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Growth of Zinc-Blende/Wurtzite Polytypic InP on Epitaxial Graphene

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Abstract: van der Waals epitaxy is an attractive alternative to direct heteroepitaxial growth of semiconductor materials where the forced coherency at the interface cannot sustain large differences in lattice parameters and thermal expansion coefficients between the substrate and the epilayer. In this work, we demonstrate the growth of monocrystalline InP on Ge and SiO₂/Si substrates using graphene as an interfacial layer. Micron-sized InP crystals were found to grow with interfaces of high crystalline quality. Depending on the growth conditions, these crystals coalesce to form continuous film-like structures. This coalescence is more pronounced on as-grown graphene layers as compared to transferred ones. Some InP crystals were found to possess a polytypic structure, consisting of zinc-blende and wurtzite phases. We demonstrate that the zinc-blende and wurtzite close packed structures form a type-II homojunction with well (barrier) width of about 10 nm. The optical properties, investigated using room temperature nanocathodoluminescence, indicated the signatures of the direct optical transitions at 1.34 eV across the gap of the zinc-blende phase and the indirect transitions at ~1.31 eV originating from the close packed phase. In addition to crystals, we also observed InP nanorods growing mainly on graphene transferred onto SiO₂/Si substrate. These nanorods showed optical transition across the gap of the wurtzite phase at ~1.42 eV. This demonstration of InP direct growth on graphene and the correlative study between the structure and optical properties pave the way to develop InP-graphene hybrid structures for potential applications in integrated photonic and optoelectronic devices.

Keywords: Indium Phosphide; Graphene; van der Waals heteroepitaxy; Polytypic crystal phase; Homojunctions; Optical emission
Besides its use in variety of emerging devices,\textsuperscript{1–3} graphene also provides an attractive platform to exploit van der Waals epitaxy to grow novel heterostructures and develop new functionalities.\textsuperscript{4–11} van der Waals epitaxy was first established by Koma in 1984 as an alternative route to conventional epitaxy with the growth of Se/Te and NbS\textsubscript{2}/MoS\textsubscript{2} heterostructures,\textsuperscript{12} and was later extended to the heteroepitaxial growth of a variety of inorganic\textsuperscript{13,14} and organic\textsuperscript{15,16} material systems, and potentially two-dimensional (2D) heterostructures.\textsuperscript{17,18} van der Waals epitaxy on any 2D layered material exploits the fact that the surface lacks dangling bonds. This means that the growing layer essentially floats over the van der Waals gap, forming a loosely interacting system. Compared to the strong interaction and forced coherency in conventional epitaxy (involving actual covalent/metallic bonds), the van der Waals process is suitable for the growth of strain-free and defect-free interfaces.

It is noteworthy that the growth of covalent semiconductors on a van der Waals material can be slightly different from the growth of layered materials in that the epilayer now has dangling bonds. Consequently, instead of floating over the van der Waals gap, the epilayer’s dangling bonds interact with the 2D layer with forces that might not be purely van der Waals in nature. This process is known as quasi van der Waals heteroepitaxy,\textsuperscript{4,5} which has been recently exploited to grow thin films\textsuperscript{9–11} and nanowires,\textsuperscript{6–8} otherwise unachievable by conventional heteroepitaxy. Based on this process, we demonstrate here the growth of InP crystals atop group IV substrates. Detailed investigations of the structural properties and luminescence from as-grown InP are presented. InP is a high performance III-V semiconductor with supreme light emitting properties and high carrier velocity with a wide range of applications in telecommunication, high speed optoelectronics and photovoltaic devices.\textsuperscript{19,20} This work shows that quasi van der Waals heteroepitaxy can be a plausible path for monolithic integration of high quality InP on a group IV semiconductor platform.
Graphene layers used in this work were grown on two different substrates, Ge(111) and Cu(111), using chemical vapor deposition (CVD). More details about the growth are provided in the Supplementary Information (SI). The layers grown on Cu(111) were subsequently transferred onto SiO$_2$/Si(111) before InP growth. Figure 1(a) shows the scanning electron microscope (SEM) image of as-grown graphene on Ge. The white particles are probably small SiO$_2$ contaminants from the quartz tube that was used for growth. The faint lines running through the images are wrinkles formed during post-growth cooling. The inset in Figure 1(a) shows a typical 10 × 10 μm$^2$ atomic force microscopy (AFM) image. The corresponding root mean squared roughness was found to be 1.6 nm. The graphene layers transferred onto SiO$_2$/Si substrate (not shown here) are less smooth and show more defects (wrinkles, grains of bi and multi-layered graphene) when compared to the graphene grown on Ge. The InP$_{Gr/Ge}$ (InP-on-graphene/Ge) and InP$_{Gr/SiO_2}$ (InP-on-graphene/SiO$_2$) samples were grown in a cold wall metal-organic chemical vapor deposition (MOCVD) reactor using trimethylindium (TMIn) and tertiarybutylphosphine (TBP) precursors at partial pressures of 1.98 and 15.8 mTorr (V/III ~80), respectively. H$_2$ was used as the carrier gas. The optimal growth temperature was 600°C while the total pressure of the reactor during the growth was held at 40 Torr. Prior to growth, the substrates were annealed in H$_2$ at 450°C for 30 min to desorb the impurities on the surface. The growth temperature and pressure were adjusted with a continuous TBP flow. The growth started with the introduction of TMIn into the growth chamber. The growth ended with the stoppage of TMIn flow, after which the reactor temperature was ramped down to 200°C in presence of TBP flow before unloading.

Figure 1(b)-(d) display a selected set of SEM images of the grown InP crystals, which were found to display a variety of shapes such as regular and irregular polygons (mostly hexagons and triangles) with sharp edges, and truncated pyramids bound by low index surface planes. This
morphology reflects the symmetry of the (111)-oriented growth surface. Depending on the growth time, the lateral size of the structures varies from ~30 nm to a few tens of microns and their heights from ~20 nm to ~1 µm. Table 1 in the SI summarizes the evolution of the morphology of the InP crystals grown as a function of the growth time. The recorded lateral growth rate after 1 min was found to be in the ~0.5 – 2.1 nm/s range. This rate increases drastically after an additional 2 min of the growth reaching ~4 – 13 nm/s, but it decreases slightly (~5 – 9 nm/s) for growth times above 3 min. Note that the observed morphology of the grown structures is common to both InP<sub>Gr</sub>/Ge and InP<sub>Gr</sub>/SiO<sub>2</sub>. However, under the same experimental conditions, the growth on graphene/Ge leads to higher density and faster lateral growth, favoring the coalescence and leading to continuous films of several tens of microns (Figure S1 (b)). The relatively limited growth on transferred graphene can be attributed to a higher density of defects as compared to as-grown graphene/Ge, which reduces surface diffusion and transport of atoms between nucleating islands thus suppressing the coalescence. In addition, nanorods were also observed but only for the InP<sub>Gr</sub>/SiO<sub>2</sub> samples (Figure S1 (a)). Similar one-dimensional growth on graphene was also recently reported for GaAs.<sup>9</sup>

A key process in growing a layer-by-layer InP thin film on graphene surface is the suppressed nucleation of sp<sup>3</sup> bonded semiconductor on sp<sup>2</sup> bonded 2D graphene.<sup>23</sup> Moreover, the low surface energy of pristine graphene ~50 mJ/m<sup>2</sup>,<sup>24</sup> is an order of magnitude lower than the surface energy value ~50 meV/Å<sup>2</sup> (~800 mJ/m<sup>2</sup>) reported for InP,<sup>25</sup> making the chances of InP wetting the graphene surface rather slim. The final shape of the InP crystals is therefore determined by the system’s attempts to lower its total energy by minimizing the InP-vacuum interface area. The high growth temperature, in addition to the fact that the graphene surface is chemically inert, should make the diffusion lengths of In and P atoms exceptionally large.
Therefore, the kinetic effects, like the migration rate of the adatoms on the graphene surface, exchange rate of atoms between neighboring crystals, and the rate at which the atoms bind to the graphene surface by quasi van der Waals forces all have a role to play in determining the growth rate and the morphology of the InP crystals. In the following, we focus on elucidating the basic properties of these InP/graphene hybrid structures.

Figure 2 (a) shows the micro-Raman spectra collected from a single InP\(_{\text{Gr/Ge}}\) crystal while (b) and (c) show those collected from InP\(_{\text{Gr/SiO}_2}\) crystals (details of Raman measurements are given in SI). The estimated lateral dimension of the crystals were \(\sim 2 - 3 \ \mu\text{m}\). The inset in each of the three figures highlights the phonon modes of interest. The measurements reveal that each TO and LO Raman mode in some InP crystals is composed of two distinct peaks, as in Figure 2 (a) and (b). This is more prominent for the LO mode than TO mode. This dual-peak is indicative of the folding of the Brillouin zone due to the presence of a zinc-blende/wurtzite polytypic structure. Although there has been several reports on zinc-blende and wurtzite polytypic\(^{26-28}\) as well as pure wurtzite\(^{29,30}\) InP nanowires, to the best of our knowledge, polytypism was never reported for III-V films and large structures. Note, however, that some structures (e.g., Figure 2 (c)) do not show the splitting of the Raman line which is indicative of the growth in the thermodynamically stable zinc-blende phase. Additionally, we have also highlighted Raman modes of the underlying graphene layer. Along with the G and the G’ bands, a broad D band at 1350 \(\pm 0.5 \ \text{cm}^{-1}\) of the underlying graphene layer is visible in Figure 2(a) and (c), showing that these crystals have nucleated at defect sites on the graphene layer. In general, defect sites on graphene, such as multilayer graphene patch edges and wrinkles, can be regarded as favorable nucleation sites. Indeed, during the graphene-assisted quasi van der Waals heteroepitaxy of GaN and AlN, the crystals were found to nucleate preferentially at defect sites and graphene-coated step edges of the
underlying substrates.\textsuperscript{31} However, in Figure 2(b) we did not find any discernable graphene D band indicating that InP structures can also nucleate on defect-free graphene.

The observations in Raman spectra indicating the growth of both cubic zinc-blende and hexagonal wurtzite phases called for deeper investigations of their structure. Towards this end, high resolution transmission electron microscopy (HRTEM) and high angle annular dark field (HAADF) aberration corrected atomic resolution scanning transmission electron microscopy (STEM) investigations were carried out. The technical details of the HRTEM and HAADF-STEM measurements are provided in the SI section. Figure 3(a) displays the cross-sectional HRTEM image of a typical $\text{InP}_{\text{Gr}}/\text{SiO}_2$ crystal, as shown by the SEM image. The HRTEM image cross-section was recorded from the InP [110] zone-axis. The inset in Figure 3(a) shows a HRTEM close-up image of the InP/graphene/SiO\textsubscript{2} interfaces. The crystal can be seen to have grown over graphene, which consists of at least a few layers. The presence of the multilayer graphene in between the InP and the SiO\textsubscript{2} is also confirmed by the electron energy loss spectroscopy compositional images, as shown in Figure S3. As it is seen in Figure 3(b), the graphene layer is not flat all throughout, but rather it follows the roughness of the SiO\textsubscript{2} underneath. Figure 3(c) shows the polytypic structure with the zinc-blende and the wurtzite regions and intermediate polytypes as a result of the presence of twin boundaries.\textsuperscript{32} This agrees with the Raman measurements described earlier. The width of the zinc-blende and wurtzite layers in Figure 3(a) is about 10 nm. The twin boundaries are present not only along the (111) horizontal planes parallel to the graphene/SiO\textsubscript{2} interface, but also along the \{111\} family of planes that are inclined to the graphene/SiO\textsubscript{2} interface. It is worth mentioning here that the observed crystal phase switching occurs naturally and could not be controlled or altered even by changing the growth parameters. We performed a control experiment by changing the growth temperature to 500 °C from 600 °C
and TMIn partial pressures to 2.15 mTorr from 1.98 mTorr. Subsequent Raman analysis like the ones done in Figure 2, indicated the presence of both polytypic as well as pure zinc-blende InP crystals on the same sample. Such observations differ from recent observations in metalorganic vapor phase epitaxial growth of InP nanowires\(^ {33}\) and InGaAs microstructures,\(^ {34}\) where the crystal phase can be controlled by the growth conditions. This indicates that rather than the global parameters like the reactor temperature, partial pressure of the precursors, and the V/III ratio, the local factors such as the local stress on the graphene layer, the presence of defects atop the graphene layer, and the density of nucleation sites, diffusion and exchange rate of atoms around a growing crystal may all have an influence on the crystal phase.

Further insights into the nature of graphene enabled quasi van der Waals heteroepitaxy of InP were obtained by employing the geometric phase analysis (GPA)\(^ {35}\) which provided the local lattice dilatation and rotation of the InP crystals. The dilatation and rotation of the three different atomic planes, the (\(\bar{1}11\)), (\(\bar{1}1\bar{1}\)), and (00\(\bar{2}\)) were measured along the two twin-related [110] and [\(\bar{1}\bar{1}0\)] zone axes as shown in the fast Fourier transform (within the black rectangular box (bottom) alongside Figure 3d). The configuration allows us to selectively map two different zinc-blend orientations related by twin boundaries along the growth plane depending on the chosen Bragg spots. The reference for the dilatation maps was chosen by the GPA software, by setting the mean interplanar distance to zero and then rescaling the local lattice dilatation with respect to this mean interplanar distance. The same was done for the rotation maps. Figure 3(d) shows the dilatation and rotation maps of the (\(\bar{1}11\)) planes along [110] and [\(\bar{1}\bar{1}0\)] zone axes of the InP crystal. The dilatation and rotation maps cover the whole height of the InP crystal shown within the black rectangular box (top). The dilatation and rotation maps of the (\(\bar{1}1\bar{1}\)) and (00\(\bar{2}\)) planes are shown in Figure S4(a) of SI. Going by the color bars shown atop the dilatation and rotation maps in Figure
3(d) and (e), the green-brown region corresponds to ~0% strain and ~0º rotation. We notice no meaningful variation in the InP lattice parameters across the whole height of the structure signifying that the crystal is predominantly relaxed, however with two prominent exceptions. First, the twin boundaries such as the ones along the oblique (1-11) planes starting at the base of the crystal (marked by white arrows in Figure 3(d)) appear strained, showing a local dilatation of the interplanar distances. Second, Figure 3(e) shows the dilatation and rotation maps of the (1-11) planes along [110] and [11-0] zone axes, zoomed in at the base of the InP crystal, at areas where the substrate and consequently the graphene layer is highly uneven (see atomic resolution HAADF STEM image alongside Figure 3(e), within the black rectangular box). We see hot spots in the dilatation and rotation maps (bright red-yellow, marked by white arrows in Figure 3(e)) which symbolized a significant variation in the lattice parameters (both strain and rotation). This is possibly due to the fact that the substrate surface is not perfectly flat, causing the nucleation of InP at different heights, whose lattice parameters do not match perfectly thereby generating strain and rotation of the lattice as they coalesce. The dilatation and rotation maps of the (1-11) and (002) planes, at the base of the InP crystal, are shown in Figure S4(b) of SI.

One of the straightforward benefits of the quasi van der Waals heteroepitaxy growth of III-V semiconductors on graphene is to effectively generate light on a graphene-platform.\textsuperscript{11,36} In order to achieve this ultimate goal of fabricating graphene-based devices with enhanced functionalities, the first most crucial step is to evaluate the basic optical properties of InP/graphene hybrid structures. With this objective in mind, we have performed room temperature hyperspectral nanoscale cathodoluminescent (CL) analysis on the InP\textsubscript{Gr}/Ge and InP\textsubscript{Gr}/SiO\textsubscript{2} crystals to investigate their optical properties. The details of the CL experiment are provided in the SI section. Theoretical calculations predict the edge of the conduction band and
the valence band of wurtzite InP to be higher by 129 meV and 45 meV respectively with respect to the zinc-blende InP. Polytypic InP therefore has a staggered type-II band alignment across the homojunctions, as shown schematically in Figure 4(a). At room temperature, the gap at the zinc-blende section is 1.34 eV while that at the wurtzite section is 1.42 eV. Three types of luminescent transitions are therefore expected in polytypic InP: first, across the 1.34 eV wide gap of a zinc-blende section (designated in Figure 4(a) in blue as $\alpha$ transition); second, across the 1.42 eV wide gap of a wurtzite section (designated in green as $\beta$ transition). Whenever there is a zinc-blende/wurtzite/zinc-blende closed packed structure such as the InP$_{Gr}$/SiO$_2$ crystal shown in the HRTEM image (Figure 3(c)), the band offset between the two phases makes the zinc-blende section an effective electron potential well (hole barrier) and the wurtzite section a hole potential well (electron barrier). Hence, a third type of transition from a localized level at the zinc-blende to a localized level at the wurtzite is also possible (designated in red as $\gamma$ transition).

Figure 4(c) and (d) shows the CL data collected from individual structures. False color RGB maps (in the wavelength range of 850 to 950 nm) of the crystal recorded during the CL measurement are shown in the insets of all the spectrum. It helps to visualize the differences in emission between different crystal and from position to position on a given crystal. The raw data was normalized with respect to the strongest peak and fitted with single or multiple Voigt line profile(s) to extract the peak position of the various transitions. In Figure 4(c) we clearly see the CL line corresponding to the $\alpha$ transition at 1.34 eV, indicating that the crystal has a pure zinc-blende phase. In Figure 4(d), we see the lines corresponding to the $\alpha$ and $\gamma$ transitions at 1.34 eV and 1.31 eV, respectively. Three observations could be made from Figure 4(c) and (d): 1) While the $\alpha$ transition is located exactly at the zinc-blende band gap energy, the $\gamma$ transition is located $\sim15 – 20$ meV above the band edge-to-edge transition energy (which should be at 1.34 eV –
0.045 eV = 1.295 eV); 2) We do not see any β transition at 1.42 eV; and 3) The strength of the γ transition is much weaker than the α transition. The reason for the first observation might be twofold. Firstly, due to quantum confinement, the electron (hole) bound states in the potential well is located above (below) the bottom (top) of the well. The narrower the well, the higher (lower) are the bound states, as shown schematically in Figure 4(b). Secondly, the electron and the hole being spatially separated into the zinc-blende and wurtzite parts of the closed packed structure, create a space charge. This induces an electric field which can lead to additional splitting of the electron and hole energy levels via the Stark effect. The reason for the second observation could be either that the electrons were not excited across the wurtzite band gap or that after being excited across the wurtzite gap they relaxed non-radiatively to the lower energy zinc-blende conduction band by emission of optical phonons.

To explain the third observation, we need to refer to Figure 4(b). While α and β transitions are spatially direct, the γ transitions are indirect (diagonal). The probability of these transitions depends on the overlap of the electron and hole wave functions. As can be seen in the schematics, while the wave functions overlap strongly in real space in the zinc-blende (or the wurtzite) part, the overlap is weak in the zinc-blende/wurtzite/zinc-blende close packed part. The height of the electron and hole potential wells being finite, the wave functions do not vanish at the respective well boundaries resulting in the leakage of the electron and the hole wave functions into the adjacent wurtzite and zinc-blende section respectively. Thus, it is only the tail of the electron wave function that overlaps with the hole wave function and vice versa. This makes the probability of a γ transitions much less than that of α or β transitions, explaining its weaker intensity.

Figure S5 in SI, shows other examples of CL spectra collected from individual InP$_{Gr/Ge}$ structures. The data show that the strength of the γ transition is comparable to the α transition.
This is possibly due to the fact, that the volume of the zinc-blende/wurtzite/zinc-blende close packed part is significantly larger than the pure zinc-blende part. The signal strength being proportional to the excitation volume might explain the strong \( \gamma \) signal, despite its low transitional probability. In Figure S5(b) and (c), we see a peak at around \( 1.20 \) eV, in addition to the \( \alpha \) and \( \gamma \) transitions. The origin of this peak could be due luminescence from any unintentionally introduced impurity. For CL measurements on InP\(_{Gr/SiO_2}\), we found many crystals which share the common features observed in InP\(_{Gr/Ge}\). Some crystals again show only \( \alpha \) transitions, an \( \alpha \) (\( \alpha \) and \( \gamma \)) transitions along with a transition line due to impurity (results are not shown here). Figure 4(e) and (f) highlight features that are peculiar to light emission from InP\(_{Gr/SiO_2}\) structures. Figure 4(e) shows the CL spectra collected from nanorods (indicated by the red arrows in the false color RGB map). The nanowires show a single spectral line at \( \sim 1.42 \) eV (RGB map of the nanowires are blueish), corresponding to a \( \beta \) transition. The absence of any \( \alpha \) and/or \( \gamma \) transitions highlights the fact that the nanorods grew in a pure wurtzite phase. At the nanoscale, the surface energy becomes a crucial parameter determining the total free energy change for crystal formation. Since the wurtzite phase has a lower surface energy compared to the zinc-blende phase\(^{41}\), the high surface to volume ratio of the nanorods causes the wurtzite phase to become favorable. Figure 4(f) shows the CL spectra collected from two different InP\(_{Gr/SiO_2}\) crystals. The one on top in Figure 4(f) shows a prominent peak due to the \( \alpha \) transition, a small peak due to the \( \gamma \) transition in addition to a peak originating from impurity. The spectra at that at the bottom show only the \( \alpha \) transition while the peak due to the \( \gamma \) transition is virtually non-existent. However, one key feature of the spectra is that the \( \alpha \) transitions from both crystals are blue-shifted from the zinc-blende band gap value (RGB map of the crystals are light-green). Although the exact reason for this is not very clear at the moment, something similar was observed from RT photoluminescence measurements on polytypic
InP nanowires with rotational twins perpendicular to the growth axis, wherein the transition was recorded at 903 nm (1.38 eV). The reason for this was attributed to the intimate mixture of the zinc-blende and the wurtzite domains within a nanowire. Additionally, we observe in the bottom spectra in Figure 4(f), that the RGB map (inset) at the top-left corner is slightly bluish-green while the rest of the crystal is greenish. We took a line scan from the corner (marked in red as ‘1’ in the RGB scan) to the center (marked in red as ‘2’ in the RGB scan) of the crystal. We found that indeed the CL peak shifts down continuously, by about 20 meV (12.5 nm), as we move from the edge to the center. The average over CL intensity over the whole crystal has a peak at 1.376 eV. The reason for this shift in the CL peak might perhaps come from some edge-induced band bending.

Additionally, we observed a distinctive difference in the directional properties of the light emitted from different crystals. For example, Figure 4 (c) and (d) show luminescence from two different InP_{Gr/Ge} crystals but their RGB scans (inset) are markedly different. Note that the wavelength range in all the RGB scans were kept the same. In Figure 4 (c), the light is seen to be emitted only from the edges of the crystal whereas the top flat (111) surface is completely dark. Note, that Figure S5(c) in the SI also shows a similar RGB scan with light emission only from the edges of a InP_{Gr/Ge} crystal. In Figure 4 (d) the light is emitted not only from the edges of the crystal but also from the top surface (except right at the dead-center of the crystal which appears dark in the RGB scan). One possible explanation for this observation might come from the nature in which the angular distribution (in both polar direction (θ) and azimuthal (ϕ) direction) of the emitted light from different crystals couple to the far field detector. To investigate the same, we performed angle-resolved CL measurements but they did not provide any conclusive evidence as to why certain crystals show light emission only from their edges. Therefore, we do not discuss them in
detail here, rather in Figure S6 and its associated discussion in the SI we simply highlight some key findings of the angle-resolved measurements. The angle resolved CL maps collected from two different crystals and their corresponding zenith cross-cut are shown in Figure S6. The maps indicate that the \((\theta, \phi)\) distribution of the emitted light can indeed be very different from one crystal to the other. We also found the \((\theta, \phi)\) distribution of the emitted light to vary on the same structure, depending on the exact location at which the crystal was excited (not shown here). Notwithstanding these new insights, the angle resolved CL investigations did not unravel the exact origin of the observed emission from some InP structures where only the edges where found to emit light (as in Figure 4 (c) and S5 (c)). This behavior might be attributed to several factors such as the location and the orientation of the wurtzite domains, the close-packed structure relative to the top flat (111) facet, and the local optical density of states at the excitation point. Further systematic studies targeting each one of these factors are needed to elucidate this peculiar behavior of light emission from InP/graphene hybrid structures.

In summary, we have demonstrated the growth of micron-sized InP crystals using quasi van der Waals heteroepitaxy process on two different substrates, SiO\(_2\)/Si and Ge, using graphene as an interfacial layer. Raman spectroscopy showed that while some of the crystals grew in the thermodynamically stable zinc-blende phase, others exhibit a polytypic nature, showing a nanoscale natural crystal phase switching between the zinc-blende and the wurtzite phases. The phase switching was also confirmed by the HRTEM and HAADF STEM analyses. The possible reason for this polytypic growth could be related to the ultrafast diffusion of adatoms on graphene surface that may lower the barrier for the nucleation of the thermodynamically less stable wurtzite phase. We also found no meaningful variation in the lattice parameter of the InP crystal except at the twin boundaries and the InP/graphene interface, the latter originating due to the roughness
and variation of height of the underneath substrate. The CL analysis of the crystals showed a prominent peak due to carrier recombination in the zinc-blende section as well as the zinc-blende/wurtzite/zinc-blende closed packed structure within the crystals. The intensity of the CL line from the latter was in general but not always much weaker compared to the former. The CL analysis of the nanorods showed the prominent signature of carrier recombination across the wurtzite gap. Additionally, the RGB scans associated with CL spectra and the angle-resolved CL maps suggested that there could be a significant difference in the way light is emitted out of a crystal. However, the exact origin of this difference remains unclear. The described correlative studies between the structural and optical properties of the crystals provide an alternative route to combine the high performance of the InP semiconductors on a group IV based platform. Additionally, the flexibility and transferability, which come from using graphene as a buffer layer, lay the groundwork to develop a novel class of hybrid optoelectronic and photonic devices.

**Conflict of interest**

TC is employee of DELMIC BV, a startup company that develops and sells the SPARC cathodoluminescence system that was used in this work.

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