SUPPORTING INFORMATION

Chemical Intercalation of Zero-Valent Metals into 2D Layered Bi_2Se_3 Nanoribbons

Kristie J. Koski[1], Colin D. Wessells[1], Bryan W. Reed[2], Judy J. Cha[1], Desheng Kong[1], Yi Cui[1,3]

[1]Department of Materials Science & Engineering, Stanford University, Stanford, California 94305, USA

[2]Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550, USA

[3]Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA

Transmission Electron Microscopy

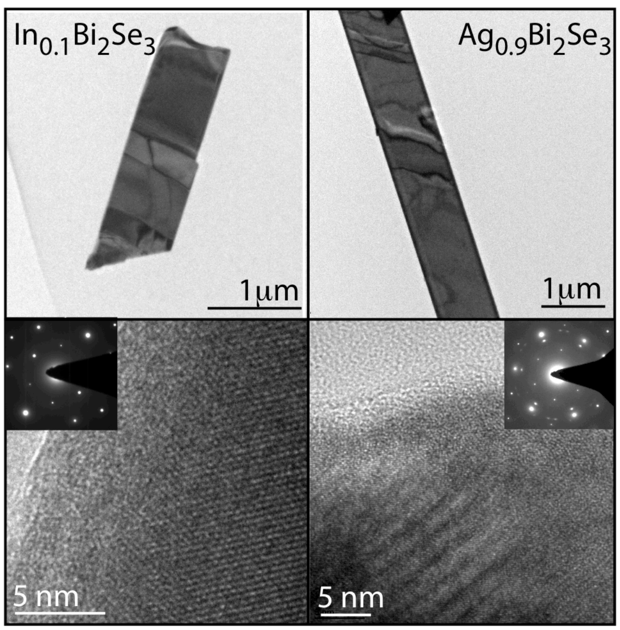

Figure 1S: Supplemental high-resolution TEM images of silver and indium-intercalated Bi_2Se_3 nanoribbons further demonstrate that no secondary phases and no metal precipitates or particles are observed. Electron diffraction of intercalated nanoribbons shows no polycrystalline rings confirming no precipitates or adsorbates on the surface of the nanoribbons. Nanoribbon lengths and morphology are not destroyed nor altered with intercalation. A characteristic superlattice pattern and associated stripe phase of the charge density wave is observed in Ag-intercalated Bi_2Se_3 nanoribbons.

X-ray Photoelectron Spectroscopy: Characterization and Electron Transfer

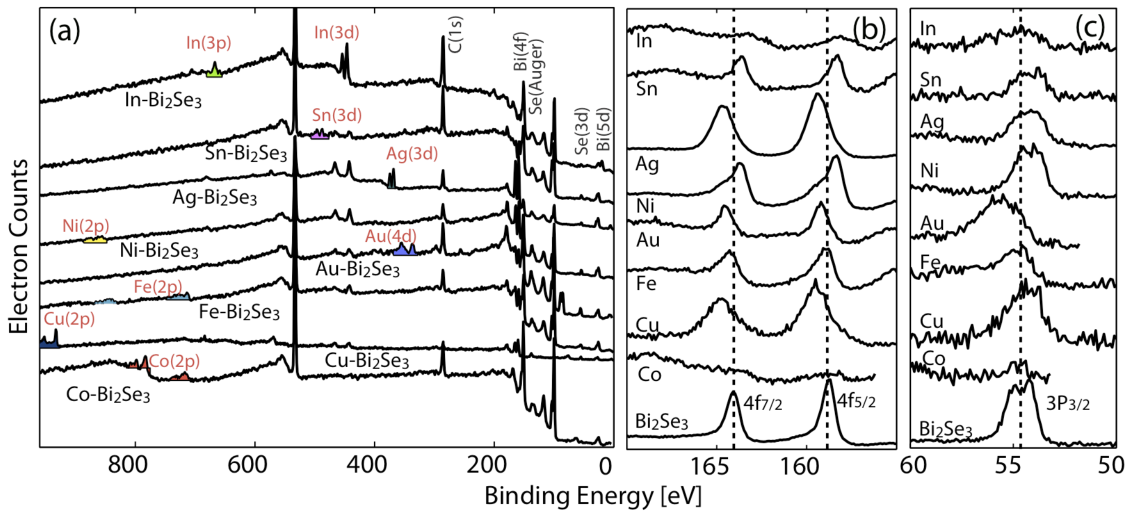

Figure 2S: (a) The atom % metal intercalated into Bi_2Se_3 nanoribbons, as determined by EDX (see manuscript Fig. 2), is confirmed using X-ray photoelectron spectroscopy (XPS). Emissions of the intercalated metals are identified by color in the spectra. All spectra are normalized to the Bi (5d) peak. The atom % of intercalated Au (20%) is determined using only XPS since Bi and Se peaks overlap Au peaks in EDX (see manuscript text). (b) Bismuth 4f peaks and (c) Selenium 3p peaks are shown as possible indicators of charge transfer, or the lack thereof, between the intercalant guest and host Bi_2Se_3.

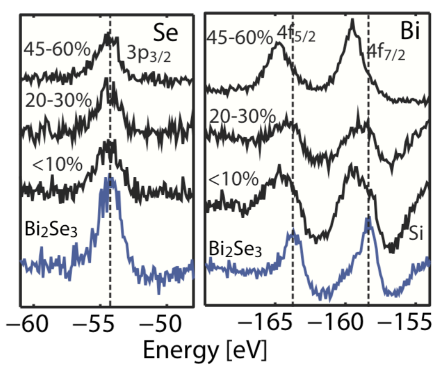

Figure 3S: A systematic study of the Bi and Se peaks detected by XPS on Cu-intercalated Bi_2Se_3 as a function of Cu concentration demonstrates that the Se peak essentially does not shift with increasing copper concentration but the bismuth peak does. In terms of charge transfer from the guest to the host, this would seem to be a strong indication of no charge transfer to the Se but possible (though quite small) charge transfer to the host overall. No apparent chemical interaction between copper and selenium is observed based on these emission peaks.

X-ray Diffraction

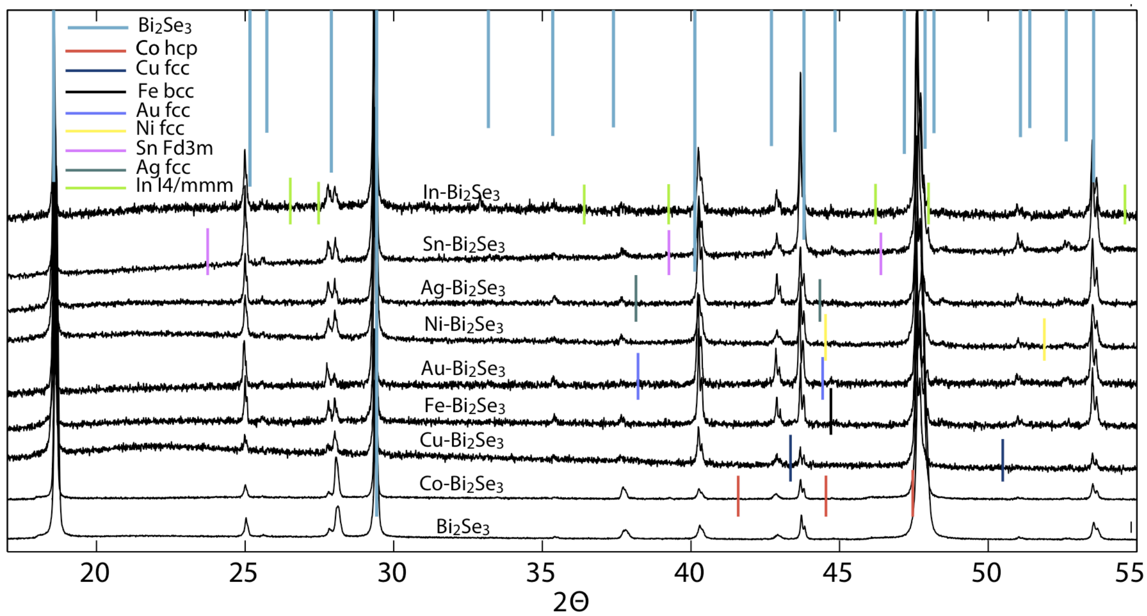

Figure 4S: Stacked plot of experimental XRD data shows no new structural phases as metal atoms are intercalated. Bi_2Se_3 peak positions are identified on the top of the plot. No diffraction peaks are observed for any bulk metal intercalant (fcc, hcp, bcc, etcetera) confirming that no metal precipitates are on the nanoribbons. Intensities of diffraction peaks, however, may change with intercalation.

Intercalant	Atom %	a [Å]	c [Å]
None	0	4.1364	28.5330
Copper	0.4-6.5%	4.1400	28.6190
Copper	23%	4.1453	28.5782
Cobalt	0.9-9.5%	4.1574	28.4930
Gold	0-4.9%	4.1420	28.6440
Indium	0.2-6.6%	4.1399	28.6124
Iron	0.3-7.0%	4.1540	28.5670
Nickel	0.2-1.3%	4.1387	28.6126
Silver	0.7-18.3%	4.1394	28.6231
Tin	1.6-4.2%	4.13854	28.6153
Tin	6%	4.1396	28.6155

Table 1: Lattice constants for all intercalated Bi_2Se_3 nanoribbons and atomic percent intercalated for data presented in Figure 4 above and Fig. 5 in the manuscript determined through Rietveld refinement of XRD patterns. Rietveld refinement was performed using the program Maud[1]. Errors for the *a* and *c* lattice constants are +/- 0.0005 **Å** and +/- 0.003 **Å** respectively.

Superlattice Intercalant Ordering With Heating

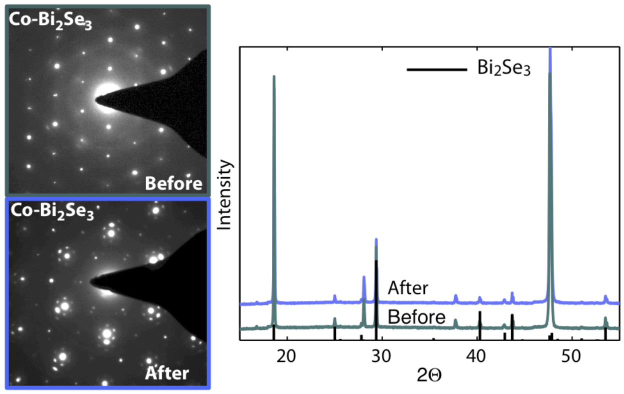

Figure 5S: Superlattice ordering is visible in copper and silver electron diffraction without heating. In cobalt, heating to 250°C for 5minutes under nitrogen or vacuum induces intercalant ordering, giving rise to superlattice diffraction patterns. No obvious indicator of superlattice ordering is seen in bulk XRD (right) but ordering is observed in electron diffraction (left).

References

(1) Lutterotti, L. Matthies, S.; Wenk, H. -R. *Proceeding of the Twelfth International Conference on Textures of Materials* (ICOTOM-12), **1999**, 1, 1599.