Electronic Supplementary Information (ESI)

Atomistic study of the alloying behavior of crystalline $SnSe_{1-x}S_x$

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Average alloying degree for S atoms

Some areas in the boundary of SnSe and SnS local phases might have ambiguity in identifying the positions of S atoms. So, the alloying degree for S atoms is averaged from several images where S atomic positions are differently chosen at the same region. In spite of some ambiguity, we find that the alloying degree J for S atoms are still close to 60% regardless of S contents.

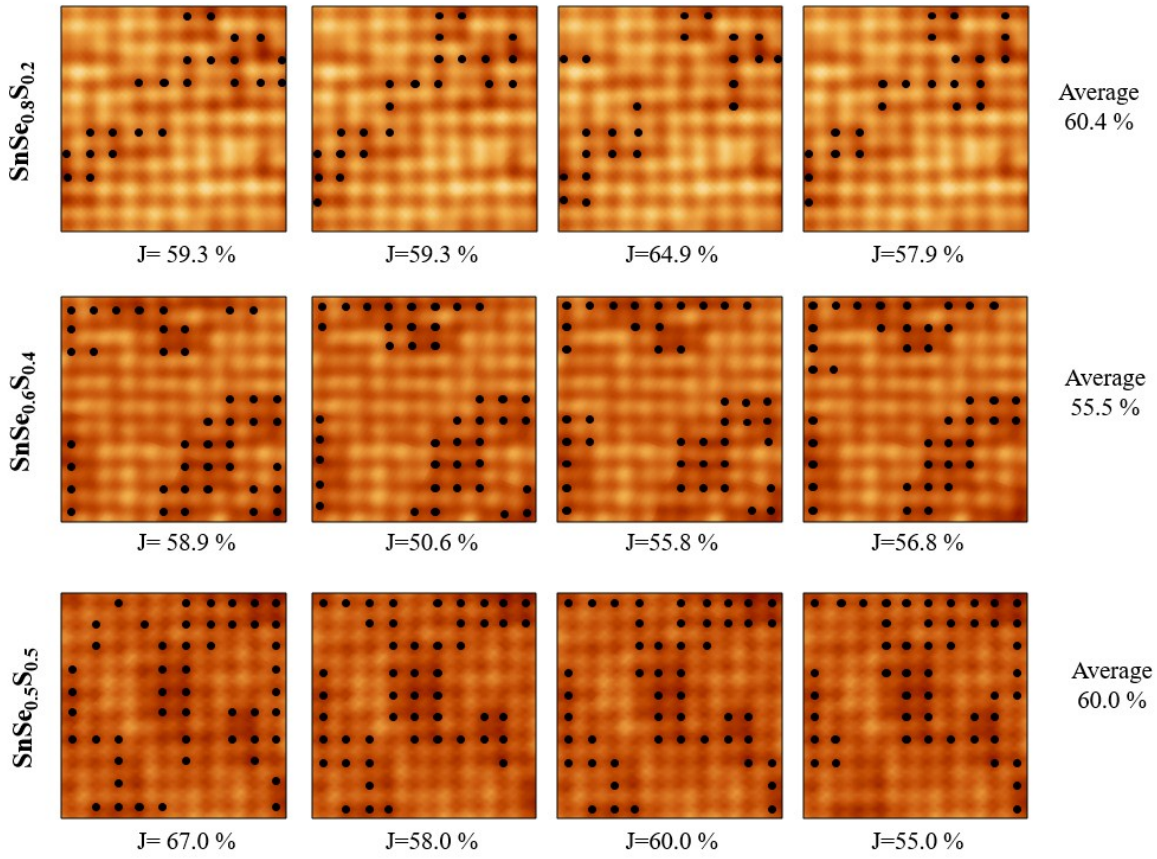

Fig. S1 S atomic positions are differently chosen from the same image, and then the alloying degree for S atoms is calculated.

Comparison of lattice constants: Theory vs. Experiment

Both experimental results and DFT calculations show that lattice constants of $SnSe_{1-x}S_x$ alloys change gradually with S content (x). This suggests that Vegard's law can be applied for this alloy system. Theoretical lattice constants are in good agreement with experimental results within 3%.

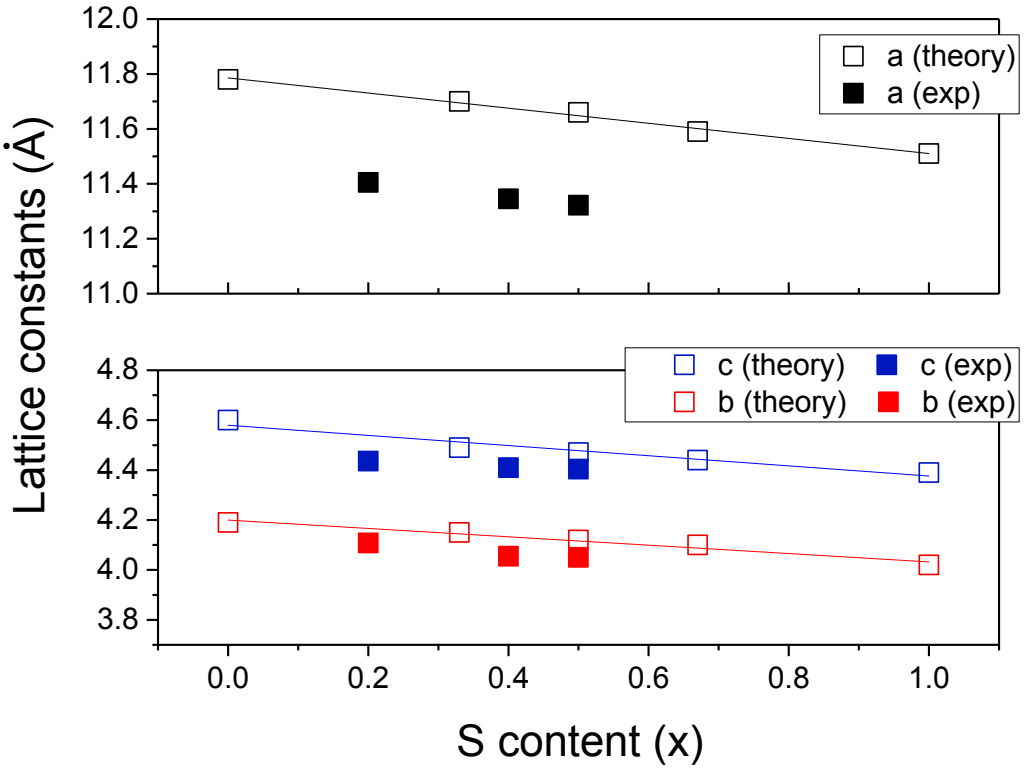

Fig. S2 Comparison of lattice constants: Theory vs. Experiment.

More examples of STM topographic images of $SnSe_{1-x}S_x$

We confirmed that STM images obtained from different locations show very consistent topographic features. Also, general topographic features didn't change after cleaving many layers. The dark areas in the top panel images were mapped with a red color in the bottom panel images by subtracting ideal lattices with uniform intensity

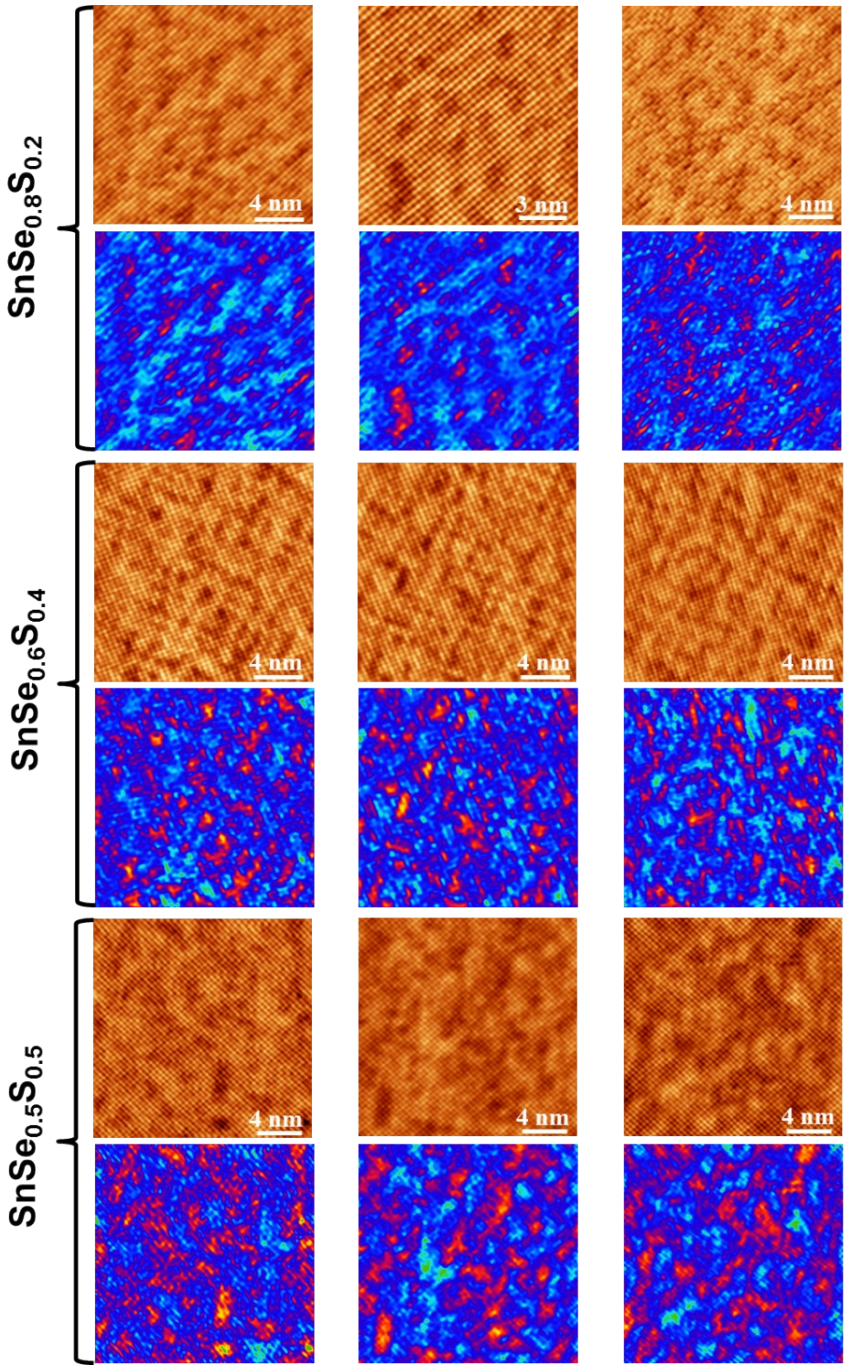

Fig. S3 STM topographic images of $SnSe_{1-x}S_x$.

Phase diagram of $SnSe_{1-x}S_x$ alloy

To estimate the phase diagram of $SnSe_{1-x}S_x$ alloy, the mixing Helmholtz free energy (ΔF_{mix}) is calculated from the DFT mixing energy results. According to the regular-solution model, ΔF_{mix} is described as $\Delta F_{mix} = \Delta E_{mix} - \Delta S_{mix} T$, where ΔE_{mix}, ΔS_{mix}, and T represent the mixing energy, mixing entropy, and temperature, respectively. The mixing energy at various compositions were fitted by a second-order polynomial $\Delta E_{mix} = \Omega x(1-x)$ based on the quasi-chemical model, where Ω is called interaction energy. The mixing entropy is evaluated by $\Delta S_{mix} = -R[x\, lnx + (1-x)\ln(1-x)]$. Thus, the mixing Helmholtz free energy can be written as $\Delta F_{mix} = \Omega x(1-x) + RT[x\, lnx + (1-x)\ln(1-x)]$. The binodal solubility curve (blue) and the spinodal decomposition curve (red) for $SnSe_{1-x}S_x$ alloy are obtained from $\frac{\partial F_{mix}}{\partial x} = 0$ and $\frac{\partial^2 F_{mix}}{\partial x^2} = 0$, which are calculated by $RT[\, lnx - \ln(1-x)] + (1-2x)\Omega = 0$ and $RT - 2x(1-x)\Omega = 0$ as shown below. Ω and critical temperature T_c are estimated to be about 20 meV and 520 K, respectively.

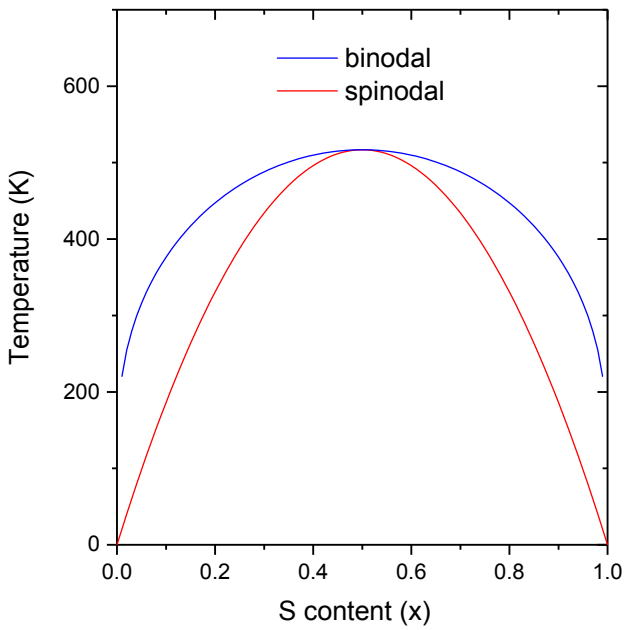

Fig. S4 Phase diagram of $SnSe_{1-x}S_x$ alloy

From our growth condition, the temperature of power ampoules was gradually increased to 960 ^{0}C

and slowly cooled (1 ^{0}C/h) from 960 ^{0}C to 600 ^{0}C, then rapidly cooled (20 ^{0}C/h) from 600 ^{0}C to room temperature. Therefore, the solid solution phase of $SnSe_{1-x}S_x$ alloy is formed from 960 ^{0}C to 600 ^{0}C, which is indeed consistent with the calculated phase diagram of $SnSe_{1-x}S_x$ alloy.