Two-Dimensional Covalent Crystals by Chemical Conversion of Thin van der Waals Materials [1]

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Abstract

Most of the studied two-dimensional (2D) materials have been obtained by exfoliation of van der Waals crystals[2]. Recently, there has been growing interest in fabricating synthetic 2D crystals which have no layered bulk analogues[3,4]. These efforts have been focused mainly on the surface growth of molecules in high vacuum[5]. Here, we report an approach to making 2D crystals of covalent solids by chemical conversion of van der Waals layers[1]. As an example, we used 2D indium selenide (InSe) obtained by exfoliation and converted it by direct fluorination into indium fluoride (InF_3), which has a nonlayered, rhombohedral structure and therefore cannot possibly be obtained by exfoliation. The conversion of InSe into InF_3 is found to be feasible for thicknesses down to three layers of InSe, and the obtained stable InF_3 layers are doped with selenium. We study this new 2D material by optical, electron transport, and Raman measurements and show that it is a semiconductor with a direct bandgap of 2.2 eV, exhibiting high optical transparency across the visible and infrared spectral ranges. We also demonstrate the scalability of our approach by chemical conversion of large-area, thin InSe laminates obtained by liquid exfoliation, into InF_3 films. The concept of chemical conversion of cleavable thin van der Waals crystals into covalently bonded noncleavable ones opens exciting prospects for synthesizing a wide variety of novel atomically thin covalent crystals.

References

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Figures

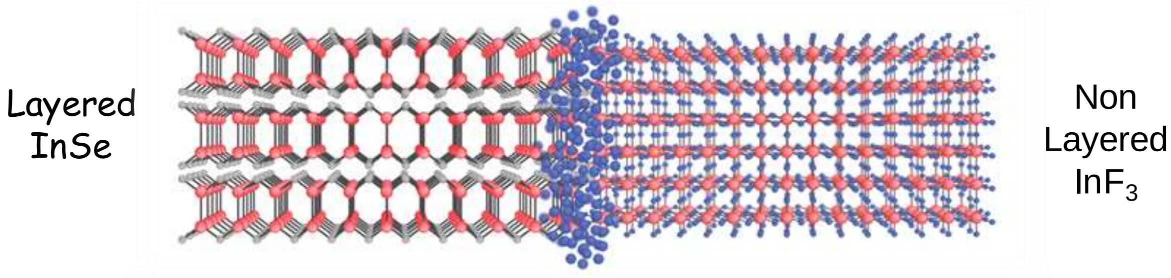

Figure 1: Schematic showing chemical conversion of 2D InSe to InF_3 nanosheets.

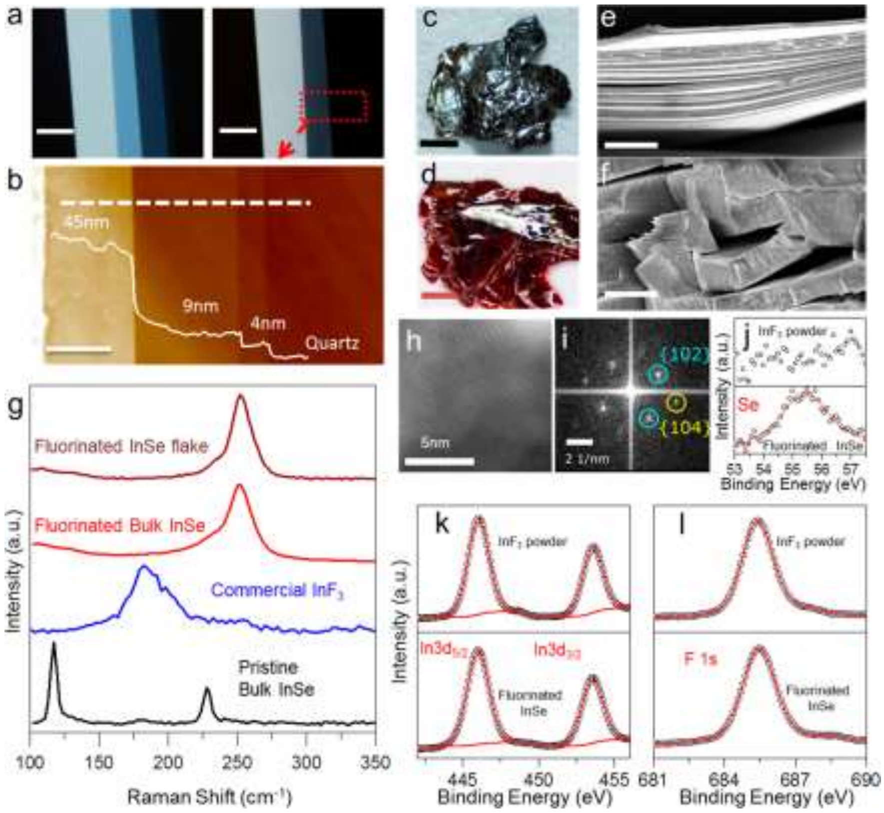

Figure 2: Characterization of fluorinated InSe. (a) Optical microscope images of InSe flakes on quartz substrate before (top left) and after (top right) fluorination. Scale bars, 7 µm. (b) An AFM image of the area marked with the red rectangle in Figure 1a. Scale bar, 5 µm. White curve: height profile along the dashed line. (c,d) Photographs of bulk InSe before and after the fluorination, respectively. Scale bars, 1 mm. (e,f) Cross-sectional SEM images of bulk pristine InSe and fluorinated InSe, respectively. Scale bars, 5 µm. (g) Raman spectra of a fluorinated InSe flake (~10 nm thick), fluorinated bulk InSe, commercial InF_3, and pristine bulk InSe. (h) HAADF STEM image of fluorinated InSe. Scale bar, 5 nm. (i) Fast Fourier transform from the region in Figure 1h, showing {102} and {104} planes in k-space. Scale bar, 2 nm^{-1}. XPS spectra of bulk fluorinated InSe crystal and commercial InF_3 powder showing (j) selenium, (k) indium, and (l) fluorine peaks.