Stacking-dependent energetics and electronic structure of ultrathin polymorphic $V_2VI_3$ topological insulator nanofilms

Can Li,$^{1,2}$ Torben Winzer,$^1$ Aron Walsh,$^3,1$ Binghai Yan,$^4,5$ Catherine Stampfl,$^6,1$ and Aloysius Soon$^1$

$^1$Global E3 Institute, Department of Materials Science and Engineering, Yonsei University, Seoul, Korea
$^2$Centre for Sustainable Chemical Technologies, Department of Chemistry, University of Bath, Bath, UK
$^3$Max Planck Institute for Chemical Physics of Solids, NöthnitzerStr. 40, 01187 Dresden, Germany
$^4$School of Physics, University of Sydney, NSW 2006, Australia

(Dated: August 25, 2014)

Topological insulators represent a paradigm shift in surface physics. The most extensively studied Bi$_2$Se$_3$-type topological insulators exhibit layered structures, wherein neighboring layers are weakly bonded by van der Waals interactions. Using first principles density-functional theory calculations, we investigate the impact of the stacking sequence on the energetics and band structure properties of three polymorphs of Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$. Considering their ultrathin films up to 6 nm as a function of its layer thickness, the overall dispersion of the band structure is found to be insensitive to the stacking sequence, while the band gap is highly sensitive, which may also affect the critical thickness for the onset of the topologically nontrivial phase. Our calculations are consistent with both experimental and theoretical results, where available. We further investigate tribological layer slippage, where we find a relatively low energy barrier between two of the considered structures. Both the stacking-dependent band gap and low slippage energy barriers, suggest that polymorphic stacking modification may offer an alternative route for controlling the properties of this new state of matter.

PACS numbers: 71.20.-b, 73.20.At, 73.43.Nq, 75.70.Tj
Keywords: Topological insulators, chalcogenide materials, ultrathin nanofilms, electronic band gap

Topological insulators (TIs) have remarkable electronic properties since the role of relativistic interactions \{e.g. spin-orbit coupling (SOC)\} is fundamentally different from conventional insulators and semiconductors.\cite{2,3} TIs combine an insulating band gap in the bulk of the material with conductive surface states that are protected by time-reversal symmetry.\cite{2,3} The topological behavior has been theoretically predicted and experimentally observed in a variety of systems\cite{2,3} such as HgTe quantum wells,\cite{25} the Bi$_2$Se$_3$ family of compounds\cite{26,27} Heusler compounds\cite{28,29} pyrochlores\cite{30,31} Kondo insulators\cite{32,33} and thallium-based ternary chalcogenides.\cite{34} Besides the fundamental research in condensed matter physics, TIs have great potential to impact multiple areas of application \{e.g. electronic, optoelectronic, and spintronic materials, thermoelectric materials, phase-change-memory and catalytic chemistry\}.\cite{35,36}

To effectively explore the surface conductivity of TIs, ultrathin films with a large surface-to-volume ratio provide attractive systems for transport studies, which are highly relevant for electronic device applications.\cite{37,38} For this purpose, the $V_2VI_3$ compounds Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ are a good choice owing to their layered rhombohedral crystal structure with space group $R\overline{3}m$. The structure contains five atomic layers as a basic unit, denoted as a quintuple layer (QL). There is strong chemical bonding within a QL, with weak van der Waals (vdW) interactions between different QLs. $V_2VI_3$ compounds can be easily grown as two-dimensional thin films by molecular beam epitaxy.\cite{39,40} The two-dimensional nanostructures of Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ have been researched both theoretically and experimentally.\cite{41,42,43} Their electronic structure depends on the thickness of the film: Above a critical thickness ($D$), films will transform from a normal insulator (NI) to a TI.\cite{44,45} For the Bi$_2$Se$_3$ system, $D = 6$ QL (about 6 nm),\cite{41,42} while $D = 2$ or 3 QL (about 2 or 3 nm) for Bi$_2$Te$_3$ and 4 QL (about 4 nm) for Sb$_2$Te$_3$.\cite{46} Below the critical thickness, a surface band gap opens, due to hybridization of overlapping surface state wavefunctions.\cite{47} Thus, a minimum film thickness is suggested for topological electronic device applications.

Although the critical thicknesses of Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ have been studied in theory and experiment, the effect of pressure and stress, which are critical factors in real environments, have not been clearly explored.\cite{48,49} Liu et al. have indicated that uniaxial strain in the $\langle 111 \rangle$ direction is an important parameter for influencing the topological insulating phase and the direct band gap of Bi$_2$Se$_3$ at the $\Gamma$ point.\cite{50,51} However, besides uniaxial strain, shear strain could also be important in applications for ultrathin layered material: such as graphite,\cite{52} boron nitride,\cite{53} and $V_2VI_3$ compounds. The weak van der Waals force between these layers leads to the possibility of layer slippage and polytypism. When layered materials are used as mechanical components of nanodevices, the properties of friction are extremely important. The nanotribologies of bilayer graphene and boron nitride layers have been intensively researched; the results show that the associated energy barriers are extremely low.\cite{54,55} The influence of layer sequencing and slippage in $V_2VI_3$ TI compounds, which directly relates to their usage in electronic device applications, is the
subject of this study.

In these $V_2VI_3$ compounds, there are three QLs in each bulk conventional hexagonal unit cell, as shown in Fig. 1. There are also three unique lattice sites (A, B and C). Different polymorphic stacking types are labeled by the group VI atoms. The stacking sequence is labeled by the group VI atomic layer according to the numbers (given in red).

| Polymorph | Stacking Sequence |
|-----------|-------------------|
| Top       | ABC-BCA-CAB       |
| FCC       | ABC-ABC-ABC       |
| Normal    | ABC-BCA-ABC       |

Different polymorphic stacking types are labeled by the group VI atoms. Large spheres (blue) are used to represent the group V atoms, while the small ones (green, yellow, and white) for group VI atoms. The stacking sequence is labeled by the group VI atomic layer corresponding to the numbers (given in red).

FIG. 1. (Color online) The atomic structures of $V_2VI_3$ polymorphs – the top (ABC-CAB-BCA), FCC (ABC-ABC-ABC) and normal (ABC-BCA-ABC) stacking sequence. Large spheres (blue) are used to represent the group V atoms, while the small ones (green, yellow, and white) for group VI atoms. The stacking sequence is labeled by the group VI atomic layer corresponding to the numbers (given in red).

In this paper, we employ density-functional theory (DFT) calculations to study the effects of polymorphic stacking and planar slippage on the electronic structures and the critical thickness of the polymorphs of $V_2VI_3$ (namely, $Bi_2Se_3$, $Bi_2Te_3$ and $Sb_2Te_3$) ultrathin nanofilms as a function of film thickness.

I. METHODOLOGY AND COMPUTATIONAL APPROACH

All DFT calculations, including geometry relaxation and electronic structure, are performed on the basis of the projector augmented wave method implemented in the Vienna $Ab$ $Initio$ Simulation Package (VASP) code. The exchange-correlation functional used is the generalized gradient approximation (GGA) due to Perdew, Burke, and Ernzerhof (PBE) including scalar-relativistic effects in addition to SOC. The latter is known to be of great importance in accounting for the topologically protected surface states in TIs. The kinetic energy cutoff of electron wavefunctions is set to 500 eV and a $k$-point sampling of $12\times12\times1$ for all films was found to be converged. A vacuum region of 20 Å is used to avoid spurious interactions between repeating slabs. Both the shape and size of the unit cell and the relative atomic positions are relaxed with a force tolerance of 0.01 eV/Å. The dispersion-corrected DFT approach due to Grimme et al. (DFT+D2) has been used in which long-range dispersion interactions are empirically described by a pair-potential of the $C_6/R_0$ form. The Grimme-D2 coefficients are obtained from values tabulated in terms of the chemical identity of the atoms: $C_6 = 63.565$, 38.459, 12.643 and 31.750; $R_0 = 1.725$, 1.710, 1.610 and 1.720 for Bi, Sb, Se and Te atoms, respectively.

In addition, hybrid DFT calculations at the level of HSE06+SOC for $Bi_2Se_3$ nanofilms have been used to study the electronic band structure. This is because the HSE06 hybrid functional typically presents a considerable improvement over semi-local density-functional descriptions of the band gaps of solid-state systems. This, in turn, is compared to available results using the van der Waals density functional with Cooper’s exchange (vdW-DF$^2$) and $GW$ calculations in the literature.

The QL-QL interaction energies of ultrathin nanofilms, $E^{QL}$ from 1 QL to 6 QLs have been calculated using:

$$E^{QL} = \frac{E^{sys} - N^{QL}E^{QL}}{N^{QL}},$$

where $E^{sys}$ and $E^{QL}$ are the total energy of the system in question and that of 1 QL, respectively, and $N^{QL}$ is the number of QLs in that system. Since the base unit is 1 QL, $E^{QL}$ denotes the relative thermodynamic stability of the ultrathin film stacked per QL. In addition, to investigate the planar slippage energy barriers for these $V_2VI_3$ polymorphs, we employ the climbing-image nudged elastic band (CI-NEB) method at the level of PBE+D2.

II. RESULTS AND DISCUSSION

A. Bulk structures of $V_2VI_3$ compounds

The crystal structures for three different polymorphic stacking sequences: normal, FCC and top are shown in Fig. 1 with the optimized lattice constants listed in Tab. 1. The DFT+D2 optimized bulk structures are found to be in good agreement with the available experimental results and the vdW-DF$^2$ values and are much...
closer to these results than previously calculated theoretical results (which do not include vdW corrections). This signals that the DFT+D2 approach is adequate for describing these weakly-bonded layered systems. Cohesive energies of the bulk $\text{V}_2\text{VI}_3$ polymorphs are calculated and we find that all bulk structures yield a negative value, i.e., stable with respect to their corresponding atomic energies (See Tab. I). The normal structure is the most favored bulk polymorph, while the top structure is least stable. However, for $\text{Bi}_2\text{Te}_3$ and $\text{Sb}_2\text{Te}_3$ the differences between normal, fcc, and top structures are marginal. Only the normal stacking of $\text{Bi}_2\text{Se}_3$ is notably more stable compared to the other polymorphs. We have calculated the electronic band structures of bulk normal $\text{Bi}_2\text{Se}_3$ with PBE+SOC and HSE+SOC. The band gap energy, $E_g$ of bulk $\text{Bi}_2\text{Se}_3$ is calculated to be 0.36 eV for PBE+SOC and 0.28 eV for HSE06+SOC, respectively. Surprisingly, the PBE+SOC $E_g$ seems to be in a better agreement with other theoretical reports (0.30 eV) and experimental data (0.35 eV) than the slightly underestimated HSE06+SOC value. We note that for $\text{Bi}_2\text{Se}_3$ GW corrections are known to change the character of the band gap from an indirect to a direct one. 

B. Ultrathin $\text{V}_2\text{VI}_3$ nanofilms

1. Energetics and thermodynamic stability of $\text{V}_2\text{VI}_3$ nanofilms

For the nanofilms of these $\text{V}_2\text{VI}_3$ materials, we perform PBE+D2(+SOC) calculations to study their QL-QL interaction energy, $E^{\text{QL}}$, as well as to understand their electronic band properties as a function of increasing number of QLs, $N^{\text{QL}}$. Figure 2 shows the variation of $E^{\text{QL}}$ for normal, fcc, and top structured nanofilms as a function of $N^{\text{QL}}$ for $\text{Bi}_2\text{Se}_3$ (Fig. 2a), $\text{Bi}_2\text{Te}_3$ (Fig. 2b), and $\text{Sb}_2\text{Te}_3$ (Fig. 2c), respectively. $E^{\text{QL}}$ for all three stackings considered in this work are calculated to be negative, and converge to the bulk-like values ($E^{\text{QL}}_{\text{bulk}}$) with increasing $N^{\text{QL}}$. Taking the bulk-stacked normal structure as an example, we find that $E^{\text{QL}}_{\text{bulk}} = -0.41$, $-0.61$, and $-0.51$ eV for $\text{Bi}_2\text{Se}_3$, $\text{Bi}_2\text{Te}_3$, and $\text{Sb}_2\text{Te}_3$, respectively. The top structured nanofilms have the least favorable $E^{\text{QL}}$, while the naturally forming normal structure yield the most favorable $E^{\text{QL}}$, with almost similar values for fcc stacked nanofilms. These results are also consistent with the calculated cohesive energies of their bulk polymorphs, as illustrated above. Given that the calculated average difference in $E^{\text{QL}}$ between the normal and fcc polymorphs is only about 0.06 eV, it is not difficult to imagine metastable fcc forming from normal stacked films via a martensitic-like (i.e., diffusionless) planar displacement, especially when the film thickness is in the nanometer range.

To study the energetic profile of this possible planar displacement, we use the the simplest 2 QL nanofilms for each $\text{V}_2\text{VI}_3$ to study planar displacement (here, we term this as slippage). Similar to the slippage in other 2D materials e.g., bilayer graphene and boron nitride, the upper QL may slip along the (1100) or (110) directions as shown in Fig. 3. In these two directions, normal, fcc, and top structure will appear when the bottom Se atomic layer in the upper QL is located in B, C and A sites, respectively. Since each QL is one unit, movement appears only between adjoining QLs. To understand the barrier needed to undergo this slippage in the (1100) direction, we have also considered possible transition states (TS) structures between the normal and the fcc structured nanofilm. For the other (1100) direction, the pathway goes via the top polymorph. These mid-way configurations are consistent with the slippage in bilayer graphene and boron nitride.

To calculate these slippage energy barriers, the energies of $E_1 (= E^{\text{fcc}} - E^{\text{normal}})$, $E_2 (= E^{\text{TS}} - E^{\text{normal}})$ and $E_3 (= E^{\text{top}} - E^{\text{normal}})$ have been defined in Fig. 3, where $E^{\text{normal}}$, $E^{\text{fcc}}$, $E^{\text{top}}$, and $E^{\text{TS}}$ denote the energies of normal, fcc, and top structure as well as the transition state, respectively. As shown in Figs. 4 to 9, the energies of top with respect to normal structured films, $E_1$ is calculated to be 0.049, 0.064, and 0.074 eV for $\text{Bi}_2\text{Se}_3$, $\text{Bi}_2\text{Te}_3$, and $\text{Sb}_2\text{Te}_3$, respectively. And based on our CI-NEB calculations, for the energy barrier in the (1100) direction, $E_2$ is found to be 0.075, 0.108, and 0.117 eV for $\text{Bi}_2\text{Se}_3$, $\text{Bi}_2\text{Te}_3$, and $\text{Sb}_2\text{Te}_3$, respectively, while for the (1100) direction, $E_3$ is found to be 0.205, 0.254, and 0.295 eV, correspondingly. We see that $E_2$ is at least two to three times larger than $E_2$ for all cases. Compared to the reported $E^{\text{QL}}$ (19.3 meV) and area-normalized $E_2$ (1.6 meV/Å²) values for bilayer graphene, we find rather similar orders of magnitude for the $\text{V}_2\text{VI}_3$ chalcogenide nanofilms: 13.8 and 4.8 meV/Å² for $\text{Bi}_2\text{Se}_3$ films, 18.3 and 5.5 meV/Å² for $\text{Bi}_2\text{Te}_3$ films, and 16.4 and 6.5 meV/Å² for $\text{Sb}_2\text{Te}_3$ films, respectively. This would then imply that the martensitic normal-to-
TABLE I. Lattice constants, electronic band gap, and cohesive energy of bulk V$_2$VI$_3$ compounds. The lattice constants, $a$ and $c$, and cohesive energy, $E_{\text{coh}}$, are calculated using PBE+D2+SOC and are reported in Å and eV, respectively. The electronic band gap, $E_g$, is in eV and is calculated using PBE+SOC (the HSE06+SOC derived $E_g$ for Bi$_2$Se$_3$ is 0.28 eV). Our results are compared to available experimental and theoretical values in the literature. The van der Waals density functional with Cooper’s exchange (vdW-DF$_{C09}^{\text{vD}}$) was used in Ref. [40].

|       | Bi$_2$Se$_3$ | Bi$_2$Te$_3$ | Sb$_2$Te$_3$ |
|-------|--------------|--------------|--------------|
| $a$   |              |              |              |
| normal| 4.092        | 4.349        | 4.195        |
| fcc   | 4.071        | 4.290        | 4.144        |
| top   | 4.057        | 4.282        | 4.142        |
| Experiment | 4.138$^a$ | 4.383$^a$    | 4.250$^a$    |
| Theory (normal) | 4.125$^b$ | 4.360$^c$    | 4.530$^c$    |
| $c$   |              |              |              |
| normal| 28.91        | 31.09        | 30.81        |
| fcc   | 29.60        | 32.03        | 31.85        |
| top   | 32.15        | 34.74        | 34.53        |
| Experiment | 28.64$^a$ | 30.49$^a$    | 30.35$^a$    |
| Theory (normal) | 28.76$^b$ | 30.17$^b$, 30.63$^c$ | 30.29$^c$ |
| $E_g$ |              |              |              |
| Experiment | 0.35$^d$ | 0.17$^e$, 0.15$^d$, 0.13$^f$ | 0.30$^d$, 0.21$^f$ |
| Theory (normal) | 0.30$^g$, 0.31$^h$ | 0.08$^h$, 0.05$^c$ | 0.03$^c$ |
| $E_{\text{coh}}$ |              |              |              |
| normal| −4.30        | −3.82        | −3.17        |
| fcc   | −4.00        | −3.80        | −3.16        |
| top   | −3.98        | −3.76        | −3.04        |

$^a$ Reference [43]  
$^b$ Reference [40]  
$^c$ Reference [44]  
$^d$ Reference [45]  
$^e$ Reference [48]  
$^f$ Reference [49]  
$^g$ Reference [8]  
$^h$ Reference [41]

fcc slippage would most probably occur for these V$_2$VI$_3$ chalcogenide nanofilms via the ⟨1100⟩ rather than the ⟨1100⟩ direction.

2. Electronic structure of V$_2$VI$_3$ nanofilms

Turning to the electronic structure of the normal and fcc stacked nanofilms of V$_2$VI$_3$, we study both the electronic band dispersion, as well as the electron density plots (at the band-edges) to understand how their topological insulating properties might be influenced by both stacking and film thickness in these nanosystems. In Fig. 4, we calculate and plot the electronic band structures (using PBE+SOC), showing only the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) for different numbers of QLs. The full band structures are shown in Fig. 7 of the Appendix section, where the number of bands necessarily increases linearly with the thickness of the films. The overall band dispersion profile (especially near the Γ point) of the normal structured films are found to be rather similar to those of the corresponding fcc polymorph, but the clear difference lies in the variation in the magnitude of $E_g$. To cross-check our PBE+SOC results, we have also selectively calculated the electronic structure of 1 and 2 QL normal and fcc stacking of Bi$_2$Se$_3$ using HSE06+SOC where the predicted $E_g$ are plotted in Fig. 5.

For Bi$_2$Se$_3$, $E_g$ decreases to zero when the N$^\text{QL}$ of normal structured nanofilms increases to 6, while that of all fcc-like films remain greater than zero. The predicted $E_g$ of Bi$_2$Se$_3$ normal structured films are in good agreement with other theoretical reports[22,24,40,41] but differ from the reported experimental data for Bi$_2$Se$_3$ films[21] as shown in Fig. 5a. Interestingly, the predicted $E_g$ of the fcc polymorphs, except for the 6 QL nanofilm, seem to agree closely with the experimental $E_g$ of Bi$_2$Se$_3$ films. Accordingly, the predicted $E_g$ of Bi$_2$Se$_3$ fcc structured
films are systematically larger than that of the Bi$_2$Se$_3$ normal stacked. Our HSE06+SOC derived $E_g$ for 2 QL normal and fcc structure show the same tendency (albeit having larger absolute values of $E_g$, and poorer agreement with reported experimental values). The $E_g$ of the fcc structured 6 QL is close to zero (0.02 eV), which may lead to a closure of the band gap when the $N^{QL}$ increases continually. For Bi$_2$Te$_3$, as shown in Fig.5b, the $E_g$ of the normal polymorph decreases to zero when $N^{QL}$ is increased to 3, again agreeing with other theoretical reports. In contrast to Bi$_2$Se$_3$, the $E_g$ of the fcc structured films quickly reaches zero when $N^{QL}$ reaches 2. For Sb$_2$Te$_3$, $E_g$ of all normal structural films are greater than (or close to) zero for $N^{QL}$ less than 5 while $E_g$ decreases to zero when the $N^{QL}$ of fcc stacked films increases to 4, cf. Fig.5c. Again, the reported experimental data seems to agree better with the predicted $E_g$ of the fcc polymorph.

Based on the above comparison, within the accuracy of PBE+SOC DFT, the experimentally measured values of $E_g$ for these V$_2$VI$_3$ nanofilms seem to better match those of V$_2$VI$_3$ fcc structured nanofilms, rather than the assumed more stable normal stacking. Although from our bulk calculations of Bi$_2$Se$_3$, we find that the PBE+SOC $E_g$ value is found to agree better with available experimental and GW values, we cannot rule out the intrinsic deficiencies of semi-local DFT which could underestimate the predicted $E_g$ values for these polymorphic nanofilms. We also note that a self-consistent relativistic quasiparticle treatment may change the qualitative nature of our results, but the qualitative trends discussed here are expected to be reliable.

Although vanishing values of $E_g$ for some nanofilms are predicted, this is not sufficient information to conclude that these states are topologically protected. For systems with inversion symmetry, such as the V$_2$VI$_3$ compounds considered in this work, the $Z_2$ topological order can be determined by a parity analysis of the occupied states at time-reversal points in the Brillouin zone. As a first approximation to this full $Z_2$ topological analysis, we plot and study the $\Gamma$ point electron density distributions.
normal fcc since the may be due to a reduced overlap of the surface states, $N$ function of the number of QL, $E$ films matches the experimental results better. We illustrate this for the 5 QL film, and vice versa. This inversion of the orbital character suggests a possible transition from a normal insulator (NI) to a TI, which has been observed in experimental measurements. However, for the $fcc$ stacked $Bi_2Se_3$ films, the calculated HOCO and LUCO plots for $N^QL$ ranging from 1 to 6 show very similar orbital character, suggesting that no such NI to TI inversion has taken place. We illustrate this for the 5 and 6 QL $fcc$ structured films in Fig. 6. For the $Bi_2Te_3$ nanofilms, an orbital parity inversion is observed for both stackings $normal$ and $fcc$, taking place at the increase from 3 QL to 4 QL for the $normal$ structure, cf. Fig. 6, and for the $fcc$-like films the inversion is observed when $N^QL$ is increased from 2 to 3. And likewise, based on the electron density distribution for $Sb_2Te_3$, the orbital parity is predicted to be inverted for both $normal$ and $fcc$ structure (i.e. 4 to 5 QL for $normal$ and 3 to 4 QL for $fcc$). Thus, when these layered $V_2VI_3$ nanofilms are used in nano-devices, due to the weak interaction between these QLS, a mechanical slip could easily be experienced and thus the desired topological insulating character of these films could be intentionally exploited for new technologies.

**FIG. 5.** (Color online) $\Gamma$-point band gap energies, $E_g$, as a function of the number of QL, $N^QL$: (a) $Bi_2Se_3$, (b) $Bi_2Te_3$, and (c) $Sb_2Te_3$. $normal$ (PBE) and $fcc$ (PBE) denote the PBE+SOC value, while $normal$ (HSE) and $fcc$ (HSE) denote that calculated by the HSE06+SOC hybrid functional, respectively. The absolute values for these $E_g$ are listed in Table II of the Appendix section.

**FIG. 6.** (Color online) $\Gamma$-point electron density distributions (namely the HOCO and LUCO states): (a) 5 and 6 QL $normal$ structured films of $Bi_2Se_3$, (b) 5 and 6 QL $fcc$ structured films of $Bi_2Se_3$, (c) 3 and 4 QL $normal$ structured films of $Bi_2Te_3$, (d) 2 and 3 QL $fcc$ structured films of $Bi_2Te_3$, (e) 3 and 4 QL $normal$ structured films of $Sb_2Te_3$, and (f) 3 and 4 QL $fcc$ structured films of $Sb_2Te_3$. 

Upon studying the band gap, $E_g$, and orbital character inversion as a function of $N^QL$ for the $normal$ and $fcc$ structure of these $V_2VI_3$ nanofilms, it seems to suggest that given the very low energy barriers for the $normal$-to-$fcc$ slippage, metastable $fcc$ structured nanofilms of these $V_2VI_3$ compounds could well form and offer different electronic band properties (e.g. critical $N^QL$ for orbital parity inversion), especially for $Bi_2Se_3$ nanofilms. Therefore, when these layered $V_2VI_3$ nanofilms are used in nano-devices, due to the weak interaction between these QLS, a mechanical slip could easily be experienced and thus the desired topological insulating character of these films could be intentionally exploited for new technologies.
III. CONCLUSION AND SUMMARY

The energetics of stacking sequences and their effect on the transition from normal to topological insulating behavior in Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ nanofilms have been investigated via first-principles DFT calculations. We find that the overall band dispersion is relatively insensitive to the stacking sequence, while the magnitude of the band gap, and the critical thickness for a band edge parity inversion, is more sensitive. Relatively low energy barriers may allow for martensitic normal-to-fcc slip-page, which are predicted to change the electronic structure and alter the topological behavior of these V$_2$VI$_3$ nanofilms. Thus, the effect of mechanical shear stress should be carefully considered in applications of topological insulators, e.g. the nanotribological conversion from TI to NI may be exploited in nano-circuit switches. In this context, a more detailed experimental analysis of the present and accessible stacking sequences is called for.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support by the Global Frontier R&D Program (2013M3A6B1078881) on Center for Global Frontier Hybrid Interface Materials (GFHIM) funded by the Korean Ministry of Science, ICT & Future Planning, as well as the Australian Research Council (ARC). This work was also supported by the third Stage of Brain Korea 21 Plus Project Division of Creative Materials. Computational resources have been provided by the Australian National Computational Infrastructure (NCI) and by the KISTI supercomputing center (KSC-2013-C3-040). A. W. and B. Y. acknowledge support from the Royal Society University Research Fellowship scheme, and the European Research Council Advanced Grant (ERC 291472), respectively.
APPENDIX: SUPPORTING INFORMATION

FIG. 7. (Color online) PBE+SOC DFT-derived electronic band structures of normal structured nanofilms of Bi$_2$Se$_3$: (a) $N^{QL} = 1$, (b) $N^{QL} = 3$, and (c) $N^{QL} = 6$. The band-edges due to the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) are shown in red lines.

TABLE II. Γ-point band gap energies, $E_g$, for normal and fcc structured nanofilms calculated using PBE+SOC (values in parenthesis by HSE06+SOC) as a function of the number of QL, $N^{QL}$ for Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$. These are compared to available experimental as well as theoretical values. All values are reported in eV.

| $N^{QL}$ | normal | fcc | Experiment | Theory |
|----------|---------|-----|------------|--------|
| 1        | 0.86 (1.19) | 0.86 (1.19) | 0.25$^a$ | 0.95$^b$, 0.72$^c$, 0.73$^c$, 0.71$^e$ |
| 2        | 0.15 (0.36) | 0.26 (0.48) | 0.14$^b$ | 0.35$^b$, 0.12$^c$, 0.11$^d$, 0.098$^e$ |
| Bi$_2$Se$_3$ | 3 | 0.04 | 0.13 | 0.07$^a$ | 0.11$^b$, 0.01$^c$, 0.03$^d$, 0.01$^e$ |
| 4 | 0.01 | 0.04 | 0.04$^a$ | 0.08$^b$, 0.00$^c$ |
| 5 | 0.01 | 0.02 | 0.00$^a$ |
| 6 | 0.00 | 0.00 | 0.00$^b$ | 0.00$^c$ |
| 1 | 0.34 | 0.34 | 0.63$^b$, 0.40$^c$, 0.34$^d$, 0.39$^e$ |
| 2 | 0.14 | 0.00 | 0.07$^b$, 0.11$^c$, 0.14$^d$, 0.15$^e$ |
| Bi$_2$Te$_3$ | 3 | 0.00 | 0.00 | 0.02$^b$, 0.02$^c$, 0.05$^d$, 0.04$^e$ |
| 4 | 0.00 | 0.00 | 0.01$^b$, 0.01$^c$, 0.02$^d$, 0.005$^e$ |
| 5 | 0.00 | 0.00 | 0.01$^b$, 0.00$^c$, 0.00$^d$ |
| 6 | 0.00 | 0.00 | 0.00$^b$, 0.00$^c$ |
| 1 | 0.73 | 0.73 | 0.67$^f$ |
| 2 | 0.10 | 0.19 | 0.26$^f$ |
| Sb$_2$Te$_3$ | 3 | 0.01 | 0.06 | 0.06$^g$ |
| 4 | 0.03 | 0.00 | 0.00$^g$ |
| 5 | 0.00 | 0.00 |
| 6 | 0.00 | 0.00 |

$^a$ Experiment, Reference 14
$^b$ G$_0$W$_0$, Reference 38
$^c$ LDA, Reference 38
$^d$ PBE, Reference 24
$^e$ PBE, Reference 22
$^f$ Experiment, Reference 20
