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Quantum Spin-Quantum Anomalous Hall Insulators and Topological Transitions in Functionalized Sb(111) Monolayers

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Supporting Information

ABSTRACT: Electronic and topological behaviors of Sb(111) monolayers decorated with H and certain magnetic atoms are investigated by using ab initio methods. The drastic exchange field induced by the magnetic atoms, together with strong spinorbit coupling (SOC) of Sb atoms, generates one new category of valley polarized topological insulators, called quantum spinquantum anomalous Hall (QSQAH) insulators in the monolayer, with a band gap up to 53 meV. The strong SOC is closely related to Sb p_x and p_y orbitals, instead of p_z orbitals in usual two-dimensional (2D) materials. Topological transitions from quantum anomalous Hall states to QSQAH states and then to time-reversal-symmetry-broken quantum spin Hall states are achieved by tuning the SOC strength. The behind mechanism is revealed. Our work is helpful for future valleytronic and spintronic applications in 2D materials.



KEYWORDS: Quantum spin-quantum anomalous Hall effect, 2D material, topological phase transition, valleytronics, spintronics

wo-dimensional (2D) materials with a honeycomb lattice, such as graphene, silicene, and so forth, have band structures with two degenerate but inequivalent valleys located at the corners of the hexagonal Brillouin zone. Intervalley scattering is generally suppressed much in the pure samples due to their large separation in momentum space.¹ The degeneracy and independence of the valley degree of freedom make it possible to control an electronic device,² similar to the electron spin adopted in spintronics. Graphene and its derivatives 3^{-7} are the early star materials employed to explore the valleytronic physics. The valley contrasting Hall transport (valley Hall effect) with the carriers in different valleys turning into opposite directions transverse to an in-plane electric field, was first predicted in graphene.⁵ Several valleytronic prototypes, such as valley filters,^{3,7} valley valves,³ and devices generating pure valley current,⁶ were also proposed based on graphene. Because the band gap (about 1.6 eV) of MoS2 monolayers, also with hexagonal lattices, is in the visible frequency range, optoelectronic measurements are relatively straightforward in MoS₂ monolayers.⁹ Rich experimental evidence of the valleydependent optical selection rules in MoS₂ monolayers were given based on polarization-sensitive photoluminescence measurements.¹⁰⁻¹² These progresses undoubtedly help move valleytronics steps closer to the reality.

Because of the strong spin-orbit coupling (SOC), Bi(111) and Sb(111) thin films have been studied much in the field of topological insulators, recently.¹³⁻¹⁷ Especially, Song et al. found a fully hydrogenated Sb(111) monolayer (SbH) is a 2D quantum spin Hall (QSH)¹⁸⁻²⁰ insulator with a pretty large

band gap (410 meV) and its atomic structure remains stable even at 600 K.¹³ Charming topological states, such as quantum anomalous Hall $(QAH)^{21}$ states, desirable for low-dissipation electronics, are expected to emerge in the system if magnetism is introduced to the materials,²² by such as doping transition metal (TM) atoms.^{23,24} In this Letter, we report an exotic valley-dependent topological insulator called quantum spinquantum anomalous Hall (QSQAH)²⁵ insulator, where the QAH effect occurs at one valley and the QSH effect occurs at the other valley, in the decorated Sb(111) monolayers (Figure 1), based on density functional theory (DFT). The concept of QSQAH was first proposed from a tight-binding model.²⁵ However, how it can be realized in experiments and what its behaviors are in the materials have been absent up to the present.

The QSQAH phase acquired in the decorated Sb(111) monolayers has a Chern number (*C*) of 1 and a spin Chern number (*C*_s) of ~1/2. Fascinatingly, the nontrivial band gap of the QSQAH state is opened exactly around the Fermi level (E_F) with a considerably large value (up to 53 meV), making the experimental observations of the QSQAH phase facile. With the current photoluminescene technologies,^{10–12} the QAH or QSH states may be achieved in one sample by valley-dependent optical excitations in the mid-infrared regime. The topological transitions in the decorated Sb(111) monolayers

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Figure 1. (a) Top view of 1×1 , 2×2 , or 3×3 supercells of the Sb hydride sheet with a TM atom (Cr/Mo/W) deposited. The *l* is the lattice constant of the 1×1 unit cell. (b) The first Brillouin zone of the 1×1 unit cell and the points with high symmetry. (c) Side view of the functionalized Sb monolayers. d_1 (d_2) is the distance between H (TM) and Sb_A (Sb_B). (d) A schematic diagram for chiral interconnect devices made of different functionalized Sb(111) monolayers. In the left region, the TM atoms are deposited on the upper surface. There is no TM atom in the middle region. In the right region, TM atoms are deposited below the lower surface. The red and blue dashed arrows indicate the charge and spin edge states, respectively, happening at the K or K' valleys. The solid arrows on the dashed lines indicate the spin directions of the edge states.

are also explored by tuning the SOC strength and the concentration of the magnetic (Cr/Mo/W) atoms. On the basis of the QSQAH effect, a device prototype of lowdissipation chiral interconnects is proposed in which chiral valley-polarized charge current and spin flow emerge along the sample boundaries. It should have potential applications in future valleytronics and spintronics.

Results and Discussion. Some obtained results for the functionalized Sb(111) monolayers are given in Table 1. As

Table 1. Some Obtained Results for the Functionalized Sb(111) Monolayer with One TM Atom in the 1 × 1 Unit Cell, Including Relaxed Lattice Constant (*l*), Relaxed Distance of d_1 (d_2) between H (TM) and Sb_A (Sb_B) as Indicated in Figure 1c, Binding Energy (E_b), Total Magnetic Moment Per Unit Cell (M_{tot}) of the System, Local Magnetic Moment of TM Atoms (M_{TM}), Tensile Strain Applied to Obtain the QSQAH State

gap (meV)
21
27
53

shown in Figure 1, when one of the H atoms on the SbH upper surface is replaced by a TM (Cr, Mo, or W) atom, the optimized lattice parameters (*l*) remain that of the pristine SbH monolayer¹³ (Table 1), independent of the type of the TM atoms deposited. The distances between H and Sb atoms have the same tendency, even if the bond length (d_1) between H and Sb_A is not varied by the TM atoms (Figure 1). The negligible structural distortion induced by the TM atoms can be ascribed to the same bonding behavior in essence of the added TM atoms as that of the removed H, to be discussed. Strong interactions are found between the deposited metal atoms and the exposed Sb_B atoms in the SbH monolayers, as evidenced by the calculated bond lengths (d_2) of 2.66, 2.71, and 2.68 Å for Cr, Mo, and W systems, respectively. The high structural stability is also confirmed by the calculation of binding energies $(E_{\rm b})$, defined as $E_{\rm b} = E_{\rm TM} + E_{\rm SbH} - E_{\rm TM@SbH}$, where $E_{\rm TM}$, $E_{\rm SbH}$, and $E_{\rm TM@SbH}$ denote the total energies of the single metal atom, pristine SbH with one H atom removed, and SbH with one H atom substituted by a TM atom in the unit cell, respectively. The obtained binding energies for the three systems (1.78-2.36 eV) are comparable to those of most elemental crystalline solids.²⁶ From Cr to W, the binding energy increases (Table 1), due to the strengthening of the electron nonlocality. The especially large binding energy in the W case can be ascribed to the W 5d orbitals occupying closer to the $E_{\rm F}$ than Mo 4d and Cr 3d. Thus, very strong interactions between W 5d and Sb 5p orbitals are induced, also explaining well why the bond length between W and Sb is slightly shorter than that between Mo and Sb. Note that the bond length also depends on the radius of the TM atoms.

Magnetism is a vital factor to understand the electronic and topological behaviors of the system. To find the magnetic ground states of the functionalized Sb(111) monolayers, we calculate the total energies of different magnetic configurations, including ferromagnetic (FM) and antiferromagnetic (AFM) structures for the system. The magnetization axis of the FM state is set as the z-direction, found to be more favorable than that of the xy plane by 1.3, 1.2, and 1.0 meV/unit cell in total energies for Cr@SbH, Mo@SbH, and W@SbH, respectively. Because of the trigonal lattice formed by the TM atoms, its stable AFM configuration is a coplanar noncollinear AFM ordering with 120 angles between the magnetic moments of the neighboring TM atoms. The total energies of the FM states of the Cr, Mo, and W systems are found to be 1.6, 1.4, and 1.3 meV/unit cell lower than those of the AFM states, respectively. We also find when the distances between the TM atoms are increased by strain or diluting the density of TM atoms, all of the compounds still prefer the FM states with the magnetization axis along the z-direction, crucial to produce the QAH effect.²⁷ The magnetic moments obtained for the three systems (M_{tot}) are all around 5.0 μ_B (Table 1), contributed predominately by the TM atoms. For a Cr (Mo) atom, its initial valence configuration is $3d^54s^1$ ($4d^55s^1$), rationalizing well the 5.0 $\mu_{\rm B}$ obtained in the system. However, for a W atom, the valence configuration is $5d^46s^2$. After the W atom is deposited to the SbH monolayers, the energy of the W 5d orbitals is lowered due to the interaction with the Sb 5p orbitals. Thus, one 6s electron can transfer to the 5d orbitals, leading to the nearly half occupied 5d orbitals of the W ions, similar to the other two cases. Therefore, in Cr/Mo/W@SbH, the 3d/4d/5d orbitals are all nearly half filled, relatively stable states, meanwhile there is only one electron occupied at 4s/5s/ 6s orbitals, respectively, making the bonding behaviors of these TM atoms very similar to that of the H atoms. This should be the reason why the TM atoms do not trigger much structural distortion in the pristine SbH monolayers (Table 1). The local magnetic moment on the TM atom $(M_{\rm TM})$ is also given in Table 1, less than the total one in the system due to the neglect of the magnetic moment in the interstitial region.

We now focus on the band structures of the decorated Sb(111) monolayers. The Mo case is taken as an example to be investigated intensively. The bands for the Mo@SbH with one

Mo atom in the 1×1 unit cell without turning on the SOC are illustrated in Figure 2a, where the Dirac points are clearly seen,



Figure 2. (a,b) Band structures for Mo@SbH in the case of the 1×1 unit cell without and with SOC considered, respectively. (c,d) The same as (a,b) but with a 3% tensile strain applied to the sheet. The red and black curves in (a,c) denote the spin-up and spin-down states, respectively. (e,f) The calculated PDOSs of Sb_B and Mo atoms, respectively, without the SOC. The solid and dotted curves in (e,f) indicate the PDOSs without strain and with a 3% tensile strain, respectively. The positive and negative values in (e,f) express the spin-up and spin-down states, respectively.

but with large variations, compared to that in the pristine Sb hydride.¹³ Because of the interactions with the magnetic Mo atoms, the bands around the K and K' points near the $E_{\rm F}$ are spin polarized drastically, leading to inversion of the bands around the Dirac cones (Figure 2a).²⁸ After the SOC is considered, local energy gaps of about 27 and 124 meV are opened around the K and K' points, respectively (Figure 2b), which may correspond to certain topologically nontrivial states.^{13,28,29} The flaw in the bands of Figure 2a,b is the bands at the Γ points also crossing the $E_{\rm F}$, which will lead to trivial electric current in the transport measurement and should be moved away from the $E_{\rm F}$.

Strain has been proved to be an effective route to tune band structures.^{30–32} Tensile strain in the *xy* plane is employed in the functionalized Sb(111) monolayers, where the lattice constant in the *xy* plane is stretched to certain value (*l*) and then the atom positions in the unit cell are relaxed fully. The magnitude of the tensile strain can be characterized by $(l - l_0)/l_0$, where l_0 is the equilibrium lattice constant. A 3% tensile strain can tune the bands very obviously. The bands of 1×1 unit cell of Mo@ SbH with a 3% tensile strain without and with SOC are plotted in Figure 2c,d, respectively. With the strain applied, the bands at the Γ point move up in energy, reaching our goals. Simultaneously, the bands at the K and K' points move down unexpectedly, giving rise to a global 27 meV gap appearing just around the E_{F} , favorable for the transport measurements of topological insulators.

Now we analyze the mechanism of the strain effects. Without the SOC, the states of the K and K' around the $E_{\rm F}$ are degenerate and composed primarily of the Sb p_x and p_y orbitals in the Sb plane,¹³ which can produce stronger SOC interactions than the usual p_z orbitals do in graphene and silicene etc.^{33,34} While the states at the Γ point originate mainly from spin-down Mo dz^2 and Sb p_z orbitals. With the strain applied, the spindown Mo dz² and Sb p_z orbitals at the Γ point move up in energy while Sb p_x and p_y orbitals at the K and K' points move down (Figure 2c,d). After the tensile strain is applied in the SbH sheet, the bond length between the Mo and Sb_B atoms (d_2) shrinks by 0.03 Å, indicating the increase of the interactions between the Mo dz^2 and the Sb p_z orbitals. Because of the large electronegativity of Sb atom, more charge is transferred from the Mo to SbH sheet from the Mo dz^2 orbitals in the process. This tendency is confirmed by the Bader analysis,³⁵ which shows that the charge transferred from Mo to Sb_B increases from 0.13e to 0.14e with a 3% tensile strain exerted. Thus, after the strain is considered, the $Sb_B p_z$ orbitals move up in energy with the Mo dz^2 , both becoming unoccupied orbitals at the Γ point (Figure 2c). Also, the original occupied electrons of those states move to the Sb p_x and p_{u} orbitals at the K and K' points. The moving up of Sb_B p_{z} and Mo dz^2 orbitals in energy and the moving down of Sb_B p_x and p_v orbitals with the tensile strain can be clearly seen in the partial densities of states (PDOSs) of these states around the $E_{\rm F}$, displayed in Figure 2e,f. The bands of the SbH sheet with Cr or W atoms around the $E_{\rm F}$ (shown in Supporting Information Figure S1) are very similar to those of the Mo case. Global gaps of 21 and 53 meV can be opened at the Dirac cones (also just at the $E_{\rm F}$) for the Cr and W systems, respectively, when a tensile strain of 5% is applied (Table 1). Previously, the topological states are usually found in p_z system such as graphene and silicene of which the nontrivial gaps are often very small.³⁶ In our cases, the topological states with larger gaps are obtained due to the contribution of p_x and p_y orbitals of Sb atoms, where the large SOC is from the on-site spin-orbit interactions,^{13,37} instead of the next-nearestneighbor spin-orbit interactions in the p_z cases.^{28,36}

The influences of TM concentrations on the results are also explored (Figure 3a,c,e). For lower TM concentration, the case of 2×2 supercell with one of the H atoms substituted by one Mo atom is calculated (Figure 1). Its total magnetic moment is found being 5 $\mu_{\rm B}$ per supercell. Also, the binding energy is 2.12 eV, larger than that of the 1×1 case (1.95 eV). It can be ascribed to the weakening of the repulsive interactions between the neighboring Mo atoms. If larger supercells of 3×3 or 4×4 with only one Mo atom in the supercell are adopted, the binding energy is saturated (only changing by 0.01 eV), inferring no interactions between the neighboring Mo atoms due to the very large distance. The black dashed curves in Figure 3a,c show the bands of the case of the 1×1 unit cell with SOC, while those in Figure 3e are the bands of the 2×2 supercell case. The bands around the K and K' points in Figure 3e are also spin polarized, similar to that of the 1×1 unit cell case. The exchange splitting in Figure 3e is, however, smaller than that in Figure 3a,c due to the low Mo concentration in Figure 3e, resulting in no band inversion around the Dirac cones (even at the K point) after the SOC is turned on (Figure 3e). Thus, very large energy gaps (214 and 349 meV) are opened around both the K and K' points, making the systems get into TRSB-QSH states,³⁸ to be verified in the next section. With the further decrease of the TM concentration, the energy



Figure 3. (a) Berry curvatures (red dots) for the whole valence bands (in atomic units (au)) of Mo@SbH in the case of 1×1 unit cell with a 3% tensile strain applied. The corresponding band structures (black dashed curves) are also displayed. (b) The distributions of the Berry curvatures in 2D momentum space for the same system as in (a). (c,d) The same as in (a,b), respectively, except for spin Berry curvatures (blue dots in (c)) instead. (e,f) The same as in (c,d), except for the case of 2×2 supercell. The bands in (e) are shown by black solid curves. No strain is applied in (e,f).

gaps increase synchronously. They hardly change when the TM concentration is lower than the 4×4 supercell case. For example, the global gap of the 4×4 supercell case is about 402 meV, very close to the gap (410 meV) of the pristine Sb hydride sheet (without the TM atoms).¹³

Exotic characteristics of the bands around the $E_{\rm F}$ in Figure 3a,c are the different behaviors at the K and K' points, which may lead to drastic valley-dependent electronics. For honeycomb structures, breaking the inversion symmetry can generally produce valley-dependent bands, such as valley-polarized metals^{28,29} and valley-polarized quantum anomalous-Hall effects,³⁹ where the inequality of the AB-sublattice potential is introduced by considering the Rashba interactions or the electric field, and so forth.40,41 The valley-dependent bands achieved in Figure 3a,c are completely different from above two types, which looks QAH states at K point and QSH states at K' point, namely QSQAH states. The different behaviors occurring at the K and K' points are associated with the inequality of the bands at the two points (Figure 3), which originates from the TM atoms deposited on the $Sb(Sb_B)$ top position (Figure 1). Thus, the strengths of the exchange fields at K and K' points around the $E_{\rm F}$ are different (Figure 3), similar to the valley Hall effect induced by the local staggered interactions in the A and B sublattices supposed in graphene.4,5

Topological invariants of C and C_s are calculated to identify the QAH and QSH states, respectively. Their definitions can be written as $C = [1/(2\pi)] \sum_n \int_{BZ} d^2k \Omega_n$ and $C_s = [e/$ $(2\pi)^2]\sum_n \int_{BZ} d^2k \Omega_n^s$. The Berry curvatures $\Omega(\mathbf{k})$ can be expressed by means of the Kubo formalism^{42,43} as follows

$$\Omega(\mathbf{k}) = \sum_{n} f_{n} \Omega_{n}(\mathbf{k}),$$

$$\Omega_{n}(\mathbf{k}) = -2 \operatorname{Im} \sum_{m \neq n} \frac{\langle \psi_{nk} | \nu_{x} | \psi_{mk} \rangle \langle \psi_{mk} | \nu_{y} | \psi_{nk} \rangle \hbar^{2}}{(E_{m} - E_{n})^{2}}$$
(1)

For the spin Berry curvatures $\Omega^{s}(\mathbf{k})$,^{8,44}

 $\alpha(\mathbf{1})$

$$\Omega^{s}(\mathbf{k}) = \sum_{n} f_{n} \Omega^{s}_{n}(\mathbf{k}),$$

$$\Omega^{s}_{n}(\mathbf{k}) = -2 \operatorname{Im} \sum_{m \neq n} \frac{\langle \psi_{n\mathbf{k}} | j_{x} | \psi_{m\mathbf{k}} \rangle \langle \psi_{m\mathbf{k}} | \nu_{y} | \psi_{n\mathbf{k}} \rangle \hbar^{2}}{(E_{m} - E_{n})^{2}}$$
(2)

In eqs 1 and 2, the summation is over all of the occupied states, E_n is the eigenvalue of the Bloch functions $|\psi_{nk}\rangle$, f_n is the Fermi–Dirac distribution function, and j_x is the spin current operator defined as $(s_z \nu_x + \nu_x s_z)/2$, where ν_x and ν_y are the velocity operators and s_z is the spin operator. The Berry curvatures and spin Berry curvatures are calculated in Wannier function bases⁴⁵ with the maximally localized algorithm.^{8,46}

The obtained Berry curvatures $\Omega(\mathbf{k})$ and spin Berry curvatures $\Omega^{s}(\mathbf{k})$ along the high-symmetry lines and their distributions in the 2D momentum space are plotted in Figure 3. In Figure 3a,c, the most nonzero $\Omega(\mathbf{k})$ only happens at the SOC-induced band gaps around the K point, while the $\Omega^{s}(\mathbf{k})$ only distributes around the K' point (The integral of $\Omega^{s}(\mathbf{k})$ around the K point is counteracted due to the both positive and negative values of $\Omega^{s}(\mathbf{k})$ around the point). By integrating the $\Omega(\mathbf{k})$ and $\Omega^{s}(\mathbf{k})$ over the first Brillouin zone (BZ), we amazingly find C and C_s of all occupied states reach value of 1 and $\sim 1/2$, respectively. It confirms a new type of topological insulators born: the QAH effect is realized at the K point while the QSH effect is realized at the K' point.²⁵ To our best knowledge, it is the first time to carry out this unique QSQAH state in a real material. For the 2×2 and larger supercell cases, the integral Chern number and spin Chern number are found to be 0 and \sim 1, respectively. The spin Berry curvature and its distributions are displayed in Figure 3e,f, respectively. We find the $\Omega^{s}(\mathbf{k})$ happens at both around the K and K' points. Although the time symmetry is broken, the calculated spin Chern number is found to be very close to an integer value of 1, meaning the system is in time-reversal-symmetry-broken quantum spin Hall (TRSB-QSH) states.³⁸ For lower TM concentrations, the systems are all in TRSB-QSH states of which the band gap is increased as the TM concentration decreases.

Above results show that the functionalized Sb(111) sheet with one TM atom deposited in a 1×1 unit cell is in QSQAH states. If the TM concentration is lowered, the system is in TRSB-QSH states. Therefore, the concentration of TM atoms can induce the topological transition. This phase transition can be ascribed to the competition between the SOC strength (λ) and the exchange field (M) resulting from the magnetic TM atoms in which the M is tuned through the TM concentration. To fully understand the competition between *M* and λ terms, we tune the λ term in the 1 \times 1 and 2 \times 2 supercell cases, which may be realized in experiments by studying PH, AsH, or BiH^{37} with group VI_{B} atoms and so forth.

The phase diagrams as a function of the SOC strength for the 1×1 and 2×2 supercell cases of Mo@SbH are given in Figure 4a,b, respectively. As shown in Figure 4a, the system is first a

Nano Letters



Figure 4. (a,b) Band gaps as a function of the SOC strength for Mo@ SbH in the cases of 1×1 and 2×2 supercells, respectively. The squares and stars denote the local band gaps at K' and K points, respectively. The solid curves denote the global band gaps in the system. (c-g) The band evolution as a function of the SOC strength (λ) for Mo@SbH with the 2 × 2 supercell model. λ_0 is the real SOC strength of the system. A 3% tensile strain is applied for the 1 × 1 case and no strain is applied for the 2 × 2 case.

Chern insulator with C = 2 when $\lambda < 0.5\lambda_0$. Then the system turns into QSQAH states with $0.5\lambda_0 < \lambda < 1.9\lambda_0$, consistent with above results that the system is a QSQAH insulator with a real SOC strength ($\lambda = 1.0\lambda_0$). QSH states can be achieved if the λ is further increased, judged by the calculations of the spin Chern number ($C_{\rm s} \sim 1$). The phase transitions of the 2 \times 2 case are very similar to those of 1×1 case, except for the smaller λ/λ_0 values of the critical points in the phase transitions. The phase diagrams can be understood as following. When M is much larger than λ , the band inversion happens at both of the K and K' points with the consideration of SOC, giving rise to QAH states in the system. When M is of the same order of λ_i QSQAH phases emerge (Figure 2d). As M is smaller than λ_i the system is in the TRSB-QSH phases (Figure 3e). Since in the 2×2 supercell case, the TM concentration is less than that in 1×1 unit cell case, the exchange field is weaker in the 2×2 supercell case, leading to the smaller critical points of the phase transition in Figure 4b. Actually, we also explore the functionalized Bi(111) monolayers (Mo@BiH) of 1×1 unit cell and find the system is in TRSB-QSH states (showed in Supporting Information Figure S2), instead of QSQAH states in the corresponding Sb case due to the particularly strong SOC in the BiH system. Therefore, the competition of the exchange field determined by TM concentrations and the SOC strength in such systems results in different phases. When $M \gg$ λ , the system can be in QAH states. When $M \sim \lambda$, the system is in QSQAH states. When $M \ll \lambda$, the system is in TRSB-QSH states. Thus, the TM concentration can efficiently tune the topological states. When a suitable insulating and nonmagnetic substrate is appended to the sheet, the topological states should remain intact which will be explored in the near future.

The concrete band evolutions with the SOC strength for Mo@SbH in the case of the 2 × 2 supercell are displayed in Figure 4c–g. The three panels of Figure 4c,e,g correspond to QAH, QSQAH, and TRSB-QSH states, respectively. The other two panels of Figure 4d,f indicate the critical states from QAH to QSQAH ($\lambda = 0.12\lambda_0$) states and from QSQAH to QSH ($\lambda = 0.47\lambda_0$) states, respectively. As shown in these panels, λ tends to enlarge the band gaps between the valence and conduction bands of the Dirac cones at the K and K' points. At the initial

stage, the band-inversion scope at K is stronger than that at K' (Figure 4c). With λ increasing to $0.12\lambda_0$ (Figure 4d), the band inversion at K' disappears first, namely, the gap at K' closes, indicating a topological phase transition may happen.⁴⁷ With the SOC strength increasing further to $0.47\lambda_0$ (Figure 4f), the band inversion at K point then vanishes. Thus, another topological phase transition can occur. Above analyses infer the inequality of the band inversion at K and K' points at the initial stage (Figure 4c) is of significance to generate the later phase transitions. This initially different exchange fields at K and K' points come from the inequality of the Sb AB-sublattice in the decorated Sb(111) monolayers, induced by the TM atoms. When TM atoms are deposited to Sb_A from the lower surface of Sb(111) monolayers, the band structures at K and K' will exchange, as displayed in Supporting Information Figure S3, that is, the QSH effect ($C_{\rm s} \sim 1/2$) emerges at the K point while the QAH effect (C = -1) happens at the K' point due to the exchange of the Sb AB-sublattice magnetization.

The functionalized Sb(111) monolayers discussed in this work can be realized in two steps based on Sb(111) ultrathin films, which have been fabricated in experiments.¹⁶ (1) Hydrogenate the Sb(111) films. Four different experimental methods have been designed to hydrogenate the Sb sheet by Song et al. in ref 13. Among them, the relatively easy method may be the one similar to synthesizing graphane (fully hydrogenated graphene) from graphene, carried out in experiments.⁴⁸ Partially hydrogenated Sb sheets can be achieved by selectively removed the hydrogen atoms by using scanning tunneling microscope⁴⁹ or by the usual deposit method.^{50,51} (2) Deposit the TM atoms to the partially hydrogenated Sb films. Because the p_z orbitals of the Sb atoms without H atoms are unbonded, the TM atoms prefer to be adsorbed and bond with the Sb atoms without H atoms. This surface-chemistry route is a powerful tool and generally employed to create new materials with desirable features in physics and chemistry. Thus, it is promising to fabricate the functionalized Sb(111) films in experiments. We also explore the influences of defects and randomizations of TM atoms on the results. The calculations show that the QSQAH state remains intact with the defect concentration up to 25% (Supporting Information Figure S4). In addition, the disorder of TM atoms does not affect much the results obtained (Supporting Information Figure S5). The topological states are robust against defects and randomizations of TM atoms, facilitating the observation of the effects in experiments.

As a potential application of the QSQAH effect, a device prototype of low-dissipation chiral interconnects is proposed in Figure 1d. In the left region of the junction, the TM atoms are deposited on the upper surface. There is no TM atom in the middle region. In the right region, the TM atoms are deposited below the lower surface. With polarization-sensitive photo-luminescence control, $^{10-12}$ various combinations between valley polarized charge and spin edge states can emerge along the borders showed in Figure 1d. The red and blue dashed arrows indicate the charge and spin edge states, respectively, happening at the K or K' valleys. For example, when the left and right regions are excited by K and K'-valley-dependent lights, respectively, fully valley-polarized charge currents emerge along the boundaries. Inversely, when the right and left regions are excited by K and K'-valley-dependent lights, respectively, spin flow transports along the borders. Such flexible manipulations of the valley and spin degrees of freedom are most useful in electronics, spintronics, and valleytronics.

Conclusions. We systematically investigated the electronic and topological properties of magnetic Sb hydride monolayers. All three types of magnetic atoms (Cr, Mo, and W) are found to have very strong binding to the exposed Sb atoms in the SbH monolayers. A small tensile strain can make the functionalized Sb(111) sheets translate from a normal metal to a QSQAH state with C = 1 and $C_s \sim 1/2$. The band gaps of the obtained QSQAH states are opened exactly around the $E_{\rm F}$ with considerably large values (up to 53 meV), beneficial to experimental observations of the effect. The large nontrivial band gaps originate from the strong SOC of Sb p, and p, orbitals, different from the traditional cases of the p_z orbitals in honeycomb structure. This QSQAH effect may make QSH and QAH states carried out in one sample possible through valleydependent optoelectronics. Phase transitions from QAH to QSQAH states and then to QSH states happen if the SOC strength of the system is tuned, ascribed to the competition of the exchange field and the SOC strength.

Methods. The electronic structures of the functionalized Sb(111) monolayers are studied with projector augmented wave formalism based on density functional theory.^{52,53} The Perdew-Burke-Ernzerhof gradient approximation⁵⁴ is used to describe the exchange and correlation functional. The planewave cutoff energy is set to be 500 eV and a vacuum space larger than 15 Å is set to avoid the interaction between the two adjacent layers. The convergence criterion for the total energy is 10^{-6} eV. The conjugated gradient algorithm is employed to perform the structural optimization. All the atoms in the unit cell are allowed to move until the Hellmann-Feynman force on each atom is smaller than 0.01 eV/Å. As shown in Figure 1a, supercells of 1×1 , 2×2 , or 3×3 with one of the H atoms in the supercell substituted by one TM atom are employed to explore the influence of the TM concentration. The 12 \times 12 \times 1, $9 \times 9 \times 1$, and $6 \times 6 \times 1$ gamma central Monkhorst–Pack grids are set for the 1 \times 1, 2 \times 2, and 3 \times 3 supercells, respectively, to perform the first BZ integral. It has been confirmed that the correlation effect of TM d orbitals has no obvious influence on the bands around the Dirac cones due to the primary Sb p_x and p_y orbitals in the bands. The Berry curvatures and spin Berry curvatures are calculated in Wannier function bases⁴⁵ with the maximally localized algorithm.⁴⁰

ASSOCIATED CONTENT

S Supporting Information

The calculated bands of Cr@SbH and W@SbH in the 1×1 unit cell case with 5% strains applied, calculated bands and spin Berry curvatures of the BiH sheet in the 1×1 unit cell case with Mo atoms deposited on the upper surface, and calculated bands, Berry curvatures, and spin Berry curvatures of the SbH sheet with Mo atoms deposited below the lower surface, the figures of the calculations of defects and randomizations of the TM atoms are shown in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b01373.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Gorbachev, R. V.; Tikhonenko, F. V.; Mayorov, A. S.; Horsell, D. W.; Savchenko, A. K. *Phys. Rev. Lett.* **2007**, *98*, 176805.

- (2) Behnia, K. Nat. Nanotechnol. 2012, 7, 488–489.
- (3) Rycerz, A.; Tworzydlo, J.; Beenakker, C. W. J. Nat. Phys. 2007, 3, 172–175.
- (4) Xiao, D.; Yao, W.; Niu, Q. Phys. Rev. Lett. 2007, 99, 236809.
- (5) Yao, W.; Xiao, D.; Niu, Q. Phys. Rev. B: Condens. Matter Mater. Phys. 2008, 77, 235406.
- (6) Jiang, Y.; Low, T.; Chang, K.; Katsnelson, M. I.; Guinea, F. *Phys. Rev. Lett.* **2013**, *110*, 046601.
- (7) Fujita, T.; Jalil, M. B. A.; Tan, S. G. Appl. Phys. Lett. 2010, 97, 043508.
- (8) Feng, W. X.; Yao, Y. G.; Zhu, W. G.; Zhou, J. J.; Yao, W.; Xiao, D. Phys. Rev. B: Condens. Matter Mater. Phys. 2012, 86, 165108.
- (9) Xiao, D.; Liu, G. B.; Feng, W.; Xu, X.; Yao, W. Phys. Rev. Lett. **2012**, 108, 196802.

(10) Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X. Nat. Nanotechnol. 2012, 7, 490–493.

(11) Mak, K. F.; McGill, K. L.; Park, J.; McEuen, P. L. Science 2014, 344, 1489–1492.

(12) Xu, X.; Yao, W.; Xiao, D.; Heinz, T. F. Nat. Phys. 2014, 10, 343–350.

(13) Song, Z.; Liu, C.-C.; Yang, J.; Han, J.; Ye, M.; Fu, B.; Yang, Y.; Niu, Q.; Lu, J.; Yao, Y. NPG Asia Mater. **2014**, *6*, e147.

(14) Liu, Z.; Liu, C.-X.; Wu, Y.-S.; Duan, W.-H.; Liu, F.; Wu, J. Phys. Rev. Lett. 2011, 107, 136805.

(15) Niu, C. W.; Bihlmayer, G.; Zhang, H. B.; Wortmann, D.; Blöugel, S.; Mokrousov, Y. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 041303(R).

(16) Bian, G.; Wang, X.; Liu, Y.; Miller, T.; Chiang, T.-C. Phys. Rev. Lett. 2012, 108, 176401.

(17) Zhang, P.; Liu, Z.; Duan, W.; Liu, F.; Wu, J. Phys. Rev. B: Condens. Matter Mater. Phys. 2012, 85, 201410(R).

(18) König, M.; Wiedmann, S.; Bröune, C.; Roth, A.; Buhmann, H.; Molenkamp, L. W.; Qi, X. L.; Zhang, S.-C. *Science* **2007**, *318*, 766– 770.

- (19) Kane, C. L.; Mele, E. J. Phys. Rev. Lett. 2005, 95, 226801.
- (20) Kane, C. L.; Mele, E. J. Phys. Rev. Lett. 2005, 95, 146802.
- (21) Chang, C. Z.; Zhang, J.; Feng, X.; Shen, J.; Zhang, Z. C.; Guo,
- M. H.; Li, K.; Ou, Y. B.; Wei, P.; Wang, L. L.; Ji, Z. Q.; Feng, Y.; Ji, S.; Chen, X.; Jia, J. F.; Dai, X.; Fang, Z.; Zhang, S. C.; He, K.; Wang, Y. Y.; Lu, L.; Ma, X. C.; Xue, Q. K. *Science* **2013**, *340*, 167–170.
- (22) Qi, X. L.; Zhang, S. C. Rev. Mod. Phys. 2011, 83, 1057-1110.
- (23) Kaloni, T. P.; Singh, N.; Schwingenschlogl, U. Phys. Rev. B: Condens. Matter Mater. Phys. **2014**, 89, 035409.
- (24) Kaloni, T. P. J. Phys. Chem. C 2014, 118, 25200-25208.
- (25) Ezawa, M. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 155415.
- (26) Kittel, C. Introduction to Solid State Physics, 5th ed.; Wiley: New York, 1976.
- (27) Liu, X.; Hsu, H.-C.; Liu, C.-X. Phys. Rev. Lett. 2013, 111, 086802.
- (28) Zhang, J. Y.; Zhao, B.; Yang, Z. Q. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 88, 165422.
- (29) Ezawa, M. Phys. Rev. Lett. 2012, 109, 055502.
- (30) Garrity, K. F.; Vanderbilt, D. Phys. Rev. B: Condens. Matter Mater. Phys. 2014, 90, 121103(R).

- Rev. B: Condens. Matter Mater. Phys. 2011, 84, 245105.
- (32) Ma, D.; Li, Z.; Yang, Z. Carbon 2012, 50, 297-305.

⁽³¹⁾ Liu, W.; Peng, X.; Tang, C.; Sun, L.; Zhang, K.; Zhong, J. Phys.

Nano Letters

(33) Liu, C. C.; Feng, W. X.; Yao, Y. G. Phys. Rev. Lett. 2011, 107, 076802.

- (34) Kaloni, T. P.; Kou, L.; Frauenheim, T.; Schwingenschlögl, U. *Appl. Phys. Lett.* **2014**, *105*, 233112.
- (35) Tang, W.; Sanville, E.; Henkelman, G. J. J. Phys.: Condens. Matter 2009, 21, 084204.

(36) Qiao, Z.; Ren, W.; Chen, H.; Bellaiche, L.; Zhang, Z.; MacDonald, A. H.; Niu, Q. *Phys. Rev. Lett.* **2014**, *112*, 116404.

(37) Liu, C.-C.; Guan, S.; Song, Z.; Yang, S. A.; Yang, J.; Yao, Y. Phys. Rev. B: Condens. Matter Mater. Phys. 2014, 90, 085431.

(38) Yang, Y.; Xu, Z.; Sheng, L.; Wang, B.; Xing, D. Y.; Sheng, D. N. *Phys. Rev. Lett.* **2011**, *107*, 066602.

(39) Pan, H.; Li, Z.; Liu, C.-C.; Zhu, G.; Qiao, Z.; Yao, Y. Phys. Rev. Lett. 2014, 112, 106802.

(40) Ezawa, M. New J. Phys. 2012, 14, 033003.

(41) Kaloni, T. P.; Tahir, M.; Schwingenschlögl, U. Sci. Rep. 2013, 3, 3192.

(42) Yao, Y. G.; Kleinman, L.; MacDonald, A. H.; Sinova, J.; Jungwirth, T.; Wang, D.-S.; Wang, E.; Niu, Q. *Phys. Rev. Lett.* **2004**, *92*, 037204.

(43) Yao, Y. G.; Fang, Z. Phys. Rev. Lett. 2005, 95, 156601.

(44) Zhang, H.; Freimuth, F.; Bihlmayer, G.; Blügel, S.; Mokrousov, Y. Phys. Rev. B: Condens. Matter Mater. Phys. 2012, 86, 035104.

(45) Mostofi, A. A.; Yates, J. R.; Lee, Y.-S.; Souza, I.; Vanderbilt, D.; Marzari, N. *Comput. Phys. Commun.* **2008**, 178, 685–699.

(46) Marzari, N.; Mostofi, A. A.; Yates, J. R.; Souza, I.; Vanderbilt, D. *Rev. Mod. Phys.* **2012**, *84*, 1419–1475.

(47) Murakami, S.; Iso, S.; Avishai, Y.; Onoda, M.; Nagaosa, N. Phys. Rev. B: Condens. Matter Mater. Phys. 2007, 76, 205304.

(48) Elias, D. C.; Nair, R. R.; Mohiuddin, T. M. G.; Morozov, S. V.; Blake, P.; Halsall, M. P.; Ferrari, A. C.; Katsnelson, D. W.; Geim, A. K.; Novoselov, K. S. *Science* **2009**, *323*, 610–613.

(49) Schofield, S. R.; Studer, P.; Hirjibehedin, C. F.; Curson, N. J.; Aeppli, G.; Bowler, D. R. *Nat. Commun.* **2013**, *4*, 1649.

(50) Robinson, J. T.; Burgess, J. S.; Junkermeier, C. E.; Badescu, S. C.; Reinecke, T. L.; Perkins, F. K.; Zalalutdniov, M. K.; Baldwin, J. W.; Culbertson, J. C.; Sheehan, P. E.; Snow, E. S. *Nano Lett.* **2010**, *10*, 3001–3005.

(51) Balog, R.; Jørgensen, B.; Nilsson, L.; Andersen, M.; Rienks, E.; Bianchi, M.; Fanetti, M.; Lægsgaard, E.; Baraldi, A.; Lizzit. *Nat. Mater.* **2010**, *9*, 315–319.

(52) Kresse, G.; Joubert, D. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758–1775.

(53) Kresse, G.; Furthmuller, J. Phys. Rev. B: Condens. Matter Mater. Phys. **1996**, 54, 11169–11186.

(54) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865-3868.

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