Ethynyl-functionalized stanene film: a promising candidate as large-gap quantum spin Hall insulator

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Abstract

Quantum spin Hall (QSH) effect is promising for achieving dissipationless transport devices which can be achieved only at extremely low temperature presently. The research for new large-gap QSH insulators is critical for their realistic applications at room temperature. Based on first-principles calculations, we propose a QSH insulator with a sizable bulk gap as large as \( \sim 0.22 \text{ eV} \) in stanene film functionalized with the organic molecule ethynyl (SnC2H), whose topological electronic properties are highly tunable by the external strain. This large-gap is mainly due to the result of the strong spin–orbit coupling related to the \( p_{xy} \) orbitals at the \( \Gamma \) point of the honeycomb lattice, significantly different from that consisting of the \( p_z \) orbital as in free-standing group IV ones. The topological characteristic of SnC2H film is confirmed by the \( Z_2 \) topological order and an explicit demonstration of the topological helical Dirac type edge states. The SnC2H film on BN substrate is observed to support a nontrivial large-gap QSH, which harbors a Dirac cone lying within the band gap. Owing to their high structural stability, this two-dimensional large-gap QSH insulator is promising platforms for topological phenomena and new quantum devices operating at room temperature in spintronics.

1. Introduction

The quantum spin Hall (QSH) insulators, also known as two-dimensional (2D) topological insulators (TIs), have generated great interest in condensed matter physics and materials science because of their scientific importance as a novel quantum state ranging from spintronics to topological quantum computation [1–5]. The unique characteristic of TI phase is their gapless boundary state inside a bulk band gap, which is spin-locked due to the protection of time-reversal symmetry (TRS), namely the propagation direction of surface electrons is robustly linked to their spin orientation [6], leading to dissipationless transport edge channels. Although being intensively explored for fundamental research and technological applications, the vast family of 2D materials has been largely underexploited for QSH insulators [7–10].

The prototypical concept of QSH insulator is first proposed by Kane and Mele in graphene [11, 12], in which the spin–orbit coupling (SOC) opened a band gap at the Dirac point. However, the associated gap due to rather weak second-order effective SOC is too small (\( \sim 10^{-3} \text{ meV} \)), which makes the QSH effect in graphene only appear at an unrealistically low temperature [13, 14]. Subsequently, other honeycomb-like group IV materials, such as silicene, germanene, and stanene [15–20], are reported to host QSH effect with experimental accessible gaps, but their gaps were still smaller than 26 meV. Up to date, quantized conductance through QSH edge states have only been experimentally demonstrated in HgTe/CdTe [21, 22], Bi bilayer film [23] and InAs/GaSb [24, 25] quantum wells. These existing systems have serious limitations like toxicity, difficulty in processing, and small bulk gap opened by SOC. To realize the QSH effect at room temperature, TIs with a large-gap are more desirable because of their ability to stabilize the edge current against the interference of thermally activated carriers in the bulk. Therefore, the search for new TIs with large-gap is urgently required.
Chemical functionalization of 2D materials is an effective way to realize QSH state with desirable large-gaps. The examples include halogenated germanene [26] and stanene [27] films. Both 2D films are found to be QSH insulators with a gap as large as 0.2–0.3 eV, sufficiently large for practical applications at room temperature. Group V elements, including Bi [28, 29], Sb [30] thin films are also found to be large-gap QSH insulators, when functionalized with hydrogen or halogen atoms. More recently, functionalized group III–V materials GaAs and GaBi have also reported to be large-gap QSH insulators [31, 32]. These large-gap QSH insulators are essential for realizing many exotic phenomena and for fabricating new quantum devices that can operate at room temperature. Unfortunately, the experiments [33, 34] reveal that plasma fluorination and hydrogenation exhibit quick kinetics, with rapid increase of defects and lattice disorder even under short plasma exposures. Also, the hydrogen-functionalized systems are not stable long-term and are greatly air reactive, as there is extreme propensity to oxidize under ambient condition [33]. Thus, the achievement of fluorinated or hydrogenated systems of high quality is rather challengeable, demonstrating the observation of QSH effect is difficult in experiments.

Tin (Sn) atom, the counterpart of carbon atom among IV honeycomb-like structures, is well known for their strongest SOC effect which can drive and stabilize the nontrivial TI states, thus it is wise to search for new QSH insulators in stanene film. Experimentally, ultrathin stanene film with buckled configuration in the honeycomb lattice is observed by molecular beam epitaxy experiments [33, 34]. Motivated by the excellent works on QSH effect by Zhang et al. [27], here, we propose a large-gap QSH insulator in stanene film functionalized with organic molecule ethynyl (labeled as SnC2H) based on first-principles calculations and phonon modes. We find that the organic molecule ethynyl is particularly suitable for surface passivation over hydrogen and halogen atoms, considerably enhancing the thermostability of stanene film, and thus allowing for achieving QSH effect. Remarkably, we find a large-gap of ~0.22 eV related to the p_{xy} orbitals of Sn atoms, effectively tuned by external strain. The topological characteristic of SnC2H film is confirmed by the Z_2 topological order and an explicit demonstration of the topological helical Dirac type edge states. Thus, the organic molecule functionalization on 2D thin films may provide a new platform to design large-gap QSH insulator, which is important for device application.

2. Computational method and details

First-principles calculations based on density-functional theory (DFT) are performed by the Vienna ab initio simulation package [35], using the projector-augmented-wave potential with 4d electrons of tin described as valence and the plane-wave basis. The exchange-correlation functional is treated using the Perdew–Burke–Ernzerhof [36] generalized-gradient approximation. The energy cutoff of the plane waves is set to 500 eV with the energy precision of 10^{-5} eV. For the 2D structures, the Brillouin zone (BZ) is sampled by using a 21 × 21 × 1 Gamma-centered Monkhorst–Pack grid, whereas a 1 × 21 × 1 grid was used for the nanoribbon. The vacuum space is set to 20 Å in the calculations to minimize artificial interactions between neighboring slabs. All structures are fully optimized, including cell parameters and atomic coordinates, until the residual forces are less than 0.01 eV Å^{-1}. The SOC is included in the self-consistent calculations of electronic structure. The phonon spectra are calculated using a supercell approach within the PHONON code [37].

3. Results and discussion

Figure 1(a) shows the geometric structures of 2D SnC2H film after structural optimization. The SnC2H film prefers a buckled configuration, analogous to germanane [24] and stanane [25] films, with the ethynyl bonding on both sides of the stanene plane in an alternating way (figure 1(b)). Thus, the crystal structure of SnC2H presents a hexagonal Bravais lattice, possessing inversion symmetry. The optimized lattice constant equals to 4.756 Å, with the buckling (Δ) between Sn planes being 0.77 Å. The thermodynamic stability of SnC2H is verified by the formation energy defined by

\[ ΔE = E\left(\text{SnC}_2\text{H}\right) - E\left(\text{Sn}\right) - E\left(\text{C}_2\text{H}\right), \]

where \( E(\text{SnC}_2\text{H}) \) and \( E(\text{Sn}) \) are the total energies of ethynyl functionalized and free-standing stanene film, respectively. \( E(\text{C}_2\text{H}) \) is the chemical potentials of \( \text{C}_2\text{H} \) molecule. The calculated formation energy (\( ΔE \)) for SnC2H is ~3.34 eV, suggesting that ethynyl molecules are chemically bonded to Sn film, indicating a higher thermodynamic stability relative to their elemental reservoirs. The dynamic stability is confirmed by the phonon spectrum calculated along the highly symmetric directions, as shown in figure 1(c). There are no modes with imaginary frequencies in the spectrum and the film is therefore expected to be dynamically stable.

Now, we turn to electronic properties of SnC2H film with and without SOC effect, as displayed in figure 2. Compared to free-standing stanene [13], its bandgap at the \( K \) point is substantially enlarged due to the saturation.
of the π orbital of Sn atoms. Without considering SOC, the band structure of SnC₂H exhibits a semiconductor feature with a direct band gap of ~0.21 eV at Γ point (figure 2(a)). By projecting the bands onto different atomic orbitals, we find that the valence band maximum (VBM) near the Fermi level is twofold degenerated with the features of binding states of pₓ,y orbitals from Sn atoms, whereas the conduction band minimum (CBM) has the anti-binding state features of s-orbital. When turn on SOC, the degenerate pₓ,y level is split significantly by a gap of 28 meV (figure 2(b)). Except for this, no significant change is caused by SOC for the band feature. The CBM at

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**Figure 1.** (a) Side and (b) top views of the atomic structures of SnC₂H. Red, blue, and green balls denote H, C, and Sn atoms, respectively. Shadow area in (a) present the unit cell. Phonon band dispersions of (c) denote Sn-C₂H film. The invariants s can be derived from the parities of wave function at the four time-reversal-invariant momenta (TRIM) points Kᵣ, namely one Γ point and three equivalent M points in the Brillouin zone are shown (d).

**Figure 2.** Orbital-resolved band structures with and without SOC based on DFT calculations. (a) SnC₂H (ε = 0.0%) without SOC, (b) Sn-C₂H (ε = 0.0%) with SOC, (c) Sn-C₂H (ε ≥ 2.0%) without SOC, and (d) SnC₂H (ε ≥ 2.0%) with SOC. The green dots represent the contributions from the s atomic orbital of Sn atom and the red dots represent contributions from the pₓ and pᵧ atomic orbitals of Sn atom.
the Γ point is still occupied by the Sn-5s orbitals, while the VBM near the Fermi level are still dominated by Sn-5p orbitals. Thus, no inverted band order is observed, suggesting that it is a trivial QSH insulator.

Generally, the mechanical strain can induce the s–p band inversion and hence lead to a nontrivial TI state [21, 22, 24, 38–40]. Thus, one might speculate if this system can become a QSH insulator under mechanical strain? Here, we employ an external strain on SnC2H maintaining the crystal symmetry by changing its lattices as $\varepsilon = (a - a_0)/a_0$, where $a$ ($a_0$) is the strained (equilibrium) lattice constants. The SnC2H lattice is expanded uniformly along both zigzag and armchair directions in the $ab$ plane and is relaxed along the $c$-axis. With increasing the strain, we find that the CBM is driven continuously to shift downward to the Fermi level, while the VBM increase reversibly, leading the band gap to decrease significantly. Throughout the changes under strain, it has a direct band gap with the VBM and CBM both located at the Γ point. Notably, at the critical value of 2.0%, the two Sn-p$_{x,y}$ bands touch each other at the Fermi level, which can be considered as a gapless semiconductor, or alternatively, as a semi-metal with zero density of states at the Fermi level. When the strain increases beyond 2.0%, as shown in figure 2(c), the contributions of the s-type orbital stay in the valence band, resulting in band inversion at the Γ point.

The strong SOC from Sn atoms is expected to have significant impact on the electronic band structures of SnC2H film, which is confirmed in figure 2(d), but the feature of s–p$_{x,y}$ inversion is preserved. In this case, the degeneracy of p$_{x,y}$ orbital at the Γ point is lifted, yielding a sizable large-gap, due to the result of the first-order relativistic effect of SOC related to Sn elements. In contrast to one without SOC, away from the Γ point, the CBM is also downshifted, whereas the VBM is upshifted, which produces a global indirect band gap. Figure 3 gives the variation of the nontrivial QSH gap (direct, $E_\Gamma$) at Γ point and bulk gap (indirect, $E_g$) with respect to the external strain. It can be seen that both the direct and indirect band gaps in TI phase decrease steadily with respect to tensile strain, especially $E_\Gamma$ and $E_g$ being equal to strain beyond 30.0%. Remarkably, for the strain of 3.0%, we can find a largest gap of $\sim 0.33$ eV opened at Γ point, along with a global indirect band gap of $\sim 0.22$ eV, which is significantly greater than $k_B T$ ($\sim 26$ meV), so the QSH effect can be realized easily at room temperature. Here, we point out that, although the s–p$_{x,y}$ band inversion is caused mainly by the external tensile strain, the SOC is still indispensable because it lifts degeneracy of valence and conduction bands around the Fermi level.

To identify the 2D TI phase, we calculate the $Z_2$ invariants $\nu$ following the approach proposed by Fu and Kane [41], due to the presence of structural inversion symmetry in SnC2H. Here, the invariants $\nu$ can be derived from the parities of wave function at the four time-reversal-invariant momenta (TRIM) points $K_i$, namely one Γ point and three equivalent M points in the BZ, as shown in figure 1(d). Accordingly, the topological indexes $\nu$ are established by

$$\delta(K_i) = \prod_{m=1}^{N} \xi_{2m}^i (-1)^\nu = \prod_{i=1}^{4} \delta(K_i) = \delta(\Gamma) \delta(M)^3,$$

where $\delta$ is the product of parity eigenvalues at the TRIM points, $\xi = \pm 1$ are the parity eigenvalues and $N$ is the number of the occupied bands. According to the $Z_2$ classification, $\nu = 1$ characterizes a QSH insulator, whereas $\nu = 0$ represents a trivial band topology. There are 13 spin–degenerate bands for 26 valence electrons. We calculate the parity eigenvalues of the Bloch wave function for the 13 occupied spin-degenerate bands at all

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**Figure 3.** The calculated energy gaps at Γ point ($E_\Gamma$) and the global energy gap ($E_g$) of Sn-C$_2$H with SOC as a function of external strain. Notably, a phase transition from normal insulator (NI) to TI, the strain 2.0% is critical point. Insets in panel show the trend of band gaps of TI phase as a function of external strain.
TRIM points, the corresponding results are listed in Table 1. As expected, in the equilibrium state, the products of the parity eigenvalues at these two symmetry points: \( \Gamma (0.0, 0.0) \) and \( M (0.5, 0.5) \) are both \(-1\), while at the \( M (0.0, 0.5) \) and \( M (0.5, 0.0) \) display \( 1 \), yielding a trivial topological invariant \( Z_2 = 0 \). With the strain increasing beyond 2.0\%, band inversion at the \( \Gamma \) point takes place. The parity eigenvalue of the VBM changes sign to become \(+\), while those at the \( M (0.5, 0.0), (0.0, 0.5), (0.5, 0.5) \) points remain \(+, +, −\), respectively. Thus, the products of the parity eigenvalues at these two points are now distinct and the system becomes TI with \( Z_2 = 1 \), suggesting that the QSH effect can be realized by adsorption of organic molecule ethynyl. Thus, the QSH effect can be steadily achieved in the 2D honeycomb \( \text{SnC}_2\text{H} \) with a nontrivial large SOC gap.

The QSH effect in 2D \( \text{SnC}_2\text{H} \) leads to helical edge states that is protected from elastic backscattering by TRS. To demonstrate these edge states explicitly, we take \( \text{SnC}_2\text{H} \) with the external strain \( \varepsilon = 2.0\% \) as an example to introduce edges on the Sn sheet by forming a nanoribbon. The edge Sn atoms are passivated by hydrogen atoms to eliminate the dangling bonds. The width of the nanoribbon is large enough to avoid interactions between the edge states of the two sides. Figure 4(a) shows the zigzag-type edge states of \( \text{SnC}_2\text{H} \), where a Dirac point at the \( \Gamma \) point is located inside the band gap with a high velocity of \( \sim 1.0 \times 10^5 \text{ ms}^{-1} \), comparable to that of \( 5.5 \times 10^5 \text{ ms}^{-1} \) in HgTe/CdTe quantum well [42], both of which are larger than that of \( 3.0 \times 10^4 \text{ ms}^{-1} \) in InAs/ GaSb quantum well [43]. Without loss of generality, we also consider armchair-type edges, which it is the existence of helical gapless edge states in TI, as shown in figure 4(b). Helical edge states are very useful for electronics and spintronics owning to their robustness against scattering.

Table 1. Parities of occupied spin-degenerate bands at the TRIM Points for \( \text{Sn-C}_2\text{H} \). Here, we show the parities of 13 occupied spin-degenerate bands for \( \text{Sn-C}_2\text{H} (\varepsilon = 0\% \) and \( \varepsilon \geq 2.0\% \). Positive and negative signs denote even and odd parities, respectively. The sign in parentheses is the product of the parity eigenvalues of the occupied spin-degenerate bands.

| \( \Gamma_i \) | Parity of \( \tilde{c}_{2\alpha} \) of occupied bands | \( \delta_i \) |
|--------------|-----------------------------------|--------|
| (0, 0)       | + - + - + + + + - - + + - - - + | −      |
| (0.5, 0)     | + + + + - - - - + + + + + + + + | +      |
| (0, 0.5)     | + - + - + + + + + + + + + + + | +      |
| (0.5, 0.5)   | - + - - - - - - - - + + + - + | −      |
| \( \varepsilon = 0\% \) | \( Z_2 \) topological invariant | \( \nu = 0 \) |
| (0, 0)       | + - + - + + + + - - + + - - - + | −      |
| (0.5, 0)     | + + + + - - - - + + + + + + + + | +      |
| (0, 0.5)     | + - + - + + + + + + + + + + + | +      |
| (0.5, 0.5)   | - + - - - - - - - - + + + - + | −      |
| \( \varepsilon \geq 2\% \) | \( Z_2 \) topological invariant | \( \nu = 1 \) |

Figure 4. Calculated electronic band structures of the zigzag-type and armchair-type nanoribbons of \( \text{SnC}_2\text{H} (\varepsilon = 2.0\%) \) with SOC. The Fermi energy is set to 0 eV.
Now we focus on the origin of the QSH nature, in which the band inversion is driven by mechanical strain instead of SOC. Thus the physics of band inversion can be understood without SOC. This new mechanism is similar to that in the HgTe quantum well [42], but different from the nontrivial topology of graphene and silicene films in the previous works, which originates from the massive Dirac cone, and there is no band inversion. Figure 5 presents systematically the band evolution at the $\Gamma$ point for SnC$_2$H film. The energy levels near the Fermi level are mainly composed of Sn-5s and Sn-5p$_{x,y}$ orbitals. Technically, there has been already some studies on (P$_{x,y}$) model (instead of P$_z$ model) of QSH. According the crystal field splitting theory, the chemical bonding between Sn–Sn atoms makes the s and p$_{xy}$ orbital split into the bonding and anti-bonding states, i.e., $|s\rangle$ and $|p_{xy}\rangle$, which the superscripts + and − represent the parities of corresponding states, respectively. In the equilibrium state, as shown in figures 5(a) and (b), the bands near the Fermi level are contributed by $|p_{xy}^+\rangle$ and $|s^-\rangle$, with the $|s^-\rangle$ being above the $|p_{xy}^+\rangle$ level. When SOC is turn on, the degeneracy of the level is split into $|p_{xy}^{\pm3/2}\rangle$ and $|p_{xy}^{\pm1/2}\rangle$, opening a full energy gap. When considering the tensile strain, as can be seen in figures 5(c) and (d), the enlarged lattice constant weakens the interaction between the Sn atoms, decreasing the splitting between the bonding and anti-bonding states, which lowers $|s^-\rangle$ level and raises $|p_{xy}^+\rangle$ level. Thus, depending on the strength of strain, the band gap of SnC$_2$H can be continuously tuned, and the order is reversed at critical point of 2.0%. Also, the $|s^-\rangle$ will be occupied, while the quadruply degenerate $|p_{xy}^+\rangle$ is half occupied, resulting in that the Fermi level stays at $|p_{xy}^+\rangle$ level, exhibiting a semimetal feature. When SOC is switched on, the degeneracy of the $P_x$ orbital is split into $|p_x, \pm3/2\rangle$ and $|p_x, \pm1/2\rangle$, opening a larger energy gap. We also note that this mechanism is consistent with that of the previous reported B$_6$@H-Si(111) nanostructure [44]. To further elucidate these phenomena, we illustrate the s–p band inversion diagram in figures 5(e) and (f) relative to the external strain. Taken together, the level crossing leads to a parity exchange between occupied and unoccupied bands, inducing a TI phase transition. While the trivial side has no band inversion, the nontrivial side shows band inversion where the conduction and valence bands swap their band character at the time reversal invariant point. Thus, the strain-driven s–p band inversion [34] is a strong indication of the existence of topologically nontrivial phases.
The substrate materials are evitable in device application, thus a free-standing film must eventually be deposited or grown on a substrate. Previous works indicate that the nontrivial TI features of graphene, silicene, and germanene [12–17] are easily destroyed by the substrate, thus introducing a trivial gap. In contrast, although the TI feature of SnC$_2$H film are for free-standing structure, their nontrivial QSH would be quite robust when they are on the substrate, because their band inversion occurs at the $\Gamma$ point rather than the $K$ point, as well as the full saturation of Sn-$p_z$ orbitals ensures a weak interaction with the substrate. In this regard, some recent works have already demonstrated this possibility [45, 46]. To check this idea, here we select BN as a possible substrate to form SnC$_2$H/BN heterobilayer, as shown in figure 6(a). The calculated binding energy is found to be $-64$ meV, indicating that it is a typical van der Waals heterobilayer. The optimized lattice constant of SnC$_2$H is 5.32 Å, fall in the range of TI feature. In this case, it has a small lattice mismatch ($\sim 0.48\%$) in comparison to BN (2 × 2), showing that it is feasible to grown SnC$_2$H film on the BN substrate. Remarkably, in this weakly coupled system, the nontrivial TI phase still remains observable, as shown in figure 6(b), although the band gap reduces slightly by 44 meV than free-standing SnC$_2$H film. These demonstrate that it is a robust QSH insulator for the SnC$_2$H/BN heterobilayer.

4. Conclusion

In summary, we perform the first-principles calculations to predict a new QSH insulator of SnC$_2$H film with a large-gap of 0.22 eV, allowing for viable applications in spintronic devices. Two factors i.e., the strongest SOC and mechanical strain are essential for QSH phase transition. This large-gap opening is mainly due to the result of the strong SOC related to the $p_x$ and $p_y$ orbitals of the Sn atoms at the $\Gamma$ point, significantly different from that of the $p_z$ orbital as in free-standing group IV ones. The topological characteristic of Sn-C$_2$H film is confirmed by the $Z_2$ topological order due to $s$–$p_{xy}$ band inversion and an explicit demonstration of the topological edge states. When it deposits on BN substrate, both the band gaps and low-energy electronic structures are only slightly affected by the interlayer coupling. These results represent a significant advance in the study of TIs and expected to stimulate further work to synthesize, characterize and utilize these new 2D TIs for fundamental exploration and practical applications at room temperature.

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