Realization of Vertically Aligned, Ultrahigh Aspect Ratio InAsSb Nanowires on Graphite

E. A. Anyebe, † A. M. Sanchez, ‡ S. Hindmarsh, ‡ X. Chen, § J. Shao, § M. K. Rajpalke, † T. D. Veal, † B. J. Robinson, † O. Kolosov, † F. Anderson, † R. Sundaram, † Z. M. Wang, # V. Falko, † and Q. Zhuang*, †

†Physics Department, Lancaster University, Lancaster LA1 4YB, U.K.
‡Department of Physics, Warwick University, Coventry CV4 7AL, U.K.
§National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, 200083 Shanghai, People’s Republic of China
∥Stephenson Institute for Renewable Energy and Department of Physics, University of Liverpool, Liverpool L69 7ZF, U.K.
⊥Oxford Instruments, Tubney Woods, Abingdon OX13 5QX, U.K.
#Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, People’s Republic of China

ABSTRACT: The monolithic integration of InAs$_{1-x}$Sb$_x$ semiconductor nanowires on graphitic substrates holds enormous promise for cost-effective, high-performance, and flexible devices in optoelectronics and high-speed electronics. However, the growth of InAs$_{1-x}$Sb$_x$ nanowires with high aspect ratio essential for device applications is extremely challenging due to Sb-induced suppression of axial growth and enhancement in radial growth. We report the realization of high quality, vertically aligned, nontapered and ultrahigh aspect ratio InAs$_{1-x}$Sb$_x$ nanowires with Sb composition ($x_{Sb}$%) up to $\sim$12% grown by indium-droplet assisted molecular beam epitaxy on graphite substrate. Low temperature photoluminescence measurements show that the InAs$_{1-x}$Sb$_x$ nanowires exhibit bright band-to-band related emission with a distinct redshift as a function of Sb composition providing further confirmation of successful Sb incorporation in as-grown nanowires. This study reveals that the graphite substrate is a more favorable platform for InAs$_{1-x}$Sb$_x$ nanowires that could lead to hybrid heterostructures possessing potential device applications in optoelectronics.

KEYWORDS: InAsSb, nanowire, self-catalyzed, molecular beam epitaxy, van der Waals, aspect ratio, graphite, graphene

InAs$_{1-x}$Sb$_x$ materials have long been recognized as highly suitable candidates for infrared photodetectors since it possess the narrowest bandgap energy among all the III–V semiconductors (0.1 eV at room temperature). Therefore, the InAs$_{1-x}$Sb$_x$ tunable band gap would cover the two most important atmospheric infrared windows, i.e., 3–5 and 8–12 $\mu$m. This enables a number of important applications such as industrial and pollution monitoring (e.g., CO$_2$, CH$_4$, N$_2$O, O$_3$, and CO gases), surveillance, health, and security. InAs$_{1-x}$Sb$_x$ infrared photodetectors (PDs) have attracted enormous research interest as a potential alternative to current state-of-the-art CdHgTe-based detectors, which suffer from costly growth and processing, nonuniformity and toxicity concerns.

Semiconductor nanowires (NWs) offer the possibility to significantly improve the sensitivity of PDs owing to their ultrasensitivity, low power consumption, and fast response evidenced by the demonstration of highly sensitive NWs based detectors. Specifically, thin and long NWs, i.e., high aspect ratio (AR), would significantly improve the sensing characteristics of PDs due to their larger effective surfaces. Such NWs...
materials also enable investigation of other important material related properties such as spin–orbit coupling and quantum confinement.

In addition, the monolithic integration of high AR InAs1−xSbx NWs on graphitic substrates (GS) holds promise for the development of high performance, flexible, and cost-effective functional devices. In such hybrid architectures, the two-dimensional graphene substrate can function as an ideal electrode because of its high transparency, high conductance, and excellent chemical stability.12,13 Over the past few years, several graphene-based devices including light emitting diodes,14 transistors,15,16 solar cells,17,18 supercapacitor,18 nanogenerator,20 photodetector,21,22 and gas detector22 have been reported. Furthermore, GS are ideal platforms for NW growth via van der Waals (VDW) epitaxy due to the absence of dangling bonds.23−25 Binary InP and GaP,26 GaAs,26,27 and ZnO28,29 NWs have been demonstrated on GS. InAs NWs/GS hybrid structures is also been synthesized though was limited to Au-catalyzed molecular beam epitaxy (MBE)26 or self-catalyzed metal−organic vapor phase epitaxy (MOVPE).23−25 Recently, we reported the MBE growth of InAs NWs on GS,30 but the NWs exhibited a low AR and areal density. In addition, the growth of ternary compound alloys on GS has been focused on InGaAs alloys.17,25 To date, InAs1−xSbx NW growth has only been demonstrated on Si.31−33 However, these studies revealed that InAs1−xSbx NWs generally have a low AR due to the surfactant effect of antimony (Sb), which suppresses axial growth while promoting radial expansion.31,32,34

In this letter, we demonstrate for the first time, the self-catalyzed growth of ultrahigh AR InAs1−xSbx NWs on GS. Although the InAs1−xSbx NWs on the graphitic platform also show an expansion in radial dimension and suppression of axial growth with increased Sb content, we observed that the Sb-induced modifications in NWs geometry is dramatically less in comparison to that on Si. Through optimizing growth conditions, we successfully obtained InAs1−xSbx NWs with ultrahigh AR up to 100:1. The optical properties of InAsSb NWs with different Sb composition (up to xSb/(xSb + 12%) are also presented.

High AR InAs NWs were first realized on the GS at As-rich conditions by MBE for a growth duration of 60 min via an In-assisted growth technique35 (more details in Methods). Scanning electron microscope (SEM) image of the InAs NWs in Figure 1a reveals a uniform NW diameter along the entire length with no visible tapering (see inset). The NWs have an estimated length (LNW) of 2.58 ± 0.34 μm, diameter (Dnw) of 31.2 ± 6.6 nm and density of 8.09 × 108 cm−2 showing a high AR of ~83. This corresponds to over three times increase in NW AR compared to previously reported self-catalyzed MBE grown InAs NWs/graphite.30 This significant improvement is attributed to the well optimized growth conditions. The SEM image also reveals that the NWs grown on GS are vertically well-aligned with a high degree of size uniformity evidenced by the small standard deviation both in LNW and Dnw. This superior NWs morphology represents a considerable improvement in the geometry and density compared to that of previously reported Au26 and self-catalyzed MOCVD grown InAs NWs on GS23−25 with diameters in the range of ~40−87 nm and density of (2−7) × 106 cm−2. The high yield of vertically well-aligned InAs NWs (InAs[111][graphite[0001]) could be attributed to the nearly coherent in-plane lattice matching between InAs (110) and graphene (100).5,24,27 High resolution annular dark field (ADF) scanning transmission electron microscope (STEM) images (see Figure 1b) of an InAs/GS indicates that the NWs are composed of mixed zinc blende (ZB) and wurtzite (WZ)
InAs$_1$ subsequently converted into InAs in the presence of excess In droplets deposited in the graphitic substrate are (111) ZB/(0001) WZ planes produce the streaks in the diffraction pattern. This behavior is related to the lower surface energy of the WZ phase compared to the ZB phase, which results in a more stable WZ phase in NWs structures. Aiming to gain insight into the structure of the graphite–InAs NWs interface, a focused ion beam (FIB) specimen containing both NW on the graphitic substrate was analyzed. High resolution ADF-STEM images (see Figure 1c) demonstrated a small “seed” of material just underneath the NW into the graphitic substrate (which is brighter than the substrate and marked with a green circle in the image), i.e., it seems the NW is pinned to the substrate. EDX spectra were carried out in areas 1 and 2 (yellow areas in Figure 1d). The atomic composition areas 1 and 2 were 48% − As and 49% − In, respectively. Therefore, the “seed” is InAs, which originated during the initial growth stage; In droplets deposited in the graphitic substrate are subsequently converted into InAs in the presence of excess As. This seed acts as nucleation site to initiate NW growth.

In order to elucidate the conditions for realizing high AR InAs$_{1-x}$Sb$_x$ NWs, a series of samples were grown on GS by MBE. The growths were performed under moderately As-rich (M-As) conditions (samples A and B) and highly As-rich (H-As) conditions (sample C) (see Methods for growth details). The Sb composition ($x_{Sb(M)}$) in the NWs was controlled by varying the Sb fractional flux ($\Psi_{Sb}$) in the range of 1.64−2.93% [where $\Psi_{Sb}$ represents the ratio of Sb flux (\(\Psi_{Sb}\)) to the overall group V (\(\Psi_{As} + \Psi_{Sb}\)) fluxes]. X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX) measurements were used to determine the Sb composition in the InAs$_{1-x}$Sb$_x$ NWs. Figure 2 shows that two diffraction peaks are present in all samples. The one at 26.5° is indexed to graphite (002), and the other at a lower diffraction angle is associated with the (111) ZB InAs$_{1-x}$Sb$_x$. Compared to the InAs ZB (111) peak at 25.4°, the diffraction peak of (111) InAs$_{1-x}$Sb$_x$ NWs shifts to lower angles with increase of Sb composition. Based on an assumption of Vegard's law and full relaxation, the Sb composition ($x_{Sb(M)}$) was deduced to be 6.2%, 0.5%, and 3.1% for samples A−C, respectively. Due to the formation of parasitic islands during the growth (see Figure 1a), there is likelihood of contribution from the islands to the diffraction peaks in the XRD measurements. In order to confirm the presence of Sb in the NWs and determine the content more precisely, we performed EDX measurements in SEM on all the samples. To ensure validity and consistency of the measurements, several EDX measurements were taken, e.g., measured on the NWs from side (tilted 45°) along the NWs at different positions near the bottom and the tip as well as top view images. All of these measurements gave quite consistent values (see Figures S1 and S2 in Supporting Information for further details) and also close to the values deduced from XRD measurements (summarized in Table 1). These measurements confirm the presence of Sb in the NWs. To further verify Sb composition in the NWs as well as exclude any possibility of contributions from the parasitic islands, thickness of sample, the substrate and geometry such as tilt and detector position, and EDX measurements were also performed in TEM. Figure 3a,b shows the bright field images of typical InAs$_{1-x}$Sb$_x$ NWs (samples A and B, respectively). EDX spectra in TEM mode were taken along the length of the NWs. The measured Sb content in the samples A and B was ∼8% and ∼1%, respectively, with a slight variation along the NW length. Please note that we provided only two decimals for the resulting composition deduced from EDX. This is due to the unknown uncertainties of the nominal Clin−Lorimer $k$-factors used in the quantification calculation though the material thickness and its density are known reasonably well. The EDX spectra in EDX-TEM also show that the Sb compositions closely correlate with the EDX-SEM and XRD data, which implies the Sb incorporation is quite close in both NW growth and parasitic growth. We therefore adopt the average of EDX deduced data for this work with the Sb content determined from the average Sb composition taken along the different positions of the tilted NWs and top view images. It is worth noting that the X-ray deduced compositions are generally less than that determined from EDX measurements. This disparity could be attributed to the modification of the phases in the presence of Sb as previously observed.

Figure 4a,b shows the representative low and high magnification SEM images of InAs$_{1-x}$Sb$_x$ NWs grown on GS within the M-As regime. The NWs exhibit a 6-fold symmetry

**Figure 2.** X-ray diffraction patterns of InAs$_{1-x}$Sb$_x$ nanowires grown on graphite with different Sb compositions.

| Sample | Substrate | Series | Growth time (min) | Sb fractional flux ($\Psi_{Sb}$) | Sb content (%) (XRD) | Sb content (%) (EDX) |
|--------|-----------|--------|-------------------|---------------------------------|---------------------|---------------------|
| A      | graphite  | M-As   | 120               | 1.64                            | 6.2                 | 8                   |
| B      | graphite  | M-As   | 120               | 2.93                            | 0.5                 | 1                   |
| C      | graphite  | H-As   | 120               | 1.82                            | 3.1                 | 5                   |
| D      | silicon   | M-As   | 120               | 2.93                            | 0.5                 | 2                   |
| E      | silicon   | M-As   | 120               | 4.68                            | 11.1                | 7                   |
| F      | silicon   | H-As   | 120               | 1.82                            | 4.7                 | 4                   |

*Moderately As-rich conditions. **Highly As-rich conditions.
Analysis of the SEM images reveals that the NWs are ∼72−101 nm thick and ∼1.7−2.3 μm long. No In droplet is present at the NW tip, which can be attributed to their consumption under excess As flux. Figure 4c shows the SEM image of sample C, grown in the H-As regime (i.e., higher As-flux), while the In-flux and ΨR (1.82%) are comparable to that of sample A (Table 1). It reveals a high yield of NWs with an average density of 1.46 × 10⁸ cm⁻², typical length of ∼4.70 ± 0.89 μm, and diameter of ∼46.0 ± 6.9 nm. In addition, this optimal growth condition led to a high yield of vertically well-aligned and nontapered NWs (highly uniform diameter along the entire length). The side-view close-up image of a representative NW (inset Figure 4c) shows no diameter broadening or wire bending along the entire length despite the high AR. This is a distinct signature of morphologically superior NWs. Figure 5 reveals the strong dependence of the NWs geometry, aspect ratio, and density on Sb composition (xSb(%)). The NWs length (LNW) and diameter (DNW) as a function of xSb(%) is plotted in Figure 5a. A total NW population of ∼150 NWs was utilized for the calculation of NWs density while employing Gaussian approximations; >70% of measurable NWs were used for the determination of the error bars of the NWs geometry (LNW and DNW), which is expressed as the deviation from the mean geometry of normally distributed NWs. The data for the InAs NWs on graphite is also shown for comparison. The monotonic decrease in LNW and expansion of DNW with increasing Sb content within the M-As regime clearly indicates a suppression of axial NWs growth with a corresponding enhancement in radial growth. This is consistent with previous reports and is attributed to Sb surfactant effect. In sharp contrast, the H-As conditions promote axial NW growth evidenced by the large LNW and small DNW as exhibited in sample C. The observed trend is more evident in Figure 5b, which shows the dependence of NW AR on xSb(%). As can be seen, the samples grown within the M-As regime show a monotonic decrease in AR with a maximum of ∼32 for sample B (xSb(%) = 1%). Such a behavior is attributed to the Sb-induced modifications in thermodynamic and kinetic processes. The InAs NWs are relatively longer and thinner than all the M-AR samples with an AR of ∼83, even though
they were grown for only 60 min (half the duration of the M-AR samples). Intriguingly, NWs with exceptionally high AR (≈102) were obtained in sample C, which was grown within the H-As regime (over 3× the maximum AR of the M-As samples) despite the relatively high Sb content ($x_{Sb(%) = 5\%}$). It has been previously reported$^{32,41}$ that trace Sb concentration induces an increase in radial growth with a suppression of axial growth leading to the growth of short and thick NWs. This trend is clearly different from the observations reported in a previous study,$^{31}$ which demonstrated that the introduction of small amount of Sb (4%) induces a significant increase in radial growth. Consequently, the observed high AR of sample C can be correlated to an enhancement in axial growth resulting from the availability of excess As flux. To further explore the effect of As-rich conditions on the AR of droplet-assisted NWs on GS, a series of InAs NWs samples were grown on graphite at various As-fluxes (see Methods for growth details). At a relatively low As-flux, no NW growth was obtained; however, an increase in As-flux (As-rich conditions) resulted in the growth of NWs. Further increase in As-flux promoted axial NW growth, which is evidenced by the significant increase in AR (see Figure S4 in Supporting Information). This indicates that As-rich condition favors the growth of high AR NWs on the GS which is similar to a previous report.$^{42}$ It has recently been demonstrated that the elongation rate of self-catalyzed NWs is highly dependent on the group V flux.$^{43,44}$ As a result, the radial NW growth promoted at moderately As-rich condition due to the surfactant effect of Sb can be inhibited by employing significantly high As flux. Also, Sb incorporation has a significant effect on NW density (Figure 5c). Compared to the high yield of InAs NWs, the density of InAs$_{1-x}$Sb$_x$ NWs was significantly reduced with an increase in Sb composition ($x_{Sb(%) = 5\%}$). This is attributed to the reduced NW nucleation probability due to the enhanced lateral growth$^{32}$ and the increased nucleation barrier, which results from a lowering of the interfacial energy with increased Sb content.$^{26}$ An evaluation of sample A (Figure 4a) reveals that the resulting NWs are nonuniform in both length and diameter. This suggests the onset of the evolution from 3D NWs to 2D thin film in the presence of 8% Sb. Sb incorporation in InAs generally favors the growth of a dominant 2D film due to a kinetically inhibited In adatom mobility$^{31}$ in the presence of Sb. Surfactant Sb is known to delay 2D → 3D growth mode transition while promoting layer by layer growth,$^{45}$ as demonstrated by Copel et al.$^{46}$ They showed that trace Sb content could induce a change in growth mode. To further validate our inference on the suppression of radial growth by As-rich conditions and to elucidate the superiority of the graphitic substrate for InAsSb NW growth, we evaluated the morphology of InAs$_{1-x}$Sb$_x$ NWs grown on bare Si(111) substrates at identical conditions to that on the GS (see Methods for growth details). Samples D and F on Si were grown with identical conditions as samples B and C (on GS), respectively, and sample E was grown under M-AR conditions with a high Sb fractional flux ($\Psi_R$) of 4.68. The Sb compositions were determined by EDX-SEM analysis (see Figure S3 in Supporting Information) to be 2%, 7%, and 4% in samples D, E, and F, respectively (Table 1). It is a surprise that the Sb incorporation ([$x_{Sb(%) = 5\%}$]) in the NWs scales inversely with the Sb fractional flux ($\Psi_R$) for $\Psi_R \leq 2.93$ on both Si and GS. Incidentally, this corresponds to the region within which NW growth was realized. For instance, sample B contain less Sb in the NWs despite the higher Sb flux compared with that of Sample A. This abnormal behavior could be associated with the Sb surfactant effect,$^{31}$ which is more pronounced in NW structures owing to their high surface to volume ratio. The higher $\Psi_R$ increases Sb surface coverage, results in increased Sb segregation and surface site blocking,$^{47,48}$ and thereby reduces the incorporation probability and composition of Sb in the NWs. A disproportionate Sb incorporation has previously been reported in the literature.$^{51,48}$ A similar behavior was demonstrated by Sourribes et al.$^{33}$ It was shown that the Sb composition monotonically increases with an increase in $\Psi_R$ in the range of 0–1.31%, while a slight increase in $\Psi_R$ (1.53%) led to a decline in Sb composition. However, it is worth noting that this behavior could be highly dependent on growth conditions and growth mode. For instance, the 2D growth of sample E resulted in higher Sb composition at increased $\Psi_R$ ($\Psi_R = 4.68$, $x_{Sb(%) = 7\%}$). The SEM images of as-grown InAs$_{1-x}$Sb$_x$ NWs on Si are shown in Figure S5 in Supporting Information. We observed

Figure 5. Measured InAs$_{1-x}$Sb$_x$ nanowire (a) length ($l_{NW}$) and diameter ($D_{NW}$); (b) aspect ratio and (c) number density and fraction of vertically aligned nanowires (%) as a function of Sb content ($x_{Sb(%) = 5\%}$) for moderately As-rich (M-As) and highly As-rich (H-As) samples. Sample names are also shown.
that an increase of Sb composition reduced the NW areal density for the NWs grown on Si (Figure 6). This dependence is indicative of Sb-induced quenching of NWs nucleation probability, which is similar to the observation in the NWs grown on GS. The presence of 7% Sb completely suppressed NW growth on Si (sample E). The plot of $L_{NW}$ as a function of $x_{Sb}$ (Figure 6) indicates a suppression of axial NW growth with increased $x_{Sb}$ for the samples grown within the M-As regime, which is consistent with the InAs$_{1-x}$Sb$_{x}$/GS samples. However, the NWs on GS are relatively longer than the ones on Si. At $x_{Sb}$ of 2.9%, the NWs on Si are only about 1.17 μm long (sample D, $x_{Sb}$(%) = 2%), while the corresponding NWs on GS (sample B) is almost double that length (∼2.33 μm). Similarly, for the samples grown with excess As-flux (H-As), at $x_{Sb}$ of 1.82%, NWs of ∼3.89 μm long were obtained on Si (sample F, $x_{Sb}$(%) = 4%) while ∼4.70 μm long NWs were obtained on GS (sample C, $x_{Sb}$(%) = 5%). This suggests that GS favors the growth of high AR NWs in comparison to that on Si possibly due to differences in adatom mobility. It has been shown theoretically and experimentally that the axial growth rate of MBE grown NWs is strongly dependent on adatom diffusion from the substrate to the droplet but not so strongly on adsorption on the drop.\textsuperscript{59,60} We recently demonstrated that the elongation rate of In-catalyzed NWs is significantly influenced by adatom diffusion from the side facets to the droplet.\textsuperscript{59,61,63} Consequently, any slight variation in adatom diffusion length owing to the changes along the substrate would translate to significant variations in axial growth rate and hence the NWs aspect ratio. In addition, among the NW samples on Si, sample F exhibits the highest AR (inset of Figure 6) although it has a relatively high Sb content ($x_{Sb}$(%) = 4%), which is again associated with the H-As condition that favors axial growth. This corroborates the observed dependence of NWs AR on As-flux and further confirms that highly As-rich conditions are essential for the suppression of radial growth in favor of enhanced axial growth in InAs$_{1-x}$Sb$_{x}$ NWs.

We also investigated the percentage of vertically aligned NWs grown on GS as a function of $x_{Sb}$ (Figure 5c). A low yield of vertically aligned NWs was obtained in sample B ($x_{Sb}$(%) = 1%) (see also the SEM image in Figure 4b) compared to the other InAs$_{1-x}$Sb$_{x}$ NWs samples (A and C) on graphite. To clarify the effect of the GS on the vertical directionality of NWs, we evaluated the morphology of sample D grown on Si at identical growth conditions to sample B. The SEM image indicates a high yield (∼95%) of vertically well-aligned NWs was realized on Si (refer to Figure S5a in Supporting Information). This suggests that the observed high density of randomly aligned NWs in sample B (on GS) could be attributed to the influence of the graphitic substrate. A close evaluation of the SEM image for sample B reveals that the unaligned NWs grew on the islands (see Figure 4b signified by arrows). Mohseni et al.\textsuperscript{25} observed a similar growth of nonvertical NWs on islands, which themselves preferentially grew along graphene line defects. It is likely that the rough sections on the GS promote the formation of large and dense InAs islands, which in turn mitigates the epitaxial growth of NWs on the GS and is in agreement with previous report.\textsuperscript{24}

Finally, in order to investigate the optical properties of InAsSb NWs/graphite, low temperature (10 K) photoluminescence (PL) was performed on a Fourier transform infrared (FTIR) spectrometer (Bruker Vertex 80v), which runs in the step-scan mode. A Kr$^+$-ion laser operating at a 647 nm spectral line was used to excite the samples. PL signal was detected by a liquid–nitrogen cooled HgCdTe detector with a lock-in amplifier. The detailed setup has been reported previously.\textsuperscript{51} Figure 7 shows the PL spectra of three samples with Sb composition of 0, ∼2%, and ∼12%. The sample of pure InAs NWs exhibits three emission peaks centered at ∼0.389, 0.415, and 0.434 eV, which have been associated with impurity-related transition, type II alignment transition, and band-to-band (BtB) transition, respectively, due to the polytypic nature of the NWs, e.g., the phase mixture of WZ and ZB.\textsuperscript{52} The sample of InAs$_{0.88}$Sb$_{0.12}$ NWs shows one emission at 0.406 eV with a weak shoulder emission peaked at 0.442 eV, which originate from BtB transition of ZB and WZ InAsSb, respectively. The sample of InAs$_{0.88}$Sb$_{0.12}$ NWs shows one emission at 0.324 eV, which gives bandgap energy of 0.400 and 0.324 eV, which are very close to the dominant peak emission present in the samples of InAs$_{0.98}$Sb$_{0.02}$ NWs (0.406 eV) and InAs$_{0.88}$Sb$_{0.12}$ NWs (0.323 eV), respectively. These spectra clearly show the redshift of the emission related to Sb incorporation due to bandgap shrinkage. It should be noted that type II related emission could possibly...
contribute to the dominant emission from the InAs$_{1-x}$Sb$_x$ samples due to the polytypic nature of the NWs. Detailed PL measurements at varied temperature and laser excitation power are ongoing to clarify other possible origins and to understand the optical evolution with Sb incorporation. The shoulder emission at 0.442 eV in the sample of InAs$_{0.98}$Sb$_{0.02}$ NWs could be associated with the BtB transition of WZ InAsSb, which has higher bandgap energy than that of ZB InAs$_{0.98}$Sb$_{0.02}$ NWs by 42 meV. This is in good agreement with previous studies of InAs NWs (46 meV). A previous report indicates that the WZ phase InAs NWs has larger bandgap energy in comparison with that of ZB InAs,53−55 at a predicted value of 40−66 meV.54,56,57 This was confirmed with an experimentally observed value of ∼0.46 eV.55 In addition, these PL spectra also show an increase of line width with the increase of Sb incorporation.

In summary, we have demonstrated for the first time, the self-catalyzed growth of dense, vertically aligned, and high aspect ratio InAs$_{1-x}$Sb$_x$ NWs on graphite substrate by molecular beam epitaxy. Sb-induced radial NWs expansion coupled with axial growth suppression results in the growth of short and thick NWs at moderately As-rich conditions. Such modification in morphology is significantly reduced by growing NWs on GS platform. We also demonstrated that highly As-rich condition enables the realization of ultrahigh aspect ratio NWs. Photoluminescence measurements demonstrate a distinct redshift in the band-to-band related emission with increasing Sb composition confirming the presence of Sb in as-grown nanowires. Our study elucidates a promising technique for the monolithic integration of InAs$_{1-x}$Sb$_x$ NWs on graphitic thin films for high-performance, flexible, and cost-effective optoelectronic devices.

Methods. InAs$_{1-x}$Sb$_x$ NWs samples were grown on graphite substrate by MBE. The graphitic films were mechanically exfoliated from highly oriented pyrolytic graphite (HOPG) and transferred onto Si(111) substrates and subsequently loaded into the system and outgassed for over 2 h. Prior to NW growth, the substrates were activated by optimal indium (In) droplets35 with a diameter of ∼70 nm to facilitate NW nucleation. The substrates were then warmed up to 420−500 °C while keeping the In source closed followed by the simultaneous introduction of all growth precursors using a fixed In beam equivalent pressure (BEP). Moderately As-rich (M-As) samples (A and B) were grown with an As-flux in the range of 10$^{-6}$ mbar, while sample C was grown in a highly As-rich (H-As) regime using a higher As-flux in the range of 10$^{-5}$ mbar. A series of M-As (D and E) and H-As (F) InAsSb NW samples were also grown on bare Si(111) substrates at identical conditions to the corresponding InAs$_{1-x}$Sb$_x$ NWs/graphite samples. Prior to NW growth, the Si substrates were chemically cleaned by 12% HF solutions for 4 min to remove the native oxide and quickly loaded into the MBE system to avoid reoxidation, then thermally outgassed. The InAs NW sample was deposited on the graphite at M-As conditions for a growth duration of 60 min and temperatures of 420−500 °C. In order to investigate the influence of As-flux on NW aspect ratio, a set of InAs NWs samples were grown on graphite at a constant temperature for 20 min growth duration. The In BEP was fixed, while the As-flux was varied in the range of (2−8) × 10$^{-6}$ mbar. The surface morphology of as-grown NWs was investigated by FEI XL30 SFEG scanning electron microscope (SEM) with an energy-dispersive X-ray spectroscopy (EDX) for composition determination. X-ray diffraction (XRD) measurements were performed on a Philips PW 1720. High-resolution transmission electron microscope (HRTEM) and annular dark field (ADF) scanning transmission electron microscopy (STEM) images were taken in a JEOL-JEM 2100 and ARM-200F microscopes both working at 200 kV. Focused ion beam (FIB) specimens were prepared using a JIB4500 to investigate the interface with the substrate. EDX measurements were carried out with an Oxford Instrument X-MAX 80.

# ASSOCIATED CONTENT

5 Supporting Information

Further details of SEM images of InAs nanowires on graphite and InAs$_{1-x}$Sb$_x$ NWs on Si (111) as well as energy dispersive X-ray spectroscopy (EDX) spectra of InAs$_{1-x}$Sb$_x$ NWs on graphite and Si (111) substrates. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b00411.

# AUTHOR INFORMATION

Corresponding Authors

*E-mail: q.zhuang@lancaster.ac.uk.
*E-mail: zhmwang@gmail.com.

Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

The authors would like to thank the EPSRC Lancaster Impact Acceleration Account and Gas Sensing Solutions for their financial support.

# REFERENCES

(1) Vurgaftman, I.; Meyer, J. R.; Ram-Mohan, L. R. J. Appl. Phys. 2001, 89, 5815−5875.
(2) Thelander, C.; Caroff, P.; Plissard, S.; Dick, K. A. Appl. Phys. Lett. 2012, 100, 232105.
(3) Yen, M. Y.; People, R.; Wecht, K. W.; Cho, A. Y. Appl. Phys. Lett. 1988, 52, 489−491.
(4) Borg, B. M.; Dick, K. A.; Eymery, J.; Wernersson, L.-E. Appl. Phys. Lett. 2011, 98, 113104.
(5) Rogalski, A. Prog. Quantum Electron. 2003, 27, 59−210.
(6) Pea, M.; Ercolani, D.; Li, A.; Gemmi, M.; Rossi, F.; Beltram, F.; Sorba, L. J. Cryst. Growth 2013, 366, 8−14.
(7) Chen, X.; Wong, C. K. Y.; Yuan, C. A.; Zhang, G. Sens. Actuators, B 2013, 177, 178−195.
(8) Liao, L.; Lu, H. B.; Shuai, M.; Li, J. C.; Liu, Y. L.; Liu, C.; Shen, Z. X.; Yu, T. Nanotechnology 2008, 19, 175501.
(9) Guo, J.; Zhang, J.; Zhu, M.; Ju, D.; Xu, H.; Cao, B. Sens. Actuators, B 2014, 199, 339−345.
(10) Liao, L.; Lu, H. B.; Li, J. C.; He, H.; Wang, D. F.; Fu, D. J.; Liu, C.; Zhang, W. F. J. Phys. Chem. C 2007, 111, 1900−1903.
