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Abstract

Previous studies showed that, as ferroelectric films become thinner, their Curie temperature (T_c) and polarization below T_c both typically decrease. In contrast, a recent experiment [Chang *et al.*, Science **353**, 274 (2016)] observed that atomic-thick SnTe films have a higher T_c than their bulk counterpart, which was attributed to *extrinsic* effects. Here, we find, using first-principles calculations, that the 0K energy barrier for the polarization switching (which is a quantity directly related to T_c) is higher in most investigated *defect-free* SnTe ultrathin films than that in bulk SnTe, and that the 5-unit-cell (UC) SnTe thin film has the largest energy barrier as a result of an interplay between hybridization interactions and Pauli repulsions. Further simulations, employing a presently developed effective Hamiltonian, confirm that free-standing defect-free SnTe thin films have a higher T_c than bulk SnTe, except for the 1-UC case. Our work therefore demonstrates the possibility to *intrinsically* enhance ferroelectricity of ultrathin films by reducing their thickness.

Ferroelectric (FE) materials in which a spontaneous polarization can be switchable by an electric field have wide applications such as high-density nonvolatile memories [1-3]. The continuous demand for device miniaturization has resulted in the increased demand of nanometric FE thin films [2-6]. Nanoscale ferroelectrics are also fascinating from a fundamental point of view, since their properties can be dramatically different from that in of bulk ferroelectrics [7,8].

A suppression of the out-of-plane polarization is known to occur in thin films under open-circuit-like electrical boundary condition, because of depolarization field effects [9]. Regarding the in-plane component of the polarization, finite-size scaling theory predicts that FE Curie temperature (T_c) shifts to lower temperatures as compared to the bulk value, as FE films become thinner [10,11]. Such features are consistent with measurements and computations demonstrating that, typically, the FE T_c becomes lower, and, as a result, the electrical polarization becomes smaller for any temperature below T_c, as the thickness of FE thin films is reduced [9,12-16]. It is therefore rather surprising that Chang *et al.* recently observed that the T_c of atomic-thick SnTe is *higher* than that of SnTe bulk [17]. In order to reconcile such observation with the aforementioned features, this unusual phenomenon was mainly explained in terms of an *extrinsic* effect, namely that there are less Sn vacancies and lower free carrier density in SnTe thin films. It is, however, interesting to investigate how T_c *intrinsically* changes with the thickness in perfectly defect-free SnTe thin films. In particular, is this currently unknown dependency in line with the common belief that T_c should decrease as the films become thinner, or are there any new effects awaiting to be revealed in SnTe thin films leading to an *intrinsic* enhancement of their ferroelectricity when their thickness is reduced?

In this Letter, we carry out first-principles calculations to determine such intrinsic dependency. We find that the 0K energy barrier for the polarization switching in SnTe thin films is higher than that in bulk SnTe when the thickness is larger than 2-unit cell (UC), and that the 5-UC SnTe thin films has the largest energy barrier. Such results strongly suggest that T_c of SnTe thin films is not only larger than that of bulk SnTe but also reaches its maximum for the 5-UC thickness. These unusual phenomena are

found to originate from the subtle interplay between hybridization interactions (HIs), which are essential for stabilizing ferroelectricity, and Pauli repulsions (PRs), that tend to suppress ferroelectricity. More precisely, (i) the increase of energy barrier when decreasing the thickness from 13-UC to 5-UC, is due to the fact that the surface Sn atoms have weaker PRs and thus a smaller force constant than the inner Sn atoms; and (ii) the decrease of energy barrier from 5-UC to 1-UC arises from the concomitant decrease of HIs. We also developed an effective Hamiltonian for free-standing defect-free SnTe thin films under open-circuit electrical boundary conditions, which does confirm that SnTe films intrinsically have a higher T_c than bulk SnTe, except for the 1-UC case. Our work therefore suggests that, unlike commonly believed, it is possible to intrinsically enhance ferroelectricity by reducing the thickness of ultrathin films.

Let us first recall that bulk SnTe is a narrow-gap (~0.2 eV) semiconductor that possesses the rock-salt structure [18]. At the FE T_c (98 K in a sample with low carrier density [19]), bulk SnTe goes through a cubic paraelectric (PE) to rhombohedral FE phase transition, and the two sublattices of Sn and Te atoms are displaced from each other along the [111] direction -- giving rise to a spontaneous polarization along that direction [20]. On the other hand, in SnTe ultrathin films being under open-circuit electrical boundary conditions, the polarization is along the in-plane [110] direction because the depolarization field annihilates the out-of-plane polarization [17,21-23]. Here, we perform density function theory (DFT) calculations [see Section 1 of Supplemental Material (SM) [24]] to relax the structures of the FE phase. Regarding the centrosymmetric PE phase of thin films, we optimize the slab cut from the cubic bulk SnTe but keeping the same symmetry. The PE and FE structures of 1-UC and 2-UC SnTe thin films are shown in Fig. 1. For the 1-UC SnTe thin film, all Sn^{2+} ions move along the [110] direction so that each Sn^{2+} ion is three-fold coordinated. The resulting FE phase with two puckered atomic layers is similar to monolayer black phosphorus [45]. The optimized in-plane lattice constants are slightly anisotropic (a = 4.58 Å and b = 4.55 Å) [17]. The multilayer FE SnTe thin films can be regarded as a stacking of 1-UC FE SnTe films along the c-axis [see Fig. 1(b) for the case of 2-UC

thin film].

Since the magnitude of the polarization (see Section 2 of SM [24]) is related to ionic displacements, we plot in Fig. 1(e) the FE displacements of Sn^{2+} ions at different layers for different SnTe thin films (1-UC, 2-UC, 5-UC, and 10-UC). The FE displacements of Sn^{2+} ions are computed by assuming that the positions of the Te^{2-} ions are fixed to those of the PE phase. Note that each SnTe unit-cell contains a double layer. Several interesting trends can be seen: i) For a SnTe thin film with a given thickness, the surface Sn^{2+} ions displace more than the inner Sn^{2+} ions; ii) For very thin films (i.e., 1-UC and 2-UC), FE displacements become smaller as the films become thinner; and iii) For multilayer SnTe thin films (i.e., 5-UC or 10-UC), the FE displacements of Sn^{2+} ions display an odd-even oscillating behavior with respect to the layer number, e.g., the motion of the Sn^{2+} ion of the second layer is smaller than that of both the first and third layers.

To study the stability of ferroelectricity in SnTe thin films, we calculate the energy difference between the PE and FE phases (i.e., the energy barrier between two FE states with opposite polarizations) of SnTe thin films as a function of thickness (see the red line in Fig. 2). One can see that this barrier first increases with the thickness from 1-UC to 5-UC, and decreases as the thickness increases for films thicker than 5-UC. Strikingly, the energy barriers of SnTe thin films from 2-UC to 13-UC are higher than that of bulk SnTe, which strongly suggests that defect-free SnTe thin films have a higher Curie temperature than bulk SnTe with no defects (as we will confirm later) -- in contrast to the previous belief that ferroelectricity in thin films is reduced with respect to the bulk case.

To check the effect of strain on the dependence of energy barrier on the film thickness, we also computed the energy barriers in the case where the in-plane lattice constants of the PE and FE phases are fixed to those of bulk SnTe ($a = 4.5254$ Å). The energy barrier also has a maximum for 5-UC [see Fig. 2(b)], implying that strain does not qualitatively affect the dependence of energy barrier on film thickness. Therefore, the interactions related to Sn displacements are responsible for the intriguing thickness dependency of the energy barrier. To investigate the interactions related to

Sn displacements in more details, we determined the layer force constant k_{DFT}^i (see Ref. [46] for more details) by computing and fitting the total energy E as a function of the Sn displacement x in the i-th layer by the form $E = \frac{1}{2}k_{DFT}^i x^2 + E_{PE}$ (where E_{PE} is the total energy of the PE phase). The chosen displacement x is so small (e.g., ~0.01 Å) that fourth and higher order terms can be neglected here. The layer force constants for 1-UC, 2-UC, 5-UC and 10-UC SnTe thin films are plotted in Fig. 3. The Sn^{2+} ions of the surface layer have a smaller force constant than the Sn^{2+} ions of the inner layers for multilayer thin films. Moreover, the layer force constant of the surface layer basically increases as the films become thinner, as shown in the inset of Fig. 3. In particular, the layer force constants of the surface layer for films thinner than 3-UC (see also Fig. S4) is significantly larger than those in thicker films. For a given thin film (e.g., 5-UC and 10-UC thin films), the layer force constants display an oscillating odd-even behavior with respect to the layer number. The dependence of the layer force constants is in line with the dependence of the FE displacements [see Fig. 1(e)] since a smaller force constant indicates a stronger FE instability [47]. The dependence of the layer force constants can also explain the dependence of the energy barrier on the film thickness. In fact, why the energy barrier does not always increase with thickness can be understood as follows: since the Sn^{2+} ions of the surface layer have a smaller force constant than the Sn^{2+} ions of the inner layer, thinner films tend to display stronger ferroelectricity (higher energy barrier) as they have a larger surface-to-volume ratio. Furthermore, the reason why 5-UC SnTe thin film has the highest energy barrier is that the layer force constants in the thinnest films (i.e., 1-UC and 2-UC) are in average much larger than those in films thicker than 3-UC, as shown in Fig. 3.

Now we attempt to understand the microscopic mechanisms for the unusual behavior of the layer force constants. It is well-known that ferroelectricity in bulk SnTe is mainly caused by the hybridization between the empty 5p orbitals of the lone-pair Sn^{2+} ion and the occupied 5p orbitals of the Te^{2-} ion, i.e., second-order Jahn-Teller effects [48,49]. To see the effect of orbital hybridization on the layer force

constants, we computed these constants by using the band energies from the Tight-Binding (TB) simulations (see Section 1 of SM [24]). As shown in Fig. 4(a), the layer force constants contributed by the HIs are found to be negative, suggesting that HIs favor FE displacements, in agreement with a previous study [50]. The oscillating odd-even behavior of the dependence of the HIs-related layer force constants and the fact that the second layer (i.e., subsurface) has the largest force constant are in line with the dependence of the total layer force constants from the DFT calculations [compare Figs. 3 and 4(a)]. The HIs-related layer force constants in 1-UC and 2-UC thin films are much larger than those in thicker films, most likely because the much larger band gaps arising from the quantum confinement in ultrathin films weaken the HIs. If considering only the HIs-related layer force constants, ferroelectricity in thinner films would always be weaker than that in thicker films since thinner films have the largest averaged HIs-related layer force constants. Therefore, although the consideration of sole HIs can explain some of the trends of the energy barrier, it cannot solely provide an explanation of why the 5-UC thin film has the highest energy barrier.

To resolve this issue, it is important to realize that the off-centric FE displacements arise due to the delicate balance between the HIs (which favors ferroelectricity [50-52]) and the Pauli repulsions (PRs) (which tends to keep systems centrosymmetric [53-55]). We will thus now see how PR affects the layer force constants. Due to the acoustic sum rule, we can decompose the layer force constant of the Sn^{2+} ions of the i-th layer (k_{DFT}^i) into intralayer (k_{intra}^i) and interlayer (k_{inter}^i) contributions (see Ref. [56] for details). Note that all the PRs within the i-th layer are reflected in the intralayer force constant k_{intra}^i. As an example, we show the intralayer and interlayer contributions of the layer force constants for the surface and inner layers of the 5-UC SnTe thin film in left part of Fig. 4(b). We find that the interlayer contributions for both the surface and inner layers are positive and of similar magnitude. The large difference in the layer force constant between the surface and inner layers arises because of the much larger positive intralayer contribution in the

inner layer case. The intralayer contribution k_{intra}^i can be seen as a sum of the HI-related contribution and the PR-related contribution between the Sn^{2+} ion and the in-plane Te^{2-} ion. Since the HI-related contribution to k_{intra}^i of the surface layer is not less than that of the inner layer, the much larger positive intralayer contribution in the inner layer case must be due to the fact that the PR-related contribution to k_{intra}^i of the surface layer is more negative than that of the inner layer. Actually, this can be understood by a simple ionic radius argument: the surface Sn^{2+} and Te^{2-} ions in the PE SnTe thin film are five-fold coordinated while the inner Sn^{2+} and Te^{2-} ions are six-fold coordinated, and it is well known that the radius of an ion with smaller coordination number is smaller than that with a larger coordination number. Since the Sn-Te bond length of the surface layer is similar to that of the inner layer in the PE phase, it is expected that the Sn-Te bond of the surface layer can be compressed much more easily than that of the inner layer. Our argument is further supported by considering a hypothetical 5-UC SnTe thin film being under 7.2% tensile strain. In this case, the layer force constants of the surface and inner layers become negative [(see right part of Fig. 4(b)], suggesting that the FE instability is enhanced, in agreement with the fact that tensile strain strengthens in-plane ferroelectricity. Interestingly, the layer force constants of the inner layer is now close to that of the surface layer. This is because the Sn-Te PR is greatly reduced, as the Sn-Te bond length is now larger than the sum of the Sn^{2+} and Te^{2-} ionic radii. Our above argument that there is less PR in a surface layer should be generally applicable to other systems. In fact, this holds even in a non-FE ionic system (see Section 4 of SM [24]).

For comparison, we also examine ferroelectricity in thin films made of other IV–VI compounds (i.e., GeTe and PbTe). For the GeTe thin films, the energy barrier increases with the film thickness, i.e., there is no maximum in the energy barrier curve (see Section 5 of SM [24]). This can be understood since the HI in GeTe is so strong that the PR contribution to the layer force constant is less important. The intriguing behavior that a thinner film may possess a stronger ferroelectricity occurs when the HI and PR are of comparable magnitude. In fact, if we reduce the PR in PbTe thin

films by applying a tensile strain, we also observe a maximum in the energy barrier curve (see Section 6 of SM [24]). Furthermore, we demonstrate that this mechanism is generally applicable to other systems. For example, we find that the energy barriers and polarizations of TiO_2-terminated $SrTiO_3$ [001] thin films under a small tensile strain (lateral lattice constants $a = b = 4.0955$ Å) decrease with the film thickness (see Section 7 of SM [24]).

Finally, we estimate the T_c of SnTe thin films by developing an effective Hamiltonian and performing parallel tempering Monte Carlo (PTMC) simulations for these 2D systems. As shown in Fig. S9, T_c increases from 1-UC to 5-UC and then decreases when further increasing the film thickness. The tendency of T_c with thickness is in line with that of the energy barrier. Our simulations show that defect-free bulk SnTe has a lower T_c (that is, 38 K) than most of SnTe thin films (i.e., T_c for 2-UC thin film is 47 K). However, the defect-free 1-UC SnTe film has a lower T_c (namely, 30 K) than defect-free bulk SnTe, in contrast with the experimental result [17]. This suggests that the high-T_c measured for the 1-UC SnTe film [17] is partly due to extrinsic effects (e.g., defects [59,60] (see Section 10 of SM [24]), van der Waals interactions between the SnTe thin film and the substrate, charge transfer between the SnTe thin film and the substrate, etc.). Although T_c is underestimated in our simulations for bulk SnTe and SnTe thin films, the qualitative trend from the simulations should be correct. In fact, with more accurate (and more demanding) methods that predict a larger energy barrier and thus a higher T_c, the qualitative dependence of the energy barriers on the film thickness remains unchanged (see Section 9 of SM [24]). We also perform additional PTMC simulations on a model Hamiltonian to prove that the smaller force constant for the surface ion is indeed the key to the non-monotonic behavior of T_c as a function of the thickness (see Section 11 of SM [24]).

In summary, based on first-principles calculations and effective Hamiltonian simulations, we revealed that the FE switching energy barrier and T_c in free-standing defect-free SnTe thin films first increase with thickness when the film thickness is less than 5-UC, and then decreases with thickness for thicker films. These atypical

behaviors originate from a subtle interplay between HIs and PRs. Our work is thus promising towards the realization of miniaturized FE devices utilizing ultrathin films.

[1] J. F. Scott, Science **315**, 954 (2007).

[2] N. Setter *et al.*, J. Appl. Phys. **100**, 051606 (2006).

[3] M. Dawber, K. M. Rabe, and J. F. Scott, Rev. Mod. Phys. **77**, 1083 (2005).

[4] D. G. Schlom, J. H. Haeni, J. Lettieri, C. D. Theis, W. Tian, J. C. Jiang, and X. Q. Pan, Mater. Sci. Eng., B **87**, 282 (2001).

[5] K. Rabe, Ch. H. Ahn, J.-M. Triscone, Eds., Physics of Ferroelectrics: A Modern Perspective (Springer, 2007).

[6] J. L. Lu, W. Luo, J. S. Feng and H. J. Xiang, Nano. Lett. **18**, 595 (2018)

[7] I. I. Naumov, L. Bellaiche, and H. X. Fu, Nature **432**, 737 (2004).

[8] A. K. Yadav *et al.*, Nature **530**, 198 (2016).

[9] D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, Science **304**, 1650 (2004).

[10] M. E. Fisher and M. N. Barber, Phys. Rev. Lett. **28**, 1516 (1972).

[11] G. A. T. Allan, Phys. Rev. B **1**, 352 (1970).

[12] I. A. Kornev, H. Fu, and L. Bellaiche, J. Mater. Sci. **41**, 137 (2006).

[13] D. D. Fong et al., Phys. Rev. Lett. **96**, 127601 (2006).

[14] D. A. Tenne et al., Phys. Rev. Lett. **103**, 177601 (2009).

[15] K. Sheshadri, R. Lahiri, P. Ayyub, and S. Bhattacharya, J. Phys: Condens. Matter. **11**, 2459 (1999).

[16] E. Almahmoud, I. Kornev, and L. Bellaiche, Phys. Rev. B **81**, 064105 (2010).

[17] K. Chang *et al.*, Science **353**, 274 (2016).

[18] J. O. Dimmock, Melngail.I, and A. J. Strauss, Phys. Rev. Lett. **16**, 1193 (1966).

[19] M. Iizumi, Y. Hamaguchi, K. F. Komatsubara, and Y. Kato, J. Phys. Soc. Jpn. **38**, 443 (1975).

[20] S. Sugai, K. Murase, and H. Kawamura, Solid State Commun. **23**, 127 (1977).

[21] R. Fei, W. Kang, and L. Yang, Phys. Rev. Lett. **117**, 097601 (2016).

[22] M. Mehboudi, B. M. Fregoso, Y. Yang, W. Zhu, A. van der Zande, J. Ferrer, L. Bellaiche, P. Kumar, and S. Barraza-Lopez, Phys. Rev. Lett. **117**, 246802 (2016).

[23] M. Wu and X. C. Zeng, Nano Lett. **16**, 3236 (2016).

[24] See Supplemental Material, which includes Refs. [25-44], for computational details, the spontaneous polarizations and lattice distortions, layer force constants, energy barriers and dependence of T_c on film thickness.

[25] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[26] G. Kresse and J. Furthmuller, Comp. Mater. Sci. **6**, 15 (1996).

[27] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).

[28] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[29] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[30] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun. **178**, 685 (2008).

[31] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Rev. Mod. Phys. **84**, 1419 (2012).

[32] P. S. Wang, W. Ren, L. Bellaiche, and H. J. Xiang, Phys. Rev. Lett. **114**, 147204 (2015).

[33] K. Hukushima and K. Nemoto, J. Phys. Soc. Jpn. **65**, 1604 (1996).

[34] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. B **52**, 6301 (1995).

[35] L. Bellaiche, A. Garcia, and D. Vanderbilt, Phys. Rev. Lett. **84**, 5427 (2000).

[36] C. Falter, G. A. Hoffmann, and M. Klenner, Phys. Rev. B **53**, 14917 (1996).

[37] H. A. Alperin, S. J. Pickart, J. J. Rhyne, and V. J. Minkiewi, Phys. Lett. **40A**, 295 (1972).

[38] R. T. Bate, D. L. Carter, and J. S. Wrobel, Phys. Rev. Lett. **25**, 159 (1970).

[39] B. J. Kooi and B. Noheda, Science **353**, 221 (2016).

[40] K. Chang *et al.*, Science **353**, 274 (2016).

[41] E. Almahmoud, I. Kornev, and L. Bellaiche, Phys. Rev. B **81**, 064105 (2010).

[42] M. E. Fisher and M. N. Barber, Phys. Rev. Lett. **28**, 1516 (1972).

[43] G. A. T. Allan, Phys. Rev. B **1**, 352 (1970).

[44] K. Sheshadri, R. Lahiri, P. Ayyub, and S. Bhattacharya, J. Phys: Condens. Matter. **11**, 2459 (1999).

[45] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, Nat. Nanotech. **9**, 372 (2014).

[46] To compute the layer force constant k_{DFT}^i of the Sn^{2+} ions of the *i*-th layer, we can displace the Sn^{2+} ions of the *i*-th layer along the *x*-axis by δ and calculate the force F_{ix}^{Sn} exerted on it with DFT. One then gets $k_{\mathrm{DFT}}^i = -\dfrac{F_{ix}^{\mathrm{Sn}}}{\delta}$. One can further decompose the layer force constant into an intralayer contribution and an interlayer contribution using the acoustic sum rule. Due to translational invariance, the sum of all the forces on all atoms should vanish: $\sum_j (F_{jx}^{\mathrm{Sn}} + F_{jx}^{\mathrm{Te}}) = 0$, where *j* is the layer-index. Thus, $k_{\mathrm{DFT}}^i = k_{\mathrm{intra}}^i + k_{\mathrm{inter}}^i$, where the intralayer contribution is $k_{\mathrm{intra}}^i = \dfrac{F_{ix}^{\mathrm{Te}}}{\delta}$ and the interlayer contribution is $k_{\mathrm{inter}}^i = \dfrac{1}{\delta} \sum_{j \neq i} (F_{jx}^{\mathrm{Sn}} + F_{jx}^{\mathrm{Te}})$.

[47] W. Zhong, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **72**, 3618 (1994).

[48] I. B. Bersuker, Chem. Rev. **113**, 1351 (2013).

[49] J. M. Rondinelli, A. S. Eidelson, and N. A. Spaldin, Phys. Rev. B **79**, 205119 (2009).

[50] R. E. Cohen, Nature **358**, 136 (1992).

[51] A. Filippetti and N. A. Hill, Phys. Rev. B **65**, 195120 (2002).

[52] M.-A. Oak, J.-H. Lee, H. M. Jang, J. S. Goh, H. J. Choi, and J. F. Scott, Phys. Rev. Lett. **106**, 047601 (2011).

[53] P. S. Wang and H. J. Xiang, Phys. Rev. X **4**, 011035 (2014).

[54] S. E. Rowley, Y.-S. Chai, S.-P. Shen, Y. Sun, A. T. Jones, B. E. Watts, and J. F. Scott, Sci. Rep. **6**, 25724 (2016).

[55] Ph. Ghosez, X. Gonze and J.-P. Michenaud, Europhys. Lett. **33**, 713 (1996)

[56] R. T. Bate, D. L. Carter, and J. S. Wrobel, Phys. Rev. Lett. **25**, 159 (1970).

[57] H. A. Alperin, S. J. Pickart, J. J. Rhyne, and V. J. Minkiewi, Phys. Lett. **40A**, 295 (1972).

[58] B. J. Kooi and B. Noheda, Science **353**, 221 (2016).

[59] C. Cazorla, Phys. Rev. Appl. **7**, 044025 (2017).

[60] S. B. Hu, Y. Wang, C. Cazorla, and J. Seidel, Chemistry of Materials **29**, 708 (2017).
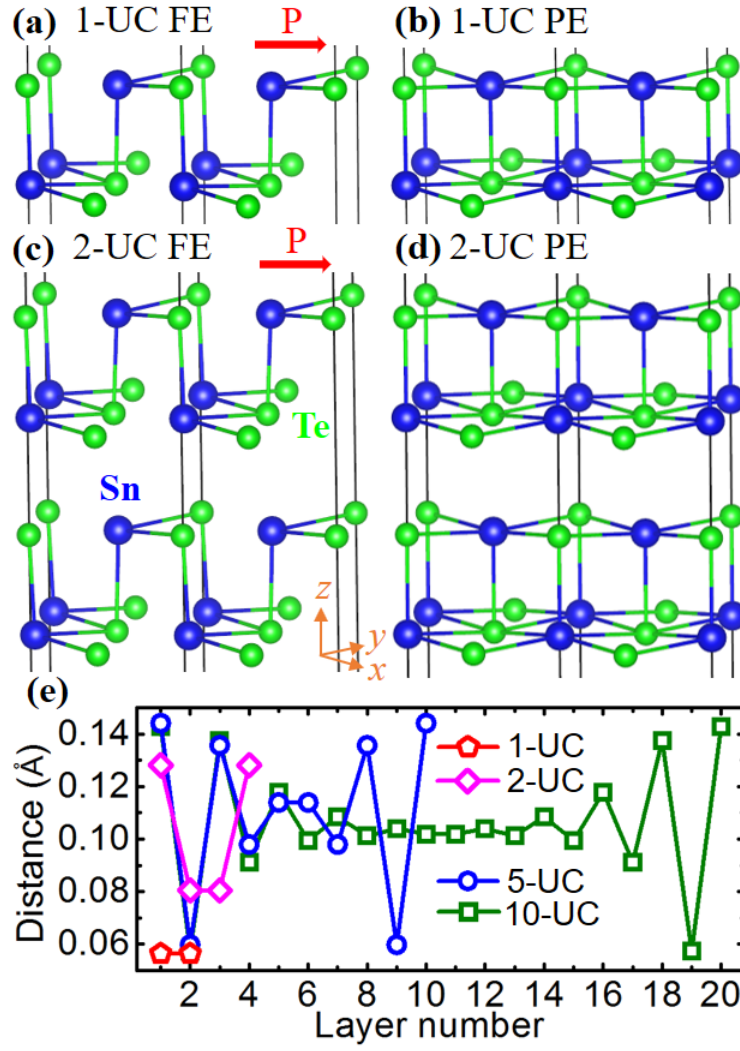
Figure 1. Crystal structures of SnTe thin films. Ferroelectric (FE) phases of (a) 1-UC and (c) 2-UC SnTe thin films. The corresponding paraelectric phases are shown in (b) (d). The red arrows indicate that polarizations are along the [110] direction. (e) The FE displacements of Sn^{2+} ions at different layers as a function of the layer number.
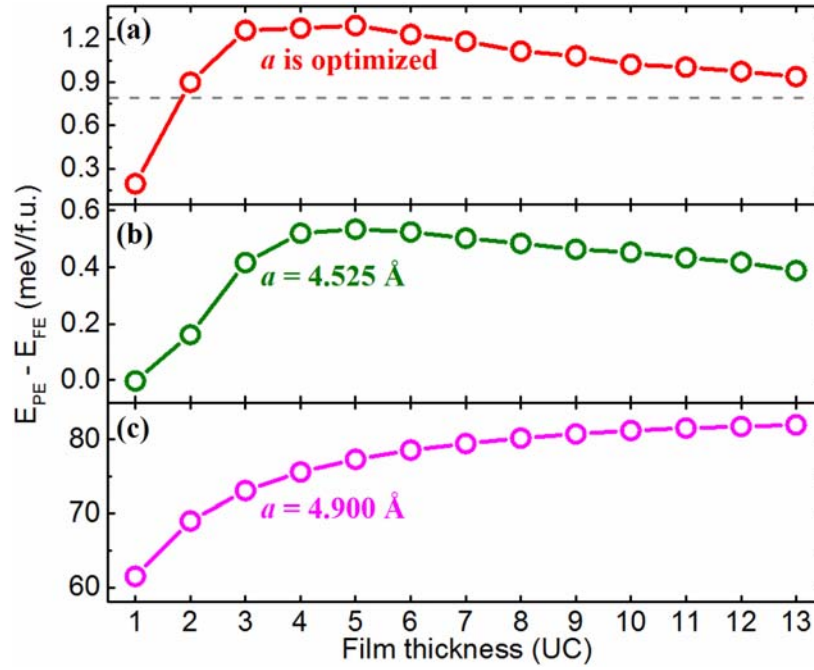
Figure 2. Energy differences between the PE and FE phases of SnTe films. (a) The lateral lattice constants a and b are fully optimized; (b) lattice constants a and b are fixed to the bulk lattice constant of 4.525 Å; and (c) lattice constants a=b=4.900 (a 7.2% tensile strain). The horizontal dashed line shows the result of bulk SnTe.
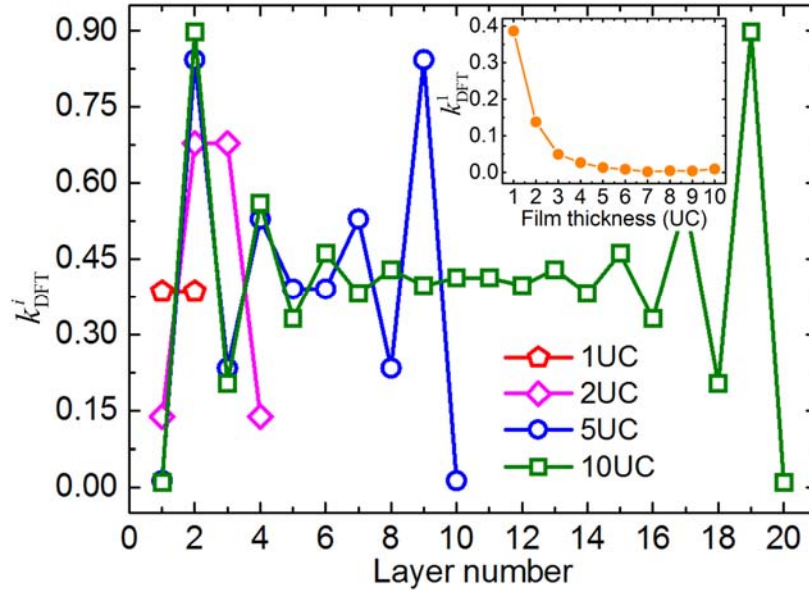

Figure 3. Layer force constants of Sn^{2+} ions as a function of the layer number, as fitted with the DFT total energies. The insert displays the force constant of the surface Sn^{2+} ion as a function of film thickness.
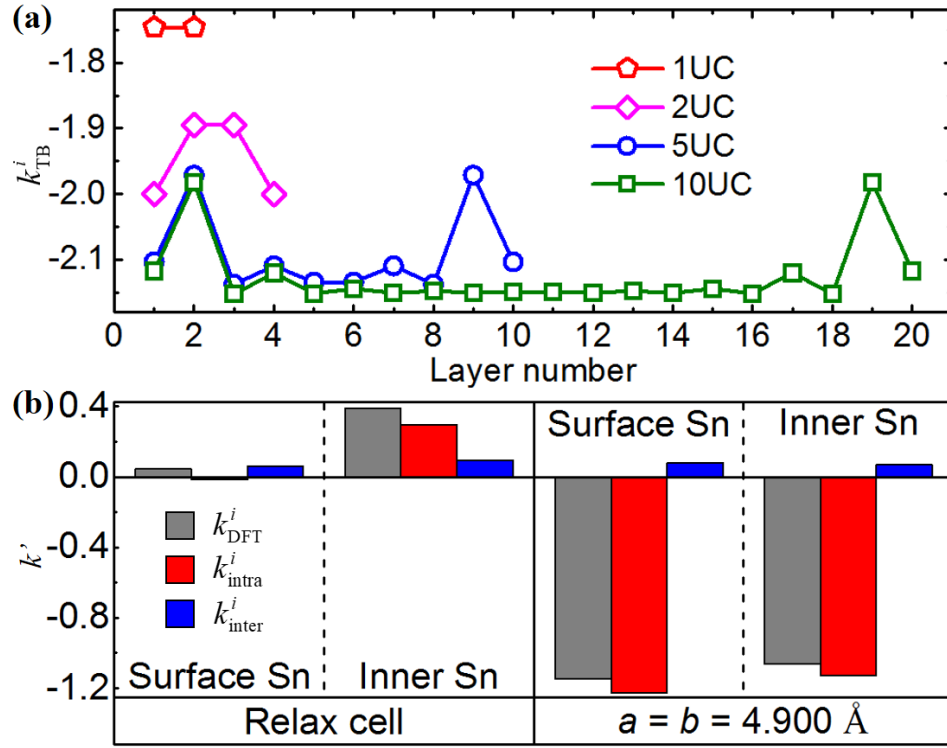
Figure 4. (a) Layer force constants of Sn^{2+} ions as a function of layer number, as fitted with the TB band energies. (b) Decomposition of layer force constants k_{DFT}^i into k_{intra}^i and k_{inter}^i for the 5-UC SnTe thin film (see main text).