Two-dimensional graphene-like Xenes as potential topological materials

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ABSTRACT
Since the discovery of quantum spin Hall (QSH) effect in graphene, searching for two-dimensional (2D) QSH materials with larger bulk gap has been an active field in the past decade. As cousins of graphene, the elemental graphene-like 2D materials (Xenes, X refers to group-IV, group-V, or group-VI elements) have been particularly interested in search of the QSH state as they share a similar honeycomb lattice with graphene. For those Xenes with heavier elements, theory predicted an extraordinarily large bulk gap suitable for room-temperature applications that have been experimentally verified in recent epitaxially grown bismuthene and stanene samples. We briefly review the progress in theoretical and experimental investigations of 2D Xenes as possible QSH topological materials.

INTRODUCTION
The successful experimental realization of graphene inspired the study of single-element two-dimensional (2D) materials. Graphene itself is a single-layer ultraflat 2D material with a honeycomb atomic structure. Its discovery has broken the conventional speculation that the single-layer 2D crystal is unstable. The unique honeycomb structure and band structure of graphene make it have excellent physical properties, including Dirac electronic behavior, ultra-high mobility, and quantum Hall effect, which have accelerated broad scientific investigations and engineering applications. Shortly after the discovery of graphene, it was envisaged to experimentally realize similar 2D honeycomb-structured materials composed of other elements. These 2D materials can be referred to as Xenes following the nomenclature of graphene, in which X refers to the main group elements ranging from group III to group VI. These elements and the corresponding Xene materials include silicon (silicene), germanium (germanene), tin (stanene), lead (plumbene), phosphorus (phosphorene), arsenic (arsenene), antimony (antimonene), bismuth (bismuthene), selenium (selenene), and tellurium (tellurene). We also include the hydrogenated or halogenated derivatives of Xenes within the framework of elemental graphene-like 2D materials since they could also host/inherit intriguing properties of the corresponding Xenes. Among the many exotic properties of Xenes in physics and chemistry, the most intriguing one is the quantum spin Hall (QSH) effect predicted in Xenes and derived materials. The 2D material with QSH effect, also called QSH insulator, has a topological energy gap opened by spin-orbit coupling (SOC) in the bulk and spin-filtered gapless states at the edge, which allows topologically protected conductive channels along the edge [Figs. 1(a) and 1(b)]. These edge states are of significance since they are particularly useful for realizing non-dissipative conduction, spintronic devices, Majorana fermions, and even quantum computing. The concept and theory of 2D topological insulators with QSH effect originated from two theoretical groups in late 2005 and early 2006. Kane and Mele proposed the QSH effect in graphene by considering the SOC effect, and Bernevig and Zhang proposed the QSH effect in a 2D semiconductor system in the presence of a strain gradient. In 2006, Bernevig et al. further predicted that the (Hg, Cd)Te/HgTe/(Hg, Cd)Te quantum wells have QSH states, and the topological QSH state was experimentally verified in 2007.
2D topological insulators, i.e., the Kane–Mele (KM) model and the Bernevig–Hughes–Zhang (BHZ) model, have been established. In both models, the size of the energy gap opening in the bulk material is decided by the strength of the SOC. However, because carbon is a very light element, its SOC is weak, and the opened topological energy gap is only in the microelectronvolts level, corresponding to an extremely low implementation temperature without practical application. If we want to build a QSH device that can operate at liquid nitrogen or even room temperature, a topological energy gap of tens or hundreds of millielectronvolts near the Fermi surface is needed all the way. This requires the design and discovery of 2D topological materials composed of heavy elements with a strong SOC. Inspired by the first QSH insulator of graphane, in the past 10 years, a few new mono-elemental graphene-like 2D topological materials have been proposed theoretically and pursued experimentally, becoming a new and promising topic in the research of low-dimensional materials and physics. \footnote{Molle et al., Nat. Mater. 16, 163 (2017). Copyright 2017 Springer Nature.}

A milestone review was given by Molle et al. in 2017, which provides insightful perspectives for the concept of making Xenes as topological materials. Since then, there have been more exciting updates in this appealing topic. For example, ultraflat stanene on Cu(111)\footnote{Molle et al., Nat. Mater. 16, 163 (2017). Copyright 2017 Springer Nature.} and flat bismuthene on SiC(0001)\footnote{Grifoni et al., Phys. Rev. B 95, 041401(R) (2017). Copyright 2017 American Physical Society.} were experimentally demonstrated to show topological features, and the spectral properties of a helical Tomonaga–Luttinger liquid were verified for the 1D edge states of the latter, further confirming the existence of the QSH state of the material. \footnote{Yao et al., Phys. Rev. B 75, 041401(R) (2007). Copyright 2007 American Physical Society.}

We are happy to see that, in the past decade, many Xenes have been fabricated as monolayers and some of them have been experimentally confirmed to be topologically nontrivial. At present, the effective preparation methods for fabricating 2D graphene-like materials include mechanical exfoliation, chemical exfoliation, chemical vapor deposition (CVD), and molecular beam epitaxy (MBE). Among them, mechanical exfoliation requires the existence of a corresponding layered bulk material. Therefore, the Xenes of Group IV elements except carbon cannot be prepared by this method. Chemical exfoliation is not a general method and is only effective for specific systems. CVD has been very successful in the preparation of many 2D materials, such as transition metal dichalcogenide compounds, but it is difficult for fabricating some elemental graphene-like 2D Xenes because most of them have a buckled structure with reactive dangling bonds and are thus easily to be affected by chemical species in the vapor atmosphere. The MBE method is used to evaporate atoms and molecular clusters by heating a bulk material in an ultrahigh vacuum environment and then depositing them on the surface to form a 2D material. This process does not require a chemical atmosphere, and the ultrahigh vacuum environment ensures that the Xene will not be oxidized and hydrogenated. So far, the MBE has become a successful and important method for the preparation of many types of graphene-like 2D materials. In addition, the MBE method can seamlessly work with scanning tunneling microscopy/scanning tunneling spectroscopy (STM/STS) and angle-resolved photoemission spectroscopy (ARPES), which also work in ultrahigh vacuum environments, without exposing the surface of the sample to atmosphere. Therefore, the MBE method can minimize the influence of impurities and adsorbates, enabling the exact verification of its intrinsic atomic structure and topological properties. Once we have a well-prepared material, it is important to verify whether it possesses the topological states. For the 2D QSH material, the topological properties are represented by a Dirac-like band crossing at the edge of the material, which is expected to be identified by observing the band crossing by ARPES and detecting enhanced density of states (DOS) by STS. In ARPES measurements, the Dirac-like band crossing at the edge is very hard to be directly observed since the detection cross section of the edge is too small, however, it is still possible to resolve the band inversion and the topological bulk gap opened by SOC using ARPES. For conductive edge states, indirect evidence can be given by STM/STS to compare the DOS at the bulk to that at the edges. Therefore, to spectroscopically identify the topological properties of a 2D material in experiment, it is necessary to use both ARPES and STM/STS methods.

We noted that there have been several great reviews summarizing research progress on Xenes and their derivatives. For example, Mannix et al. reviewed the synthesis and chemistry of elemental 2D materials. \footnote{Mannix et al., Acc. Chem. Res. 52, 2629 (2019). Copyright 2019 American Chemical Society.}

Grazianetti et al. reviewed the epitaxial
**RESEARCH UPDATE**

**Pb (plumbene)** 
Yes
0.8–1 eV

**Sn (stanene)**
Yes
0.1–0.3 eV

**Ge (germanene)**
Yes
24–30 meV

**Si (silicene)**
Yes
1.5–2.0 meV

**S (sulfur)**
Yes

**O (oxygen)**
Yes

**N (nitrogen)**
Yes

**P (phosphorus)**
Yes

**As (arsenic)**
Yes

**Sb (antimony)**
Yes

**Bi (bismuth)**
Yes

**Te (tellurium)**
Yes

**Po (polonium)**
Yes

**TABLE I. A survey of research status for Xenes as potential topological materials.**

| Group-IV element (Xene) | QSH state predicted | SOC-induced bulk gap | Group-V element (Xene) | QSH state predicted | SOC-induced bulk gap | Group-VI element (Xene) | QSH state predicted | SOC-induced bulk gap |
|------------------------|---------------------|---------------------|------------------------|---------------------|---------------------|------------------------|---------------------|---------------------|
| C (graphene)           | Yes                 | 25–50 μeV           | N (…)                  | …                   | …                   | O (…)                  | …                   | …                   |
| Si (silicene)          | Yes                 | 1.5–2.0 meV         | P (phosphorene)        | Yes                 | 28–85 meV           | S (…)                  | …                   | …                   |
| Ge (germanene)         | Yes                 | 24–30 meV           | As (arsenene)          | Yes                 | 70–193 meV          | Se (selenene)          | Yes                 | 0.13 eV             |
| Sn (stanene)           | Yes                 | 0.1–0.3 eV          | Sb (antimonene)        | Yes                 | ~270 meV            | Te (tellurene)         | Yes                 | 0.16 eV             |
| Pb (plumbene)          | Yes                 | 0.8–1 eV            | Bi (bismuthene)        | Yes                 | ~1 eV               | Po (…)                 | …                   | …                   |

methodologies and configurational details toward the nanotechnology applications of the Xenes and the ongoing efforts to devise and realize applications based on the Xenes. Antonatos et al. reviewed current state and perspectives of monolayer Xenes deposition by a bottom-up approach, stressing on the preparation techniques. In this mini review, we sort out the progress and prospects for the experimental pursuit of the above-mentioned graphene-like 2D materials, mainly focusing on their topological properties. The purpose of this review is to draw a map of the zoo of Xenes as potential QSH materials, which has not been systematically summarized before. A survey of research status for all group IV, V, and VI elements is given in Table I. We start from the silicene, the first cousin of graphene in the family of graphene-like materials.

**SILICENE AND GERMANENE**

As early as 1994, Takeda and Shiraishi theoretically predicted the possibility of forming graphene-like honeycomb structures with silicon and germanium, i.e., silicene and germanene. Different from graphene, the six-membered rings in single-layer silicon and germanium tend to form buckled structures according to their calculations. This result did not attract much attention until the single-layer graphene was discovered. In 2009, Cahangirov et al. revisited the graphene analogs of silicon and germanium and reproduced the previous results. Although the geometry is buckled, its band structure is still like that of graphene, with a Dirac cone with $p_z$ orbital contribution at the K point in the Brillouin zone and a large energy gap at the Γ point. More importantly, Liu et al. predicted by theoretical calculations that 2D buckled silicene and germanene may also have nontrivial topological properties in the freestanding states due to SOC. For both silicene and germanene, the SOC opens a topological bandgap at the Dirac point based on the KM model, analogous to that in graphene. For silicene, the size of the gap can reach 1.5–2.0 meV, corresponding to an experimentally accessible temperature of about 18 K. For germanene, the size of the SOC bandgap was predicted to reach 23.9 meV, much higher than the thermal energy of liquid nitrogen temperature (~6.6 meV). This work sheds light on the realization of practical QSH devices using silicene and germanene.

It has been thought that it is extremely difficult to fabricate single-layer silicene since silicon is naturally presented in the form of $sp^3$ hybridization and tends to form 3D clusters rather than a layered structure. The breakthrough was made in 2012, when Vogt et al. and Feng et al. independently reported the successful fabrication of silicene on the Ag(111) surface by the MBE method. The reported silicene has multiple superstructures with respect to the underlying Ag substrate, including (4 × 4), (√7 × √7), and (√3 × √3), as shown in Fig. 2, and some other superstructures. So far, silicene has been successfully fabricated on various substrates, for example, ZrB$_2$(0001) and Ir(111) surfaces. However, due to the strong interaction between silicene and these substrates, it is...
difficult to characterize the intrinsic properties of the silicene layer. In addition, since the theoretically predicted topological gap for silicene is on the order of 1 meV, it is still difficult for ARPES or STS to identify the gap at this resolution. Therefore, after 2014, more attention was paid on germanene and stanene that may have much larger topological energy gaps. Silicene is not only the first graphene-like group-IV 2D material that was predicted to be a QSH insulator but also the first one that was successfully fabricated in experiment. These pioneer works also demonstrated that MBE is the most powerful method toward the fabrication of such elemental 2D materials and inspired future research on heavier group-IV Xenes. A comprehensive review on the research progress of silicene is found in Ref. 36.

Freestanding germanene was theoretically calculated to have the same honeycomb buckled structure as silicene, and the band structure is also very similar. In 2013, Bianco et al. produced nanosheets of hydrogenated germanene with an electron mobility ten times than that of silicon by chemically exfoliating germanium crystals. However, the hydrogenated germanene prepared by this method is a direct bandgap semiconductor and does not have a QSH insulating state. Following the preparation of silicene, the MBE method is also used to prepare monolayers of germanene, as shown in Fig. 3. In 2014, Li et al. and Dávila et al. successfully grew layers of germanene on Pt(111) and Au(111), respectively. In 2016, Qin et al. reported the MBE growth of nearly flat bilayer and monolayer germanene on Cu(111). However, due to the complex interaction with the substrate, the Dirac electronic state was not observed for all the reported monolayer germanene.

STANENE AND PLUMBENE

Tin has a much larger atomic number than silicon and germanium, so the SOC effect in stanene is much more prominent. In 2013, Xu et al. found that SOC opens a topological energy gap at the K point of ~100 meV in buckled stanene according to the KM model, which means that freestanding stanene may host the QSH state even at room temperature. What is more interesting they found is that the pz orbitals (π bands with a Dirac cone at the K point) will be removed away from the Fermi surface if the stanene is decorated with hydrogen or halogen atoms. Instead, the transport properties of stanene will be determined by the px orbitals (σ bands) at the Brillouin center Γ point. Theoretical calculations predict that, for chemically decorated stanene, it is possible to induce an inverse band order at the Γ point in the energy diagram where the px bonding states have higher energy than the anti-bond s states. This s–p band inversion results in a nontrivial QSH phase described by the BHZ model, and the enhanced SOC of the σ orbitals opens an extraordinarily large topological gap of

![FIG. 3. Some examples of monolayer germanene epitaxially prepared on a substrate. (a) Atomic-resolution STM image and the corresponding structural model of the monolayer germanene grown on Pt(111). Reprinted with permission from Li et al., Adv. Mater. 26, 4820 (2014). Copyright 2014 Wiley. (b) Atomic-resolution STM image and the corresponding structural model of the monolayer germanene grown on Au(111). Reprinted with permission from Dávila et al., New J. Phys. 16, 095002 (2014). Copyright 2014 IOP. (c) Atomic-resolution STM image and the corresponding structural model of the monolayer germanene grown on Cu(111). Reprinted with permission from Qin et al., Adv. Mater. 29, 1606046 (2017). Copyright 2017 Wiley.](image-url)
FIG. 4. [(a) and (b)] Theoretically calculated band structures without (black dashed-dotted lines) and with (red solid lines) SOC for freestanding stanene and fluorinated stanene, respectively. The inset of (a) shows a zoomed-in view of energy dispersion near the K point. Parities of the Bloch states at the Γ point are denoted by +, −. (c) Theoretically calculated energy gap of stanene (none) and its derivatives at their equilibrium lattice constants. Red squares and blue circles mark topological and trivial insulators, respectively. Reprinted with permission from Xu et al., Phys. Rev. Lett. 111, 136804 (2013). Copyright 2013 American Physical Society. [(d) and (e)] Top view and side view of the atomic structure and molecular orbitals as well as the low-energy bands with (red solid lines) and without (black dashed lines) SOC for bare stanene (d) and chemically decorated stanene (e). Reprinted with permission from Molle et al., Nat. Mater. 16, 163 (2017). Copyright 2017 Springer Nature.

∼0.3 eV at the Γ point near the Fermi level, which is about three times larger than that of the QSH phase in unsaturated stanene described with the KM model, as shown in Fig. 4(c). This means that the topological states of stanene are highly tunable and both the KM and BHZ models can be studied in stanene, offering an ideal platform to explore 2D topological physics. Furthermore, this topological phase is quite robust: First, the size of the large energy gap depends on the strength of SOC and is nearly constant. Second, this topological band inversion is determined by the in-plane $p_x$ orbitals between the tin atoms, so it is natively protected from out-of-plane adsorbates and impurities. Figures 4(d) and 4(e) show the geometric structure of pristine stanene and chemically decorated stanene as well as their topological bandgap described by KM and BHZ models, respectively. Moreover, the topological phase chemically decorated stanene can even be changed from the trivial phase to nontrivial and vice versa by tuning the lattice strain or substituting the chemical species, enabling the so-called topological phase transition. Besides the intriguing topological properties, stanene was also predicted to host topological superconductivity, superior thermoelectric effect, and high-temperature quantum anomalous Hall effect.

Before 2015, the synthesis of stanene has been a challenge. It cannot be obtained by mechanical or chemical exfoliation from bulk tin, which is a soft crystalline metal at room temperature. It is also hard to be prepared with the CVD method since the tin atoms prefer to form 3D clusters on many substrates. In 2015, Zhu et al. made the breakthrough by growing a first stanene sample with the MBE method on a Bi$_2$Te$_3$(111) surface, which has a slightly smaller lattice parameter than freestanding stanene (Fig. 5). The atomic-resolution STM images showed that the stanene film has a buckled honeycomb structure in accordance with the theoretically predicted monolayer stanene. Due to the commensurate epitaxy of stanene on the Bi$_2$Te$_3$ substrate, the lattice constant of the buckled stanene is compressed to 4.38 Å to match that of the Bi$_2$Te$_3$(111) surface. The successful synthesis of stanene stimulated further experimental investigation of stanene and its derivatives. For example, in 2017, Gou et al. reported the epitaxial growth of stanene film and stanene nanoribbons on a Sb(111) substrate. The stanene film also showed a compressed lattice constant of 4.3 Å following that of the Sb substrate. In 2018, Zang et al. successfully prepared a single layer of stanene hydride on a PbTe(111) substrate with a lattice constant of 4.52 Å and observed an insulator gap by ARPES. However, none of these stanene samples show topological properties due to the compressed lattice constant inherited from the substrates. According to the theory, band inversion should occur with an enlarged lattice constant (>4.8 Å). In 2018, Yuhara et al. reported the epitaxial growth of a single layer of nearly flat stanene on the Ag(111) substrate with a lattice constant of 5.0 Å, meeting the requirement of suitable lattice stretching. However, the stanene film was actually grown on a corrugated Ag$_2$Sn surface alloy, whether it exhibits topological band features or not remains unknown.

In order to obtain stanene with topologically nontrivial states, the accurate control over substrate/interface structures at the atomic level during the epitaxial growth is required. In 2018, Deng et al. achieved this goal by growing monolayer stanene on Cu(111)
substrates with a modified MBE method. A Cu(111) single crystal was selected as the substrate in this work since the surface has a lattice constant of 2.55 Å (Fig. 6). By carefully controlling the substrate temperature, stanene can be grown in a true 2D mode on the surface and forms a perfect 2 × 2 honeycomb superlattice with a lattice constant of 5.1 Å [Figs. 6(b) and 6(c)], satisfying the lattice strain required for the topological phase. Interestingly, the stanene layer shows an ultraflat geometry like graphene: the two sublattice atoms in a unit cell of the honeycomb lattice are chemically indistinguishable, representing a true analog of graphene, as shown in Figs. 6(d) and 6(e). Theoretical analysis showed that the Cu substrate not only stabilizes the stretched and ultraflat structure of the stanene layer but also plays the role of orbital filtering. It selectively filters out the $p_z$ orbitals of tin atoms so that the epitaxial stanene can be viewed as a honeycomb lattice of in-plane $p_{xy}$ orbitals only. This orbital-filter effect removes the $p_z$ bands away from the Fermi level at K points and effectively mimics the chemical decoration in hydrogenated or halogenated stanene [Fig. 6(f)], making the ultraflat stanene on Cu(111) have the similar topological properties described by the BHZ model. High-resolution ARPES spectra indeed show that the SOC opens an energy gap of about 0.3 eV in the $p_{xy}$ band at the $\Gamma$ point [Figs. 6(g) and 6(h)], in accordance with the theoretical calculations. Such a large topological energy gap is of great significance for the implementation of topological quantum devices operating at room temperature. Moreover, further theoretical calculations predict that germanene and plumbene can also be grown and stabilized on Cu(111) in the same ultraflat honeycomb structure, and both of them show an s–p band inversion together with a SOC-induced gap at the $\Gamma$ point. Therefore, these materials form a distinct class of ultraflat graphene-like materials that are stabilized by the substrate.

Like stanene, plumbene was also predicted to become a QSH insulator with extraordinarily giant bulk gaps larger than 1 eV by chemical decoration with halogen elements. A recent work by Yuhara et al. reported the compelling evidence of the plumbene epitaxially grown by segregation on a Pd$_1$–Pb$_5$(111) alloy. However, they did not show ARPES results on this sample, so whether there is a band inversion or not remains to be verified.

**PHOSPHORENE AND ARSENENE**

Group-V elements can form stable graphene-like 2D layered materials, except nitrogen. Among these materials, some were predicted to host topological properties in certain circumstances. The lightest stable elemental group-V Xene, phosphorene, also known as a single layer of phosphorus. There are multiple allotropes of phosphorene, including black phosphorene and blue phosphorene. The structure of black phosphorene has an orthorhombic structure, and the blue phosphorene has a bucked honeycomb structure as other graphene-like Xenes do. For few-layer black phosphorene, theory predicted that it can be continuously tuned from a normal semiconductor to a topological insulator in the QSH phase by simply applying a perpendicular electric field. However, due to the weak SOC effect, the resulting topological energy gap is only about 5 meV. In addition, technically, it is not easy to apply such a vertical electric field, so whether the topological phase transition can be realized in phosphorene has not been experimentally verified so far. For blue phosphorene, theoretical calculations predict that an s–p band inversion can be induced at the $\Gamma$ point in the band structure by applying tensile strain on monolayer phosphorene to about 17%, similar to the s–p band inversion in stanene. The SOC induced bulk gaps are calculated to be sizable from 28 to 85 meV with tunable strain. In addition, fluorination of monolayer blue phosphorene was predicted to have a Dirac cone at the K points and a bandgap opens when the SOC is turned on, similar to graphene and silicene, making the fluorinated blue phosphorene a promising QSH material.

Although few-layer or single-layer black phosphorene can be readily obtained by exfoliation from bulk black phosphorus, the preparation of blue phosphorene is a challenge since no bulk blue phosphorus has been discovered. In 2016, Zhang et al. reported the epitaxial growth of single layer blue phosphorene on Au(111) by using black phosphorus as a precursor. Their STM investigation showed that the blue phosphorene has a (5 × 5)-Au(111) supercell structure and a 1.10 eV bandgap. However, this structural model is still under strong debate, and their recent calculations indicated that the single-layer phosphorus structure grown on Au(111) is not a full layer of blue phosphorene but a single layer structure.
FIG. 6. (a) Schematic sample preparation setup for ultraflat stanene epitaxially grown on Cu(111). (b) STM image of a stanene nanoflake on Cu(111). (c) High-resolution STM image of the stanene flake showing a flat honeycomb structure. (d) and (e) Top view and side view of optimized structural model for (c) with a \(2 \times 2\) superlattice. The inset is a simulated STM image. (f) Theoretically calculated energy band structure of ultraflat stanene on Cu(111) with SOC. (g) and (h) ARPES spectra of 0.9 ML stanene on Cu(111) along the M–\(\Gamma\)–K–M and M–\(\Gamma\)–M’–\(\Gamma\) directions. The orange lines outline the energy bands that are contributed mainly by orbitals of Sn. Reprinted with permission from Deng et al., Nat. Mater. 17, 1081 (2018). Copyright 2018 Springer Nature.

composed of Au atom-connected blue phosphorene fragments owing to the strong Au–P interaction. These results show that it is still a challenging task to prepare uniform monolayer blue phosphorene with a well-defined honeycomb structure.

In search of possible group-V QSH materials with larger SOC-induced topological bulk gap, arsenene was subjected to investigation. In 2015, Zhang et al. theoretically predicted that atomically thin arsenene and antimonene in a buckled honeycomb structure can be converted from indirect bandgap semiconductors to direct bandgap semiconductors under biaxial strain. One year later, Wang et al. proposed by theoretical calculation that further increasing the strain of arsenene to larger than 11.14% will result in a typical s–p band inversion at the \(\Gamma\) point, which is a nontrivial QSH state [Figs. 7(a) and 7(b)]. That is to say, monolayer arsenene can also be tuned into topological phase transition like monolayer blue phosphorene. The SOC-induced bandgap under a strain of 16% is
predicted to reach a considerably large value of \( \sim 70 \text{ meV} \). More interestingly, Wang et al.\(^\text{25}\) also discovered another possible approach to make arsenene a topological insulator by chemical decoration, following the idea proposed for stanene by Xu et al. in 2013.\(^\text{26}\) In their prediction, hydrogenated arsenene can stably exist in a flat honeycomb structure under high tensile strain as large as 28% [Fig. 7(c)]. In this case, a new \( \sigma \)-type Dirac cone related to the \( p_x \) orbital of As atoms will show up at the K point, and SOC opens a large QSH gap of 193 meV at the Dirac cone [Fig. 7(d)]. These results are exciting and promising because such a tensile strain is not difficult to reach, considering the highly buckled structure of arsenene. However, the deposition of As is not compatible with the standard MBE method because it is hard to crack small As clusters during evaporation. So far, the experimentally fabricated high-quality monolayer arsenene still remains challenging, not to mention the hydrogenated arsenene.

**ANTIMONENE AND BISMUTHENE**

Antimonene is predicted to be a semiconductor\(^\text{53}\) and is expected to be used in high-performance electronic and optoelectronic devices.\(^\text{54,55}\) Much like arsenene, theoretical calculations by Zhao et al.\(^\text{27}\) also suggest that a large tensile strain (\( \sim 15\% \)) applied on monolayer antimonene will lead to an \( s\text{-}p \) topological band inversion at the \( \Gamma \) point, transforming it from a normal insulator to a topological insulator with a QSH gap of up to 270 meV [Figs. 8(a) and 8(b)]. In 2014, Song et al.\(^\text{28}\) found that if antimonene and bismuthene monolayers are chemically decorated by hydrogen or halogen atoms, the resulting hydrogenated or halogenated Xenes (\( X = \text{Sb}, \text{Bi} \)) are also 2D QSH insulators with an extraordinarily large bulk bandgap (\( \sim 0.4 \text{ eV} \) for Sb and \( \sim 1 \text{ eV} \) for Bi) due to the large SOC effect of Sb and Bi, sharing the same mechanism with that for hydrogenated arsenene [Figs. 8(c)–8(f)].

The above theoretical calculations point out that there are two approaches toward the realization of QSH insulator with antimonene, one is to introduce enough tensile strain in the lattice and the other is to chemically decorate the Sb atoms. For undecorated antimonene, it can be prepared in a variety of methods including mechanical exfoliation using antimony crystals\(^\text{29}\) and epitaxial growth on various substrates.\(^\text{37–62}\) However, only two of these antimonene samples show large lattice strain. In 2018, Shao et al.\(^\text{63}\) used the MBE method to prepare a monolayer antimonene of purely flat honeycomb structure on the Ag(111) surface. Independently, Mao et al.\(^\text{64}\) prepared buckled structured monolayer antimonene on a layer of the Sb–Ag surface alloy on the same Ag(111) substrate. In both works, antimonene showed a superstructure of \( (\sqrt{3} \times \sqrt{3}) \text{R}30^\circ \) with respect to the Ag(111) substrate, and the lattice constants reached 5 Å, that is, with a lattice stretch of 20% comparing to that of freestanding antimonene. This tensile strain in the Sb lattice is large enough to meet the requirement for topological band inversion. However, none of these reports showed ARPES for the epitaxially grown monolayer antimonene; thus, the existence of topological states was not verified.

Unlike the nonmetallic lighter elements P, As, and Sb in group-V with a layered structure, bulk Bi is a rhombohedral metallic crystal. The melting point of Bi is low, and it will not form molecular clusters when evaporated. Therefore, high quality crystalline sheets of Bi can be readily deposited with the MBE method.\(^\text{63}\) As early as 2013, Huang et al.\(^\text{64}\) predicted that in the case of lattice stretching, bismuthene can be tuned into a nontrivial topological phase with band inversion, opening a large topological bulk bandgap, in analogous to arsenene and antimonene. Huang et al. also predicted that single-layer bismuthene can be fabricated on the SiC(0001) surface with a \( (\sqrt{3} \times \sqrt{3}) \text{R}30^\circ \) superstructure and a flat planar honeycomb lattice. Two years later, Hsu et al.\(^\text{65}\) from the same group further studied the topological properties of monolayer bismuthene on SiC (0001). They found that, in this system, bismuthene has a Dirac cone band structure at the K point with a topological energy gap opened by SOC. Due to the huge SOC in Bi, this gap is the largest one predicted among all QSH insulators of group-IV and group-V. Interestingly, the simulated band structure with SOC for bismuthene on SiC(0001) is similar to that for hydrogenated or halogenated...
bismuthene simulated previously by Song et al. in 2014, indicating that the bonding of bismuthene to the Si adatoms on the SiC surface can effectively mimic the bonding of Bi to hydrogen and halogen atoms.

These pioneer theoretical proposals were finally realized and verified until 2017, when Reis et al. successfully synthesized monolayer bismuthene on the SiC (0001) surface with the MBE method. The bismuthene layer shows a $\sqrt{3} \times \sqrt{3} R30^\circ$ superstructure with a flat honeycomb lattice consistent with theoretical predictions. The results are shown in Figs. 9(a)–9(d). Each of the Bi atoms is located at the top of a Si atom and is chemically bonded to it so that the low-energy bands of bismuthene are described by a Dirac cone at the K point contributed mostly by $p_x$ and $p_y$ orbitals. To verify the band structure, they performed ARPES measurement and found that there are two occupied parabolic energy bands near the K point [Fig. 9(f)], which are attributed to the SOC induced bandgap opening to the Dirac cone [Fig. 9(e)]. The STS spectra measured in the bulk of the bismuthene domain show an energy gap of about 0.8 eV ($\approx 0.2$ eV to 0.6 eV) near the Fermi level, while those measured at the edge show an enhanced electron density of states in the gap. The measured size of the bulk gap as well as the band structure near the Fermi level is in good agreement with the theoretical predictions of the SOC-induced topologically nontrivial QSH state. Such a large gap suggests that the bulk of the monolayer bismuthene can remain topologically insulating well above room temperature. More importantly, the chemical potential of bismuthene resides in the global system gap of the SiC substrate, which is a wide-gap semiconductor. This means that the conducting edge channels will not be smeared by substrate conduction electrons, making the epitaxial system a judicious choice for realizing practical room-temperature QSH devices.

**SELENENE AND TELLURENE**

Selenene and tellurene are a new family of Xenes defined recently as 2D structures of selenium and tellurium. Although they are also named as Xenes, they do not host the honeycomb or buckled honeycomb structure as group-IV and group-V Xenes do and cannot be classified into graphene-like Xenes. Therefore, one cannot simply expect similar QSH phases in selenene and tellurene as those predicted in those graphene-like Xenes. Xian et al. predicted by theoretical calculations that selenene and tellurene could exist in chair-like buckled structures but with a square unit cell rather than a honeycomb one. More interestingly, their results show that a considerably large bandgap opened by SOC makes square selenene and tellurene promising topological insulators, hosting nontrivial QSH states. The SOC induced bulk gap opens at the $P_1$ point and is predicted to be 0.13 eV for square selenene and 0.16 eV for square tellurene. A recent experimental work by Khatun et al. reported the growth of a nonlayered tellurene monolayer through an anisotropic ultrasonication method. They also reported evidence of topological insulator behavior in this
nonlayered material by taking STS measurements on the insulating interior and metallic edge states. Although the group-IV Xenes are a new promising family for realizing 2D topological materials, the investigation on the existence of nontrivial topological properties in 2D selenene and tellurene structures is still preliminary and needs further verification from both experimental and theoretical aspects.

**SUMMARY AND OUTLOOK**

In this article, we review the theoretical and experimental progress of the elemental 2D topological materials of group IV and V elements. As this field is still in very rapid development and numerous research results were achieved, we must point out that not all of them are introduced in this mini review. Besides the group VI Xenes in non-graphene-like square structure, the main clues for graphene-like Xenes as potential topological materials can be summarized as follows: For the group-IV family, pristine freestanding Xenes (X = Si, Ge, Sn) are proposed to be QSH materials with SOC-induced bulk gaps opened at the Dirac cones, but there have been continuous challenges to fabricate and isolate such freestanding Xenes. Alternatively, Xenes (X = Ge, Sn, Pb) decorated chemically or bonded to suitable substrates, in which the pz orbitals of the Xene are saturated or filtered out and an s–p band inversion occurs, can be ideal QSH materials described by the BHZ model with even larger SOC-induced bulk gap compared to that in the freestanding Xene described by the KM model. For the group-V family, the pristine freestanding Xenes (X = P, As, Sb) are semiconductors. There are two means toward the realization of QSH insulators in general. The first one is to apply a large tensile strain on the lattice so that the band-inversion can be realized and the Xene (X = P, As, Sb, Bi) can transition from trivial semiconductors to nontrivial QSH insulators. The second one is to chemically decorate the Xenes or bond them to a suitable substrate. Along with these theoretical proposals, we are happy to see that there have been two samples to show experimental evidences of topological properties, i.e., the ultraflat stanene on Cu(111) and the flat bismuthene on SiC(0001). We also find that coincidentally the Xenes in these two samples, although belonging to group-IV and group-V, respectively, are both chemically bonded to the substrate with pz orbitals filtered. In the theoretical aspect, the hydrogenated or halogenated Xenes are highly promising QSH materials. However, to fabricate high-quality hydrogenated and halogenated Xenes is still inaccessible with current chemical techniques. On the other hand, even if we obtain a layer of hydrogenated or halogenated Xenes, we still need to place it on an insulating and inert substrate to avoid damage to its QSH state. From this practical point of view, to grow Xenes directly on a semiconductor surface with a large bandgap such as SiC or oxides is such a good idea that may be immediately compatible with modern microelectronic techniques. The progress introduced in this review has shed light on making Xene-based topological materials, although there are several difficulties that need to be overcome before the epitaxial 2D Xenes can be used for practical applications. We highly expect that significant progress in this fast-rising field can be made in the near future.

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