Graphene meets gallenene - A straightforward approach to developing large-area heterostacks by gallium self-propagation

S. Wundrack\textsuperscript{1†}, N. Schmidt\textsuperscript{2}, D. Momeni Pakdehi\textsuperscript{1}, K. Pierz\textsuperscript{1}, L. Michaliszyn\textsuperscript{1}, H. Spende\textsuperscript{2,3}, A. Schmidt\textsuperscript{2,3}, H. W. Schumacher\textsuperscript{1}, R. Stosch\textsuperscript{1}, A. Bakin\textsuperscript{2,3†}

1. Physikalisch-Technische Bundesanstalt, Bundesallee 100, D-38116 Braunschweig, Germany
2. Institut für Halbleitertechnik, Technische Universität Braunschweig, Hans-Sommer Straße 66, D-38106 Braunschweig, Germany
3. Laboratory of Emerging Nanometrology (LENA) der Technischen Universität Braunschweig, Langer Kamp 6 a/b, D-38106 Braunschweig, Germany

† Correspondence and requests for materials should be addressed to S. W. (email: stefan.wundrack@ptb.de) or A. B. (email: a.bakin@tu-braunschweig.de)
Gallenene is an atomically thin two-dimensional metallene that to be considered as a potential candidate for accessing new ways of developing ultra-thin gallium-based semiconductor devices. Using the solid-melt exfoliation technique, we demonstrate the feasibility of fabricating a gallenene film on epitaxial graphene substrates with lateral sizes approaching the centimeter scale. The stepwise self-propagation of gallenene across the epitaxial graphene surface on the macroscopic scale was observed by optical microscopy at room temperature shortly after initial processing without any further physical or chemical treatment of the sample. On the other hand, evidence for the occurrence of epitaxial graphene intercalation through the gallenene propagation leading to a transformation into quasi-freestanding bilayer graphene (QFBLG) has been observed by confocal micro-Raman spectroscopy. The results reveal a new pathway for a controlled fabrication of two-dimensional heterostructures and stacks based on interaction between a liquid metal and epitaxial graphene.

1. Introduction

The fabrication of large-area high-quality graphene samples has opened new fields of research to investigate the feasibility of creating new two-dimensional crystal structures, particularly of semiconducting materials as well as the fabrication of van der Waals heterostructures exploring their physical interactions at the nanoscale of condensed matter\(^1\)–\(^9\). Ever since the isolation of graphene was first achieved in 2004\(^10\), a whole family of two-dimensional materials has been discovered and fabricated by means of the very simple exfoliation technique\(^11\)–\(^16\). For instance, hexagonal boron nitride (hBN) or transition-metal dichalcogenides (TMDC) such as tungsten disulfide (WS\(_2\)) and molybdenum disulfide (MoS\(_2\)) can be easily obtained by exfoliation from their bulk crystals based on breaking the weak interlayer bonding similar to that of graphite\(^14\)–\(^16\). On the contrary, the fabrication of large areas of the respective material is virtually impossible with this procedure which allows only crystal flakes with lateral dimensions of a few microns to be prepared. Using metals with a low melting point such as elemental gallium, tin or even their alloys could fundamentally change this simple deposition technique due to their physical and chemical properties. Finally, the so-called solid-melt exfoliation might be a suitable approach to fabricate 2D materials in sizes up to the wafer-scale as demonstrated in previous studies\(^17\)–\(^19\).

Gallium (Ga) is an metallic element with an unusually low melting point of 29.7°C\(^20\),\(^21\) as compared to other metals. Strong electronic bonding states exist between two Ga atoms forming a Ga pair, whereas the bonding energy between Ga pairs is significantly lower\(^22\). Besides the liquid phase, Ga can exist in several different solid state modifications referred to as \(\alpha\)- to \(\gamma\)-Ga phase occurring at different temperatures as measured under defined pressure and temperature conditions\(^23\) as well as in a metastable supercooling phases\(^24\),\(^25\). The investigation of atomically thin Ga films on semiconducting
substrates and their surface reconstruction behavior on these surfaces is still a matter of scientific studies. The discovery of ultra-thin gallium oxide sheets as well as the monochalcogenide gallium sulfide (GaS) has recently attracted attention since it provides a new approach of the exfoliation technique utilizing the liquid instead of a solid phase of a metal. Carey et al. have exfoliated atomically thin layers of gallium oxide from the surface of the liquid phase of Ga onto an oxidized silicon wafer which was previously hydrophobized with a silane to create a patterned gallium oxide layer. Using surface chemistry, they converted the oxide layer into two-dimensional GaS. Recently, Kochat et al. have demonstrated the exfoliation of “gallenene” – an atomically thin sheet of Ga – from the liquid Ga phase onto different substrates by means of a solid-melt exfoliation technique. In this context, they demonstrated the extraction of the (010) and (100) crystal planes (zigzag and honeycomb-like structure) from α-Ga, which were stabilized at ambient conditions due to strong interactions with the underlying substrates as underpinned by DFT calculations. The honeycomb phase of gallenene occurs even in an epitaxially grown monocrystalline bilayer which is stabilized on the (0001) plane of gallium nitride (GaN). The gallenene layer has a thickness of only 0.55 nm and exhibits superconductivity at a higher transition temperature as compared to bulk Ga due to polarization effects from the underlying GaN substrate. Recently, the epitaxial growth of gallenene on a Si(111) surface has been demonstrated by Tao et al. Also, of technological interest is the conversion of Ga into 2D GaN semiconductor layers by the chemical process of ammonolysis as described by Balushi et al. was shown. There, a thin Ga layer was prepared by incorporation of Ga atoms between an epitaxial graphene sheet and the SiC substrate in a high temperature trimethylgallium atmosphere.

The preliminary work of different research groups has shown a large versatility of liquid Ga by downsizing the bulk material to the two-dimensional level. Based on the solid-melt exfoliation technique we demonstrate here a far more extensive large-scale deposition of gallenene by self-propagation of gallium atoms. Taking into account the observed physical effects, we reveal at the same time a possible intercalation mechanism of epitaxially grown graphene. The physical properties of gallenene were investigated by optical microscopy, micro-reflection spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM) as well as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). In addition, confocal micro-Raman spectroscopy was used to evaluate the interlayer interactions between gallenene and graphene.
2. Results and discussion

**Deposition of gallenene on epitaxial graphene substrate.** Optical images of large gallenene-covered areas as well as from regions acquired shortly after the solid-melt exfoliation are shown in Fig. 1b and c. A schematic representation of the fabrication process is depicted in Fig. 1a including the observed self-propagation of gallenene. In general, the deposition of a large gallenene layer has been achieved by depositing a droplet of liquid Ga ($V \approx 10 \, \mu$l) onto the surface center of the SiC substrate (Fig. 1a, I) which is covered with epitaxial graphene on top of the (0001) plane of 6H-SiC. The latter consists of monolayer graphene and the buffer layer which is covalently bonded to the Si-terminated side of the SiC substrate\(^{32,33}\). The solid-melt exfoliation was initiated by placing a Ga droplet and the epitaxial graphene sample onto an object slide and heating them up to $T \approx 120$ °C. This treatment results in a temperature gradient from the annealing source to the sample surface so that a lower surface temperature of epitaxial graphene sample can be assumed. However, since a higher process temperature could cause structural lattice defects in the graphene, the mentioned process temperature has not been exceeded. As indicated in Fig. 1a (I), the Ga droplet was spread only to the lower side of the sample by wiping the liquid metal across the substrate surface using a Teflon squeegee. The graphene layer on top of the buffer layer withstands this treatment and has neither been removed nor damaged throughout the solid-melt exfoliation as examined by Raman spectroscopy. Hence, we suggest, that liquid Ga acts as a lubricant during the solid-melt exfoliation decreasing the frictional force between the Teflon squeegee and the substrate surface. Figure 1b (I-III) represents three stages of a typical time-depending self-propagation of gallenene, which was recorded shortly after spreading of the liquid Ga droplet. The color contrast in Fig. 1b (I-III) clearly reveals large bright and dark areas across the substrate. Examining these regions by LA-ICP-MS measurements unambiguously proves the existence of Ga within the bright regions from its isotopic fingerprint (as shown later), while the dark areas correspond to uncovered epitaxial graphene grown on 6H-SiC. A stepwise broadening of the bright colored areas can easily be observed using the red auxiliary line as the starting point.

The propagation velocity of gallenene across the sample surface varies over time. Figure 1b (I-II) reveals a low propagation within the first 20 min, followed by a significant increase in the subsequent period (Fig. 1b, II-III) which resulted in complete coverage of the investigated area within the next 10 min (Fig. 1b, III). A corresponding time lapse video of the gallenene self-propagation is
available in the supplementary information. Figure 1b contains three images extracted from the video showing different
Fig. 1 a) Schematical drawing of gallenene self-propagation caused by solid-melt exfoliation. I. Initiation of solid-melt exfoliation by liquid Ga deposition and wiping the metal across the substrate. The inset shows schematically the sample structure consisting of monolayer graphene sheet on top of a graphene buffer layer which is covalently bonded to the underlying SiC substrate. II. Self-propagation of gallenene shortly after processing. III. Self-propagation of gallenene after 2 hours. IV. Gallenene completely covering the epitaxial graphene sample after >24 hours.

b) I-III. time-dependent self-propagation of gallenene. The red dashed line is used as start marker. IV. AFM topography of pure epitaxial graphene surface. V. Line profile of the substrate surface extracted from AFM topography. c) Optical micrograph of the gallenene-covered epitaxial graphene sample.
states of the self-propagation of gallenene that occurred fitfully in a non-continuous motion. The video as well as Fig. 1b (III) reveal the existence of two different propagation directions indicated by the vectors $\vec{a}$ and $\vec{b}$ with the propagation velocity along $\vec{b}$ being significantly larger as compared to the direction of vector $\vec{a}$. A detailed AFM analysis of the uncovered graphene surface shows an orthogonal direction of terrace steps to $\vec{a}$ having an average step height of $(0.66 \pm 0.09)$ nm (Fig. 1b, IV-V). We therefore suggest that the propagation of gallenene is energetically favored along the SiC terrace ($\vec{b}$), whereas the terrace steps presumably form an energetic barrier retarding the gallenene propagation along $\vec{a}$. Figure 1c clearly demonstrates that gallenene covers almost the whole width of the sample substrate while residues of Ga remain at the lower sample side. Finally, the self-propagation of gallenene affects the entire sample surface keeping the upper side of the sample free from any bulk Ga residues. The upper region of the sample thus allows further analytical investigations (e.g. SEM or Raman spectroscopy) to be carried out and enables the post-processing of the gallenene-graphene heterostack for preparing further experiments. The propagation velocity of gallenene decreased with progressing time and it took a few hours until the lower sample side was completely covered (Fig. 1a, II - III). The total coverage of the top half, however, was completed only after a few days by storage of the sample at room temperature (Fig. 1a, III - IV). It is therefore indisputable that the initiation of self-propagation of gallenene on the SiC substrate is decisively influenced by temperature as a crucial parameter. So far, the implementation of this approach at room temperature has not led to fabricate gallenene films with such large dimensions.

**Topological and chemical characterization of gallenene.** Further evidence supporting the formation of a thin Ga film as metallene has been provided by means of LA-ICP-MS, SEM and AFM measurements as shown in Fig. 2. In analytical chemistry, LA-ICP-MS has been evolved to a standard technique which can be used for identifying and quantifying inorganic impurities, for instance, in semiconductor materials\textsuperscript{34–37}. Moreover, LA-ICP-MS mappings enable the lateral composition of thin films to be analyzed. Here, LA-ICP-MS mappings were measured across an area of $(80 \times 220)$ µm\(^2\) and an increment as well as laser spot size of 20 µm encompassing the sharp transition from gallenene (bright-colored area) to pure epitaxial graphene (dark-colored area) as shown in Fig. 2a (red colored box) and b. For a better visualization, the pixels in Fig. 2c were linearly interpolated. The corresponding mass spectrum shows the signals of the two stable isotopes \textsuperscript{69}Ga and \textsuperscript{71}Ga (Fig. 2c) with small fractions of these isotopes even appearing on pure epitaxial graphene, probably due to
than one order of magnitude appearing in brightly colored areas (red mass spectrum, Fig. 2c) undoubtedly demonstrates the presence of gallium on the substrate and, thus, the existence of gallenene. The gallenene coverage across the substrate was also characterized by AFM. Figure 2d shows the topography of the SiC substrate including the typical terrace structure as already shown in the previous section on the pure epitaxial graphene surface. The topography image also shows a high density of small hole-like defects on the substrate, also known as micropipes. These surface defects occur in low crystal quality SiC wafers or could have been created during graphene fabrication employing the PASG process. The origin of the micropipes can be theoretically described by the Frank
theory, according to which they often appear due to bunching of several screw dislocations to a super-screw dislocation. In addition, the growth of epitaxial graphene stops at dislocations, and under certain circumstances, these defects develop into bilayer or even few-layer graphene patches. The identification of the deposited gallenene sheets from AFM topography images is challenging because the measured gallenene topography is disturbed by the dominant SiC terraces. In addition, during the AFM measurements, the gallenene area sometimes continues to spread. On the other hand, the AFM phase contrast image readily shows changes in the material properties, thus enabling the identification of pure epitaxial graphene and of gallenene (Fig. 2e). A sharp transition boundary between areas of pure epitaxial graphene and large gallenene areas appears as a slight contrast change in the phase image (Fig. 2e). The difference in height between the pure substrate and the gallenene-covered areas is particularly evident on the terrace steps of the substrate, so that average thickness of gallenene of about 1 nm can be observed (Fig. 2d, line no. 2, red line) which is approximately four times smaller compared to the value reported by Kochat et al. In contrast, the blue line shows an average terrace height of about 0.75 nm. High resolution SEM images (Fig. 2f and 2g) were generated to investigate especially the difference between gallenene-covered and non-covered areas of graphene on the SiC substrate. Figure 2f represents in detail a gallenene-free area obtained by In-Beam SEM imaging. This figure also shows the well-resolved characteristic terrace steps of the SiC wafer as indicated by bright marked lines along the SiC terrace step edges. The appearance of gallenene is evidenced by a brighter contrast (Fig. 2g) compared to the pure epitaxial graphene region (Fig. 2f). Additionally, various dark and bright (red dashed) lines appear within the gallenene film. The origin of the former is still unknown but could indicate grain boundaries of gallenene. The latter (bright lines) presumably corresponds to the characteristic terrace steps of the SiC wafer which remain visible even throughout the gallenene film (Fig. 2g).
Optical properties of gallenene-graphene heterostack. Micro-reflection spectroscopy was used to roughly identify the optical properties of gallenene on the epitaxial graphene substrate within a spectral range from 450 to 800 nm based on the approach reported by Frisenda et al. Reflectivity measurements were carried out in a top-down backscattering optical setup using a halogen lamp. The acquired reflectance spectra (Fig. 3a) correspond to different measurement areas (see inlet of Fig. 3a) representing the pure epitaxial graphene substrate (black), gallenene (red) as well as a droplet of bulk Ga (blue). In general, the reflectance spectrum of gallenene and of the substrate reveal an almost similar spectral behavior, differing from each other only in the spectral range from 600 to 750 nm under the given conditions. The reflection efficiency of all materials rapidly decreases both below 500 nm and above 800 nm, since the spectral power distribution of the halogen lamp gradually collapses when approaching the UV or infrared range (Fig. 3a). A relatively large reflection efficiency was measured for bulk Ga resulting from its typical metallic properties (Fig. 3a, blue curve). The differential reflectance spectra of gallenene and of bulk Ga (Fig. 3b) were obtained according to the approach of Frisenda et al. by calculating the ratio \((R-R_0)/R\) which is proportional to the absorption coefficient of the investigated material\(^{40}\). This approach allows the pure reflection line shapes of gallenene and bulk Ga to be extracted which are normally superimposed by the SiC substrate and the spectral power.
distribution of the incident light source. In this context, the reflectance intensity of gallenene and of bulk Ga, respectively, (denoted $R$) as well as of the SiC substrate (denoted $R_0$) is considered. Figure 3b depicts the calculated differential reflectance spectra indicating a significant difference between bulk Ga and gallenene (blue and red lines, respectively). Finally, we have observed a differential reflectance of approximately 65% in case of bulk Ga, while the reflectance of gallenene unambiguously decreased down to roughly 12%. Therefore, the reflectance intensity might also be regarded as a parameter to distinguish between the solid and liquid phase of Ga. Kofman et al. have already demonstrated that the reflectance as well as the line shape function of the reflectance of bulk Ga changes particularly from 600 to 900 nm during the melting process from the solid phase into the liquid phase$^{20,41}$. The latter is indicated by a change of the slope of the reflectance function which results from the disappearance of interband transition levels and the rise of intraband transitions$^{20,41}$. However, no such change of the line shape function appeared in the reflectance spectra of gallenene and bulk Ga in our measurements (Fig. 3b). This might be an indication that both materials could rather exist in the liquid phase at room temperature and, thus, possibly correspond to the supercooling phase. However, it should be mentioned that Kofman et al. have carefully checked the growth conditions of the thin Ga film preparation, which has been carried out at low temperatures ($T = 77$ K) clearly below the melting point of Ga, and which might result in a higher structural order of their thin Ga films$^{41}$. Hence, a low crystallinity of gallenene cannot be excluded in our experiments since the fabrication of a thin Ga film as well as the self-propagation takes place above the melting point of Ga promoting a structural disorder of the gallenene. The work of Kofman et al. also proves the dependency of the melting point by downsizing the sample thickness of Ga$^{20}$. The melting temperature of ultra-thin films or even on a two-dimensional scale is significantly lower than for bulk materials$^{20}$.

Confocal micro-Raman spectroscopy is an optical technique which is excellently suited to the characterization of 2D crystalline lattices. It enables the investigation of the crystal structure as well as induced lateral strain effects and the change of electronic doping levels within the two-dimensional lattice. Recently, strong interactions between WSe$_2$ and hBN as a heterostack have been observed by Raman spectroscopy revealing the appearance of silent optical phonon modes of hBN due to resonant coupling to WSe$_2$ electronic states$^{42}$. Here, we used Raman spectroscopy to investigate the interactions between gallenene and epitaxial graphene considering doping and strain effects. Figure
4a depicts the micrograph of the gallenene-graphene boundary showing bright gallenene areas which are clearly separated from darker regions of uncovered epitaxial graphene. Figure 4b, c and d show the distribution of the background signal of gallenene as well as the distributions of the 2D and G peak widths of epitaxial graphene across the (20 x 20) µm² area selected for Raman mapping.

Fig. 4 a) Optical micrograph of the gallene-graphene boundary indicating the area selected for Raman mapping (red square). b) Measured Raman signal of gallenene. Dark areas represent areas of pure epitaxial graphene substrate. Green-coloured areas correspond to gallenene. c) Lateral 2D peak width distribution along the graphene-gallenene boundary. Green-coloured areas indicate regions of monolayer epitaxial graphene, whereas pink-coloured areas indicate the intercalation of epitaxial graphene caused by gallenene. Scale bar corresponds to a width of 5 µm. d) G peak width distribution indicating electronic doping within graphene on gallenene-covered areas (blue-coloured areas). e) Raman spectra of pure epitaxial graphene (black line) and gallenene-graphene heterostack (red line). Raman signal related to gallenene appears below 250 cm⁻¹ (dashed purple line). SiC phonon bands are marked with an asterisk. f) Time-dependent evolution of the phonon bands of graphene during the gallenene self-propagation. The intercalation of epitaxial graphene to QFBLG appears after 6 seconds.

are clearly separated from darker regions of uncovered epitaxial graphene. Figure 4b, c and d show the distribution of the background signal of gallenene as well as the distributions of the 2D and G peak widths of epitaxial graphene across the (20 x 20) µm² area selected for Raman mapping.
Raman spectra from pure epitaxial graphene (black) and from the gallenene - epitaxial graphene stack (red) are depicted in Fig. 4e. Both Raman spectra contain phonon bands which belong to the SiC substrate (marked with an asterisk). Characteristic phonon bands of graphene appear at 1580 and 2670 cm\(^{-1}\) corresponding to the well-known G- and 2D peak. The physical origin of the D-, G- and 2D peak of graphene has been extensively investigated and a description can be found elsewhere\(^{43-47}\).

Creighton and Withnall have analysed the space group symmetry of \(\alpha\)-Ga, whereupon 4 Ga atoms occupy the primitive unit cell of a \(D_{2h}^{18}\) space group and, thus, result in six Raman active phonon bands of \(\alpha\)-Ga\(^{22}\). Their Raman spectroscopic experiments have shown that only one characteristic Raman band of solid \(\alpha\)-Ga appears around 246 cm\(^{-1}\) corresponding to the symmetrical stretching of Ga pairs\(^{22}\). However, no such phonon band appeared in the Raman spectra of gallenene (Fig. 4e, red line), presumably due to the low structural order of the gallenene lattice at room temperature as shown by differential reflection measurements. Moreover, the symmetrical stretching mode of Ga pairs was even absent in low temperature Raman experiments (\(T = 4\) K — 303 K, results are not shown), evidencing the existence of a low crystalline phase under these conditions. On the other hand, one could reasonably expect that other Raman active phonon modes of gallenene which might differ from the space group symmetry of \(\alpha\)-Ga would arise in the Raman spectrum corresponding to the hexagonal symmetry as has already been experimentally verified by Kochat et al.\(^{18}\). For instance, silicene is a material well known for exhibiting Raman active phonon modes which are different to those obtained from bulk silicon. They are generated by surface reconstruction effects resulting from the interaction with the underlying substrate\(^{48}\). The Raman spectrum of gallenene covered areas (Fig. 4e, red line) exhibits a strong signal between 45 and 750 cm\(^{-1}\) with its maximum occurring at \(\sim 104\) cm\(^{-1}\) as compared to the Raman spectrum of the pure epitaxial graphene substrate (black line, Fig. 4e). However, the gallenene spectrum is not completely visible in the low-wavenumber range > 45 cm\(^{-1}\) as these bands have been cut by an edge filter placed in the optical path of the spectrometer (Fig. 4e, red line).

Raman spectroscopic investigations of bulk Ga droplets have revealed a comparable spectral line shape as compared to gallenene (Fig. S1) that was already observed by Lee and Kang even on thin \(\beta\)-Ga\(_2\)O\(_3\) films\(^{49}\). In their work, the growth mechanism of \(\beta\)-Ga\(_2\)O\(_3\) nanowires on amorphous substrates using a RF powder-sputtering method has been analysed by several analytical tools including Raman spectroscopy\(^{49}\). Lee and Kang have shown that the typical characteristic phonon bands belong to the
monocrystalline crystal structure of \(\beta\)-Ga\(_2\)O\(_3\), but they also observed two broadened bands at 115 and 703 cm\(^{-1}\) on thin Ga films\(^{49}\). Based on their Raman data they suggested that a low crystallinity phase exist in those thin films, which cannot be assigned to known Raman active phonon modes of pure solid Ga or \(\beta\)-Ga\(_2\)O\(_3\), but might rather indicate the presence of a Ga-rich oxide phase\(^{19}\). Hence, their data provide support to our experimental results indicating a low-crystalline gallenene to be formed after the deposition onto the SiC substrate when using the solid-liquid exfoliation technique. Nevertheless, the observed background signal in the Raman spectrum could also arise from luminescence effects which is a typical behaviour of metallic materials. Thus, the Raman spectroscopic investigations rather confirm that a nanocrystalline or even an amorphous phase exist in both materials, as also indicated by the micro-reflectance measurements. A similar signal appears in the Raman spectra of Kochat et al. showing the spectral fingerprint of pure gallenene and the gallenene-MoS\(_2\) heterostack\(^{18}\). Unfortunately, a description of this signal is missing in their work.

The lateral distribution of the individual graphene and gallenene phonon bands was measured by means of micro-confocal Raman mappings in combination with an automated non-linear fitting algorithm that extracts the characteristic parameters such as peak position and peak width (Fig. 4b, c and d). All Raman spectra were corrected by subtracting a reference spectrum obtained from a pure 6H-SiC, since the second order vibrational modes of 6H-SiC cover the Raman spectrum of graphene in a spectral range between 1200 cm\(^{-1}\) and 2000 cm\(^{-1}\) leading to a spectral superposition. The Raman mapping shown in Fig. 4b depicts the collected intensity distribution of gallenene across the epitaxial graphene. Black-coloured areas clearly reveal the absence of gallenene showing uncovered epitaxial graphene, whereas green-coloured regions indicate the rise of the gallenene background signal in the Raman spectrum. The false color image of the 2D peak width distribution in Fig. 4c illustrates a distinct contrast difference, representing a broadening of the 2D peak width on gallenene covered areas which is consistent with the gallenene background signal distribution in Fig. 4b. A statistical evaluation of the 2D peak width of Fig. 4c underpins this effect by the formation of two separated gaussian-like distributions (histogram, Fig. S2) with the 2D peak widths being (34.7 ± 5.3) and (53.9 ± 9.1) cm\(^{-1}\). The former distribution denotes 2D peak widths typically measured for epitaxially grown monolayer graphene\(^{50}\) while the latter rather indicates bilayer graphene.

Figure 4g and h depict the subtracted Raman spectra of pure epitaxial graphene (black line) as well as of the gallenene – graphene heterostack (red line). The Raman spectrum of epitaxial graphene
(Fig. 4g and h) consists of the G and 2D peak related to monolayer graphene and is accompanied by flat and broadened phonon bands of the buffer layer in the Raman spectral range from 1200 cm$^{-1}$ to 1600 cm$^{-1}$ \cite{33}. Remarkably, this buffer layer background vanishes on gallenene-covered areas as shown in Fig. 4g (red line) followed by an increase of the G peak intensity. Furthermore, the 2D peak line shape obviously changes on gallenene covered areas as depicted in Fig. 4h (red line) and can be fitted by four Lorentzian curves. The time-dependent evolution of the above-mentioned Raman spectral changes is represented in Fig. 4f showing the increase of the G peak intensity as well as the 2D peak broadening as soon as the Ga signal rises. Furthermore, Fig. 4f demonstrates a rather fast change of the spectral properties of graphene occurring within a time interval of approximately 6 s in this case. Generally, an asymmetric 2D peak line shape as well as the observed 2D peak width are prominent properties of bilayer graphene \cite{51,52,53} as well as of quasi-freestanding bilayer graphene (QFBLG). The latter results from the intercalation of epitaxial graphene, for instance, by using a gaseous intercalation agent \cite{54,55}. Since the 2D peak of a pure epitaxial graphene monolayer is commonly fitted by a single Lorentzian curve \cite{50} (blue line, Fig. 4h), the 2D peak line shape asymmetry observed in our experiments provides evidence for the intercalation of epitaxial graphene into QFBLG in the presence of gallenene. The good agreement of the 2D peak behavior to QFBLG fabricated by gaseous intercalation might therefore point to a similar mechanism for the Ga intercalation. In this process, the Ga atoms induce breaking of bonds between buffer layer and SiC substrate and saturate the remaining Si dangling bonds, thereby forming a two-dimensional gallium layer in between the SiC substrate and the QFBLG. So far, however, it is not yet clear whether gallenene was also formed in between the two graphene layers. Raman spectroscopy shows no direct spectral evidence here, for instance, resulting from different strain levels in both carbon layers which would lead to G peak splitting. Thus, other optical techniques, for example cross-sectional transmission electron spectroscopy need to be used for clarification in additional experiments.

The deposition of metals on top of monolayer graphene is also able to change the G and 2D line shape as well, resulting in a spectral splitting of both peaks, whereby each of them is then generally fitted by two Lorentzian curves \cite{56}. To avoid a misinterpretation, we have carefully checked the characteristic dispersion behavior of bilayer graphene by considering the 2D peak position and its line shape at different laser energies (1.96 eV, 2.33 eV). The dispersion behaviour of the four Lorentzian peaks of the 2D peak reveals calculated slopes between 85.8 and 93.5 cm$^{-1}$ eV$^{-1}$ in our experiments
(Fig. S3) indicating a similar behavior as described in the literature. However, a more asymmetrical line shape of the 2D peak containing two distinct shoulders occurs depending on the laser energy (Fig. S4), which is typical of bilayer graphene resulting from its phonon dispersion behavior. Since the observed line shape cannot satisfactorily be fitted by one or two Lorentzian curves (Fig. S4), we suggest that this line shape belongs to bilayer graphene. Unfortunately, the characteristic low energy out-of-plane phonon modes (around 100 cm\(^{-1}\) and 1800 cm\(^{-1}\)) of bilayer graphene are superimposed by the background signal of gallenene and the second order vibrational modes of SiC and, thus, they were not observed in our Raman measurements.

The evaluation of electronic as well as physical interactions between gallenene and graphene was also achieved using confocal micro-Raman spectroscopy. Electronic doping within graphene significantly affects its Raman spectroscopic properties by changing especially the G peak position and peak width typically resulting in stiffening and sharpening of the G peak. Fig. 4d depicts the G peak width mapping of graphene indicating predominantly blue and green-coloured areas corresponding to G peak widths of 12 and 16 cm\(^{-1}\). While the green areas indicate the absence of carrier doping in epitaxial graphene, the blue areas correspond to slight carrier doping presumably introduced due to the interaction with gallenene finally changing the carrier density of bilayer graphene. Furthermore, carrier doping originates only on gallenene covered areas and is delimited by a sharp border as shown in Fig. 4d. In addition, Fig. 4d depicts a non-homogenous distribution of the G peak width on gallenene covered areas which implies a rather heterogeneous doping across the graphene-gallenene heterostack. In this context, we have noticed a shift of the G peak position from (1598.9 ± 3.3) cm\(^{-1}\) down to (1593.8 ± 2.5) cm\(^{-1}\) (Fig. S3), indicating a slight reduction of the strain level. Nevertheless, the G peak position is also superimposed by electronic doping as has already been proved by the reduced G peak width. Considering the physical interaction between graphene and gallenene, the introduction of defects into the graphene lattice should also be taken into account. The investigated areas of our samples do not reveal any increased defect density of graphene after the gallenene spreading (Fig. S5). However, the rise of lattice defects cannot be fully excluded at this point, so further investigations are required.

The intercalation of epitaxial graphene supported by molecular gas species such as hydrogen, water vapour etc. has been extensively examined and strongly depends on the annealing temperature. Buffer layer intercalation was already achieved in air at temperatures around 250 °C and
at atmospheric pressure\textsuperscript{66}. Consequently, we have carefully checked our process conditions at an annealing temperature of 120 °C too, by annealing a pure epitaxial graphene sample. In summary, no Raman spectral changes (e.g. change of the 2D peak line shape) of epitaxial graphene similar to those found for the solid-melt exfoliation experiments have been observed so far (results are not shown). Hence, an intercalation of epitaxial graphene by ambient molecules such as oxygen or water can be excluded during the solid-melt exfoliation process in this experiment.

We suppose, however, that the appearance of substrate defects such as micropipes (as proven by AFM measurements) as well as the lateral density of such defects across the substrate surface play a key role. In this context, a decreased surface energy of the SiC substrate resulting from micropipes might act as nucleation hot spots for Ga atoms. A similar effect was observed by Balushi et al., demonstrating that graphene wrinkles enhance the nucleation process of Ga\textsuperscript{31}. Other research groups have shown that the infiltration of alkali atoms can be achieved through wrinkles which act as penetration sides\textsuperscript{67}. Hence, these micropipes present in both graphene and in SiC could support the intercalation of Ga atoms by enabling them to enter below the buffer layer. Furthermore, carbon and silicon dangling bonds are known as remnants of the epitaxial graphene growth, originating from the surface reconstruction process of the buffer layer crystal lattice, where only every third carbon atom of the buffer layer is covalently bonded to the Si-terminated substrate\textsuperscript{68}. Hence, the strong chemical reactivity of the dangling bonds results from their unsaturated bonding state which could certainly interact with Ga atoms. Indeed, the passivation of Si dangling bonds, for instance on an Si(111) plane introduced by the deposition of thin Ga films has already been observed previously\textsuperscript{28,29} and causes a surface reconstruction of the ultra-thin Ga film which itself depends on the Ga layer thickness. This leads us to the suggestion that the dangling bonds could act as a Coulomb driven capillary force in this intercalation process.

3. Conclusions

In summary, we have demonstrated the successful fabrication of a gallenene-graphene heterostack on a SiC substrate realized through the solid-melt exfoliation of liquid Ga. Although the exact mechanism of the gallenene self-propagation and a possible crystal lattice conversion of epitaxial graphene into QFBLG initiated through Ga intercalation has not yet been fully elucidated, we propose a mechanism as follows, which can be deduced from our experimental results. The graphene-
gallenene interface is particularly formed in the presence of substrate defects such as holes and micropipes enabling the infiltration of the liquid Ga film. After all, the liquid Ga penetrates holes and intercalates the epitaxial graphene which releases the buffer layer and finally converts the epitaxial graphene into QFBLG as evidenced by confocal micro Raman spectroscopy. It has been shown that a time-dependent increase of the QFBLG area associated with the gallenene self-propagation on the macroscopic scale occurs after the fabrication process. The self-organized and self-limited process at ambient conditions neither requires specific environmental conditions to be met nor any additional physical or chemical treatment. We also suggest that dangling bonds at the SiC – buffer layer interface support the intercalation process, but this needs to be confirmed in further experiments. Moreover, this approach in combination with large-area PASG grown monolayer graphene sheets could open a new route towards a controlled fabrication of homogenous large-area 2D stacks employing liquid metals. This could be followed by the conversion of the deposited metallene layer (based on Ga, In, Sn etc.) into its corresponding semiconductor derivative, such as an oxide or nitride layer, and, thus, result in 2D-stacked polytypes.

4. Materials and methods

Substrate fabrication and treatment. Epitaxial graphene was grown on the Si-face of SiC samples (5 x 10) mm² cut from a semi-insulating 6H-SiC wafer with a nominal miscut angle of about 0.06° towards [1̅1̅00] surface. The graphene samples were prepared according to the polymer-assisted sublimation growth (PASG) technique which involves polymer adsorbates to be formed on the SiC surface by liquid phase deposition from a solution of a photoresist (AZ5214E) in isopropanol followed by sonication and short rinsing with isopropanol. The graphene layer growth was processed at 1750°C (argon atmosphere ~1 bar, 6 min, zero argon flow) with a pre-vacuum-annealing at 900°C. The applied PASG method allows the growth of large-area ultra-smooth, homogenous monolayer graphene and it is therefore very well suited as the basis for the fabrication of large area two-dimensional gallenene sheets by solid-melt intercalation technique as described in this work. Commercial Ga (99.99 % purity) was purchased from Heraeus. The deposition of liquid Ga was carried out similarly to the approach described for the exfoliation of thin gallium oxide films, but in our case this method was employed on epitaxial graphene as a substrate and without the selective functionalization of the sample surface. More detailed information of the gallenene fabrication can be found in “Synthesis of gallenene on epitaxial graphene” within the section “Results and discussion”.

18
**Measuring equipment.** Raman measurements of graphene and gallene were acquired at ambient conditions with a Witec Alpha 300 RA (Witec GmbH) Raman spectrometer equipped with a frequency-doubled Nd:YAG laser emitting at 488 nm ($E_L = 2.54$ eV) and a 100x (N.A. 0.9) objective to focus the excitation laser onto the sample surface. A LabRAM Aramis Raman spectrometer (Horiba) has been used in case of excitation wavelengths of 532 nm ($E_L = 2.32$ eV) and 633 nm ($E_L = 1.96$ eV). Confocal micro-Raman mappings were recorded over (20 x 20) µm² scan areas in backscattering mode using a piezo-driven xy-stage (PI) and a scanning step size of 0.1 µm. AFM measurement was carried out using the Nanostation AFM (manufactured by S.I.S) providing pronounced resolution for precisely resolving structures down to 0.25 nm. SEM investigations were carried out inside a Tescan Mira 3 GMH FE-SEM. A high surface sensitivity was reached using acceleration voltages between 1 and 5 kV and small beam currents. The in-lens SE detector offered sufficient SNR, high contrast and high resolution for the small working distances used. Besides the topographic information mainly provided by the asymmetrically mounted SE detector, the additional in-lens SE detector also images the work function (e.g. material variations) of the sample. LA-ICP-MS mappings were measured by using a laser ablation system (NWR 213, New Wave Research Inc.), which is equipped with a frequency quintupled Nd:YAG deep UV laser emitting at 213 nm ($E_L = 5.82$ eV) focusing the laser with a pulse energy of about 0.1 mJ. Ablated materials were investigated by means of a double focusing magnetic sector field high resolution ICP mass spectrometer (Element XR, Thermo Scientific Inc.) analyzing the isotopic ratios of $^{69}$Ga and $^{71}$Ga.

5. References
1. Gong, Y. *et al.* Two-step growth of two-dimensional WSe$_2$/MoSe$_2$ heterostructures. *Nano Lett.* **15**, 6135–6141 (2015).
2. Shim, G. W. *et al.* Large-area single-layer MoSe$_2$ and its van der Waals heterostructures. *ACS Nano* **8**, 6655–6662 (2014).
3. Huang, C. *et al.* Lateral heterojunctions within monolayer MoSe$_2$–WSe$_2$ semiconductors. *Nat. Mater.* **13**, 1096–1101 (2014).
4. Hsu, W.-T. *et al.* Second harmonic generation from artificially stacked transition metal dichalcogenide twisted bilayers. *ACS Nano* **8**, 2951–2958 (2014).
5. Gong, Y. et al. Vertical and in-plane heterostructures from WS$_2$/MoS$_2$ monolayers. *Nat. Mater.* **13**, 1135–1142 (2014).

6. Duan, X. et al. Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions. *Nat. Nanotechnol.* **9**, 1024–1030 (2014).

7. Shi, Y. et al. van der Waals epitaxy of MoS$_2$ layers using graphene as growth templates. *Nano Lett.* **12**, 2784–2791 (2012).

8. Haigh, S. J. et al. Cross-sectional imaging of individual layers and buried interfaces of graphene-based heterostructures and superlattices. *Nat. Mater.* **11**, 764–767 (2012).

9. Britnell, L. et al. Field-effect tunneling transistor based on vertical graphene heterostructures. *Science* **335**, 947–950 (2012).

10. Novoselov, K. S. Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).

11. Geng, X. et al. Pure and stable metallic phase molybdenum disulfide nanosheets for hydrogen evolution reaction. *Nat. Commun.* **7**, 10672 (2016).

12. Shen, J. et al. Liquid phase exfoliation of two-dimensional materials by directly probing and matching surface tension components. *Nano Lett.* **15**, 5449–5454 (2015).

13. Zheng, J. et al. High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide. *Nat. Commun.* **5**, 2995 (2014).

14. Magda, G. Z. et al. Exfoliation of large-area transition metal chalcogenide single layers. *Sci. Rep.* **5**, 14714 (2015).

15. Iqbal, M. W. et al. High-mobility and air-stable single-layer WS$_2$ field-effect transistors sandwiched between chemical vapor deposition-grown hexagonal BN films. *Sci. Rep.* **5**, 10699 (2015).

16. Falin, A. et al. Mechanical properties of atomically thin boron nitride and the role of interlayer interactions. *Nat. Commun.* **8**, 15815 (2017).
17. Carey, B. J. *et al.* Wafer-scale two-dimensional semiconductors from printed oxide skin of liquid metals. *Nat. Commun.* **8**, 14482 (2017).

18. Kochat, V. *et al.* Atomically thin gallium layers from solid-melt exfoliation. *Sci. Adv.* **4**, e1701373 (2018).

19. Syed, N. *et al.* Printing two-dimensional gallium phosphate out of liquid metal. *Nat. Commun.* **9**, 3618 (2018).

20. Cheyssac, P., Kofman, R. & Garrigos, R. Optical behaviour of melting for a thin metal film. *Solid State Commun.* **44**, 1583–1584 (1982).

21. Kofman, R., Cheyssac, P. & Richard, J. Optical properties of Ga monocystal in the 0.3-5-eV range. *Phys. Rev. B* **16**, 5216–5224 (1977).

22. Creighton, J. A. & Withnall, R. The Raman spectrum of gallium metal. *Chem. Phys. Lett.* **326**, 311–313 (2000).

23. Comez, L., Di Cicco, A., Itié, J. P. & Polian, A. High-pressure and high-temperature x-ray absorption study of liquid and solid gallium. *Phys. Rev. B* **65**, 014114 (2001).

24. Bosio, L. & Windsor, C. G. Observation of a metastability limit in liquid Gallium. *Phys. Rev. Lett.* **35**, 1652–1655 (1975).

25. Carlson, D. G., Feder, J. & Segmüller, A. Measurement of the liquid-structure factor of supercooled gallium and mercury. *Phys. Rev. A* **9**, 400–403 (1974).

26. Tao, M.-L. *et al.* Gallene epitaxially grown on Si(1 1 1). *2D Mater.* **5**, 035009 (2018).

27. Lander, J. J. & Morrison, J. Surface reactions of silicon with aluminum and with indium. *Surf. Sci.* **2**, 553–565 (1964).

28. Kawazu, A. & Sakama, H. Geometric structure of the Si(111)V3×V3-Ga surface. *Phys. Rev. B* **37**, 2704–2706 (1988).

29. Zegenhagen, J. *et al.* X-ray standing-wave and tunneling-microscope location of gallium atoms on a silicon surface. *Phys. Rev. B* **39**, 1298–1301 (1989).
30. Zhang, H.-M. et al. Detection of a superconducting phase in a two-atom layer of hexagonal Ga film grown on semiconducting GaN(0001). Phys. Rev. Lett. 114, 107003 (2015).
31. Al Balushi, Z. Y. et al. Two-dimensional gallium nitride realized via graphene encapsulation. Nat. Mater. 15, 1166–1171 (2016).
32. Kruskopf, M. et al. Comeback of epitaxial graphene for electronics: large-area growth of bilayer-free graphene on SiC. 2D Mater. 3, 041002 (2016).
33. Fromm, F. et al. Contribution of the buffer layer to the Raman spectrum of epitaxial graphene on SiC(0001). New J. Phys. 15, 043031 (2013).
34. Seifner, M. S. et al. Direct synthesis of hyperdoped germanium nanowires. ACS Nano 12, 1236–1241 (2018).
35. Labutin, T. A., Lednev, V. N., Ilyin, A. A. & Popov, A. M. Femtosecond laser-induced breakdown spectroscopy. J. Anal. At. Spectrom. 31, 90–118 (2016).
36. Becker, J. S. & Dietze, H.-J. State-of-the-art in inorganic mass spectrometry for analysis of high-purity materials. Int. J. Mass Spectrom. 228, 127–150 (2003).
37. Chi, P.-H. et al. Direct impurity analysis of semiconductor photoresist samples with laser ablation ICP-MS. J. Anal. At. Spectrom. 17, 358–365 (2002).
38. SiC materials and devices. (World Scientific, 2006).
39. ul Hassan, J. et al. Control of epitaxial graphene thickness on 4H-SiC(0001) and buffer Layer removal through hydrogen Intercalation. Mater. Sci. Forum 717–720, 605–608 (2012).
40. Frisenda, R. et al. Micro-reflectance and transmittance spectroscopy: a versatile and powerful tool to characterize 2D materials. J. Phys. Appl. Phys. 50, 074002 (2017).
41. Kofman, R., Cheyssac, P. & Garrigos, R. Optical investigation of the solid-liquid transition in gallium. J. Phys. F Met. Phys. 9, 2345–2351 (1979).
42. Jin, C. et al. Interlayer electron–phonon coupling in WSe2/hBN heterostructures. Nat. Phys. 13, 127–131 (2017).
43. Ferrari, A. C. & Basko, D. M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat. Nanotechnol.* **8**, 235–246 (2013).

44. Cançado, L. et al. Quantifying defects in graphene via Raman spectroscopy at different excitation energies. *Nano Lett.* **11**, 3190–3196 (2011).

45. Eckmann, A. et al. Probing the nature of defects in graphene by Raman spectroscopy. *Nano Lett.* **12**, 3925–3930 (2012).

46. Ferrari, A. & Robertson, J. Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon. *Phys. Rev. B* **64**, 075414 (2001).

47. Ferrari, A. C. & Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* **61**, 14095 (2000).

48. Solonenko, D. et al. 2D vibrational properties of epitaxial silicene on Ag(111). *2D Mater.* **4**, 015008 (2017).

49. Lee, S. Y. & Kang, H. C. Synthesis and characterization of $\beta$-Ga$_2$O$_3$ nanowires on amorphous substrates using radio-frequency powder sputtering. *J. Cryst. Growth* **412**, 25–30 (2015).

50. Lee, D. et al. Raman spectra of epitaxial graphene on SiC and of epitaxial graphene transferred to SiO. *Nano Lett.* **8**, 4320–4325 (2008).

51. Ferrari, A. et al. Raman spectrum of graphene and graphene Layers. *Phys. Rev. Lett.* **97**, 187401 (2006).

52. Graf, D., Molitor, F., Ensslin, K., Stampfer, C. & Jungen, A. Spatially resolved Raman spectroscopy of single- and few-layer graphene. *Nano Lett.* **7**, 238–242 (2007).

53. Malard, L. M. et al. Probing the electronic structure of bilayer graphene by Raman scattering. *Phys. Rev. B* **76**, 201401(R) (2007).

54. Pakdehi, D. M. et al. Homogeneous Large-area quasi-free-Standing monolayer and bilayer graphene on SiC. *ACS Appl. Nano Mater.* **2**, 844–852 (2019).

55. Oliveira, M. H. et al. Formation of high-quality quasi-free-standing bilayer graphene on SiC(0001) by oxygen intercalation upon annealing in air. *Carbon* **52**, 83–89 (2013).
56. Lee, J., Novoselov, K. S. & Shin, H. S. Interaction between metal and graphene: dependence on the layer number of graphene. *ACS Nano* 5, 608–612 (2011).

57. Cançado, L. G., Reina, A., Kong, J. & Dresselhaus, M. S. Geometrical approach for the study of G’ band in the Raman spectrum of monolayer graphene, bilayer graphene, and bulk graphite. *Phys. Rev. B* 77, 245408 (2008).

58. Lui, C. H. *et al.* Observation of layer-breathing mode vibrations in few-layer graphene through combination Raman scattering. *Nano Lett.* 12, 5539–5544 (2012).

59. Pisana, S. *et al.* Breakdown of the adiabatic Born–Oppenheimer approximation in graphene. *Nat. Mater.* 6, 198–201 (2007).

60. Das, A. *et al.* Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. *Nat. Nanotechnol.* 3, 210–215 (2008).

61. Das, D., Bhattacharyya, S., Muñoz, E. & Singh, A. K. Strain-induced chiral symmetry breaking leads to large Dirac cone splitting in graphene/graphane heterostructure. *Phys. Rev. B* 94, 115438 (2016).

62. Ding, F. *et al.* Stretchable Graphene: A close look at fundamental parameters through biaxial straining. *Nano Lett.* 10, 3453–3458 (2010).

63. Lee, J. E., Ahn, G., Shim, J., Lee, Y. S. & Ryu, S. Optical separation of mechanical strain from charge doping in graphene. *Nat. Commun.* 3, 1024 (2012).

64. Neumann, C. *et al.* Raman spectroscopy as probe of nanometre-scale strain variations in graphene. *Nat. Commun.* 6, 8429 (2015).

65. Das, A. *et al.* Phonon renormalization in doped bilayer graphene. *Phys. Rev. B* 79, 155417 (2009).

66. Oida, S. *et al.* Decoupling graphene from SiC(0001) via oxidation. *Phys. Rev. B* 82, 041411(R) (2010).

67. Petrović, M. *et al.* The mechanism of caesium intercalation of graphene. *Nat. Commun.* 4, 2772 (2013).
68. Emtsev, K. V., Speck, F., Seyller, T., Ley, L. & Riley, J. D. Interaction, growth, and ordering of epitaxial graphene on SiC(0001) surfaces: A comparative photoelectron spectroscopy study. *Phys. Rev. B* **77**, 155303 (2008).

69. Momeni Pakdehi, D. et al. Minimum resistance anisotropy of epitaxial graphene on SiC. *ACS Appl. Mater. Interfaces* **10**, 6039–6045 (2018).
Supplementary: Graphene meets gallenene - A straightforward approach to developing large-area heterostacks by gallium self-propagation

S. Wundrack\textsuperscript{1†}, N. Schmidt\textsuperscript{2}, D. Momeni Pakdehi\textsuperscript{1}, K. Pierz\textsuperscript{1}, L. Michaliszyn\textsuperscript{1}, H. Spende\textsuperscript{2,3}, A. Schmidt\textsuperscript{2,3}, H. W. Schumacher\textsuperscript{1}, R. Stosch\textsuperscript{1}, A. Bakin\textsuperscript{2,3†}

1. Physikalisch-Technische Bundesanstalt, Bundesallee 100, D-38116 Braunschweig, Germany
2. Institut für Halbleitertechnik, Technische Universität Braunschweig, Hans-Sommer Straße 66, D-38106 Braunschweig, Germany
3. Laboratory of Emerging Nanometrology (LENA) der Technischen Universität Braunschweig, Langer Kamp 6 a/b, D-38106 Braunschweig, Germany

† Correspondence and requests for materials should be addressed to S. W. (email: stefan.wundrack@ptb.de) or A. B. (email: a.bakin@tu-braunschweig.de)
This supplemental material presents:

1. Raman spectrum of Ga droplet (bulk)

2. Statistical Evaluation of the 2D peak width as well as the G peak position

3. Phonon dispersion measurements of intercalated graphene by gallenene

4. Non-linear curve fitting of the 2D peak corresponding to intercalated graphene by gallenene

5. Raman mapping of gallenene-graphene area proving the absence of high defect densities during self-propagation of Ga

6. Video: Self-propagation of gallenene across epitaxial graphene sample
**Fig. S1** Raman spectrum of Ga droplet (bulk)

**Fig. S2** (a) Peak width distribution of the 2D peak. Peak widths around 35 cm\(^{-1}\) correspond to epitaxial monolayer graphene, peak widths around 54 cm\(^{-1}\) are related to bilayer graphene after solid-melt exfoliation. (b) Peak position distribution of the G peak. Peak positions around 1599 cm\(^{-1}\) corresponds to epitaxial monolayer graphene, peak positions around 1594 cm\(^{-1}\) are related to bilayer graphene after solid-melt exfoliation.
Fig. S3 Phonon dispersion of the 2D peak at different Laser energies deconvoluted by 4 Lorentzian curves (P\textsubscript{11}, P\textsubscript{12}, P\textsubscript{21}, P\textsubscript{22}) from Fig. S5c and f.
Fig. S4 Non-linear curve fitting of the 2D peak corresponding to bilayer graphene after solid-melt exfoliation showing a satisfying curve fit by using 4 Lorentzian curves as proven by a clearly reduced residual distribution.
Fig. S5 Raman mapping of epitaxial graphene sample after solid-melt exfoliation. False color mapping corresponds to the acquired Ga signal within the Raman measurements. Green colored areas indicate gallenene, whereas black colored areas prove its absence. Surrounding Raman spectra prove the absence of D peak ($\approx 1340$ cm$^{-1}$), evidencing no lattice defects in bilayer graphene in this investigated area after gallenene spreading as well as the removal of the buffer layer phonon bands.