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Topological insulators in transition metal-intercalated graphene: the role of d electrons in significantly increasing the spin-orbit gap

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We study the effect of transition metal intercalation of graphene on the formation of two-dimensional topological insulator with experimentally measurable edge states. Our first-principles calculations reveal that the spin-orbit coupling (SOC) gap in Re-intercalated graphene on SiC(0001) substrate can be as large as 100 meV. This value is five orders of magnitude larger than that of pristine graphene. Similar effect should also exist in Mn- or Tc-intercalated graphene. A tight-binding model Hamiltonian analysis establishes the role of orbital coupling between graphene p states and transition metal d states on the formation of the SOC gap. Remarkably, the gap can be larger than atomic SOC, as is the case for Mn. This finding opens the possibility of designing topological insulators comprised of only relatively light elements. Our study also reveals that the presence of the substrate should induce a splitting between the K and K' valleys with the potential to integrate spintronics with valleytronics.

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I. INTRODUCTION

Stimulated by the seminal work of Kane and Mele on a model graphene system[1], topological insulators (TI) have attracted considerable attention due to their unique fundamental properties and potential applications in quantum computing and spintronics[2,3]. A remarkable characteristic of the TI is the metallic spin-momentum locked one-dimensional edge state for two-dimensional (2D) TI and 2D surface state for three-dimensional (3D) TI across the band gap. Several intriguing physical phenomena have been predicted on the basis of the TIs, such as magnetic monopole[4], Majorana fermions[5], and quantum anomalous Hall effect[6]. Among the large number of materials and structures that have been predicted to be 2D TIs, HgTe/CdTe[7] and InAs/GaSb[8] quantum wells have been confirmed by transport experiments. Graphene, although it hosts a number of fascinating electronic properties and paves the way for TI, is still a model system due to its vanishingly small spin-orbit coupling (SOC). Graphene has an additional valley degree of freedom not present in quantum well structures to result in valley-spin coupled phenomena[9–11]. Considerable efforts have been made to enlarge the graphene SOC gap, e.g., by depositing graphene on metal substrates[12], decorating graphene with heavy metal adatoms[13–15], utilizing the proximity effect[16], or applying a strain[17].

Much of the current effort of searching for TIs focuses on heavy atoms, and most of the proposed TIs are based on p electrons. This may not be necessary nor desirable, as d electrons can also have large SOC. For example, $3d$ transition metal (TM) elements are lightweight and have SOC on the order of several tens of meV[18], comparable to k_BT at room temperature. Going from $3d$ TM to $5d$ TM, SOC increases by nearly two orders of magnitude. To realize d-electron TIs, however, requires not only d-electron dominance near the Fermi level bout also spin quenching to preserve time-reversal symmetry. In this regard, the recently predicted strongly-bound graphene/intercalated Mn on SiC(0001) substrate system[19] uniquely stands out, as in such a system the near band edge states form a Dirac cone made of primarily the Mn d states. The Dirac cone highly resembles that in free-standing graphene with no impurity states introduced around the Fermi level as well as no energy shift of the Fermi energy with respect to the Dirac point. The coupling between the Mn and graphene states quenches completely the metal magnetic moment. The system is expected to also have good thermal and mechanical stabilities necessary for the preparation of nanoribbons. Most importantly, similar graphene/intercalated Mn/SiC structures have recently been experimentally demonstrated[20]. Given that Mn, Tc, and Re are isovalent elements in the Periodic Table with rapidly increasing atomic SOC, the SOC gap may also be significantly increased if one substitutes Mn by Tc or Re.

In this paper, we show by first-principles band structure calculations that topological phases, as well as topologically protected edge states, exist in graphene/intercalated d^5-TM/SiC systems. The effects are so large that they could be readily observed. For instance, the calculated SOC gap for Re of 100 meV is nearly five orders of magnitude larger than that of pristine graphene, while a 30 meV SOC gap is opened in the Mn intercalated system that is completely constituted by light elements. A model Hamiltonian is developed to explain the SOC gap as a function of the TM elements. It points to the importance of p-d orbital coupling, to a degree even more so than atomic SOC. The removal of the inversion symmetry by the substrate further suggests that interesting spin-valley coupled phenomena can be realized in such systems.

II. COMPUTATIONAL DETAILS

The calculations were done using density-functional theory (DFT) with the projector augmented wave[21] method and the local density approximation (LDA)[22], as implemented in the Vienna *ab initio* simulation package[23]. Plane wave basis set with a kinetic energy cutoff of 400 eV was used. We adopted a $\sqrt{3} \times \sqrt{3}R30^\circ$ structural model for $6H$-SiC to accommodate a 2×2 graphene with one TM atom intercalated [see Figs. 1(a) and (b)]. The SiC substrate contains six SiC bilayers. The bottommost three layers are fixed at their respective bulk positions. All other atoms are fully relaxed without any symmetry constraint until the residual forces are less than 0.01 eV/Å. A vacuum layer larger than 10 Å is used to minimize spurious interactions between supercells.

III. RESULTS AND DISCUSSION

Among the d^5-TMs, Re has the largest atomic SOC. Hence, it will be used here for discussion, although the physics is the same for Mn and Tc. Figures 1(a) and (b) show the atomic structure for graphene/intercalated Re/SiC(0001) in the surface unit cell, where Re takes the central η_6 position and is 1.73 Å below the (flat) graphene layer. The calculated binding energy between graphene and Re-terminated SiC surface[24] is 0.51 eV per C atom, which is similar to graphene/intercalated Mn/SiC(0001). The relaxed system maintains the C_3 rotational symmetry, the mirror symmetry with respect to the short rhombohedral diagonal line in Fig. 1(a), and the time reversal symmetry.

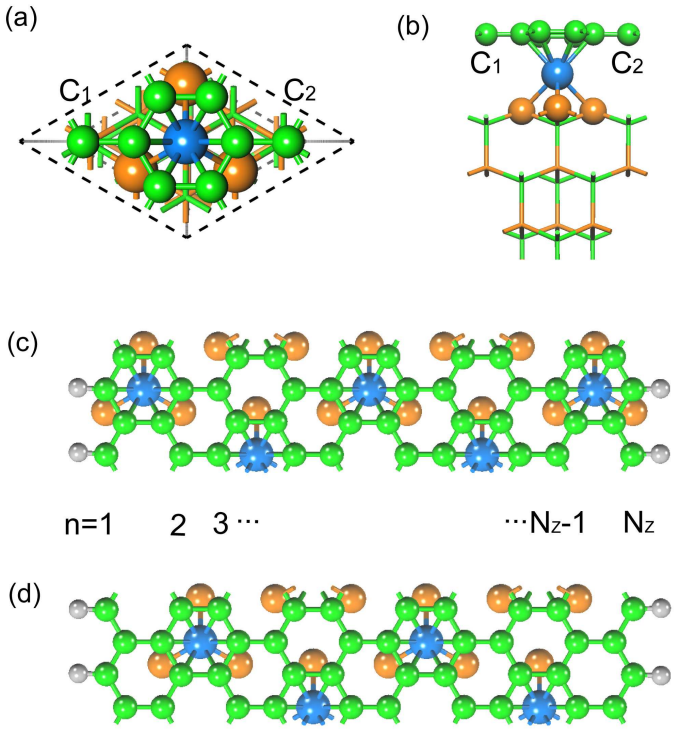

FIG. 1: (Color online) (a) Top and (b) side views of the optimized atomic structure for graphene/intercalated Re/SiC(0001) system. For clarity only half of the SiC substrate used in the simulation is shown. Dashed rhombus line denotes the surface cell. (c) and (d) Schematic drawings of $W = 10$ zigzag nanoribbon with two different edge terminations. The width W denotes the number of zigzag chains. For clarity, only the top Si layer of the SiC substrate is shown. Orange, green, gray and blue balls are Si, C, H, and Re, respectively. All dangling bonds are saturated by hydrogen.

Figure 2(a) shows the calculated band structure (left) without and (right) with SOC. Without the SOC, two bands cross each other at the Fermi level at the K (and K') point, forming a perfect Dirac cone. With the SOC, the Dirac cone splits to open up a gap of 100 meV. Such an SOC gap is considered exceptionally large, as it is nearly five orders of magnitude larger than that of pristine graphene[25]. The SOC gap is also larger than those for HgTe/CdTe (∼40 meV)[7] and InAs/GaSb (∼4 meV)[8] quantum wells.

Under the local C_{3v} symmetry, the degenerate Re d atomic states split into three different subgroups: the d_{z^2} singlet and the (d_{xy}, $d_{x^2-y^2}$) and (d_{xz}, d_{yz}) doublets. By analyzing the projected density of states, we find that the states near the Dirac point are made of predominantly the p_z states of graphene and (d_{xy}, $d_{x^2-y^2}$) states of Re. Moreover, the p_z states are localized predominantly on the carbon atoms C_1 and C_2 in Fig. 1(a) or (b), as these atoms are not directly affected by the presence of the Re.

To better understand the graphene/d^5 TM/SiC systems, we construct a simple tight-binding (TB) Hamiltonian,

$$H = H_0 + H_{\rm AB} + H_{\rm SOC} \tag{1}$$

where $H_0 = H_{\rm G} + H_{\rm TM} + H_{pd}$ accounts for the on-site energies of C p and TM d orbitals near the Dirac point and nearest-neighbor interactions between them. H_{AB} accounts for the breaking of the graphene inversion symmetry by the TM/SiC substrate. The last term $H_{\rm SOC} = \frac{1}{2}\lambda\vec{L}\cdot\vec{S}$ accounts for the SOC. Details of the Hamiltonian can be found in the Supplemental Material.[26]

Let us first consider the effect of $H_{\rm SOC}$ on the band gap. From the DFT results and using time-reversal symmetry, one can construct the following basis for the Dirac cone: $\{|\psi_1\rangle, |\psi_2\rangle\}\otimes\{|\uparrow\rangle, |\downarrow\rangle\}$, where $|\psi_1\rangle = \alpha|p_z^1\rangle + \beta|d_{2+}\rangle + \gamma|d_{2-}\rangle$ and $|\psi_2\rangle = \alpha^*|p_z^2\rangle + \gamma^*|d_{2+}\rangle + \beta^*|d_{2-}\rangle$. In these expressions, $|p_z^{1(2)}\rangle$ are the basis set for graphene near the Dirac cone and $|d_{2\pm}\rangle = \frac{1}{\sqrt{2}}(|d_{xy}\rangle \pm i|d_{x^2-y^2}\rangle)$. The corresponding matrix elements are given by

$$\langle\psi_1,\uparrow(\downarrow)|H_{\rm SOC}|\psi_1,\uparrow(\downarrow)\rangle = +(-)(\beta\cdot\beta^* - \gamma\cdot\gamma^*)\lambda \tag{2}$$

and

$$\langle\psi_2,\uparrow(\downarrow)|H_{\rm SOC}|\psi_2,\uparrow(\downarrow)\rangle = -(+)(\beta\cdot\beta^* - \gamma\cdot\gamma^*)\lambda \tag{3}$$

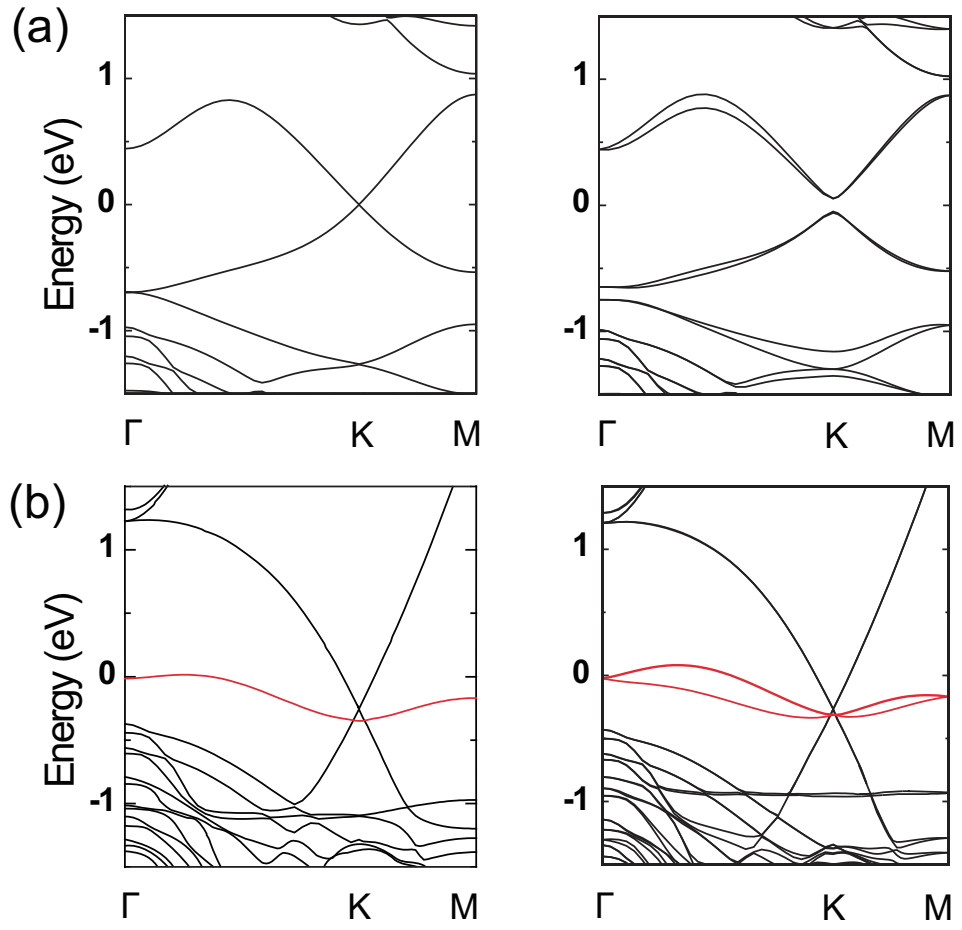

FIG. 2: (Color online) Band structures of (a) Re- and (b) Bi-intercalated graphene/SiC(0001) systems without (left) and with (right) the SOC. Fermi level is at zero. Red lines denote the Bi intercalation introduced impurity states around the Fermi level.

where the results for spin-down states are given in parentheses. Also,

$$\langle\psi_1|H_{\rm SOC}|\psi_2\rangle = \langle\psi_2|H_{\rm SOC}|\psi_1\rangle = 0. \tag{4}$$

The energy gap is at K (and K'), which is given by the difference between the diagonal elements,

$$E_g = 2|\beta\cdot\beta^* - \gamma\cdot\gamma^*|\lambda = \xi\lambda. \tag{5}$$

Equation (5) suggests that E_g is dominated by Re d states, because it does not contain α. However, this does not imply that carbon p states play no role, as the absolute values of the coefficients β and γ are still determined by the p-d coupling of states near the Dirac cone. The atomic SOCs for Mn, Tc, and Re show large differences: λ = 26, 234, 1,000 meV, respectively. The calculated SOC gaps of 30, 35, and 100 meV are, however, not in the same proportion. The reason is because the noticeable difference in ξ = 1.15, 0.15, and 0.1, as deduced from DFT calculations. These large differences in ξ are not originated from the different magnitudes of p-d coupling, but rather from a large asymmetry between β and γ, for different TMs. For Mn, β = 0.78 and γ = 0.2, but for Tc (Re) β = 0.52 (0.51) and γ = 0.45 (0.46), respectively. The large E_g for Mn suggests that it is possible to design TIs completely made of light elements.

Equation (5) also suggests that there should be no gap opening, when there is no d component in the outer shell of the atomic wavefunction regardless the mass. Indeed, this is what was found for bismuth (Bi) with atomic number Z = 83. Figure 2(b) shows the band structures (left) without and (right) with the SOC for graphene/intercalated Bi/SiC. Not only does the gap not open, but the Bi also introduces an undesirable impurity state near the Fermi level, similar to light metal intercalations such as lithium[27].

The most important character of a 2D TI is the existence of topologically protected gapless edge states[1]. Figures 1(c) and 1(d) show two low-energy edge structures with different Re arrangements for the W = 10 nanoribbons.

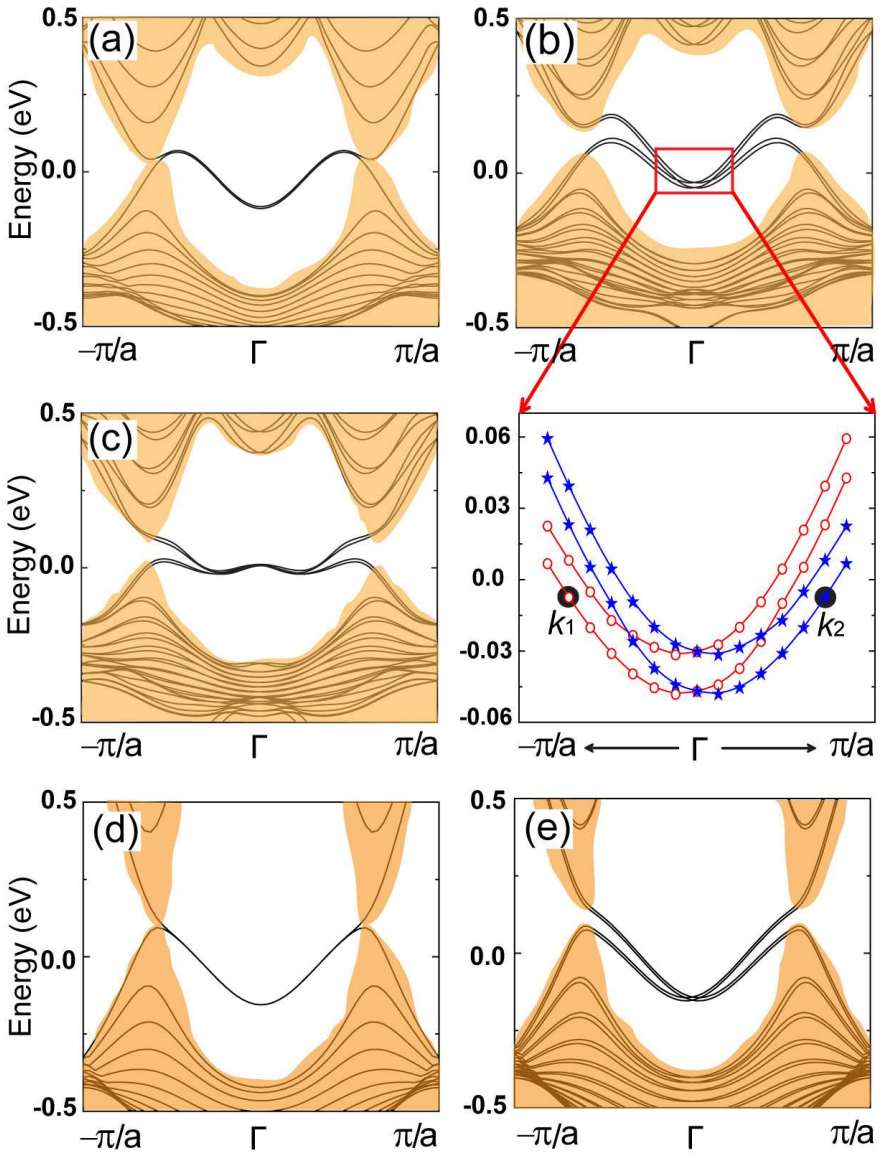

FIG. 3: (Color online) Energy dispersion of edge states for the $W = 26$ zigzag nanoribbons: (a) and (b) are for edge-termination geometry shown in Fig. 1(c) without and with SOC, respectively. In the latter case, details of the edge states near the Γ point are also shown. (c) is for edge-termination geometry shown in Fig. 1(d) with SOC. Shaded regions denote the energy spectrum of bulk. Blue lines with stars and red lines with circles are the topologically protected edge states. The Fermi level is at zero. (d) and (e) are the TB band structures without and with SOC, respectively. The TB model qualitatively reproduces the DFT results of (a) and (b).

Figure 3(a) shows the band structure of a $W = 26$ ribbon with the termination as in Fig. 1(c) without the SOC,[28] whose main feature is similar to that of free-standing zigzag graphene ribbons[29]. The edge states appear warped with about 0.2-eV dispersion. One can qualitatively understand the warpping by the TB model in Eq. (1) where the combined effect of $H_0 = H_{\rm G} + H_{\rm TM} + H_{\rm pd}$ yields a warpping of same magnitude [see Fig. 3(d)]. The large warpping prevents large density of states at the Fermi level, so the system should be nonmagnetic. Direct calculation reveals that indeed the magnetic state is about 0.1 eV higher in energy than the nonmagnetic one.

Figure 3(b) shows the band structure for the $W = 26$ ribbon with SOC. The system is in its topological phase due to SOC, as evidenced by the real-space charge distributions in Fig. 4 for states at two representative k-points, e.g., the marked $\pm k$ pair in the magnified part in Fig. 3(b). These states are located at the opposite sides of the edges with a spatial width of ∼1 nm. The fact that the in-gap edge states are mainly distributed on the Re atoms clearly demonstrates that the 1D nontrivial topological edge states can be based on not only the prevailing s and p electrons

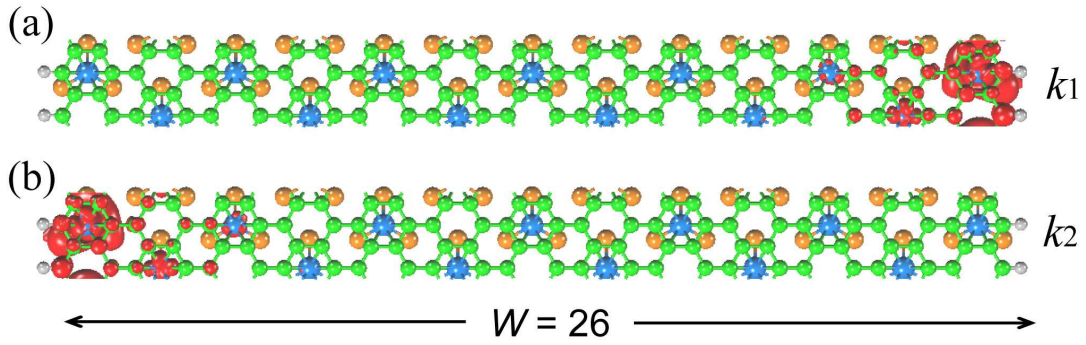

FIG. 4: (Color online) Real-space charge distribution at two representative k-points marked in the magnified part of Fig. 3(b) with an isosurface = 0.5 e/Å^3. Only the topmost Si layer of SiC substrate is shown for clarity and all the dangling bonds are saturated by hydrogen.

but also on the TM d electrons. The same picture is also qualitatively obtained by the TB model [see Fig. 3(e)]. For the ribbon structure with the termination as in Fig. 1(d), Fig. 3(c) shows the band structure with SOC. Here, the basic features of the band structure are identical to those in Fig. 3(b), except for the upward bowing of the edge states near the Γ point. The insensitivity of the nontrivial edge states on edge geometry unambiguously corroborates that the topological characters of the states are originated from bulk. Although the discussion here is based on the $W = 26$ zigzag ribbons, the conclusions apply to other zigzag ribbons as well.

The graphene/intercalated TM/SiC structure is lack of inversion symmetry. As such, one may expect that the edge states should further split. This is indeed the case as shown in Fig. 3(b), the magnified plot of Fig. 3(b), and the TB results in Fig. 3(e). Although the splitting is relatively small, only on the order of several meV, it may be enough for valley effects to be observed. For example, circularly polarized luminescence may be observed when applying circularly polarized light[11]. Because the energy splitting here is considerably smaller than the SOC gap, the topological non-trivial phase should remain to be robust. Hence, when a perpendicular electric field is applied to the system, new physics may emerge: namely, the level splitting induced by the breaking of inversion symmetry increases with increasing electric field. Eventually, phase transition will take place from the topological non-trivial quantum spin Hall state to a normal-insulator quantum valley Hall state.[9].

Recently, Hu et al. proposed that graphene decorated by 5d TM, such as Os, may be a TI, too[13]. While in both cases coupling between TM and graphene dominates electronic properties near the Fermi level, there are important differences; in particular, the SiC substrate in the present case provides a spin quenching mechanism to maintain the time-reversal symmetry for any TM coverage $\leq 1/3$ ML surface silicon. This has been a challenge in Ref. 13. To realize a true TI phase, therefore, it requires additional doping by another impurity such as Cu with exact ratio to TM, e.g., Cu/Os = 2. On top of this, clustering of the TMs on graphene is another longstanding problem. In the presence of the SiC substrate, however, not only such a clustering has not been observed experimentally[20], but the Mn intercalation energy (5.6 eV/Mn) is calculated to be larger than Mn cohesive energy (5.2 eV/Mn). In other words, clustering of the intercalated Mn is an endothermic process. Last by not least, the sandwiched graphene/intercalated TM/SiC structure has the advantage of preventing the TM atoms from being oxidized.

IV. CONCLUSIONS

In summary, we showed that graphene/intercalated d^5 TM/SiC systems are not only Dirac fermion systems, as recently proposed, but they also exhibit exceptionally large SOC gaps (perhaps the largest to date in the case of Re). We proposed a TB model to understand the gap opening, which points to the importance of orbital coupling between graphene p and metal d states near the Fermi level, more so than atomic SOC. Transition from the quantum spin Hall regime to valley Hall regime as a function of the applied electric field is proposed. The large SOC gap, the impurity-free band structure near the gap region, and the recent experimental demonstration of Mn intercalation into graphene/SiC(0001) all suggest that such a system may have a better chance of being experimentally realized.

Acknowledgments

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