

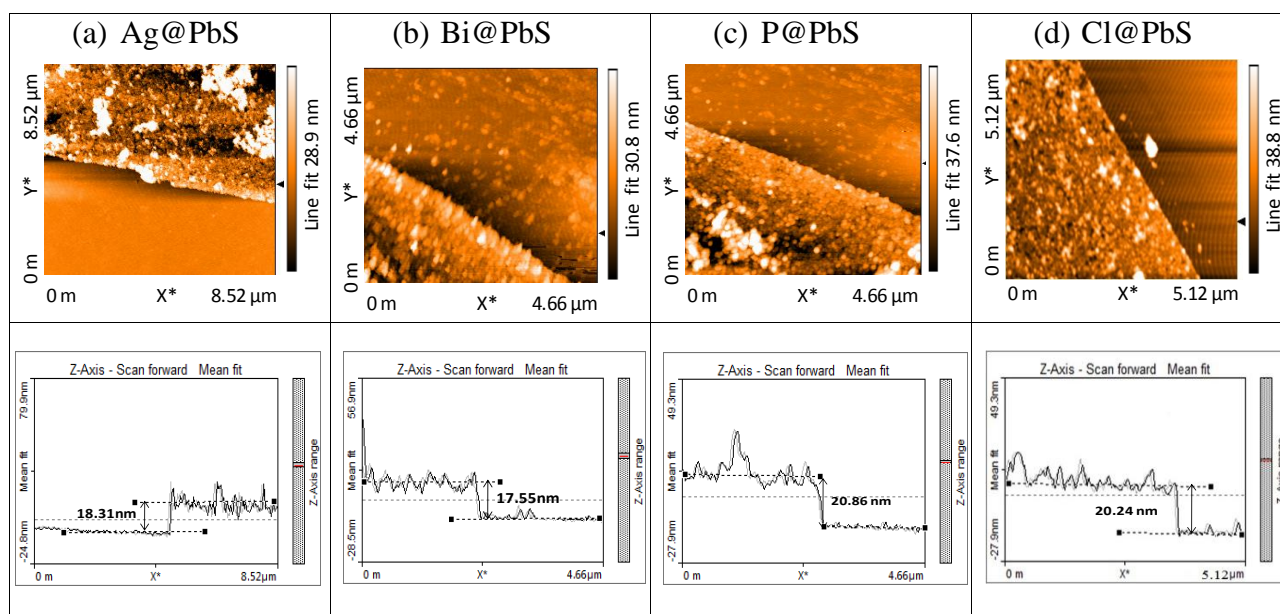
## Electronic supplementary information

Heterovalent substitution in anionic and cationic positions of PbS thin-films grown by SILAR method vis-à-vis Fermi energy measured through scanning tunneling spectroscopy

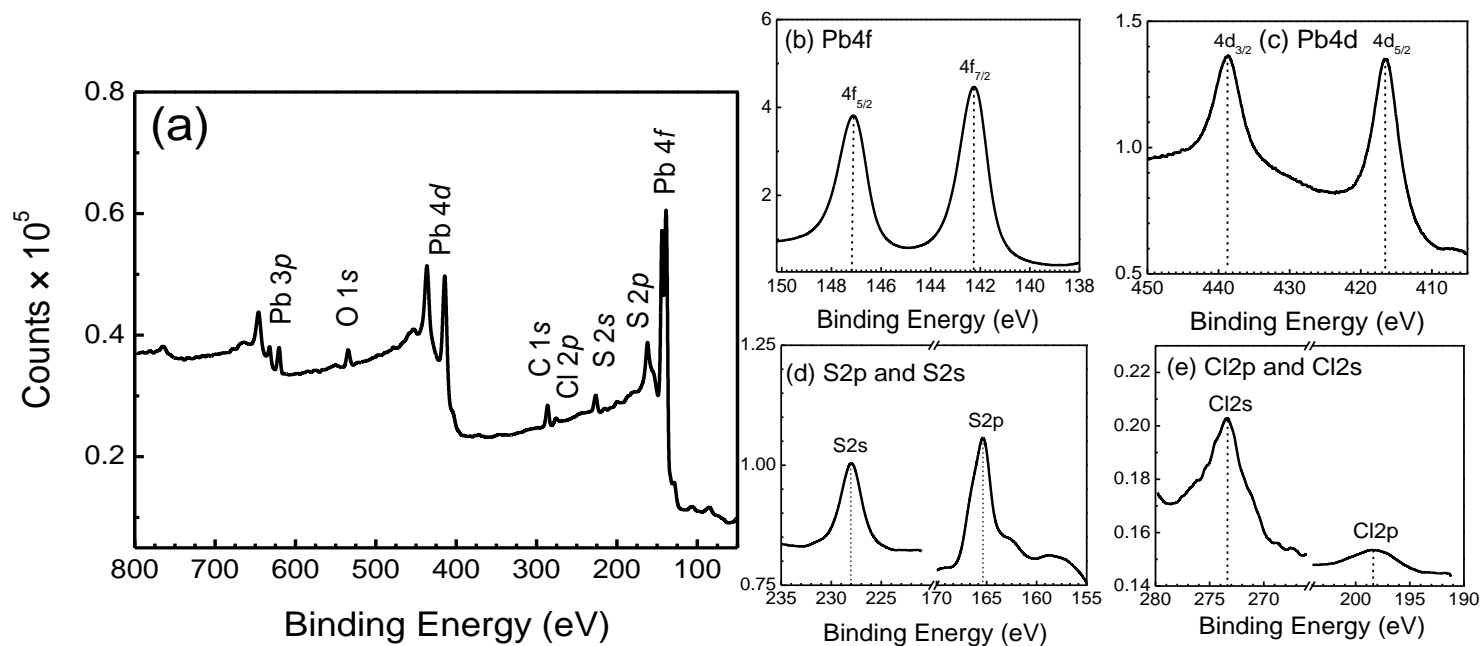
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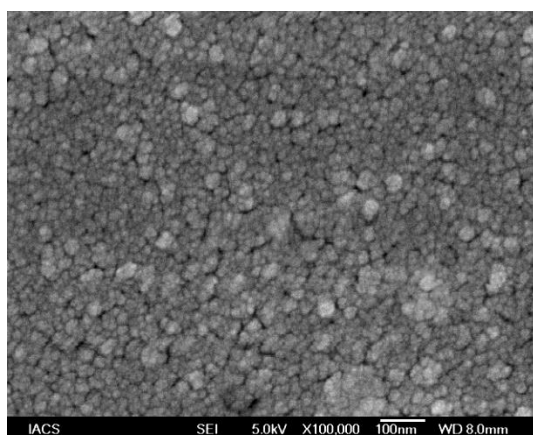
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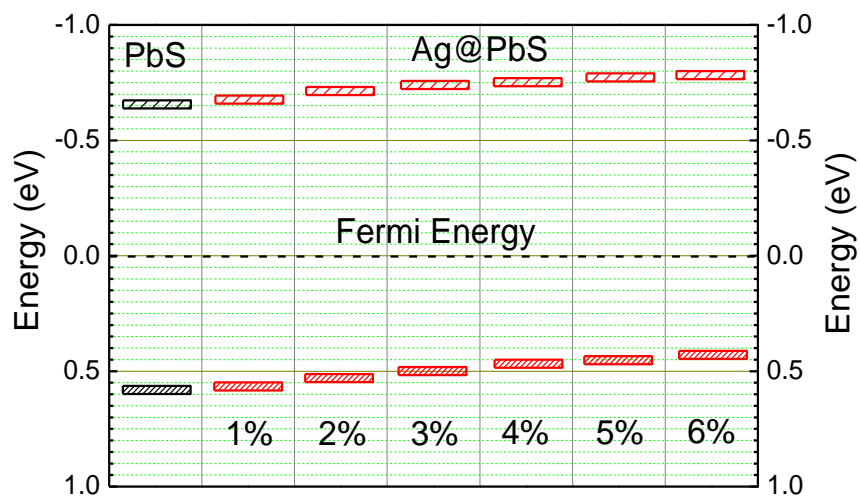
**Fig. S1** AFM images of scratched SILAR films (10 layers each) along with the depth profile of the scratch.



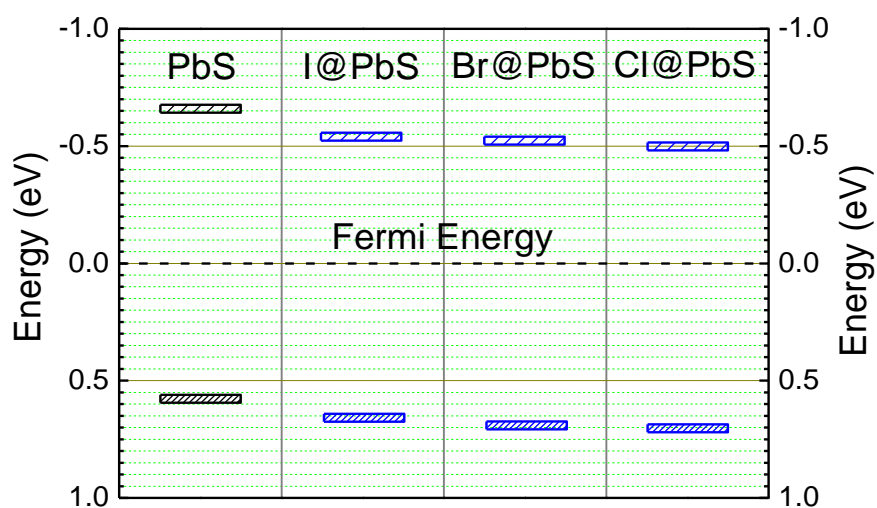
**Fig. S2** (a) Full-range XPS spectrum of Cl@PbS. High-resolution spectra of the material resolving binding energies of Pb4f, Pb4d, S2p and S2s and Cl2p and Cl2s electrons are shown in (b) through (e), in sequence.



**Fig. S3** SEM image of a pristine PbS thin film.



**Fig. S4** Schematic band diagram of Ag@PbS having a dopant content of 1-6 atomic% with respect to lead. The atomic% of silver is shown as legends. Band positions of pristine PbS are also presented in the figure. The dashed line represents each semiconductor's Fermi energy, which was aligned to 0 V.



**Fig. S5** Schematic band diagram of halide-doped PbS thin-films. Band positions of pristine PbS are also shown in the figure. The dashed line represents each semiconductor's Fermi energy, which was aligned to 0 V.