

## Supplementary information

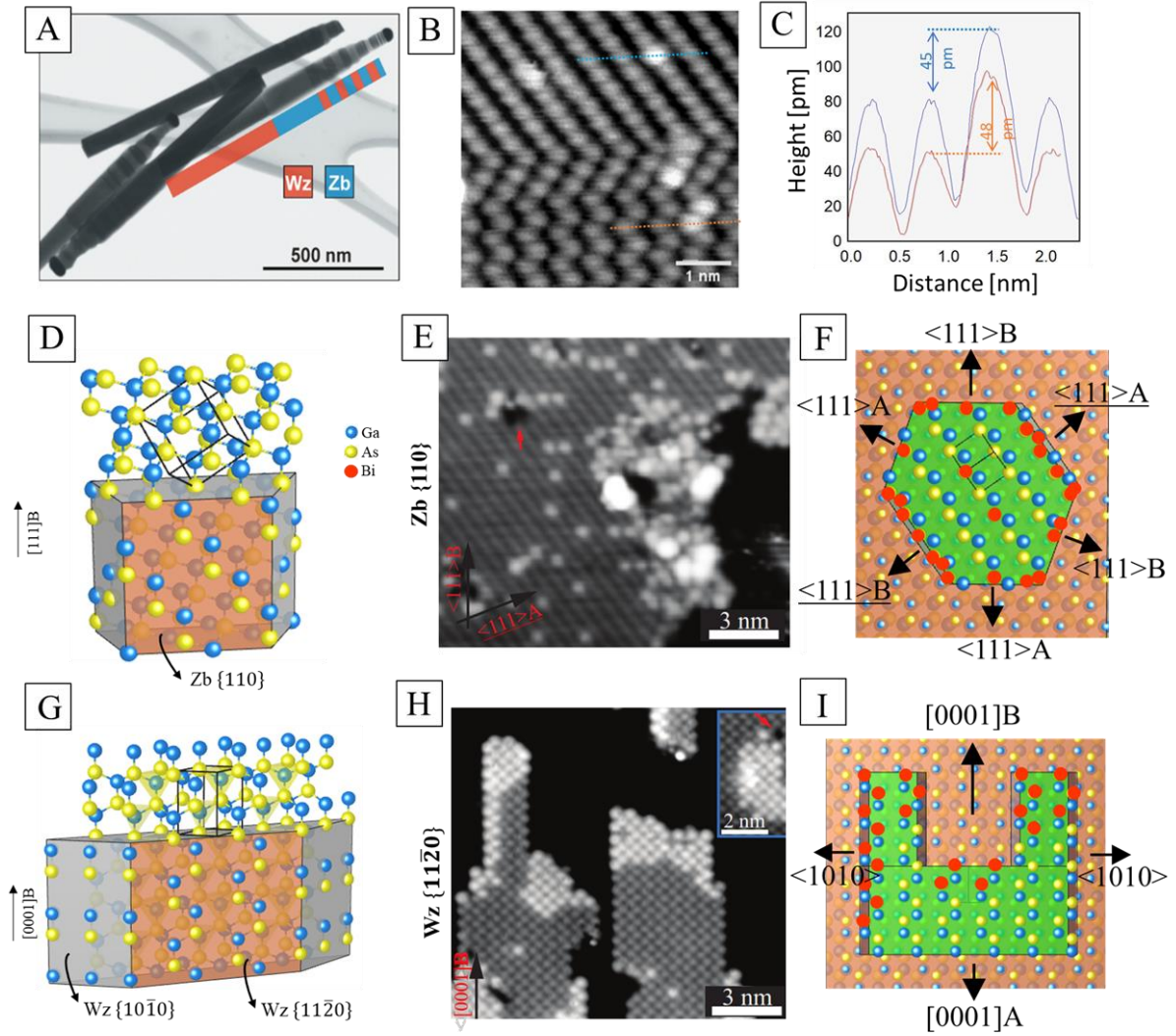


Figure 1. Bi incorporates into the surface layer of GaAs NWs. (A) Scanning electron microscopy image in transmission mode with crystal phase contrast of GaAs NWs, after transferring onto a suitable sample holder. Brighter and darker contrast corresponds to Zb and Wz, respectively, as confirmed previously by transmission electron microscopy. (B) A zoom-in filled state STM image of the Wz/Zb interface between Wz  $\{11\bar{2}0\}$ - (bottom) and Zb  $\{110\}$ - (top) type facet, showing the group-V atoms. The brighter dot-like protrusions are Bi incorporation sites, which match well with the As lattice sites. Line scan along the blue (orange) line in (C), showing the height of the protruded atom in Zb (Wz) segment, which is far less than an atomic radius. The many small bright protrusions correspond to Bi atoms. (D), (E) and (F) show an STM image of the Zb  $\{110\}$ -type surface and the corresponding 3D and 2D models. The green area in (F) represents the topmost layer of GaAs based on top of the second layer (orange area). For better illustration, the topmost layer has different types of step edges formed on surface. As can be seen, Bi atoms (red dots) incorporate via vacancies and atomic step edges which are facing  $\langle 111 \rangle A/B$  directions. The direction indexes with red underline in (F) present the projections of  $\langle 111 \rangle$ -type directions in  $\{110\}$  plane. (G), (H) and (I) show an atomically resolved STM image of the  $\{11\bar{2}0\}$ -type surface and the corresponding 3D and 2D model. The inset in (H) indicates a 2D GaBi island near a vacancy in the middle of a flat terrace. In the green topmost layer in (I), Bi enters the surface via vacancies and atomic step edges which are facing the  $[0001]B$  growth direction. Red arrows in (E) and (H) point at atomic vacancies. In (D) (F) (G) and (I), blue (yellow/red) spheres depict Ga (As/Bi) atoms. STM images were obtained at (B)  $V_T = -4.4$  V,  $I_T = 75$  pA.  $V_T = -4.4$  V,  $I_T = 100$  pA for (E) and (H). See also Yi Liu et al., Nature Commun. (submitted, 2021)