Process Pathway Controlled Evolution of Phase and Van-der-Waals Epitaxy in In/In$_2$O$_3$ on Graphene Heterostructures

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Many applications of 2D materials require deposition of non-2D metals and metal-oxides onto the 2D materials. Little is however known about the mechanisms of such non-2D/2D interfacing, particularly at the atomic scale. Here, atomically resolved scanning transmission electron microscopy (STEM) is used to follow the entire physical vapor deposition (PVD) cycle of application-relevant non-2D In/In$_2$O$_3$ nanostructures on graphene. First, a “quasi-in-situ” approach with indium being in situ evaporated onto graphene in oxygen-/water-free ultra-high-vacuum (UHV) is employed, followed by STEM imaging without vacuum break and then repeated controlled ambient air exposures and reloading into STEM. This allows stepwise monitoring of the oxidation of specific In particles toward In$_2$O$_3$ on graphene. This is then compared with conventional, scalable ex situ In PVD onto graphene in high vacuum (HV) with significant residual oxygen/water traces. The data shows that the process pathway difference of oxygen/water feeding between UHV/ambient and HV fabrication drastically impacts not only non-2D In/In$_2$O$_3$ phase evolution but also In$_2$O$_3$/graphene out-of-plane texture and in-plane rotational van-der-Waals epitaxy. Since non-2D/2D heterostructures’ properties are intimately linked to their structure and since influences like oxygen/water traces are often hard to control in scalable fabrication, this is a key finding for non-2D/2D integration process design.

1. Introduction

Metals and metal-oxides on 2D materials such as graphene are key to engineer and complement the 2D materials’ intrinsic properties in a large variety of applications.[3] This includes non-2D metals and non-2D metal-oxides as charge transfer dopants, (transparent) electrical contacts, dielectrics, environmental barrier layers, and (photo-)catalysts.[2–10] Methods for deposition of metals and metal-oxides onto 2D materials include various physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition or wet chemistry routes, all with large potential processing parameter spaces for which rational process design principles are still limited.

High resolution (scanning) transmission electron microscopy ((S)TEM) has been used in the past to discern some underlying principles in the growth of deposited metals, metal oxides, and other compound nanostructures on 2D materials.[11–38] The majority of these studies were however ex situ studies which typically involved ambient air exposure of samples after ex situ fabrication and prior to (S)TEM imaging. As a consequence intrinsic deposition results and subsequent unintentional materials modifications from an intermediate ambient air exposure (e.g., metal to metal-oxide oxidation in ambient) were often hard to disentangle. Consequently, employing an ex situ approach often fails to capture the actual state of as deposited metals on 2D materials. Ex situ sample preparation also makes it difficult to follow the dynamics of subsequent deliberate oxidation processes when, for example, intentionally transitioning from metal to metal oxide decoration of the 2D material. As a result, despite the wide application profile of non-2D metal-oxide/2D heterostructures, only little is currently known about their interfacing and their integration processes at the atomic scale, particularly for application-relevant material combinations and scalable synthesis routes.

In this context, the indium (In) and indium oxide (In$_2$O$_3$) system is a non-2D metal-oxide system not only with high relevance for applications but which is also a particularly suitable model system to study non-2D/2D heterostructures: In has a low...
melting point (≈160 °C)\(^{39}\) retains a low vapor pressure when molten and consequently avoids evaporation for a wide temperature range\(^{39}\) and shows comparatively facile oxidation behavior for thin In deposits.\(^{40–43}\) Combined these properties suggest In to be advantageous for follow-up metal/2D metal interactions and dynamic reconstructions in high-resolution (S)TEM. Likewise In may also facilitate following in situ the oxidation of a parent non-2D metal into a non-2D oxide on a 2D material. From a 2D materials application perspective, indium decoration has been advantageously used to engineer the electronic properties of graphene.\(^{44–46}\) alkbeit structural details of In growth on monolayer graphene remain unknown. In\(_2\)O\(_3\) on the other hand is the principal phase in the widely used optically transparent conductor Sn-doped In\(_2\)O\(_3\) (indium-tin-oxide, ITO) and intrinsically is a semiconductor with favorable properties for sensing.\(^{47}\) The control over texture and film morphology in the growth of In\(_2\)O\(_3\) is still a topic of considerable interest in its own right.\(^{48–52}\) Application wise for 2D materials, In\(_2\)O\(_3\)/graphene heterostructures were shown to be highly promising for device applications in the fields of sensing.\(^{53–62}\) transparent electrodes\(^{63–66}\) energy storage\(^{67}\) and catalysis.\(^{68}\) To date however largely no mechanistic insights into the interfaces of In\(_2\)O\(_3\) with 2D materials have been obtained.

We therefore use here ultrathin In and In\(_2\)O\(_3\) nanostructures on suspended monolayer graphene membranes as ideal models to follow non-2D/2D heterostructure formation by PVD throughout the entire fabrication cycle. To obtain high resolution insights, we use atomically-resolved and element-specific STEM. Importantly, we study the In/In\(_2\)O\(_3\) deposition in a “quasi-in-situ” manner where indium is first thermally evaporated in situ onto the graphene in ultra-high-vacuum (UHV, \(≈10^{-9}\) mbar base pressure) conditions and then directly transferred without vacuum break into the aberration corrected STEM instrument.\(^{69,70}\) This allows capturing the intrinsic state of In clusters on graphene in virtually oxygen- and water-free conditions. Subsequently we employ controlled ambient air exposure at variable temperatures and times, followed by reloading into the STEM to stepwise monitor the oxidation of specific In particles toward O\(_3\) on graphene. This “quasi-in-situ” oxidation allows us to discern mechanistic details of the In oxidation process. We then compare our “quasi-in-situ” results with conventional ex situ PVD onto graphene in a standard commercial high vacuum (HV, \(≈10^{-4}\) mbar base pressure) evaporation system. Interestingly, we find that the process pathway difference in oxygen feeding between “quasi-in-situ” UHV depositions and scalable ex situ HV PVD conditions translates to a dramatic impact on the resulting In/In-oxide phase evolution, structure, and rotational epitaxy.

In particular, our atomic-scale analysis of the initial “quasi-in-situ” UHV deposited In particles on graphene indicates that they form with body centered tetragonal (bct) structure with preferred out-of-plane textures of bct In(201)//graphene(001) and bct In(100)//graphene(001) but without an in-plane preferred rotational alignment between In and graphene lattices. In\(_2\)O\(_3\) particles derived from the subsequent “quasi-in-situ” oxidation route via stepwise ambient air exposure are cubic In\(_2\)O\(_3\) with a predominant In\(_2\)O\(_3\)(100)//graphene(001) out-of-plane texture (In\(_2\)O\(_3\)(100)||graphene(001)) but, consistently, show no signs of preferred in-plane rotational alignment between the In\(_2\)O\(_3\) and the graphene support. In stark contrast, the ex situ HV evaporation of In on graphene results directly in deposition of cubic In\(_2\)O\(_3\), that is, the In is readily oxidized during HV PVD already prior to ambient air exposure due to residual oxygen/water in the inferior HV base pressure. The out-of-plane texture of this ex situ In\(_2\)O\(_3\) is however In\(_2\)O\(_3\)(111)||graphene(001) (In\(_2\)O\(_3\)(111)||graphene(001)) which is in stark contrast to the “quasi-in-situ” UHV/air exposure route. Importantly, these ex situ deposited In\(_2\)O\(_3\) particles also show clear signs of in-plane rotational van-der-Waals (vdW) epitaxy with a preferred alignment of In\(_2\)O\(_3\)(10-10)||graphene(100). Thereby comparison of our “quasi-in-situ” and ex situ data highlights that in fabrication of non-2D metal and non-2D metal-oxide heterostructures on 2D materials the processing kinetics (such as oxygen feeding pathways) can drastically impact not only on non-2D phase evolution but also on non-2D/2D texture and rotational vdW epitaxy. This is of fundamental importance in future design of non-2D/2D integration routes.

Beyond 2D materials and non-2D/2D heterostructures in the wider realm of functional oxide growth, control over texture, and epitaxy in In\(_2\)O\(_3\) nanostructures and thin films is highly sought after in its own right.\(^{48–52}\) In this context, our finding that graphene can template epitaxial growth of In\(_2\)O\(_3\) also suggests graphene as a potential templating buffer layer for epitaxial In\(_2\)O\(_3\) growth on non-In\(_2\)O\(_3\)-lattice-matched device-relevant substrates.

### 2. Results and Discussion

#### 2.1. In Situ UHV Deposited In on Graphene

We first focus on the interfacing of elemental indium onto graphene in oxygen- and water-free UHV conditions. This is a model for the first step in PVD of In/In-oxide on graphene. To assess In’s atomic configuration on graphene in situ evaporation of indium onto suspended CVD graphene monolayers is carried out in UHV conditions (\(≈10^{-9}\) mbar, nominal thickness of In is 10 nm monitored by a quartz micro balance, samples not intentionally heated from room temperature (RT)). Thus produced heterostructure samples are transferred without vacuum break into an aberration-corrected STEM for imaging (Nion UltraSTEM 100, 60 kV electron acceleration voltage, high and medium angle annular dark field detectors (HAADF/MAADF)).\(^{69,70}\) See Experimental Section below for more experimental details.

As shown in Figure 1a–c, we find that the UHV evaporated indium grows as particles on the graphene support. All observed In particles exhibit a structure consistent with body-centered-tetragonal (bct) In. Two principal out-of-plane bct In textures on the supporting graphene (001) basal plane are observed: First is a texture in which the bct In(201) direction (zone-axis) is perpendicular to the graphene (001) plane, that is, bct In(201)//graphene(001) (Figure 1d). (Note that because of the non-cubic bct In structure the In(201) directional vector is not perpendicular to In(201) plane, that is, the In(201) plane is not parallel to graphene(001) support but inclined.\(^{71}\) See also Figure S1, Supporting Information). Second is a bct In(100)//graphene(001) texture (Figure 1e). The observation of

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The bct In[201] out-of-plane texture corresponds well to prior literature of In deposition on bulk graphite and bulk MoS₂. Further details on phase identification of In can be found in Figures S1, S2, and S3, Supporting Information. Electron energy loss spectroscopy (EELS, Figure 1f) of the deposited particles confirms that the indium is not oxidized under our UHV deposition and imaging conditions but metallic In. Generally, In particles on graphene are disc shaped with flat top surfaces and slightly inclined edge faces (Figure 1). Average lateral projected particle sizes of the In[100] and In[201] particles are 6.3 ± 0.3 and 5.3 ± 0.7 nm (histograms of particle sizes are shown in Figure S4, Supporting Information). The thickness of the In particles on the graphene can be estimated by examining the intensities of experimental and simulated HAADF images, as shown in Figure 1g–j. Individual indium atoms close to the edges of particles can readily be discriminated against the supporting graphene lattice (Figure 1g–j) and form the basis for the thickness estimation. For instance, based on the intensity profiles in Figure 1j, we find that typical In particles are comprised of ~12 layers of indium (i.e., ~1.6 nm). Total estimated thicknesses of In particles range from 0.9 to 16 nm. We find that the In particles on graphene appear rather round in projection with only weak signs of faceting of edges.

Selected area electron diffraction (SAED) measurements of in situ samples after their “quasi-in-situ” fabrication cycle (i.e., including subsequent air exposure as described below, see Figure S5, Supporting Information) reveal that a sharp graphene SAED pattern is retained after full “quasi-in-situ” fabrication. This sharp SAED pattern is similar to the SAED pattern of as grown CVD graphene. This observation excludes the formation of extended defects in the graphene during the “quasi-in-situ” fabrication including during UHV In deposition. This in turn implies the absence of covalent bonds between the graphene and the In at any stage of fabrication and suggests that the In/graphene interface is of vdW type, consistent with prior suggested weak vdW interactions between In and graphite.

Figure 2 demonstrates that the In particles on graphene exhibit electron beam (e-beam) induced “quasi-melting” under high-resolution STEM imaging conditions when electron dose rates are above ~5 × 10⁵ e⁻·nm⁻²·s⁻¹ (in contrast, when lower electron dose rates are used for STEM imaging the structure of particles remains unperturbed under the beam). The “quasi-melting” for high electron dose rates is related to the low melting point of In compounded with particle-sized induced melting point depression and energy transfer from the scanning e-beam. As an example in Figure 2 the structural dynamics observed for a given bct In[100] particle involve various states including amorphous In as well as poly-crystalline and single-crystalline In particles. At the beginning of imaging at this field of view, this indium particle initially becomes fully amorphous under the high dose rate e-beam. Subsequently, the particle is partially re-crystallized and then fully re-crystallized while, intermittently, forming grain boundaries between various differently in-plane rotated bct In[100] grains. Such dynamic variations in the internal structure of indium continue to be observed in all image frames. The observation of quasi-melting...
behavior of nanometer-sized In particles in STEM is in agreement with earlier literature.\cite{75,78} Despite the observed changes in the In crystals’ internal structure, we find that the projected shape of the indium particles remains largely unchanged during imaging. When crystallinity is detected within In particles, then this is of either bct In\[201\] or bct In\[100\] out-of-plane textured phase, despite the highly dynamic “quasi-liquid” overall behavior of the In particles at high electron dose rates. This suggests that the vdW interaction at the In\[201\]⊥graphene(001) and the bct In\[100\]⊥graphene(001) interfaces is rather robust.

Given this robustness of bct In\[201\]⊥graphene(001) and the bct In\[100\]⊥graphene(001) out-of-plane textures via their vdW interfaces, a key question is whether these vdW interactions also result in a preferential in-plane rotational orientation of In on graphene, that is, “rotational” vdW epitaxy. We therefore investigate the rotational alignment of In lattice and supporting graphene lattice in Figure S6, Supporting Information: We probe close up HAADF-STEM images of indium particles (ensuring that electron dose rates are too low to induce significant e-beam induced “quasi-melting” behavior) and of the directly adjacent graphene lattice. Given that CVD graphene grains have lateral extensions on the order of several \(\mu\)m,\cite{79} we can thereby safely assess the rotational alignment of a given In particles with its supporting graphene grain underneath. However, as shown in Figure S6, Supporting Information, no signs of in-plane rotational alignment are found for the bct In\[201\]⊥graphene(001) out-of-plane texture, as In particles appear to be randomly rotated with respect to the graphene. Similarly, the bct In\[100\]⊥graphene(001) texture also shows no clear preferred rotational alignment. Thus our observations suggest that the vdW interaction between In and graphene result in robust preferred out-of-plane bct In\[201\]⊥graphene(001) and the bct In\[100\]⊥graphene(001) textures but that no particular in-plane rotational alignment exists for our bct In particles on graphene.

### 2.2. “Quasi-In-Situ” Oxidation of In to \(\text{In}_2\text{O}_3\)[100] on Graphene

Having established the growth mode and vdW interfacing of elemental In on graphene in the section above, we now turn to following the controlled oxidation (Figure 3a) of these In particles on graphene toward \(\text{In}_2\text{O}_3\). To this end, we image first the atomic structure of as deposited in situ UHV-evaporated indium particles without vacuum break (Figure 3b, left panel, that is, similar to the data shown above). We then remove the imaged In/graphene sample from vacuum and expose it to ambient air atmosphere for controlled times and at controlled temperatures. After this air exposure we reload the sample into the STEM and re-image the same particles as previously imaged in as deposited state (Figure 3b, middle and right panel). In doing so we find that oxidation kinetics\cite{43} of our In particles under ambient air at RT are sufficiently slow to allow us to image intermediate states of the particles from In to \(\text{In}_2\text{O}_3\) by repeated unloading/loading into the STEM. Thereby we can follow the oxidation of the In to \(\text{In}_2\text{O}_3\) on graphene in a stepwise fashion, that is, in what we term “quasi-in-situ,” as shown for an ensemble of particles in Figure 3b.

As a close-up example, Figure 3c, left panel shows the state of an as deposited UHV-evaporated In particle. In agreement
with our findings above, we find the as deposited In to be consistent with bct In\(^{[201]}\)\textperp graphene(001). Figure 3c, middle panel then shows the same particle after exposure to ambient air at RT for \(\approx 24\) h. During this air exposure, the In particle has transformed in its lower half into what we identify as cubic In\(_2\)O\(_3\) with an In\(_2\)O\(_3\)\(^{[100]}\) out-of-plane texture on the graphene(001), that is, In\(_2\)O\(_3\)\(^{[100]}\)\textperp graphene(001). Since In\(_2\)O\(_3\) is cubic, that is, \([001]\)\textperp (100), we can also express this relation by In\(_2\)O\(_3\)\(^{[100]}\)\textperp graphene(001). For more details on phase identification of In\(_2\)O\(_3\)(100) see Figures S7, S8, and S9, Supporting Information. However, the translation of bct In\(^{[201]}\) into crystalline In\(_2\)O\(_3\)(100) is not entirely completed in ambient air at RT over the course of \(\approx 24\) h as evidenced by the undefined upper half of the particle in Figure 3c, middle panel. This is in agreement with prior literature.\(^{[41-43]}\) To therefore drive the particle to complete formation of a crystalline oxide, we remove the same sample again to ambient air and heat it in ambient air at 100 °C for 45 min. After this procedure, we find (Figure 3c, right panel) that the particle has been fully transformed into cubic In\(_2\)O\(_3\)\(^{[100]}\)\textperp graphene(001) = In\(_2\)O\(_3\)\(^{[100]}\)\textperp graphene(001). The
Figure 4. a) Atomic resolution HAADF-STEM image of another UHV evaporation/ambient air route In$_2$O$_3$(100) particle on graphene. b) Close up HAADF-STEM image of the region shown in white dashed frame in (a). Image backgrounds in (a) and (b) have been subtracted using a Gaussian blur (radius of 20 px). c) Top and side views of the atomic models showing In$_2$O$_3$(100) on graphene. d) Intensity profile recorded over the dashed lines on (b) and (e). e) Simulated HAADF image corresponding to the model shown in (c). The experimental intensity profile has been recorded on the raw image.

The data demonstrates that this typical In$_2$O$_3$(100) crystal is around 2 unit cells thick after full 100 °C/ambient air oxidation. The data demonstrates phase identification for another similarly processed particle prior to oxidation to In$_2$O$_3$(100) (average: 8.0 ± 0.3 nm, see Figure S4, Supporting Information), suggesting that volume expansion during oxidation is largely perpendicular to the graphene support. As shown for the exemplary particle in Figure 3d, we often find that a single-crystalline parent In(201) particle transforms into a polycrystalline In$_2$O$_3$(100) particle during oxidation with the individual In$_2$O$_3$ grains all showing out-of-plane In$_2$O$_3$(100) texture but with non-systematic in-plane misorientations (i.e., no in-plane rotational vdW epitaxy with graphene support). This points to severe crystallographic rearrangements happening during the oxidation. Consistent with such severe rearrangements, we also find that particles (example in Figure 3e) often undergo internal void formation during oxidation. We find no particular increase of projected size from In particles into a polycrystalline In$_2$O$_3$(100) particle transitions (Figure 3d,e). At a wider field of view, the SAED data in Figure S5, Supporting Information confirms the predominant In$_2$O$_3$(100) out-of-plane texture (as the (0-44) reflections are dominant in intensity for In$_2$O$_3$ phase) and also confirms the random in-plane orientation of the In$_2$O$_3$(100) crystallites on the graphene support (as on the single crystalline graphene domain the (0-44) reflections of multiple adjacent In$_2$O$_3$(100) particles appear overlaid into a ring in the SAED pattern), fully consistent with our STEM results. The SAED data in Figure S5, Supporting Information also shows that after the “quasi-in-situ” oxidation the graphene support displays a pattern consistent with high quality graphene, implying that the entire “quasi-in-situ” UHV/air exposure fabrication procedure does not degrade the graphene and thus that the In$_2$O$_3$(100)||graphene(001) interface is of vdW type (i.e., absence of covalent bonding to carbon layer).

The observation that In$_2$O$_3$(100)||graphene(001) is the predominant texture for In$_2$O$_3$ on graphene from our UHV In evaporation/ambient air exposure fabrication route is a surprising finding because the thermodynamically preferred texture of cubic In$_2$O$_3$ is In$_2$O$_3$(111)||support on non-lattice-matched substrates, based on the (111) surface’s lowest relative surface energy.[46] Thus our UHV evaporation/ambient air exposure route has realized on graphene an otherwise harder to achieve In$_2$O$_3$(100) texture. This finding opens the question if this non-thermodynamically preferred texture of the In$_2$O$_3$ stems from the interaction with the graphene support (i.e., is a 2D material induced effect via vdW epitaxy) or from the kinetic process conditions in the In$_2$O$_3$ deposition process pathway? In the next section we will turn to answering this question.

2.3. Ex Situ HV Deposited In$_2$O$_3$(111) on Graphene

To assess the influence of the kinetic process pathway on the structure and orientation of In$_2$O$_3$ on graphene in comparison
to our UHV evaporation/ambient air exposure “quasi-in-situ” results above, we now evaporate In onto graphene in a conventional ex situ PVD system in HV conditions (∼10⁻⁴ mbar base pressure, nominal thickness 10 nm via quartz micro balance, samples not intentionally heated), see Figure 5a. These are significantly poorer vacuum conditions compared to the UHV in situ In evaporation (∼10⁻⁹ mbar).

Surprisingly, atomic resolution HAADF-STEM images of such ex situ HV deposited In on graphene in Figures 5 and 6 show that via this route not bct In but cubic In₂O₃ is directly grown on the graphene. For details on phase identification see Figures S7, S8, and S11, Supporting Information. We suggest that this direct formation of In₂O₃ is related to sufficiently high amounts of trace oxygen and water in the poorer HV background pressure to oxidize the hot In flux during its passage from evaporation source to sample, that is, not metallic In vapor but in situ generated In-oxide species are actually deposited on the graphene.[40,52,80] We exclude that the In is here oxidized only during ambient exposure between HV PVD and microscopy by observing cubic In₂O₃ already after few minutes after evaporation in SAED, which is much faster than the >24 h oxidation at RT kinetics observed for elemental In above. The atomic structure of the as deposited HV PVD In₂O₃ crystals is further detailed in Figure 6 in which In₂O₃ formation is also corroborated by EELS (Figure 6d).[48,74] We estimate a thickness around two unit cells for the HV PVD In₂O₃ crystals (∼1.5 nm) and a projected lateral size of ≈12 ± 0.4 nm (Figure S4, Supporting Information). Thickness and size between In₂O₃ particles for in situ UHV evaporation/ambient air and ex situ HV PVD route

Figure 5. a) Schematic illustration of the setup used for ex situ HV PVD. b) HAADF- STEM image showing HV PVD route derived In₂O₃ crystals with In₂O₃[111]∥graphene(001) (= In₂O₃(111)||graphene(001)) texture. The inset shows a close-up HAADF-STEM image of the particles shown in white dashed frame. HAADF-STEM images display raw data. c) Atomic model showing In₂O₃(111)||graphene(001).

Figure 6. a) HAADF-STEM image of HV PVD In₂O₃(111) on graphene from a particle at a location different from Figure 5b. Image background has been subtracted using a Gaussian blur (radius 20 px). Simulated HAADF image is superimposed in false color. b) Intensity profiles along the white dashed lines (line 1 and line 2) in (a). c) Plan view and cross section of the model used in the image simulation. The structure shown in black dashed frame corresponds to the simulated image in (a). d) EELS spectrum (background subtracted by power-law) corresponding to (a). e) HAADF-STEM image of the edge of HV PVD In₂O₃(111) on graphene. The image is Gaussian blurred with 3 px. f) Simulated two unit cells thick In₂O₃(111) on graphene. g) Intensity profiles recorded along the white dashed lines on (e) and (f). The experimental intensity profile has been recorded on the raw image.
are therefore reasonably comparable, thus allowing comparison of orientational and interfacial properties without consideration of significant size effects. We note that the HV PVD In$_2$O$_3$ particles do not exhibit e-beam induced crystallographic or morphological changes for our STEM conditions.

The key finding for the HV PVD cubic In$_2$O$_3$ particles on graphene is that their out-of-plane texture is In$_2$O$_3$(111) perpendicular to graphene support, that is, cubic In$_2$O$_3$(111)$\parallel$ graphene(001). The prevalence of this texture is clearly shown by the observed relative abundances of In$_2$O$_3$ crystals in Figure 5b with (111) out-of-plane texture for 43 particles per 100 nm$^2$ compared to only 4 particles per 100 nm$^2$ with (100) texture. While In$_2$O$_3$(111) is the thermodynamically expected texture for cubic In$_2$O$_3$, it is in stark contrast to the In$_2$O$_3$(100)$\parallel$ graphene(001) texture observed above for the UHV evaporation/ambient air exposure route. Further inspection of the HV PVD cubic In$_2$O$_3$(111) particles on graphene in Figure 5b also immediately suggests that their projected particle shape is (elongated) hexagonal with typical inside angles of $\approx120^\circ$ and that the edges of the hexagon shapes are systematically aligned with respect to each other on their graphene support. In particular we find intervals of 60$^\circ$ of rotational alignment of the long axes of the In$_2$O$_3$(111) elongated hexagons. Given that the graphene grain in Figure 5b can be surmised to be of single crystalline orientation (as above) and that both In$_2$O$_3$(111) and graphene(001) have sixfold symmetry, this is a first indication of in-plane rotational vdW epitaxy in the In$_2$O$_3$(111)$\parallel$ graphene(001) system. This rotational epitaxy is further corroborated by the analysis of atomic resolution HAADF-STEM images and of TEM/SAED data in Figure 7. Based on the Fourier transform (FT) data obtained from the atomic resolution HAADF-STEM (Figure 7a) of a single In$_2$O$_3$(111) particle and the adjacent graphene(001) lattice, we find the in-plane [1-10] direction of the cubic In$_2$O$_3$(111) particles to be aligned with the in-plane [100] direction in graphene(001) without a rotation ($\approx0^\circ$ misorientation), that is, (In$_2$O$_3$(1-10)$\parallel$ graphene[100]). The TEM and SAED in Figure 7c,d probes the same information for a larger field of view and thus multiple particles in parallel. Consistently, the SAED data in Figure 7d indicates a preferred orientation of in-plane [1-10] directions of the cubic In$_2$O$_3$(111) and in-plane [100] direction in graphene(001) around 0$^\circ$ misorientation. We note that during the HV PVD coating process the high quality CVD graphene is not structurally degraded as observed via the sharp SAED spot pattern in Figure 7b. This confirms that the In$_2$O$_3$(111)$\parallel$ graphene(001) interface is of vdW type.

In combination, our ex situ HV PVD preparations of In$_2$O$_3$ on graphene reveal a strong out-of-plane (In$_2$O$_3$(111)$\parallel$ graphene(001)) texture and rotational in-plane (In$_2$O$_3$(1-10)$\parallel$ graphene[100]) vdW epitaxy. These are markedly different orientational relations compared to In$_2$O$_3$ on graphene from the UHV evaporation/ambient air exposure route (In$_2$O$_3$(100)$\parallel$ graphene(001) out-of-plane texture with no rotational in-plane alignment).

### 3. Conclusion

Combining our findings from the in situ UHV evaporation/ambient air exposure and the ex situ HV PVD routes, we show that for the same 2D material support (here graphene) process...
paths in the oxide deposition (here rate of oxygen/water availability\(^\text{[8]}\) via base pressure during In evaporation) can govern not only phase evolution (here intermediate elemental In growth for UHV versus direct In\(_2\)O\(_3\) growth for HV) but also can govern the type of texture and the presence/absence of rotational vdW epitaxy. Since overall properties in 2D/non-2D heterostructures are intrinsically linked to the heterostructures' internal structural arrangements and since subtle influences such as oxygen/water background traces are often hard to control in fabrication processes, this is a key finding meriting consideration when designing future non-2D/2D integration processes.

Beyond 2D materials our work also has a potential implication in the wider context of controlled In-oxide growth\(^{[8-12]}\). Graphene can be grown via CVD on a variety of device relevant materials\(^{[81,82]}\). Therefore, our finding that graphene can impose controlled vdW epitaxy to an In\(_2\)O\(_3\) overlayer also suggests that exploration of graphene as a templating buffer-layer may be promising toward the controlled growth of In\(_2\)O\(_3\) on non-In\(_2\)O\(_3\)-lattice-matched device-relevant materials.

4. Experimental Section

STEM: STEM employed a Nion UltraSTEM 100 operated at a 60 kV accelerating voltage in near-UVH (≈10\(^{-9}\) mbar) using high angle annular dark field (HAADF, 80–200 mrad collection angle) and medium angle annular dark field (MAADF, 50–70 mrad) detectors.\(^{[83]}\) Where indicated in figure captions, HAADF image backgrounds were removed by subtracting a strongly blurred copy of the image (Gaussian blur, radius 20 px). EELS used an acquisition setup involving a Gatan PEELS 666 spectrometer retrofitted with an Andor iXon 897 electron-multiplying charge-coupled device camera. The energy dispersion, the beam current and the EELS collection semi-angle were 1 eV per px, 30 pA, and 35 mrad, respectively.\(^{[83]}\) The STEM was equipped with a custom-made sample loading and transfer system to enable direct loading of samples from various preparation chambers including evaporation chamber into the STEM without vacuum break.\(^{[84]}\) Bright field TEM and SAED experiments were carried out in a Delong instruments LVEMS table-top transmission electron microscope operated at 5 kV and in a Tecnai F20 TEM at 60 kV.

Graphene Samples: Graphene substrates (Graphenea) were suspended monolayer graphene films prepared by CVD\(^{[79]}\) that were heated to 700 °C. Knudsen cell and employed In pellets (99.99% purity, Kurt J. Lesker) which were heated to 700 °C in the Knudsen cell. The resulting In flux was then directed to the desired substrates which were not intentionally heated, that is, nominally remained at RT. Nominal deposition In thickness was monitored using a quartz micro balance and kept at ≈10 nm.

Ex Situ In/In-Oxide HV PVD: HV PVD employed a commercial Mantis HEX deposition system with a base pressure of ≈10\(^{-4}\) mbar. The same type of In pellets as for the in situ UHV evaporation were used. The In was evaporated via a resistively heated tungsten boat. The target substrates were not intentionally heated and nominally remained at RT. Nominally deposited In thickness was monitored using a quartz micro balance and kept at ≈10 nm.

Other Equipment: Ambient air oxidation was carried out in standard laboratory air (≈20 °C) and ambient air heating with the samples placed on a commercial hotplate.

STEM Image and SAED Simulations: HAADF and MAADF image simulations were performed using the QSTEM software with parameters corresponding to the experiments\(^{[83]}\) chromatic aberration coefficient of 1 mm, a spherical aberration coefficient of 1 \(\mu\)m, energy spread of 0.48 eV. HAADF and MAADF detector angle ranges were set to the experimental range of 80–200 and 50–70 mrad, respectively. The convergence semi-angle was 25 mrad. SAED simulations were performed using DDView+/HighscorePlus software with PDF-4+ 2010 database. Main structure files used were (International Centre for Diffraction Data (ICDD) database entry numbers): Graphene/graphite (04-014-0362), bct In (01-080-5360), cubic In\(_2\)O\(_3\) (04-021-4783). Phase identification and out-of-plane texture analysis proceeded via comparison of FTs of measured high resolution STEM data with simulated SAED patterns. In-plane orientation analysis was done via assignment of directions in real space images (visualized via Vestal\(^{[86]}\) software) and crosschecked by comparison to simulated STEM images from the above structure files. See also Figures S1, S2, S3, S7, S8, S9, and S11. Supporting Information for phase identification details. Throughout the article in STEM, SAED, and FTs labeling the following colors were used to refer to particular phases: White refers to graphene(001), yellow to In[201] and In[100], green to In\(_2\)O\(_3\)[100] and red to In\(_2\)O\(_3\)[111].

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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