015**, *15*, 1867.
- (51) Yu, Q.; Jauregui, L. A.; Wu, W.; Colby, R.; Tian, J.; Su, Z.; Cao, H.; Liu, Z.; Pandey, D.; Wei, D.; et al. Control and Characterization of Individual Grains and Grain Boundaries in Graphene Grown by Chemical Vapour Deposition. *Nat. Mater.* **2011**, *10*, 443–449.
- (52) Artyukhov, V. I.; Hao, Y.; Ruoff, R. S.; Jakobson, B. I. Breaking of Symmetry in Graphene Growth on Metal Substrates. *Phys. Rev. Lett.* **2015**, *114*, 115502.
- (53) Lee, J.; Baek, J.; Ryu, G. H.; Lee, M. J.; Oh, S.; Hong, S. K.; Kim, B.-H.; Lee, S.-H.; Cho, B. J.; Lee, Z.; et al. High-Angle Tilt Boundary Graphene Domain Recrystallized from Mobile Hot-Wire-Assisted Chemical Vapor Deposition System. *Nano Lett.* **2014**, *14*, 4352–4359.
- (54) Walker, M. I.; Weatherup, R. S.; Bell, N. A. W.; Hofmann, S.; Keyser, U. F. Free-Standing Graphene Membranes on Glass Nanopores for Ionic Current Measurements. *Appl. Phys. Lett.* **2015**, *106*, 023119.

(55) Weatherup, R. S.; Baetz, C.; Dlubak, B.; Bayer, B. C.; Kidambi, P. R.; Blume, R.; Schloegl, R.; Hofmann, S. Introducing Carbon Diffusion Barriers for Uniform, High-Quality Graphene Growth from Solid Sources. *Nano Lett.* **2013**, *13*, 4624–4631.

(56) Zhao, H.; Lin, Y.-C.; Yeh, C.-H.; Tian, H.; Chen, Y.-C.; Xie, D.; Yang, Y.; Suenaga, K.; Ren, T.-L.; Chiu, P.-W. Growth and Raman Spectra of Single-Crystal Trilayer Graphene with Different Stacking Orientations. *ACS Nano* **2014**, *8*, 10766.

(57) Yan, Z.; Liu, Y.; Ju, L.; Peng, Z.; Lin, J.; Wang, G.; Zhou, H.; Xiang, C.; Samuel, E. L. G.; Kittrell, C.; et al. Large Hexagonal Bi- and Trilayer Graphene Single Crystals with Varied Interlayer Rotations. *Angew. Chem., Int. Ed.* **2014**, *53*, 1565.

(58) Dahal, A.; Addou, R.; Sutter, P.; Batzill, M. Graphene Monolayer Rotation on Ni(111) Facilitates Bilayer Graphene Growth. *Appl. Phys. Lett.* **2012**, *100*, 241602.

(59) Kidambi, P. R.; Blume, R.; Kling, J.; Wagner, J. B.; Baetz, C.; Weatherup, R. S.; Schloegl, R.; Bayer, B. C.; Hofmann, S. In Situ Observations during Chemical Vapor Deposition of Hexagonal Boron Nitride on Polycrystalline Copper. *Chem. Mater.* **2014**, *26*, 6380.

(60) Björk, M. T.; Ohlsson, B. J.; Sass, T.; Persson, A. I.; Thelander, C.; Magnusson, M. H.; Deppert, K.; Wallenberg, L. R.; Samuelson, L. One-Dimensional Heterostructures in Semiconductor Nanowhiskers. *Appl. Phys. Lett.* **2002**, *80*, 1058.

(61) Dlubak, B.; Kidambi, P. R.; Weatherup, R. S.; Hofmann, S.; Robertson, J. Substrate-Assisted Nucleation of Ultra-Thin Dielectric Layers on Graphene by Atomic Layer Deposition. *Appl. Phys. Lett.* **2012**, *100*, 173113.

(62) Nathan, A.; Ahnood, A.; Cole, M. T.; Lee, S.; Suzuki, Y.; Hiralal, P.; Bonaccorso, F.; Hasan, T.; Garcia-Gancedo, L.; Dyadyusha, A.; et al. Flexible Electronics: The Next Ubiquitous Platform. *Proc. IEEE* **2012**, *100*, 1486.