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The effects of surface bond relaxation on electronic structure of Sb2Te3 nano-films by first-principles calculation
C. Li, Y. F. Zhao, C. X. Fu, B. Q. Chi, Y. Y. Gong, and C. Q. Sun

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The effects of surface bond relaxation on electronic structure of Sb$_2$Te$_3$ nano-films by first-principles calculation

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The effects of vertical compressive stress on Sb$_2$Te$_3$ nano-films have been investigated by the first principles calculation, including stability, electronic structure, crystal structure, and bond order. It is found that the band gap of nano-film is sensitive to the stress in Sb$_2$Te$_3$ nano-film and the critical thickness increases under compressive stress. The band gap and band order of Sb$_2$Te$_3$ film has been affected collectively by the surface and internal crystal structures, the contraction ratio between surface bond length of nano-film and the corresponding bond length of bulk decides the band order of Sb$_2$Te$_3$ film. © 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/10.1063/1.4898143]

INTRODUCTION

A new class of quantum matter topological insulator (TI) has been found in the last years.$^{1–3}$ Different from normal insulator (NI) and metal; TI has an insulating gap in the bulk and a gapless edge on the surface or interface and is protected by time-reversal symmetry.$^{4,5}$ TI with strong spin-orbit coupling (SOC) and band inversion at Fermi level $E_F$, so it has remarkable electronic properties and great potential for electronic and optoelectronic materials,$^{6–8}$ superconductor,$^{9,10}$ catalytic chemistry and magnetic applications,$^{11,12}$ and has attracted great attention theoretically and experimentally.$^{2,13–15}$ Up to now, several topological candidates have been found, such as: HgTe,$^{3,16}$ V$_2$VI$_3$ compounds,$^{12,15,17,18}$ Heusler compounds,$^{19–21}$ thallium-based ternary chalcogenides$^{22}$ and organic TIs.$^{23–25}$

To effectively exploit the surface conductivity of TIs, nano-films with a large surface-to-volume ratio provide attractive systems for transport studies, which are highly relevant for electronic device applications. Owing to the layered rhombohedral crystal structure with space group $R$-3$m$, V$_2$VI$_3$ compounds are suitable for nano-application, and two-dimensional V$_2$VI$_3$ nano-films have been synthesized easily in laboratory by molecular beam epitaxy method (MBE).$^{15,26,27}$ In V$_2$VI$_3$ compound, each basic unit includes five atomic layers named a quintuple layer (QL) (see Fig. 1). There is strong chemical bonding within a QL, with weak $van$ $der$ $Waals$ (vdW) interactions between different QLs. Two-dimensional V$_2$VI$_3$ nano-films have been studied theoretically and experimentally, and their electronic structures depend on the film thickness in nano-range and the critical thickness ($D$) are $D = 6, 4$ and $2$ QLs for Bi$_2$Se$_3$, Sb$_2$Te$_3$ and Bi$_2$Te$_3$, respectively.$^{29–32}$ Below the critical thickness, a surface band gap opens, and it is a bond inversion between the conduction band and valence band for TIs. Thus, the critical thickness is the key of topological nano-applications.

Several researchers have reported that external stress can change the electrical structure, critical thickness and band order of TI.$^{17,32,33}$ For instance, Liu, et al. have also indicated that mechanical...
deformation could reduce the band gap at the time-reversal-invariant momentum points so that even materials with relatively weaker SOC could display a band inversion;\textsuperscript{33} Young, \textit{et al.} have indicated that uniaxial strain in the \textless 111 \textgreater direction is an important parameter for influencing the topological insulating phase and the direct band gap of bulk Bi\textsubscript{2}Se\textsubscript{3} at \textGamma\ point.\textsuperscript{34} At present, the mainstream view is when thickness of a film is smaller than its critical thickness, overlapping between the surface-state wavefunctions from the two surface of the film becomes non-negligible, and hybridization between them has to be taken into account, which leads to a hybridization gap at the Dirac point to avoid crossing of bands with the same quantum numbers.\textsuperscript{28,34} The view has been accepted by most of physicists; and the nontrivial topological of TI is calculated and confirmed based on the wavefunction parity at time reversal \textit{k}-points.\textsuperscript{35}

Although the electronic structure and wavefunction parity at time reversal \textit{k}-points of bulk and nano-film TIs have been researched widely, the relationships between electronic structure and crystal structure are ambivalent. The changes of electronic structure are surely synchronous with the changes of crystal structure of materials, the fundamental factor determining the electronic structures or topological property of materials is the chemical bonds including bond length, bond angle and electronic distribution.\textsuperscript{36,37} Thus, the surface electronic structure or topological property of nano-film will be reflected in the surface chemical bonds since the topological property or band inversion will appear at surface, and the surface chemical bonds or surface state is the synthesis result caused by both surface and interior, thought the band gap of nano-film is influenced by two effects: the quantum confinement effect in thickness direction and the interaction between the top and bottom surface states.\textsuperscript{37} Wang, \textit{et al.} have also indicated that the edge chemical adsorption of 2D TI affect the surface chemical bonds and TI edge (surface) states recently.\textsuperscript{38} Further, our previous work has indicated that the contraction ratio ($r$) of bond lengths between surface bond of film and the corresponding bond of bulk decides the band order of Bi\textsubscript{2}Te\textsubscript{3} film.\textsuperscript{39} However, the
effects of surface bond relaxation on other $V_2VI_3$ system are ambivalent; the critical contraction ratio of other system need to be studied.

In this paper, Sb$_2$Te$_3$ nano-films under three different vertical surface compressive stresses have been calculated by using the relativistic density functional theory, the crystal structure, interaction energies, chemical bond, electronic structures and critical thickness under three different vertical surface compressive stresses have been studied. The relationships between surface bond contraction and band order are discussed.

**COMPUTATIONAL METHOD**

All density functional theory calculations, including geometry relaxation, interaction energy, band structure and charge distribution, are performed on the basis of the project augmented wave method implemented in the VASP 5.2 package.\textsuperscript{40,41} The exchange-correlation functional the generalized gradient approximation (GGA) due to Perdew, Burke and Ernzerhof (PBE) have been used,\textsuperscript{42} including scalar-relativistic effects in addition to SOC. The kinetic energy cutoff of electron wave function is 400 eV, which is sufficiently large for the systems considered. A $k$-point sampling of $10 \times 10 \times 1$ for all films is found to be converged. A vacuum layer of 20 Å is used to avoid interactions between repeating slabs, and the relative atomic positions are relaxed with a force tolerance of 0.01 eV/Å. For all nano-films, the lattice constants are fixed in $ab$-plane and both outermost Sb atomic layers are fixed in $c$ axis to keep the constant film thickness before geometry relaxation (see Fig. 1). Based on the values of film thickness, four different situations have been considered: without strain with equilibrium film thickness $c_0$, vertical compressive strain with film thicknesses $c = c_0(1-2\%)$, $c = c_0(1-4\%)$ and $c = c_0(1-8\%)$, respectively, and the film thickness increases from 1 QL to 6 QL in $c$ axis.

The interaction energies of films $E^{QL}$ from 1QL to 6QLs are calculated by:

\[ E^{QL} = (E^{sys} - nE^{1QL})/n \]  

(1)

Where $E^{sys}$ is the total energy of the system, $E^{1QL}$ denotes the energy of one QL without stain in order to consider the strain energy; $n$ is the amount of QL in each system. Since the basic unit is one QL, $E^{QL}$ denotes the stability of a stacked film.

The contraction ratio ($r$) between surface bond length of the nano-film and the corresponding bond length of bulk can be calculated by:

\[ r = (L_{bulk} - L_{surface}^{nQL})/L_{bulk} \]  

(2)

Where $L_{surface}^{nQL}$ and $L_{bulk}$ denotes the surface bond length of nano-film and the corresponding bond length of the bulk (Fig. 1), respectively. The surface bond of film denotes the bond between the outermost Sb atom and the neighboring Te atom.

**RESULTS AND DISCUSSION**

Lattice constants and band gaps

We know Sb$_2$Te$_3$ has a rhombohedral structure, which exhibits a layered anisotropy with the Te and Sb atom layers arranged along the $c$-axis. Moreover, there are two adjacent Te layers connected by van der Waals bonds. The optimized lattice constant of bulk Sb$_2$Te$_3$ are 4.195 Å in $a$ and $b$ axis, 30.81 Å in $c$ axis, which are agreement with the available experiment result: 4.250 Å in $a$ and $b$ axis, 30.55 Å in $c$ axis,\textsuperscript{43} and is more accurate than other’s simulation results: 4.440 Å in $a$ and $b$ axis, 30.29 Å in $c$ axis.\textsuperscript{44} The result proves that the choice of our simulation parameters is reasonable. We have calculated the band structures 6 of bulk and 1QL film without strain by PBE+SOC and HSE+SOC methods. The band gap of bulk is 0.089 eV for PBE+SOC and 0.301 eV for HSE+SOC. The result of PBE+SOC is good agreement with the theoretical reports with LDA+SOC method (0.090 eV),\textsuperscript{45} GGA+SOC method (0.100eV)\textsuperscript{46} and experimental data (0.072eV),\textsuperscript{45} and better than the theoretical report with GW method (0.260 eV) and our HSE+SOC method. Also, the band gap of 1QL
film $\Delta$gap is 0.341 eV for PBE+SOC and 0.652 eV for HSE+SOC. The result of PBE+SOC is good agreement with the theoretical report with PW91+SOC method (0.391 eV)\(^{47}\) and experimental data (0.342 eV),\(^{48}\) and better than the theoretical report with GW method (0.630 eV)\(^{45}\) and our HSE+SOC method. It means that our calculated parameters for PBE+SOC are reasonable. Next, the same simulation parameters have been used to investigate nano-films.

**Stability of films**

To study the stability of our systems, $E^{39\text{th}}$ of all films have been calculated by first principle theory when SOC have been considered and $E^{\text{QL}}$ have been calculated by Eq. (1). In Fig. 2, it is easy found that $E^{\text{QL}}$ are related to the lattice constants of nano-films and have the relationship: $E^{\text{QL}}_{-8\%} > E^{\text{QL}}_{-4\%} > E^{\text{QL}}_{0\%}$, where the subscript denotes the corresponding strain. It is obvious with increases of the compressive stress, the $E^{\text{QL}}$ of nano-films increase. The values of $E^{\text{QL}}$ of all films become smaller and smaller when the thicknesses of them increase, it means the systems are more and more thermodynamically stable; Based on values of $E^{\text{QL}}$, nano-films with compress strain 8% are thermodynamics unstable, and will be left out next; conversely, nano-films with compress strain 2% or 4% are thermodynamically stable when the film thickness larger than 2QL and 3QL, respectively, and nano-films without strain have the lowest $E^{\text{QL}}$ values and are the most thermodynamically stable. At the same time, the interaction energy of bulk $E_{\text{bulk}} = -0.031$ eV was also calculated by Eq. (1) with $n = 3$ in order to compare the thermodynamic stability with nano-films. It is found that all nano-films are less stable than bulk materials except the 6 QL nano-film without strain $E^{\text{QL}}_{0\%} = -0.046$ eV.

**Charge distributions of films**

Since TIs have the band inversion, i.e., switching of occupied and unoccupied bands with opposite parity around the $E_F$,\(^{49}\) the value of band gap is not sufficient information and cannot conclude whether the material is TI. To confirm the topological property of our films, the charge distributions of the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) for all films have been calculated to confirm the band order, since the wavefunction parity at $\Gamma$.
points is consistent with the bond order of HOCO and LUCO.\textsuperscript{50} The charge distributions of band edges at $\Gamma$ point for the selected films are shown in Fig. 5. In which only the outermost QL have been shown. For 4QL films with lattice constant $c = c_0$ (Fig. 4(a)), the electrons of HOCO round each atom in surface QL since the Pauling electronegative of Sb atom (2.05) is similar to that of Te atom (2.10), while the LUCO of 4QL film locates around the Sb and Te atoms in both sides of surface QL but not the middle Te atom. Conversely, as the film thicknesses increase from 4QL to 5QL, the charge distributions of LUCO (or HOCO) of 4QL film is similar to that of HOCO (or LUCO) of 5QL film, it means that the band order has been changed and band inversion appears, so Sb$_2$Te$_3$ nano-films without strain has the critical thickness of 4QL, this result is consistent with other theory and experiment results. Similar as above stations, the charge distributions and band orders are inverted when the thicknesses of Sb$_2$Te$_3$ films increase from 5QL to 6QL for films with $c = c_0(1-2\%)$ (Fig. 4(b)), however, the charge distributions and band orders are constant for Sb$_2$Te$_3$ films with $c = c_0(1-4\%)$ when the thickness of film increases from 1QL to 6QL, and Fig. 4(c) shows that the charge distributions of LUCO and HOCO of corresponding 5QL and 6QL films, it means these are always NIs. Based on above analyses, compressive stress increases the critical thickness of Sb$_2$Te$_3$ nano-films.

**Bond length of films**

Just as the analysis in introduction, the topological property or bond inversion appears at the surface of film and is caused by the electronic structure and crystal structure of surface atoms. As above, the electronic structures of surface QL in film have been studied, while the crystal structure and the relationship between electronic structure and crystal structure is ambiguity. To analyze the relationship of them, the surface bond length $L_{\text{surface}}^{n\text{QL}}$ and the corresponding bond length in bulk $L_{\text{bulk}}$ of each system is obtained and listed in Tab. I where, $c_0$, $c_0(1-2\%)$, $c_0(1-4\%)$ and $c_0(1-8\%)$ denote the systems with corresponding lattice constants. It was found that the values of $L_{\text{surface}}^{n\text{QL}}$ decrease along with the lattice constant $c$, and the values of $L_{\text{surface}}^{n\text{QL}}$ with 8% compression strain are obviously larger than that of corresponding film with 2% or 4% compression strains, which induces the systems unstable (discussed above for Fig. 2). Although, compared with $L_{\text{bulk}}$, the surface bonds of all nano-films shrink, they $L_{\text{surface}}^{n\text{QL}}$ are different for films with different thicknesses, the values of $L_{\text{surface}}^{n\text{QL}}$ increase little form 6QL to 3QL films and increase a bit form 3QL to 1QL films, which is similar as our previous result for Bi$_2$Te$_3$ nano-films,\textsuperscript{39} however, the values of $L_{\text{bulk}}$ and $L_{\text{surface}}^{n\text{QL}}$ reduce linearly with the reduce lattice constants $c$ in Tab. I and Fig. 4(a), the values of $\Delta_{\text{gap}}$ with equilibrium lattice constant $c_0$ is the smallest 0.341 eV, it is different from our previous result: Bi$_2$Te$_3$ with equilibrium lattice constant $c_0$ has the biggest $\Delta_{\text{gap}}$.\textsuperscript{39} The same as Bi$_2$Te$_3$ nano-films,\textsuperscript{39} the absolute values of lattice constant or band length are unrelated to $\Delta_{\text{gap}}$, as they $L_{\text{surface}}^{n\text{QL}}$ are 2.9892 Å (for 6QL films without strain), 2.9892 Å (for 4QL film with compressive strain 2\%) and 2.9890 Å (for 1QL film with compressive strain 4\%), the $\Delta_{\text{gap}}$ of them are 0 eV, 0.090 eV and 0.701 eV, respectively (see Fig. 5). Thus, the $\Delta_{\text{gap}}$ of films is unrelated directly with the $L_{\text{surface}}^{n\text{QL}}$. Based on our previous work: the contraction ratio ($r$) of bond lengths between surface bond of film and the corresponding bond of bulk decides the band order of Bi$_2$Te$_3$ film,\textsuperscript{39} the contraction ratios ($r$) of our systems have been calculated by Eq. (2) and the results have been shown in Fig. 4(b). It is found that the values of $r$ increase along with the increasing film thickness. By combining Figs 3 and 4(b), we have found the HOCO and LUCO of all films have exchanged when the contract ratios beyond about 0.93% which is different from the critical contract ratios 0.53% for Bi$_2$Te$_3$ nano-film. Based on our analyses above, when the film thickness increases, the surface bond shrinks and electric distributions of surface bond are localized, which lead to the reduction of the film band gap; at the same time, the internal crystal structure protected by time-reversal symmetry also affects the band gap or topological property of Sb$_2$Te$_3$. Thus, the band gap and band order of Sb$_2$Te$_3$ film has been affected collectively by the surface and internal crystals structures. Regulating the contraction ratio $r$ of nano- or bulk materials by external stress, the conversion from TI to NI has potential applications in nano-circuit switches.
FIG. 3. (Colour online) The charge distributions of the HOCO and LU CO at the Γ point for (a) 4QL and 5QL Sb$_2$Te$_3$ films without strain, (b) 5QL and 6QL Sb$_2$Te$_3$ films with compressive strain 2%, (c) 5QL and 6QL Sb$_2$Te$_3$ with compressive stain 4%.

CONCLUSIONS

The stability of Sb$_2$Te$_3$ nano-films with different vertical surface compressive stresses and the effects of strains on their crystal and electronic structures have been investigated by first-principles calculation. The band gap of nano-film is sensitive to the stress in Sb$_2$Te$_3$ nano-film and the critical thickness increases under compressive stress. The band gap and band order of Sb$_2$Te$_3$ nano-film has been affected collectively by the surface and internal crystals structures, the contraction ratio...
between surface bond length of the nano-film and the corresponding bond length of bulk decides the band order or topological property of Sb$_2$Te$_3$ films. Regulating the contraction ratio $r$ of nano- or bulk materials by external stress, the conversion from TI to NI has potential application in nano-circuit switches.
FIG. 5. (Colour online) Band structures of Sb$_2$Te$_3$ films without strain (a) 1QL film and (b) 4QL film, respectively. The red lines denote the band edges.

TABLE I. $\Delta$gap denotes the band gap of 1QL film, $L_{\text{bulk}}^{nQL}$ and $L_{\text{surface}}^{nQL}$ denote the surface bond length of film and the corresponding bond length of the bulk, respectively, where $n$ is the number of QL in nano-film. $c_0$, $c_0(1-2\%)$ $c_0(1-4\%)$ and $c_0(1-8\%)$ denote the films with corresponding compressive lattice constants.

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