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## Ferroelectric switching in epitaxial GeTe films

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In this paper, using a resonance-enhanced piezoresponse force microscopy approach supported by density functional theory computer simulations, we have demonstrated the ferroelectric switching in epitaxial GeTe films. It has been shown that in films with thickness on the order of several nanometers reversible reorientation of polarization occurs due to swapping of the shorter and longer Ge-Te bonds in the interior of the material. It is also hinted that for ultra thin films consisting of just several atomic layers weakly bonded to the substrate, ferroelectric switching may proceed through exchange of Ge and Te planes within individual GeTe layers. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4881735>]

Germanium telluride GeTe has long been known as the simplest ferroelectric material with just two atoms in the primitive cell.<sup>1</sup> The origin of the rhombohedral distortion and its effect on the properties of GeTe have been extensively studied by various groups.<sup>2-4</sup> Recently, there has been increased interest in GeTe, primarily driven by industrial application of GeTe-based compounds, such as quasibinary GeTe-Sb<sub>2</sub>Te<sub>3</sub>, in phase-change memory (PCM) alloys and also by the proposal that GeTe may exhibit a giant Rashba effect in the bulk phase.<sup>5</sup> Making use of the ferroelectric properties of GeTe is an appealing possibility to enhance the functionality of PCM, especially by using so-called interfacial PCM (iPCM) structures, where GeTe and Sb<sub>2</sub>Te<sub>3</sub> are arranged into sub nanometer-thick layers. Recent reports of ferroelectric ordering in small colloidal GeTe crystals provides tangible reasons to expect the ferroelectric switching functionality of GeTe down to the nanometer scale.<sup>6</sup> The main challenge in direct studies of ferroelectric switching in GeTe by conventional electrical spectroscopic techniques, such as hysteresis loop and transient current measurements, is its high conductivity: free charge carriers screen the applied electric field inhibiting polarization reversal and result in high dielectric loss. Application of piezoresponse force microscopy (PFM) allowed visualization of ferroelectric domain structure on the nanometer scale by virtue of limiting the leakage current.<sup>7</sup> However, up to now unambiguous evidence for the switching behavior in GeTe films was still lacking. The PFM hysteresis loops obtained in the previous studies were inconclusive<sup>7,8</sup> being most likely affected by the free charge motion and switching in only one direction has been demonstrated by PFM imaging.<sup>7</sup> In this Letter, we have demonstrated the ferroelectric switching of epitaxial GeTe films by using a resonance-enhanced PFM approach supported by density functional theory (DFT) computer simulations. It has been shown that in films with thickness on the order of several nanometers reversible reorientation of polarization occurs due to swapping of the shorter and longer Ge-Te bonds in the interior of the material.

According to Bragg diffraction studies, at 625 K,<sup>9</sup> GeTe undergoes a spontaneous transition from a non-polar rock-salt structure with six identical Ge-Te bonds to a polar rhombohedral phase with

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three shorter and three longer Ge-Te bonds. In other words, the material exhibits a displacive phase transition, similar to that of perovskite ferroelectrics, with the dipole moment in the low-temperature phase stemming from the relative shift of Ge and Te sublattices.<sup>10</sup> Raman scattering studies showed some mode softening,<sup>11</sup> which provided indirect support of the proposed structural change. This description of the phase transition has been recently challenged by extended X-ray absorption fine structure (EXAFS)<sup>12</sup> and total scattering studies.<sup>13,14</sup> Both of these techniques unambiguously demonstrated that the subsets of the shorter and longer Ge-Te bonds persist across the transition and, furthermore, no bond softening characteristic of displacive transitions could be detected. Terahertz spectroscopy measurements also failed to detect critical phonon softening.<sup>15</sup> At the same time, X-ray Bragg diffraction spectra taken for control purposes on the same samples clearly showed double peaks characteristic of the low-temperature rhombohedral phase that at higher temperatures merged into a single peak indicative of the rocksalt phase. The authors concluded that the ferroelectric-to-paraelectric transition results from an order-disorder transition, where the structure remains rhombohedrally distorted locally but the distortions change from coherent at low temperatures to stochastic at higher temperatures.<sup>9-11</sup> In the latter case, the average structure becomes cubic. This discrepancy between the Bragg diffraction and the EXAFS/total scattering results is not unknown and has also been reported for other materials.<sup>16</sup> Recently, there was a report on observation of ferroelectric ordering in thin GeTe films obtained by rf-sputtering and subsequently crystallized by thermal annealing. Using capacitance measurements, the authors observed a resonant increase in the dielectric constant occurring at 632 K, i.e., very close to the value of the Curie temperature determined from diffraction measurements.<sup>8</sup>

In this Letter, we have investigated the ferroelectric response of the 22-nm-thick GeTe films (with rhombohedrally distorted rocksalt structure  $\alpha$ -GeTe(0001)) epitaxially grown on Si(111) substrates using molecular beam epitaxy (MBE) and capped with a 10-nm-thick sputtered amorphous Si<sub>x</sub>N<sub>y</sub> layer to prevent oxidation of GeTe. Experimental details regarding the growth procedure and structural characterization can be found elsewhere.<sup>17</sup> The ferroelectric switching behavior of the GeTe films has been studied using PFM local spectroscopy and imaging modes.<sup>18</sup> DFT-based computer simulations have been performed to investigate the possible structural changes associated with polarization reversal.

In PFM, the ferroelectric measurements are carried out by monitoring the piezoelectric strain in response to a periodic bias applied to a conductive probing tip in contact with the sample surface and domain mapping is performed by detecting the piezoresponse while scanning the sample. A spectroscopic PFM approach, which is based on the measurement of the local piezoresponse signal as a function of the poling dc bias swept in the cyclic manner, allows measurements of the hysteresis loops which are directly related to the process of polarization reversal underneath the probing tip.<sup>18</sup> Figure 1(a) shows PFM amplitude and phase hysteresis loops, which illustrate the ferroelectric switching behavior of the GeTe films. Measurements were performed in the pulsed mode to minimize the electrostatic contribution to the measured response. Given a finite voltage drop across the Si<sub>x</sub>N<sub>y</sub> capping layer, the actual coercive voltage should be less than  $\pm 3.3$  V as determined from the hysteresis loops. The topographic image in Figure 1(b) shows a somewhat non-uniform surface morphology, with bright features with the height of about 10–30 nm. These topographic features have been also observed on un-capped GeTe films and thus cannot be attributed to the Si<sub>x</sub>N<sub>y</sub> layer. The fact that the only peaks observed in the X-ray diffraction pattern from the same sample were only those corresponding to GeTe suggests the absence of a second phase (within our measurement sensitivity). We believe that these features correspond to GeTe inclusions with a different crystal orientation and, possibly, with a different defect concentration. Importantly, no PFM hysteresis loops have been observed on these regions. This result rules out the possibility of charge entrapment in the capping Si<sub>x</sub>N<sub>y</sub> layer as a mechanism behind the hysteresis switching behavior. Figures 1(c) and 1(d) show the PFM amplitude and phase images of the GeTe film after it has been poled by scanning with an electrically biased PFM tip. It is interesting to note that while the poled film exhibits a robust amplitude signal with the reversed phase for opposite poling voltages, only noise-level PFM signals can be measured for the bright topographic features. The PFM signal of the GeTe film did not show any sign of decay over a period of several hours, which indicates that it is not caused by electrostatic effects. The obtained results demonstrate the

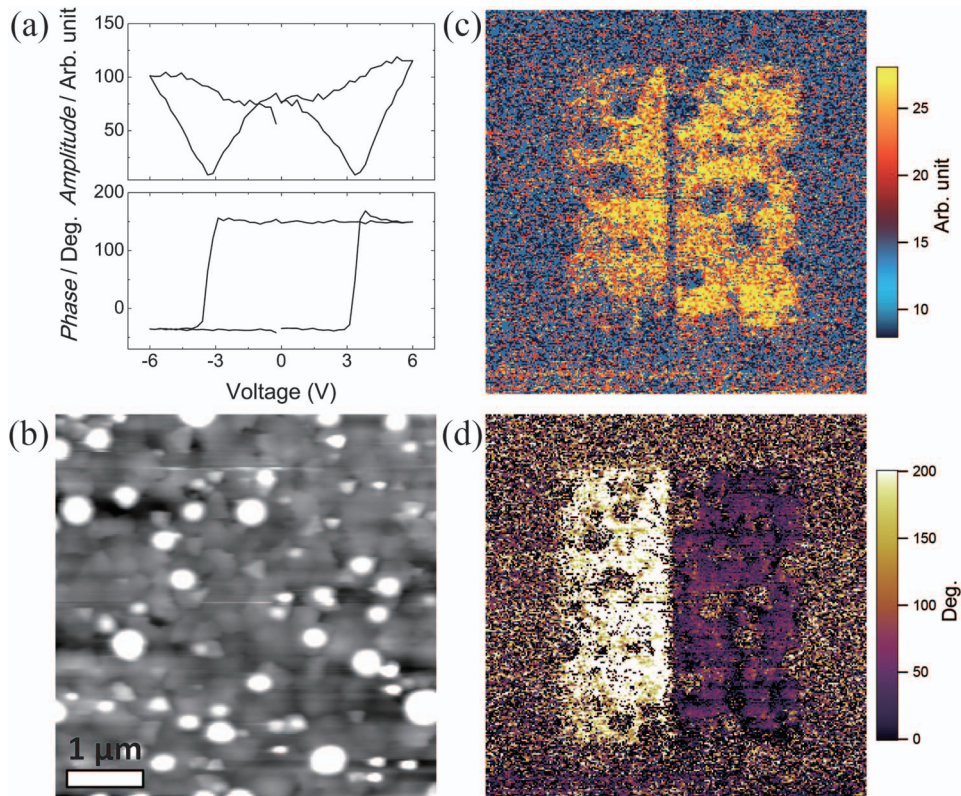


FIG. 1. (a) Local PFM hysteresis loops obtained by monitoring the amplitude (upper panel) and phase (lower panel) PFM signals of the GeTe film as a function of the external poling voltage. (b) Topography of the GeTe film. (c) and (d) PFM amplitude (c) and phase (d) images of the GeTe film after poling by scanning with a +9 V (left side) and −9 V (right side) tip bias.

switchable hysteretic electromechanical response of the GeTe films indicative of their ferroelectric nature.

We also performed simple DFT simulations to elucidate the mechanism of polarization reversal in GeTe films. The structure of the ferroelectric GeTe phase is usually described as rhombohedral, or distorted rocksalt, with subsets of three shorter and three longer Ge-Te bonds, which are characterized by a strong bonding energy hierarchy.<sup>19</sup> Our DFT simulations yield values of 2.57 eV and  $\sim 0.1$  eV for the longer and shorter bonds, respectively. The former value is typical of a covalent bond, which allows us to alternatively consider this structure as consisting of the Ge-Te layers with strong covalent-like bonds between Ge and Te atoms within the individual layers and much weaker bonding between the adjacent layers. The latter are formed using back lobes of the same p-orbitals that establish strong intralayer bonding often called resonant.<sup>20</sup> Destruction of resonant interaction is the basis of nanosecond amorphization in GeTe and its alloys.<sup>19,20</sup> Each individual Ge-Te layer includes covalently bonded three-fold coordinated Ge and Te atoms with the two species localized each on one side, top or bottom, of the Ge-Te layer (Figure 2). To underscore the fact that Ge-Te layers are in fact three-dimensional, below we use the terms such as “double layer” or “buckled layer” to refer to individual Ge-Te layers. The dipole moment is associated with different charges located on Ge and Te atoms and the asymmetry of the shorter *intralayer* and longer *interlayer* bonds.

A possible atomistic mechanism of polarization reversal in GeTe films, which we propose here, involves swapping the shorter and longer Ge-Te bonds as shown in Figure 2, where a plane of (111) Ge atoms moves closer to a different (111) plane of Te atoms in the adjacent Ge-Te layer. In this case, the Ge atoms (for the simplicity of discussion we assume only Ge atoms to move) move a small distance of about 0.3 Å upward. This process has low activation energy of 0.11 eV and can be viewed as the rupture of Ge-Te bonds within the existing buckled Ge-Te layers with subsequent re-formation

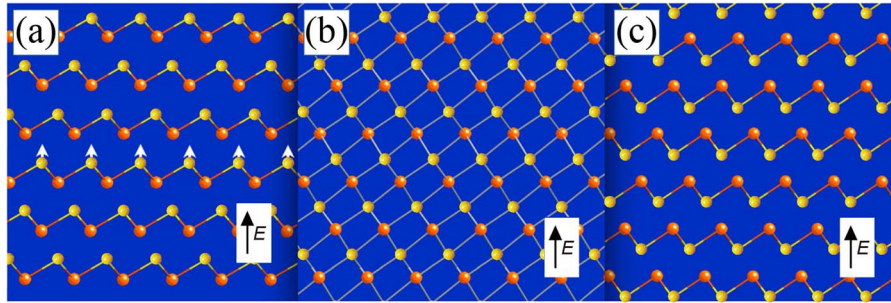


FIG. 2. Illustration of a possible mechanism of ferroelectric switching in GeTe under the applied electric field. Ge atoms are shown by yellow circles and Te atoms by larger orange circles. (a) Initial phase, (b) transient structure, and (c) switched phase. The displacement direction of the Ge atoms is indicated by white arrows. The Ge atoms move upward within the interior of the GeTe film until the three shorter and longer Ge-Te bonds swap, i.e., the existing buckled layers are destroyed and new ones are formed.

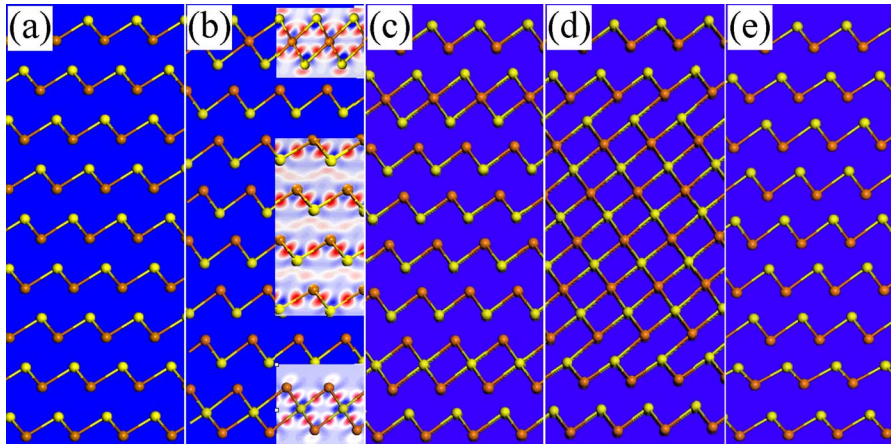


FIG. 3. Illustration of polarization switching and relaxation (backswitching) in thin (9 buckled layers) GeTe films. (a) The initial structure, identical to the one in Figure 2(a), showing Ge atoms in the buckled Ge-Te layers facing up. (b) The switched structure with Ge atoms in the buckled layers facing down and two triple-layer Ge-Te-Ge and Te-Ge-Te blocks at the top and bottom interfaces, respectively. Insets in (b) show charge density difference (CDD) maps comparing strong energy hierarchy within the “cubic” network (center) and symmetric three-center bonds in the triple-layer blocks at the interfaces. (c)-(e) Spontaneous polarization relaxation via movement of the triple-layer blocks into the interior of the film (c) and formation of the metastable mesh-like structure resulting in the original structure (e). In the figure, (covalent) bonds are shown between atoms separated by less than  $3 \text{ \AA}$ .

of different buckled layers, which remain stable after the field is turned off. Such a process is only possible in the interior of the samples because atoms at the extremities do not have the option to re-bond to the other side. Note, that at the nano- and microscopic level polarization reversal involves generation of domain nuclei, their forward growth in the polar direction and sideways expansion.<sup>21</sup> The proposed atomistic mechanism of exchange of shorter and longer bonds may play a part in the mechanism of domain wall movement.

We further investigate the stability of the switched structures as a function of the film thickness. Starting with a GeTe film consisting of a sequence of 9 buckled layers ( $\sim 3 \text{ nm}$ ) shown in Figure 3(a), we manually switch the ferroelectric orientation in the interior of the film. Since the atoms in the termination layers cannot switch,<sup>22</sup> we necessarily end up with triple atomic layers blocks located at the interfaces, one with Ge-Te-Ge atomic stacking and the other with the Te-Ge-Te stacking (Figure 3(b)). These triple layers are characterized by highly symmetrical fully resonant 3-center 4-electron bonds<sup>23</sup> as opposed to highly asymmetric, and only partially resonant, Ge-Te bonds within the interior of the slab, as evidenced by the simulated charge density maps shown in Figure 3(b), where red clouds in between atoms indicate a charge pile-up characteristic of covalent-like bonding.

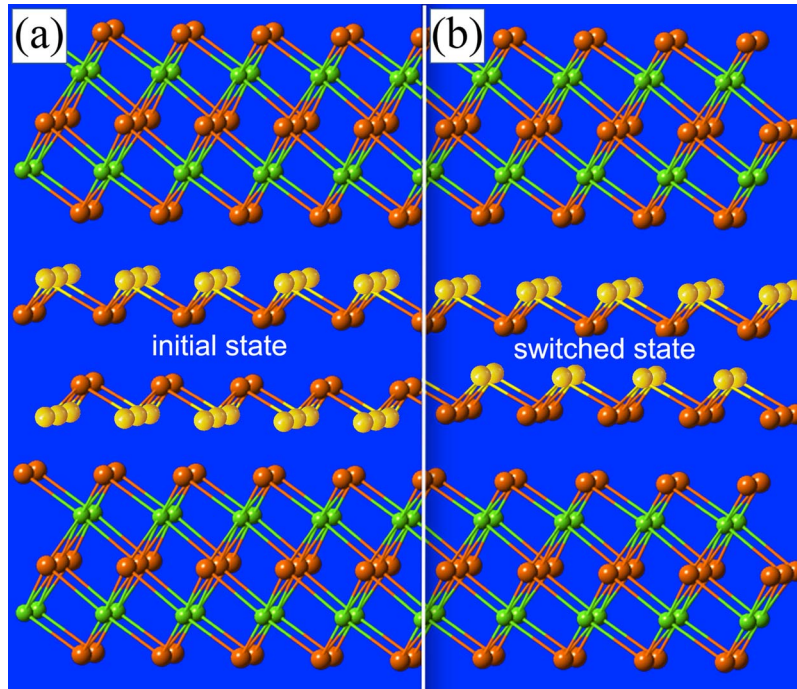


FIG. 4. Schematics of iPCM with ferroelectric functionality. (a) Initial and (b) switched ferroelectrically aligned configurations of an ultrathin  $\text{Sb}_2\text{Te}_3$ -GeTe- $\text{Sb}_2\text{Te}_3$  structure relaxed using DFT. The energy difference between the two phases is  $\sim 0.2$  eV/unit cell and the activation barrier is on the order of 2 eV.

Although both the interior of the film and the non-switchable triple layers are found to be individually stable, when the switched structure in Figure 3(b) is relaxed at 0 K, it reverts to the original state via the process that starts at the interfaces and involves movement of the resonantly bonded triple-layer blocks into the interior of the film and formation of the metastable resonantly bonded mesh-like structure (Figures 3(c)–3(e)). At the same time, simulations performed on a thicker GeTe film (15 buckled layers) demonstrated that the switched structure remains stable with the triple layers moving into the interior of the film and getting pinned there effectively separating oppositely oriented domains. These results suggest that the considered mechanism of ferroelectric reorientation, which involves swapping between the shorter and longer Ge-Te bonds in the interior of the material, can be realized only in relatively thicker GeTe films similar to those investigated by PFM in our studies. The necessity to have a certain thickness of the switched region for the stability of the switched orientation is similar to the critical nuclei size in crystal growth, where the gain in energy due to switching (crystallization) has to compensate loss in energy due to the presence of interfaces.

We note that it would be extremely interesting to investigate atomically thin GeTe layers that are weakly bonded to the substrate, since this situation is closely related to recently developed iPCM devices,<sup>24,25</sup> which have a structure of GeTe/ $\text{Sb}_2\text{Te}_3$  superlattices with the GeTe layers being located between the quintuple layers (QLs) of  $\text{Sb}_2\text{Te}_3$ .<sup>26–28</sup> Further analysis of the energetics of this polarization reversal mechanism, which involves flipping of the Ge and Te planes, is underway.

Of special interest is the situation when two GeTe layers are sandwiched between two layers of a  $\text{Sb}_2\text{Te}_3$ -like material (Figure 4). The overall symmetry of the structure would require a head-to-head or tail-to-tail polarization alignment in the two adjacent GeTe layers (Figure 4(a)), while application of an electrical field is likely to switch one of these GeTe layers generating a ferroelectric phase with polarization in both GeTe layers aligned in the same direction (Figure 4(b)). Our DFT simulations show that the energy difference between these two phases is about 0.2 eV/unit cell with an activation barrier on the order of 2 eV, a value very close to that of the activation energy in phase-change memory alloys.<sup>29</sup> Experimental verification of such a mechanism, currently underway, may open new perspectives for memory applications adding ferroelectric switchability of GeTe as a new

functional feature of memory and logic devices. This possibility is especially appealing in view of the recently proposed giant Rashba effect in GeTe,<sup>5</sup> strongly dependent on the material's symmetry, which, in turn, can be controlled using the ferroelectric switchability of GeTe.

In conclusion, we have performed direct experimental demonstration of ferroelectric switching in thin epitaxial GeTe films using PFM. Our DFT simulations show that reorientation of the dipole moment induced by swapping of the shorter and longer bonds is possible in relatively thick films (over several nanometers). We suggest that use of atomically thin GeTe layers in overall symmetric structures may add ferroelectric switching functionality to the phase-change memory and logic devices.

Epitaxial GeTe films were grown on Si(111) substrates using MBE. First, *p*-type Si(111) substrates with a 100-nm-thick thermal oxide layer were wet-cleaned to remove organic contaminants and the thermal SiO<sub>2</sub> film was stripped using 5%-diluted HF. The H-terminated substrates were immediately loaded in a custom-built MBE machine. Second, the substrates underwent multiple-step annealing at 150 °C and 350 °C in the transfer chamber to outgas residual water from the surface. Then, they were introduced into the ultrahigh vacuum growth chamber of the MBE cluster and heated up to prepare a high quality (7 × 7)-reconstructed surface. GeTe thin films were grown using Ge and Te dual-filament effusion cells. The corresponding fluxes were estimated by measuring with *ex situ* X-ray reflectivity the thickness of amorphous Ge and Te specimens, deposited at room temperature. Ge and Te growth rates were found to be ~0.13 and ~0.3 nm min<sup>-1</sup>, respectively, with a Ge-to-Te flux ratio of ~0.4. The growth process was followed in real time by means of *in situ* reflection high-energy electron diffraction and quadrupole mass spectrometry. Overall growth rates ranged from 0.2 to 0.5 nm min<sup>-1</sup>. To prevent oxidation, the GeTe layer was capped in vacuum with a 10-nm-thick layer of sputtered amorphous Si<sub>x</sub>N<sub>y</sub>. The sample thickness was 22 nm as estimated from interference fringes around the  $\alpha$ -GeTe(0003) Bragg peak.

The ferroelectric switching behavior of the GeTe films was studied using an atomic force microscopy (MFP-3D, Asylum Research) operated in a contact-resonance enhanced mode of PFM. Conducting Pt/Ti-coated cantilevers (NanoSensors) have been utilized for PFM studies. A typical frequency range of ac modulation voltage during the studies was ~350 kHz with an amplitude of 0.5–1.0 V (peak-to-peak).

The simulations of ferroelectric switching in GeTe were carried out using the plane-wave code CASTEP.<sup>30</sup> Ultrasoft pseudopotentials were used for germanium and tellurium atoms, including germanium 4s2 4p2 and tellurium 5s2 5p4 valence electrons, respectively. The DFT exchange-correlation contribution was evaluated using the generalized gradient approximation. The charge density was calculated with a plane-wave cutoff of 210 eV and a 4 × 4 × 4 Monkhorst Pack grid. For the relaxation processes, the Broyden, Fletcher, Goldfarb, and Shannon algorithm was used to relax the atomic coordinates at 0 K within a supercell of a fixed volume used to reflect the experimentally determined density.

For the bond energy calculations, we performed geometry optimization for a single buckled GeTe layer and the bonding energy for the shorter bonds was determined by subtracting from the energy of the relaxed structure those of participating isolated pseudoatoms. To estimate the energy of the weaker bonds, we compared energies of two slabs surrounded by 10 Å thick vacuum, one with two buckled layers that were sliced from the bulk phase and the same two buckled layers moved away from each other by 10 Å. The increase in energy is due to destruction of the interlayer bonds.

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