Supporting Information

Optical and Photodetector Properties of Stripe-Like InS Crystal

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InS

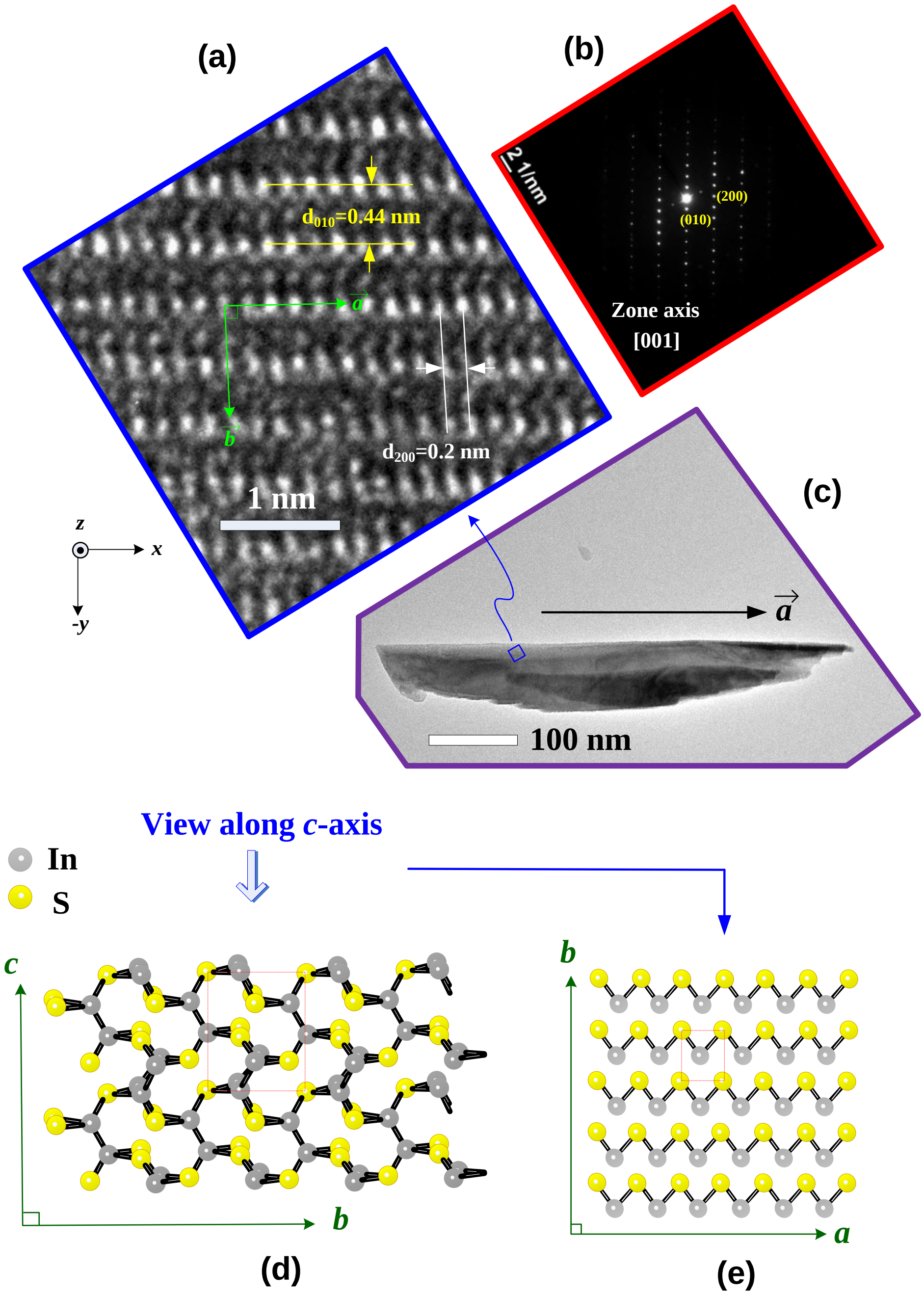
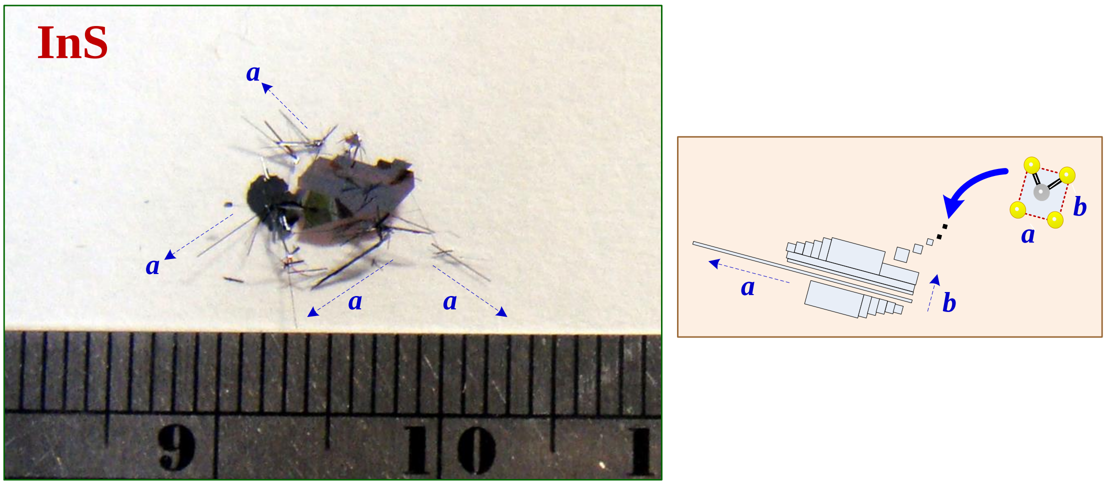
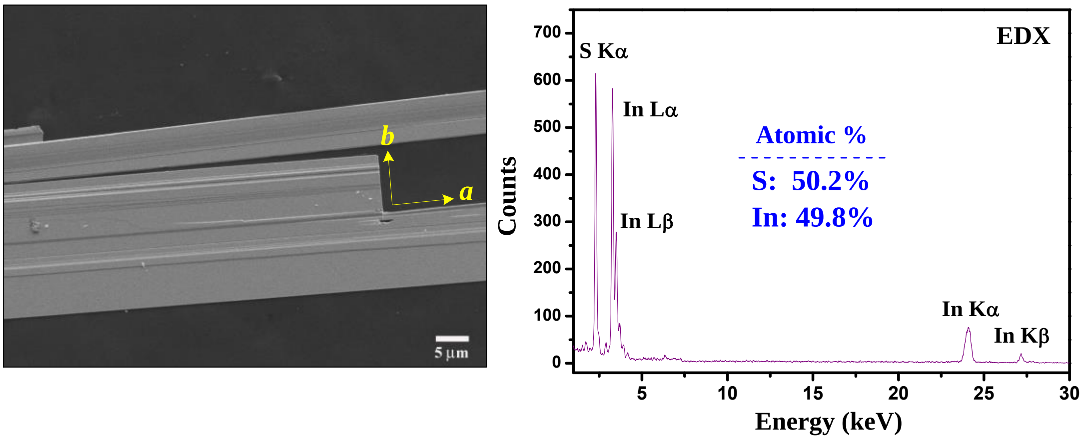


Fig. S1. (a) HRTEM image and (b) SAED pattern of a stripe-like nanoflake in (c) for a *c*-plane InS grown by physical vapor transport method. An orthorhombic lattice is clearly shown and the longest edge of the plate is along *a* axis. (d) The representative scheme of atomic arrangement in network form of orthorhombic InS. (e) The atomic sites and HRTEM image of the stripe-like InS viewing along *c* axis. The atomic arrangements show similar pattern, and which is consisted of fundamental In-S bond units that constructed and connected orthogonally.



(a)



(b)

Fig. S2. (a) Crystal morphology of the as-grown InS that includes needle, stripe, and layer like outline. The needle and stripe like InS crystals are extension along *a* axis. The large-area layer shows dark red and transparent to verify its band-edge energy. The right inset depicts the construction of nano needle, stripe, ribbon and layered orthorhombic InS from fundamental In-S bond units. (b) SEM image and EDX result of the InS microstripes. They verify orthogonality and stoichiometry of the as-grown InS nano (micro) stripes.

Figures S1(a) and 1(b) respectively show the HRTEM image as well as selective-area-electron-diffraction (SAED) pattern in a stripe-like nanoribbon displayed in Fig. S1(c) grown by PVT. The zone axis of the electron beam of the TEM images is along <001>. The clear atomic sites in Fig. S1(a) as well as obvious dot pattern in SAED image in Fig. 1(b) indicate high crystalline quality of the as-grown InS nanoflake. As shown in Fig. S1(a), the angle between *a* and *b* axes (green lines) are 90°, which reveals orthogonal and orthorhombic structure of the InS. The lattice spacing in Fig. 1(a) verifies that the lattice constants of orthorhombic InS are $a \approx 0.4$ nm (i.e. $d_{200}=0.2$ nm) and $b \approx 0.44$ nm, respectively. The *a* axis consists of the connection of zigzag chain of indium-sulfur atoms, which is the longest edge of the InS nanoribbon as displayed in Fig. S1(c). The great ionic character (ionicity) of InS that relative to the other InSe, GaS and GaSe monochalcogenides may destabilize the usual hexagonal-layer structure and becomes a network-connection structure in the orthorhombic InS.[17] The atomic arrangement of the lowest-energy network form (i.e. high-temperature phase) [9] of the S-In-In-S units with sharing corner style in InS is depicted in Fig. S1(d). A sharing-corner connection to the fundamental S-In-In-S units instead of van der Waals gap of the hexagonal layer stacking, represents for the network form of the orthorhombic InS along *c* axis. The *c* plane (*a*-*b* surface) viewed along *c* axis is depicted in Fig. S1(e). Essentially the *c* plane was formed by many top layer In-S zigzag bond units that arranged horizontally and vertically along the *a* and *b* axes.

To further understand crystallographic construction of the network InS, larger and long-range-order as-grown crystals are prepared and their crystal morphologies are displayed in the left part in Fig. S2(a). The outline shapes of the InS reveal needle, stripe, and layer-like styles that may consist of small to a larger-area crystal construction. Especially, the larger area and layer like InS shows dark red and transparent, which can be evident in Fig. S2(a). The result indicates the band gap of the InS crystal is near red-light wavelength portion.[13] The thin-plate type morphology of InS also identifies a 2D layer-like character of the monosulfide. The right part in Fig. S2(a) shows the representative scheme of building in orthorhombic InS from the basic In-S bond unit as derived in Fig. S1(e). Initially, the nearly square-shape In-S units (i.e. $a\approx0.4$ nm and $b\approx0.44$ nm) can be connected or merged together along either *a*-, *b*- or both axes to form a needle, stripe, rectangular, square-like, or polygon *c*-plane as indicated in the right side of Fig. S2(a). The binding force along *a* axis (zigzag chain) is larger than that along *b* axis, which can be verified from many of as-grown stripe and ribbon-like InS crystals were formed alongside *a* axis in Fig. S2(a). The various widths of small stripe-like InS crystals are ranged from ~tens nm to tens μm. The stripe-like outline and orthorhombic structure of the network InS can also be observed and verified by scanning electron microscope (SEM) image of InS as displayed in Fig. S2(b). The axial direction of the *c*-plane micro- and nano- stripes is along *a* axis, which may be the strongest bonding-force orientation of the InS. The angle between *a* and *b* axes is 90°. The right part in Fig. S2(b) shows the energy-dispersive X-ray (EDX) spectrum of the as-grown InS, which shows approximately 1:1 (In:S) stoichiometric content for the InS micro- and nano-stripe. The network InS structure has an orthorhombic lattice with a crystal symmetry of space group D_{2h}^{12}.[18, 19]

Supporting Information Reference:

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