Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

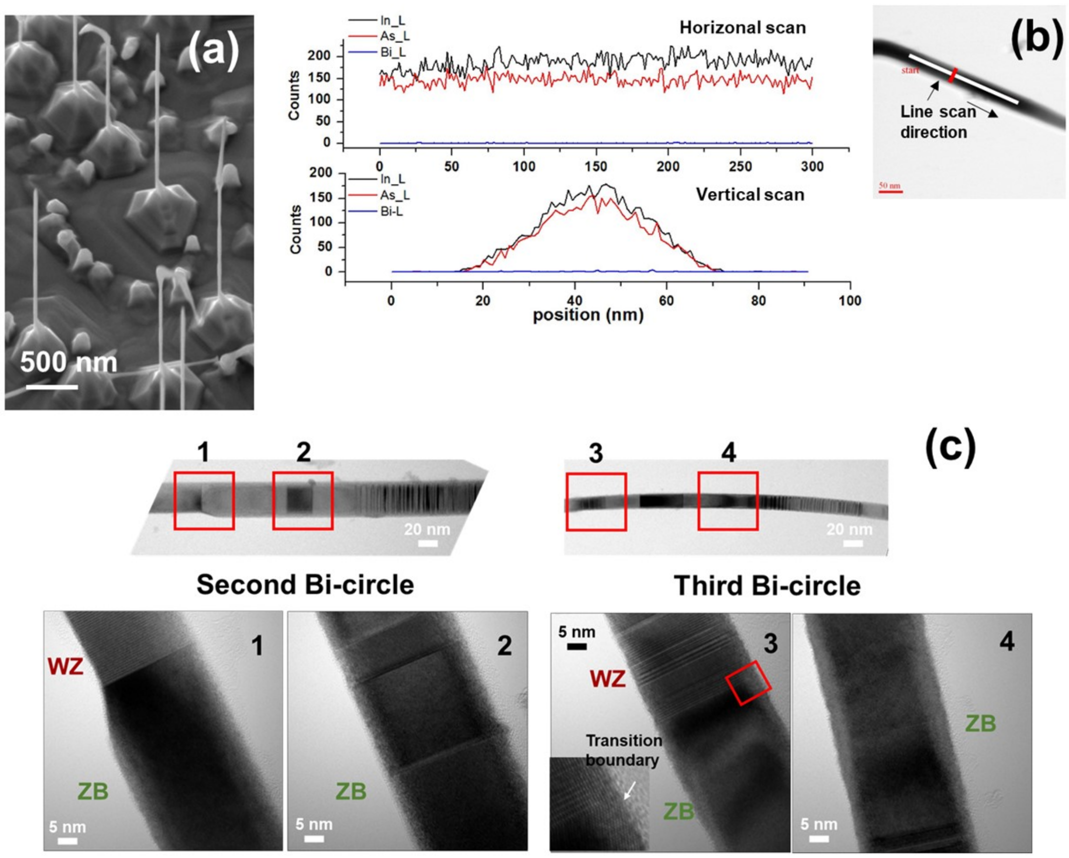

Fig. S1 (a) SEM image of InAs nanowires with a 30° tilted view. (b) TEM-EDX line scan along and pedicular to the growth direction (c) TEM images of the second and third circle of the nanowire. The 1 to 4 images are zoomed-in TEM images corresponds to the area marked with numbers 1 to 4 and red boxes.

The SEM images shows under low and interval Bi supply, the InAs nanowire remains vertical growth. To reveal the Bi incorporation condition, two line-scans are conducted alongside and pedicular to the nanowire growth direction. No obvious Bi signal is found in both scans as shown in figure S1 (b). This is due to the low Bi coverage rate that the Bi is mainly functioned as surfactant rather than incorporating into the nanowire. In figure S1 (c) shows the typical WZ to ZB transitions in the second and third cycles of Bi influenced growth. In the image marked 3, a clear boundary could be seen between the WZ to ZB phases.

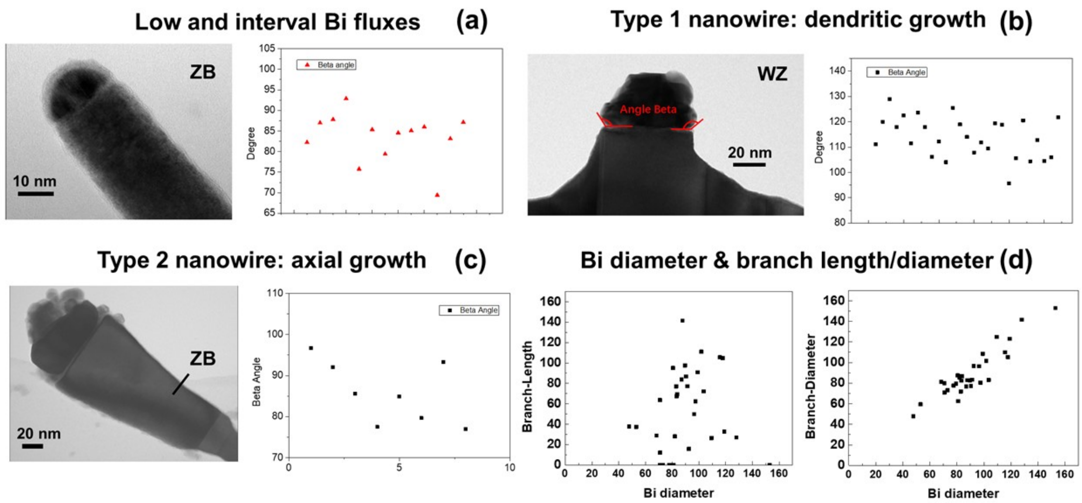

Fig. S2 (a-c) The contacting angles measured between the liquid catalyst and the nanowire top surface. (d) The dependence of Bi catalyst diameter with the length and diameter of the nanobranches.

The contacting angles of the Bi-mediated nanowires are shown in figure S2. For nanowire with low and interval Bi introduction, the contacting angle was among the range of 75°to 97° with the average contacting angle of 85°. This data range corresponds well with the theory of Panciera *et al.*[1] that WZ was formed between the angle of 100° to 125°, ZB would be formed beyond that range. For type 1 dendritic growth demonstrating WZ phase, the contacting angle was between 104°to 128°, averaged at 113°. A slight deviation beyond 125° for the maximum angle (128°) could be due to measurement error. For type 2 axial grown nanowire, the contacting angle was between 70°to 92°, averaged at 85°. Figure S2 (d) shows the dependence of Bi catalyst diameter and length/diameter of the nanobranches in type 1 nanowire. We found most of the nanobranches are short that the average length is 53 nm ranged from 0 to 141 nm. And no clear relationship is found between the length of the nanobranches with the diameter of Bi catalyst. In contrast, the diameter of the nanobranches are directly correlated with the diameter of the Bi catalyst that the branch diameter increase linearly with increasing Bi droplet diameter. This fits well with the theory of VLS growth that the diameter of the nanowire is decided by the catalyst itself.

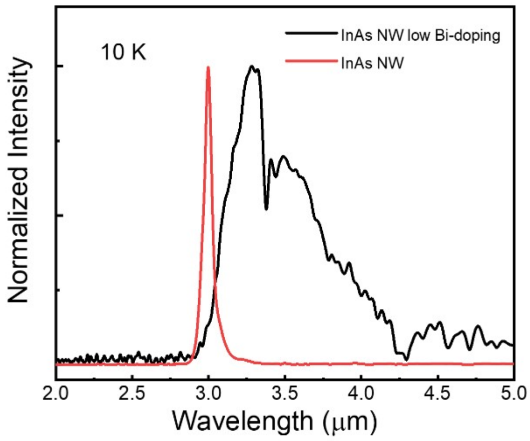

Fig. S3 PL spectrum of InAs nanowire (NW) and InAs NW with low Bi-doping.

We have characterized the PL spectra of InAsBi alloys with a nominal doping level of Bi, where the Bi content is considered around or less than 1%. For the PL measurement, we adopted the step-scan Fourier transform infrared (FTIR) spectroscopy method[2], which is renowned for its enhanced sensitivity and resolution in the mid- to far-infrared spectral regions. Specifically, we utilized a Bruker IFS 66v/S FTIR spectrometer, operating in step-scan mode, to precisely modulate the pump beam with a mechanical chopper and to detect the resultant PL signals via a liquid-nitrogen cooled HgCdTe detector. The step-scan technique's ability to maintain a fixed optical path difference during data acquisition allows for the acquisition of PL spectra with minimized system response interference and improved signal integrity[3].

Previous literature has reported that a 1% Bi incorporation in InAs can result in a bandgap reduction of 55 meV[4]. In our study, the PL peak of pure InAs is observed at 3.00 μm (0.414 eV). Upon Bi doping, we identified two distinct emission peaks: the first at 3.29 μm (0.378 eV) and the second at 3.51 μm (0.354 eV). The shift for the first peak corresponds to a reduction of 36 meV, which is consistent with the presence of less than 1% Bi in the alloy, as per the reported rate of bandgap reduction of 55 meV per Bi percent. The second peak exhibits a shift of 60 meV, which aligns closely with the expected change for approximately 1% Bi incorporation. These observations suggest that even at sub-percent levels, Bi has a significant impact on the band structure of InAs, with the potential to induce multiple emission peaks that are indicative of complex electronic transitions within the alloy. The distinct shifts in the PL peaks underscore the sensitivity of the bandgap to the Bi concentration and highlight the intricate interplay between alloy composition and optoelectronic properties.

In terms of the high Bi-containing InAsBi material, we would like to clarify the experimental challenges faced. The calculated bandgap of 0.038 eV (wavelength beyond 32 μm) of our material places it within the far-infrared region. This range is acknowledged for the inherent difficulties associated with PL measurements, particularly beyond 4 μm[3]. The robust thermal background and diminished photodetectivity, have made it extremely difficult to perform conventional PL measurements on our nanoscale material. We are actively seeking alternative approaches, such as employing more sophisticated detection techniques and advanced spectral resolution methods, to address these challenges. We anticipate that these efforts will enable us to present PL data in subsequent research.

Reference:

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