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RESEARCH ARTICLE

Local probe of the interlayer coupling strength of few-layers SnSe by contact-resonance atomic force microscopy

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Supplementary Materials

The raw measured site-specific CR-force spectroscopy is shown as Fig. S1, where the zero-loading force is normalized to the free condition, the negative value refers to attraction and the positive value means repulsion. The higher CRF and CRA on SiO_2/Si than SnSe as above can be observed, which increase differently with the approaching of the tip to sample. Note that the CRA in the paper is calculated with the first optical sensitivity.

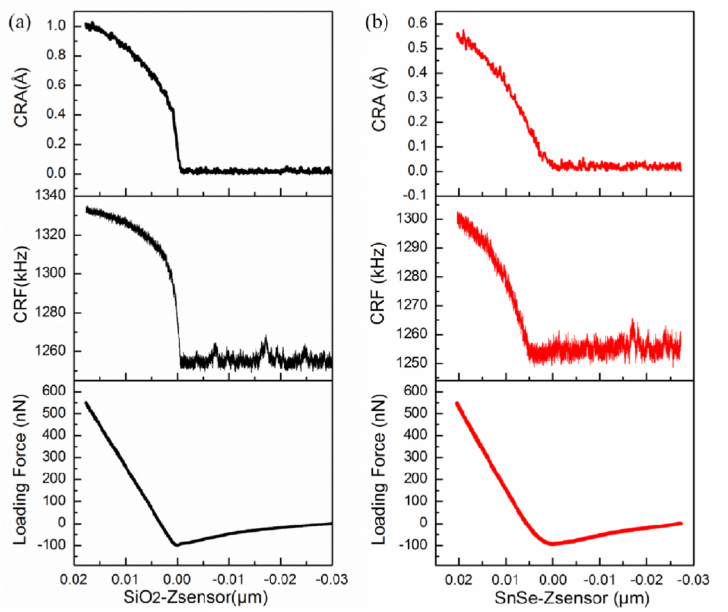

Fig. S1 Raw data of Contact-Resonance Force Spectroscopy measurements on SnSe and its supporting substrate of SiO_2/Si. **(a)** The changes of loading force, CRF and CRA with the approaching of the tip to SiO_2/Si. **(b)** The changes of loading force, CRF and CRA with the approaching of the tip to SnSe.

Table S1 Calculated lattice constant of our tested three functionals compared with experimental results. All three functionals overestimate the lattice constant along *x* direction. The functional optB86b performs best.

Lattice Constant (Å)	a (x)	b (y)	c (z)
optB86b	4.20	4.43	11.62
optB88	4.21	4.53	11.78
PBE	4.21	4.56	11.79
expt.	4.14	4.44	11.70

Calculation of force constant and Young's Modulus:

Projected inter-layer force constant. In a rigid layer vibrational mode, the whole layer can be treated as one rigid body [1]. The projected inter-layer force constant, p-ILFC k^i (i stands for the projected direction, e.g. x, y or z) was constructed by summing inter-atomic force constants over all atoms from each of the two adjacent layers, as $k_{AB}^{i} = \sum_{a,b} D_{a,b}^{i}$ ($a \in [\text{atoms in layer } A], b \in [\text{atoms in layer } B]$). The matrix of inter-atomic force constants, essentially the same as the Hessian matrix of Born-Oppenheimer energy surface, is defined as the energetic response to a distortion of atomic geometry in DFPT [2]. It reads, $D^i_{a,b} = \frac{\partial^2 E_0(\boldsymbol{R})}{\partial R^i_a \partial R^i_b}$, where R is the coordinate of each ion, $E_0(\boldsymbol{R})$ is the ground-state energy. Thus, the vertical p-ILFC defined as $\sum_{a,b} \frac{\partial^2 E_0(\boldsymbol{R})}{\partial R^i_a \partial R^i_b}$ approximately equals to the elastic constant defined as $\frac{\partial^2 E_0(\boldsymbol{R})}{\partial L^2_{ab}}$ (L_{ab} represents the distance between a and b layer) in linearization range.

Young's modulus, defined as $E = \frac{\sigma}{\varepsilon}$ (σ stands for the normal stress and ε stands for the normal strain), were obtained in this work as follows:

$$E = \frac{\Delta F/A}{\Delta h/h_0} = \frac{h_0}{A} \cdot \frac{\partial F}{\partial h}$$

Therein, F represents the external force, A is the cross-sectional area, h_0 represents the effective layer thickness and Δh is the thickness variations. In this work, h_0 was defined as $d^{\mathrm{T}} + d^{\mathrm{a}}$ (d^{T} represents the thickness between the top layer and the bottom layer and d^{a} represents average interlayer distance respectively). $\frac{\partial F}{\partial h}$ is the total vertical elastic constant of the system. An in-series-springs model was used to estimate the value of $\frac{\partial F}{\partial h}$. Each sublayer in SnSe was considered as an individual layer in this model. The elastic constant of each spring was given by p-ILFC as stated above. The total elastic constant $\frac{\partial F}{\partial h}$, therefore could be obtained according to spring series formula:

$$\frac{\partial F}{\partial h} = k_{\mathrm{tot}} \approx \frac{1}{\sum_{i=1}^{2N-1} \frac{1}{k_{i,i+1}}} = \frac{1}{\sum_{i=1}^{2N-1} \frac{1}{\sum_{a,b} D^{vertical}_{a,b}}}$$

$$a \in [\text{atoms in the } i^{th} \text{ sublayer}], b \in [\text{atoms in the } (i+1)^{th} \text{ sublayer } B]$$

Here, N is the number of SnSe layers. And $k_{i,i+1}$ represents the elastic constant between the i^{th} and $(i+1)^{\mathrm{th}}$ layers which equals to the vertical p-ILFC.

Calculation of elastic restoring force. The elastic restoring force (F_{re}) was calculated by multiplying the external pressure by the lateral surface area. The SnSe lattice was applied by a series of hydrostatic pressure from 0.0 to 3.0 kBar with a step of 0.5 kBar and fully relaxed to obtain the lattice changes. The pressure corresponding to the same value of elongation ratio with the experimental results could be obtained by interpolating the ratio-pressure curve.

References

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