Buckled two-dimensional Xene sheets — **Source link** ↗

Alessandro Molle, Joshua E. Goldberger, Michel Houssa, Yong Xu ...+2 more authors

Institutions: Olivetti, Ohio State University, Katholieke Universiteit Leuven, Tsinghua University ...+2 more institutions

Related papers:

- Electric Field Effect in Atomically Thin Carbon Films

- Generalized Gradient Approximation Made Simple

- Epitaxial growth of two-dimensional stanene

- Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon

- Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set.

Buckled Two-Dimensional Xene Sheets

Alessandro Molle[1], Joshua Goldberger[2], Michel Houssa[3], Yong Xu[4,5,6], Shou-Cheng Zhang[7,8,9], and Deji Akinwande[10]

[1] Laboratorio MDM, IMM-CNR, via C. Olivetti 2, Agrate Brianza, I-20864, Italy
[2] Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210, USA
[3] Department of Physics and Astronomy, University of Leuven, B-3001 Leuven, Belgium
[4] State Key Laboratory of Low Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China
[5] Collaborative Innovation Center of Quantum Matter, Beijing 100084, People's Republic of China
[6] RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan
[7] Department of Physics, McCullough Building, Stanford University, Stanford, California 94305-4045, USA
[8] Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA
[9] Institute for Advanced Study, Tsinghua University, Beijing 100084, People's Republic of China
[10] Microelectronics Research Center, The University of Texas at Austin, Texas 78758, USA

33

34   **Abstract**

35   Silicene, germanene, and stanene, are part of a monoelemental class of two-dimensional

36   (2D) crystals termed 2D-Xenes (X=Si, Ge, Sn) which, together with their ligand-

37   functionalized derivatives referred to as Xanes, are comprised of group IVA atoms

38   arranged in a honeycomb lattice – similar to graphene but with varying degrees of

39   buckling. Their electronic structure range from trivial insulators, to semiconductors with

40   tunable gaps, to semimetallic, depending on the substrate, chemical functionalization, and

41   strain. More than a dozen different topological insulator states are predicted to emerge,

42   including the quantum spin Hall state at room temperature, which, if realized, would

43   enable new classes of nanoelectronic and spintronic devices, such as the topological field

44   effect transistor. The electronic structure can be tuned, for example, by changing the

45   group IVA element, the degree of spin-orbit coupling, the functionalization chemistry, or

46   the substrate, making the 2D-Xene systems promising multifunctional 2D materials for

47   nanotechnology. This Perspective Article highlights the current state-of-the art and future

48   opportunities in the manipulation and stability of these materials, their functions and

49   applications, and novel device concepts.

50

51

52

53

54

55   The rise of graphene has inspired the flourish of a so-called "flatland" of two-

56   dimensional (2D) materials with complementary properties and functionalities enabling

57   rapid advances in science and engineering, and an accelerated global development in

58   nanotechnology applications that can address societal challenges in energy, electronics,

59   sensors and health.[1,2,3] One closely related class of 2D crystals are the single-element

60   "2D-Xenes", which take their etymology from the sp^2-hybridized alkene bond and are

61   generally comprised of a single-layer of atoms organized into a honeycomb-like lattice.

62   In particular, 2D-Xenes made of group-IVA elements, referred to as "silicene",

63   "germanene", and "stanene" when X=Si, Ge, and Sn respectively, are isoelectronic to

64   graphene,[4] however their larger interatomic distances result in up and down atomic

65   buckling about a honeycomb lattice[5], and also afford new routes towards covalent

66   functionalization. The buckled structure and the strong spin-orbit coupling (SOC)

67   concurrently paves a pathway for accessing the new quantum state of matter known as a

68   2D topological insulator (TI), a solid-state material that has both an insulating electronic

69   structure in the bulk and dissipation-less conducting channels along the edges that are

70   protected against back-scattering by time reversal symmetry. The potential technological

71   value of such an effect is that it enables the creation of a material that exhibits ideal

72   conduction along the edges that is immune from scattering from a variety of defects and

73   disorder. Overall, intriguing questions have come to the forefront such as: What are the

74   benefits and challenges that arise owing to the intrinsic buckling and surface sensitivity in

75   2D-Xenes? And can 2D-Xenes ultimately establish topology as a paradigm shift for

76   nanoscale opto-electronics? These questions are discussed here with highlights on the

77   opportunities and perspectives on the technical challenges.

A pseudo planar flatland

While the planar flatland has been considered the norm for the past ten years as is the case for graphene and h-BN, *anisotropy* in honeycomb lattices stemming from the extended vertical distortions (for example bond buckling in 2D-Xenes or puckering in phosphorene) is now the *new normal*.[4,5,6] The native buckling can have dramatic implications in the overall physics and chemistry of the 2D-Xenes. For instance, the degree of buckling can dictate the electronic character or influence the chemical reactivity. This highlights the concept of a pseudo-planar flatland where buckling can foster a number of potential functionalities that can be readily engineered.

An in-depth view on buckling. In their most stable form, 2D-Xenes based on Si, Ge or Sn atoms adopt a buckled hexagonal honeycomb structure[6,7], unlike graphene, which is ideally flat. For example, the larger bond length in silicene (~2.28 Å) compared to graphene (~1.42 Å), prevents the Si atoms from forming strong π-bonds, thus leading to deviations away from a sp^2 hybridization.[4,8] The buckling of the Si atoms brings them closer together to enable a stronger overlap of their π-bonding p_z orbitals, resulting in a mixed sp^2-sp^3 hybridization, which stabilizes their hexagonal arrangement. The vertical buckling distance δ between the top and bottom atoms of the 2D-Xene crystal structure (**Figure 1a**) is correlated to the bond angle between the framework atoms and the hybridization of the atomic orbitals: δ increases from 0 Å in graphene to 0.85 Å in free-standing (FS) stanene, with an associated decrease of the bond angle, from 120° (pure sp^2 hybridization of C atoms) to 110° (almost pure sp^3 hybridization of Sn atoms).

100 2D-Xenes can be described by a four-band second-nearest neighbor tight binding

101 Hamiltonian[9] near the K and K' points, involving a SOC term (λ_{SO}) and a staggered

102 external electric field term (E_z),

103 $H = \hbar v_F(\eta k_x \tau_x + k_y \tau_y) + \eta \tau_z \sigma_z \lambda_{SO} - \frac{\delta}{2} E_z \tau_z + \frac{\lambda_{R1}(\eta \tau_x \sigma_y - \tau_y \sigma_x)}{2} + \eta \tau_z a \lambda_{R2}(k_y \sigma_x -$

104 $k_x \sigma_y)$,   (1)

105 where v_F is the Fermi velocity, η=1 for K and η=-1 for K' point, $\tau_{x,y,z}$ is the Pauli matrix

106 for the sublattice pseudospin, σ is the Pauli matrix for the electron spin, and λ_{R1} and λ_{R2}

107 are the first and second Rashba coupling constants, related to the nearest and second

108 nearest neighbor hopping, respectively. E_z arises from the buckling of 2D-Xenes and

109 allows for tunability of their electronic properties.

110 When the SOC is not taken into account and no electric field is applied (Kane-Mele

111 model[10]), silicene, germanene, and stanene are predicted to be zero-gap semiconductors

112 with linear dispersions near the K and K' Dirac points. The computed Fermi velocities in

113 silicene and germanene are about 6×10^5 m/s,[6,11] roughly half of that for graphene. With

114 SOC, silicene and germanene are predicted to be 2D TIs with bulk energy gaps of about

115 1.5-2 meV and 23.9-30 meV, respectively.[9] Stanene, owing to its stronger SOC,

116 incorporates a 2D TI state with a sizeable energy gap of about 0.1 eV.[12,13]

117 **The 2D-Xene experimental Odyssey.** The tendency of FS 2D-Xenes to buckle is

118 experimentally confirmed by the *epitaxial growth* of various 2D-Xene "phases" on

119 different substrates with *commensurate* surface lattice. An extensive list of substrates

120 serving this purpose is enumerated in **Table 1**. Experimental identification of the buckled

121 2D-Xene structure has been mainly based on scanning tunneling microscopy (STM)

122 assisted by *ab initio* atomic models. Other techniques such as angle resolved

123 photoemission spectroscopy (ARPES) have been used to reveal the electronic structure.

124 Starting from the ideal FS 2D-Xene lattice as predicted from *ab initio* simulations

125 (**Figure 1a**), a historical overview of the main experimental breakthroughs is presented in

126 **Figure 1** including the STM confirmation of silicene (**b**), closely paralleled by the

127 chemical synthesis of germanane (**c**), and followed by the epitaxy of germanene (**d**), the

128 realization of a silicene transistor (**e**) and the epitaxy of stanene (**f**).

129 The forerunner of the 2D-Xene roadmap is the epitaxial silicene on metallic

130 substrates.[14,15-19] In particular, silicene-on-Ag(111) is interesting as a model of a buckled

131 elemental atomic sheet due to the wealth of commensurate phases on the host Ag(111)

132 surface.[16,17] These phases are commonly written as $n \times n / m \times m$, where $n \times n$ and $m \times m$ refer

133 to the coincidence with the FS 2D-Xene lattice and the substrate lattice, respectively; they

134 arise from different rotational alignment of the 2D-Xene sheet with respect to the

135 substrate. STM topographies of the majority silicene phases are reported in **Figure 1b**

136 along with the respective atomic structure model. This structural versatility can

137 dramatically influence the electronic structure of each 2D-Xene phase, and is a general

138 monolayer property of the 2D-Xene family (**Table 1**).[20] In spite of this, substrate orbitals

139 strongly hybridize with the Si atoms, resulting in an overall metallic character of the

140 silicene-on-metal substrate system, as follows from ARPES investigations.[11,21]

141 Following silicene, several STM studies have detailed the atomic arrangement of buckled

142 germanene phases on various metallic substrates[22,23,24-26] (**Figure 1d**), and the epitaxy of

143 stanene on Bi_2Te_3 substrates has been established soon afterwards[27] (**Figure 1f**). Most

144 recently, the epitaxy of a 2D boron sheet, termed borophene, with a metallic character

145 [28,29] and of a monolayer of (silicene-like) phosphorene with semiconducting character[30]

146 were respectively reported on Ag(111) and Au(111) substrates, thus extending the

147 realization of 2D-Xenes to elements beyond the group IVA atoms.

148 **Covalently functionalized 2D-Xenes.** The covalent functionalization into ligand-

149 terminated Xenes is an intriguing route towards tuning chemical, physical, and

150 topological properties of these materials, as well as increasing their environmental

151 stability. Here we define "Xanes" as 2D-Xene derivatives in which every atom on the

152 framework features a covalently bound ligand, thereby removing π-bonding. These

153 ligands directly couple to the half-filled p_z orbitals in 2D-Xenes, to produce a gapped,

154 semiconducting band structure, and the magnitude of this band gap depends on both the

155 framework element, and the identity of the covalent ligand.[12,31,32] Unlike Xenes, Xanes

156 can be derived by topotactic exfoliation.[31] The first reported example of topotactic

157 exfoliation of a single germanane sheet is shown in **Figure 1c**.

158 The most versatile route for preparing Xanes relies on the direct chemical conversion of

159 structurally related layered intermetallic "Zintl" phase precursors. For example, the

160 crystal structures of $CaSi_2$, $CaGe_2$, and $BaSn_2$, are comprised of anionic $[Si]_n^-$, $[Ge]_n^-$,

161 and $[Sn]_n^-$ layers in a puckered honeycomb arrangement analogous to 2D-Xenes, with

162 each layer separated by a divalent cation. These phases can be transformed directly into

163 multi-layered van der Waals crystals of Xanes by reaction with an electrophilic species

164 that will bond directly to the group IVA framework and a solvent that solubilizes the

165 divalent cation. For instance, the reaction of $CaSi_2$ in aqueous HCl produces partially –

166 H/–OH terminated silicane, a reaction first reported by Friedrich Wöhler in 1863.[33] In

7

167   aqueous acidic conditions, the Si- and Sn-based Xane frameworks become partially

168   terminated with –OH ligands, whereas the Ge-based frameworks are completely –H

169   terminated.[31,32] Organic-terminated Xanes can be created via a similar one-step reaction

170   of precursor Zintl phases with alkyl halides. For instance, $GeCH_3$ has been prepared via

171   the direct reaction of $CaGe_2$ with CH_3I.[34] Also, some Si and Ge surface functionalization

172   routes can also graft ligands onto 2D Xanes, such as the hydrosilylation of alkenes and

173   alkynes onto 2D silicane.[35] Other strategies for preparing Xanes include electrochemical

174   atomic layer epitaxy, which has been shown to be a viable route towards germanane,[36] as

175   well as the H-chemisorption to 2D-Xenes.[37]

176   The handful of emerging reports on the role of surface termination on electronic

177   properties of functionalized Xenes indicate that both the size and the electron-

178   donating/electron-withdrawing properties of the ligand have a strong influence on the

179   electronic structure. First, surface-terminating Xenes with ligands that have relatively

180   larger van der Waals radii can produce tensile strain in the 2D framework. This tensile

181   strain will lower the energy of the ligand-Si/Ge/Sn s-orbital antibonding levels at the

182   conduction band maximum (CBM), effectively reducing the band gap.[12] Increasing the

183   alkyl length by just a single methylene unit to ethyl ($-CH_2CH_3$) limits the fraction of

184   surface atoms that are functionalized with the organic substituent to functionalization to

185   80-85% whereas the remaining atoms are –H terminated.[38] While the framework of

186   functionalized Xenes might have the flexibility to accommodate the strain induced by

187   larger ligands, to date, $GeCH_3$ is the only synthesized Xene functionalization with nearly

188   uniform organic functionalization.[34] Second, more electronegative ligands will withdraw

189   electron density from the Xane framework, and similarly lower the energy of the ligand-

190   Si/Ge/Sn s-orbital antibonding levels at the CBM.[39] Consequently, replacing the –H

191   ligand in germanane with the more electron-donating –CH$_3$ ligand will increase the

192   observed band gap from 1.54 to 1.67.[12,34] These Xanes can be in the form of multi-

193   layered crystals whose length and width is determined by the size of precursor Zintl

194   phases and can be greater than millimeters, suitable for exfoliation and further device

195   processing.[31]

196

197   **The *triple S-factor* in the epitaxial 2D-Xenes.**   The experimental realization of the

198   epitaxial Xenes has been generally conditioned by three factors: Synthesis, Substrate, and

199   Stability. This *triple S-factor* brings several challenges for a full exploitation of Xene and

200   access to a broad range of characterization and/or applications. The synthesis of 2D-Xene

201   is restricted to expensive molecular beam epitaxy (MBE) methodologies requiring ultra-

202   high vacuum conditions. Moreover, substrates enabling the 2D-Xene epitaxy must be

203   commensurate with the FS 2D-Xene structure.[14,15,16,17,19] Further efforts are in progress to

204   design or synthesize 2D-Xenes on weakly interacting substrates, and the option of

205   chalcogenide templates with a selected termination is promising to host a 2D-Xene

206   lattice.[40] This is the case of the growth of hexagonal silicene sheets on semiconducting

207   MoS$_2$.[41,42] The option of Xenes on non-metallic substrates would bring obvious benefits

208   for device integration, scientific studies, and applications, and *substrate engineering* is a

209   demanding task of technological interest.

210   On the other hand, the chemical stability of 2D-Xenes under ambient condition is

211   severely restricted by the inherent thermodynamic preference of Si, Ge, and Sn for sp^3

212   bonding. Air-stability issues can be overcome by making use of a non-destructive

213   encapsulation material such as Al$_2$O$_3$.[43]

9

214   The case of silicene can be taken as a paradigmatic pathway to overcome the "triple S

215   factor" and develop a prototypical 2D-Xene nanoelectronic platform (**Figure 1e**). A

216   silicene sheet can be sandwiched in between two thin layers, the native Ag on one side

217   and Al_2O_3 encapsulation on the other side. The former layer comes from the delamination

218   of the "substrate", a cleavable Ag(111)-on-mica where the silicene is epitaxially grown.

219   The latter one is the stabilizing encapsulation sequentially deposited after silicene growth.

220   The "silicene sandwich" is easily handled as a sheet to be placed upside down on a

221   device-friendly platform, such as SiO_2/Si, and the top Ag patterned so as to obtain a Ag-

222   free silicene channel in between two (or more) "native" Ag electrodes, hence completing

223   a transistor device structure. Room temperature operation of this silicene transistor

224   revealed an ambipolar character in agreement with the predicted graphene-like nature of

225   the particular silicene phase in the experiment.[44] Despite the fast degradation of exposed

226   Ag-free silicene in ambient condition that is yet to be fully addressed, this transfer

227   methodology can be generally extended to the class of Xenes-on-substrate, and hence,

228   offer a universal route for verifying the quantum transport properties of Xenes.[45]

229

230
231   **Topology as a paradigm shift for quantum electronics**

232   2D TIs support the intriguing quantum spin Hall (QSH) effect, characterized by

233   insulating bulk states with gapless helical edge states that are protected against back-

234   scattering by time reversal symmetry (**Figure 2a).** The QSH effect was first theoretically

235   predicted and subsequently experimentally observed in a HgTe quantum well.[46,47]

236   Graphene was proposed to have the same effect,[10] but its bulk gap is extremely small

237   (~μeV). The buckled 2D-Xenes have much larger QSH gaps (up to 0.3 eV),[12] suitable for

238   room-temperature usage, and their QSH states are tunable by chemical functionalization

239   from π orbital states to σ orbital states (**Figure 2b**).[12] This tunable topology affords an

240   electronic switch where the logic state is dictated by the topological phase transition

241   rather than by the charge depletion/inversion as in conventional semiconductors.

242   **The benefit of gaining weight.**   2D-Xenes share the same Dirac physics as

243   graphene, which is a 2D Dirac semimetal when excluding the SOC and becomes a QSH

244   insulator when including the SOC (**Figure 2b**, left).[10,9,12] Notably, the SOC-induced bulk

245   gap in silicene (1.5-2 meV)[45,9] is much larger than in graphene (~μeV). The underlying

246   mechanism is two-fold. The first-order contribution of SOC, which is turned off in a

247   planar structure like graphene, is turned on in silicene because the hybridization between

248   π and σ orbitals of nearest neighbors becomes allowed in a buckled structure.[9] Moreover,

249   the SOC strength is commensurate with increasing weight. Thus enhanced SOC is

250   obtained in germanene (23.9-30.0 meV) and stanene (~0.1eV).[9,12,48] In perspective, the

251   QSH gap increases five orders of magnitude from graphene to stanene, compliments of

252   the heavier mass and structural buckling.

253   The chemical functionalization of 2D-Xenes provides an additional degree of freedom to

254   tune topological states. The saturation of the p_z orbitals opens a large energy gap at the K

255   and K' points, which destroys the Dirac physics of the π orbitals. The low-energy physics

256   is then determined by the σ orbitals around the Γ point (**Figure 2b**, right), where inverted

257   band structures may occur in 2D-Xenes composed of heavier elements.[12,48]. Take the

258   fluorinated stanene (F-stanene) as an example. The relevant states around the Fermi level

259   are comprised of s, p_x, and p_y orbitals on the Sn atoms, split into bonding and anti-

260   bonding states by the Sn-Sn interaction. Unlike undecorated graphene, the anti-bonding s

261 state is located below the bonding p_{xy} state at the Γ point, showing an inverted band order.

262 The s-p band inversion results in a nontrivial QSH phase,[12] similar to the scenario of the

263 HgTe quantum well.[46] Therefore, the QSH states are varied from π orbitals described by

264 the Kane-Mele model[10] to σ orbitals described by the Bernevig-Hughes-Zhang model[46].

265 The new QSH states derived from σ orbitals possess many advantages[12,48]. First, the QSH

266 gaps are extraordinarily large (up to 0.3 eV), since the effective SOC of σ orbitals is

267 significantly larger than that of π orbitals. Second, the electronic properties can be

268 controllably tuned. Functionalization with different chemical groups can result in

269 topologically distinct phases (**Figure 2c**). Moreover, applying external strain can

270 effectively control the emergence or disappearance of the helical edge states.

271 Third, in comparison with the π orbitals that are easily affected by substrate and

272 adsorbates,[27,49] the σ orbitals that are composed of in-plane p_{xy} states are relatively more

273 environmentally stable. Even when forming chemical bonds with the substrate, large-gap

274 σ-orbital-derived QSH states are predicted to be preserved in functionalized stanane[40].

275 Given the dependence on external factors owing to their buckled nature, 2D-Xenes may

276 offer a high degree of functional versatility. For example, in silicene, physical influences

277 such as electric and magnetic fields, mechanical strain, and temperature has been

278 predicted to produce a variety of electronic states including semimetallic,

279 semiconducting, superconducting, and trivial insulating phases, in addition to about

280 *sixteen* 2D TI phases.[50] These TI phases arise from the combination of the four defining

281 topological numbers in a honeycomb lattice, which are the Chern, spin-Chern, valley-

282 Chern and spin-valley-Chern numbers with an end result of five types of topological

283 quantum states, namely the spin-polarized quantum anomalous Hall (SQAH), quantum

284   valley Hall (QVH) and quantum spin-valley Hall (QSVH) states in addition to the already

285   mentioned QSH and QAH states (**Figure 2d**).[51]

286

A Buckled Outlook

288   The interplay of non-trivial 2D topological features and the buckled structure of 2D-

289   Xenes may also open new routes for disruptive applications like low-energy electronics,

290   piezo-magnetism, enhanced thermoelectricity and spintronics.[12] Furthermore, by

291   explicitly breaking the symmetries (for example, gauge symmetry, inversion symmetry

292   and time reversal symmetry), new emerging physics (such as topological

293   superconductivity[52], valley-polarized metal,[45] and QAH effect[45]) can be explored in 2D-

294   Xenes.

295   **From digital to topological bits.** One of the more visionary outlook about 2D-Xenes is

296   the realization of a paradigm shift from conventional to quantum electronics based on

297   field-controllable topological properties. Transport through the QSH edge states can be

298   ballistic, thus promising an exceptional advance in terms of energy saving in electronic

299   devices. In contrast to carbon nanotubes or graphene where ballistic transport can be

300   affected by defects, transport in 2D-Xenes in the QSH regime is robust against scattering.

301   Equally appealing is the opportunity to access a logic functionality based on the concept

302   of topological phase transitions. A topological phase transition occurs when the QSH

303   state characterized by ballistic edge states that can serve as information carriers ("ON"

304   state) is switched to a trivial insulator state with vanishing conductance ("OFF") state) vis-

305   à-vis an external electric field E_z (**Figure 3a**, top diagram).[50] The two ON/OFF states

306   define a logic switch mechanism, namely a *topological bit*, which can be distinguished by

307   the sequential topological gap closing and trivial gap opening as a function of the external

308   field.

309   A prototypical device structure based on the gate bias modulation can be understood as a

310   *quantum* topological insulator field-effect transistor (TI-FET)[53] as shown in the

311   corresponding sketch of **Figure 3b**. The gate bias can be employed to switch the TI-FET

312   from the ON to the OFF state, whereas the drain-source voltage facilitates one kind of

313   helical carrier through each edge. Being topologically protected and helical in character,

314   the edge states in these quantum TI-FETs serve as truly one-dimensional, spin-polarized

315   dissipationless highways for charge transport that is robust against scattering from non-

316   magnetic material defects,[12] and potentially suitable for scaled low-power nanoelectronic

317   devices.

318   The main challenge with devices based on electric field-driven topological phase

319   transitions is the relatively large critical field required ($E_c = 2\lambda_{SO}/\delta$, where $2\lambda_{SO}$ is the

320   SOC induced bandgap), which is of the order of 0.05 V/nm and 1 V/nm for silicene and

321   stanene, respectively. In light of this, a *classical* TI-FET not predicated on topological

322   phase transitions was recently proposed.[54] In this scheme, the 2D TI is configured as a

323   nanoribbon FET with the width small enough to ensure inter-edge elastic scattering

324   (namely, within an order of magnitude of the field-dependent edge-bulk tunneling length

325   scale, ~1 nm for F-stanene and ten times larger in silicene). Unlike the conventional FET

326   where the field-effect enhances the carrier density and conductivity increases, the field-

327   effect in classical TI-FET facilitates phonon-mediated scattering of edge electrons into

328   bulk states by reducing the energy barrier and hence, conductivity decreases.

329   Alternatively, a topological phase transition can be driven by applying external strain in

330   functionalized 2D-Xenes because the *s-p* band inversion at the Γ point sensitively

331   depends on the interatomic bond length.[12] In this case, the details of the topological

332   phase transition depend on the identity of the functional group. For instance, F-stanene is

333   a QSH insulator that undergoes a transition to a trivial insulator state as a function of the

334   compressive strain (over a critical value of about -7%) thus nominally mimicking the

335   same ON/OFF sequence of the electric field induced topological phase transition (**Figure**

336   **3a**, middle diagram). Conversely, H-stanene is a trivial insulator at zero applied strain

337   and enters a QSH state when applying a tensile strain over a critical value of about 2%

338   thus manifesting an inverted OFF-ON logic mechanism (**Figure 3a**, bottom diagram).

339   Both mechanisms may open unprecedented routes for 2D-Xene-based piezotronic

340   devices (see the corresponding sketches in **Figure 3b**).

341   **New emerging applications.**   The existence of large-gap, tunable and robust QSH

342   states make 2D-Xenes promising for various applications (**Figure 3c**). The large bulk gap

343   (~0.3 eV)[12] enables QSH phenomena to occur at room temperature. The helical edge

344   states are useful for low-energy electronics, since they can conduct electricity without

345   generating heat[10,46,47]. They can also induce anomalous Seebeck effect due to the strong

346   energy dependence in lifetime introduced by the edge-bulk interaction.[55] The

347   thermoelectric performance of QSH insulators can be effectively improved by optimizing

348   the morphology to maximize the edge-state contribution.[55] In addition, the helical edge

349   states may also find important applications in spintronics (for example in spin transfer

350   torque, spin Seebeck, spin-charge conversion, and spin-filter[56] based devices). However,

351   very little experimental progress has been achieved until now, mainly because high-

352   quality samples are still lacking.[27] More experimental effort is thus essential to advance

353   2D-Xenes and related materials, and ultimately realize the above-mentioned concepts.

354   **New emerging physics.**   2D-Xenes may also offer an ideal platform to study new

355   emerging physics. Exotic quantum effects would emerge upon explicitly breaking

356   different symmetries in 2D-Xenes (**Figure 3c**). For instance, breaking the *inversion*

357   *symmetry* by substrate or electric field introduces the Rashba effect, which enables the

358   spin manipulation as well as access to topological superconductivity.[52] Breaking *time*

359   *reversal symmetry* by magnetism[40,57] may induce the QAH effect, which supports chiral

360   edge states that are topologically protected against scattering. A near room-temperature

361   QAH effect has been predicted in half-functionalized stanene and germanene, where a

362   ferromagnetic order is formed between local magnetic moments of unsaturated p_z states.[57]

363   Breaking *gauge symmetry* by superconductivity may afford exotic topological

364   superconducting states bearing Majorana fermions that are useful for fault-tolerant

365   topological quantum computation.[52]

366   Even richer physics is expected by breaking different symmetries simultaneously. For

367   instance, the use of an electric field together with an exchange field ΔM (from magnetic

368   impurities or by proximity coupling with a ferromagnet) enables tuning the spin and

369   valley degrees of freedom independently, which generates a variety of phases in 2D-

370   Xenes.[45] Furthermore, the symmetries can be broken either globally or locally. The local

371   symmetry breaking, though preserving the topology, can considerably affect properties of

372   the QSH states. As an example, the helical edge states are eliminated when introducing

373   an in-plane ferromagnetic order to the edge atoms. The existence of the helical edge

16

374 states thus can be controlled by local edge manipulation, which leads to potential

375 applications in giant magnetoresistance and an ideal spin filter.[56]

376 **Perspective**

377 By virtue of their buckled character, 2D-Xenes can potentially serve as a nanotechnology

378 platform with multiple physical features for fundamental research and applications. The

379 diverse material properties in intrinsic and functionalized Xenes permit a wide degree of

380 freedom in designing efficient, on-demand or reconfigurable devices for electronic,

381 spintronic, photonic, thermal, energy, mechanical, chemical and sensor nanosystems.

382 However, many processing and technological issues are yet to be solved, the most

383 significant of which is the instability in ambient conditions which complicates the

384 establishment of scalable routes for device integration schemes. Appropriate solutions

385 including the design of device-friendly and neutral substrates, and the development of

386 large-scale production methodologies (for example chemical vapor deposition) are

387 demanding issues for a viable Xene nanotechnology. Nonetheless, the recently reported

388 technological and synthetic advances are encouraging towards the exploration of the

389 unique topological phenomena in 2D-Xenes and their exploitation in innovative device

390 concepts.

391

392

17

412

413

414

415

Table 1. Properties of 2D-Xenes. Computed structural parameters of FS 2D-Xenes, using first-principles calculations based on density functional theory (left-hand side). Experimentally observed or calculated structural parameters of epitaxial Xenes-on-substrates (right-hand side). a_X, ℓ_{X-X}, and δ are the cell lattice constant, interatomic distance, and buckling parameter in 2D-Xenes. E_g is the SOC-induced band gap. The latter branch includes a list of substrates that have been found to accommodate specific 2D-Xene lattices and their atomic reconstructions (commonly denoted as "phases") on the substrates' surface. Graphene parameters are reported for comparison. Note that graphene has nominally zero atomic buckling in the absence of rippling.

426

Figure 1: The 2D-Xene Odyssey. An evolutionary overview of the key-experimental evidences of 2D-Xenes. (a) Atomic configuration of a FS 2D-Xene lattice (top: side view, bottom: perspective view) where red and orange spheres represent X atoms at top and bottom positions, respectively. (b) Silicene epitaxy on Ag(111) substrates as a representative case of Xene-on-substrate systems. STM investigations of Silicene-on-Ag(111) has revealed a multiphase character. Left: The STM topographies of three majority phases, $3\times3/4\times4$, $\sqrt{7}\times\sqrt{7}/\sqrt{13}\times\sqrt{13}$, and $\sqrt{7}\times\sqrt{7}/2\sqrt{3}\times2\sqrt{3}$, are reported along with the atomic structure models. (c) Topotactic exfoliation of germanane as a first example of the chemical exfoliation of a Xane sheet: process schematics (left) and optical microscopy image of a single hydrogen-terminated germanane sheet (right). (d) Representative case of germanene on metal substrates: STM topography of an extended

19

438   germanene sheet on Al(111) assisted by an *ab initio* atomic model. Adapted from Ref.[24].

439   (e) Silicene integration into a transistor device after Ref. [44]: Silicene is epitaxially grown

440   on a cleavable Ag-on-mica substrate via MBE, encapsulated with a protective Al_2O_3 and

441   then delaminated as a Al_2O_3/silicene/Ag sandwich sheet; this "silicene sandwich" is

442   transferred to a device-friendly substrate (such as SiO_2/Si) and then integrated as the

443   active channel in a field-effect transistor structure by patterning the native Ag to make

444   contact electrodes. (f) Epitaxy of stanene on Bi_2Te_3 substrates based on STM

445   identification of a buckled and unreconstructed lattice structure. Adapted from Ref. [27].

446

447   **Figure 2:   Topology as a paradigm shift in nanoelectronics. a)** Top view of a 2D-

448   Xene in a QSH state bearing helical currents at the edges. **b)** Side view of the atomic

449   structure and molecular orbital, and the low-energy bands with (red solid lines) and

450   without (black dashed lines) spin-orbit coupling for pure (left) and functionalized (right)

451   Xene. The red and blue spheres denote atoms of different sublattices, and the white

452   spheres denote the chemical functional group. **c)** Energy gap as a function of the lattice

453   constant induced by the covalent functionalization of stanene. Adapted from Ref.[12].**d)**

454   The topological phase diagram as a function of perpendicular electric field E_z and the

455   exchange field ΔM, and the arrows reflect the spin polarization. Adapted from Ref.[51]

456

457   **Figure 3:   The topological bit and emerging physics based on broken symmetry.**

458   **a)** Schematic band structure diagrams of nanoribbons along the 1D Brillouin zone (Γ-X',

459   X' is a *k*-point point along the nanoribbon length direction) for (top) bare stanene,

460   (middle) and fluorine-terminated (SnF), and (bottom) hydrogen-terminated (SnH) stanane

461 and topological phase transitions induced by an out-of-plane electric field or a

462 compressive/tensile strain. The helical edge states that emerge within the bulk gap are

463 denoted by red lines. **b)** Corresponding sketches of a *quantum* TI-FET driven by an

464 electric field, by a compressive strain, and by a tensile strain. A 2D-Xene ribbon is

465 embedded in between a top gate and a substrate (for applying V_G), and source (S) and

466 drain (D) electrodes. **c)** Applications of the QSH states and new emerging physics

467 induced by breaking symmetries, including the A-B sublattice symmetry, inversion

468 symmetry P, time reversal symmetry T and gauge symmetry U.

469

470

471

472

473

474

475

476

477

478

479

480

481

482

483

	FS 2D-Xenes (predicted)					Epitaxial 2D-Xenes (Xene-on-substrate)					
	a_X (Å)	$\ell_{X\text{-}X}$ (Å)	δ (Å)	E_g	Ref.	substrate	phase	a_X (Å)	$\ell_{X\text{-}X}$ (Å)	δ (Å)	Ref.
Graphene	2.47	1.42	0	~1 μeV		metals		2.47	1.42	0	58
Silicene	3.87	2.28	0.44	1.5-2 meV	59	Ag(111)	3×3/4×4	11.78	2.34-2.39	0.71-0.79	14,15,16,17
							√7×√7/√13×√13	10.60	2.31-2.36	0.77-0.79	
							√7×√7/2√3×2√3	10.20	2.28-2.37	1.10	
						Ir(111)	√3×√3/√7×√7	7.20	2.10	0.83	18
						ZrB$_2$	√3×√3/2×2	6.72-6.78	2.24-2.26	0.90-1.35	19
						MoS$_2$	1×1/1×1	3.17	2.61	1.90	41
Germanene	4.06	2.44	0.69	23.9-30.0 meV	59	Au(111)	√3×√3/√7×√7	7.65	2.55	0.47	22
						Pt(111)	3×3/√19×√19	12.0	~2.31	0.60	23
						Al(111)	2×2/3×3	8.50	2.58	1.23	24
						MoS$_2$	1×1/1×1	3.82	2.20	0.86	42
						hex-AlN	3×3/4×4	12.31	2.37	0.70	26
Stanene	4. 68	2.83	0.85	0.1 eV	12	Bi$_2$Te$_3$	1×1/1×1	4.38	2.80	1.20	27

485

486

487

Table 1

489

490

a free-standing 2D-Xenes

c exfoliation of germanane

d germanene: atomic structure

Models of silicene and germanene

Chemical synthesis of germanane

Epitaxy of germanene

Epitaxy of borophene

Silicene transistor

Phosphorene transistor

Epitaxy of phosphorene

1994 2009 2012 2013 2014 2015 2016

Epitaxy of silicene

Epitaxy of stanene

b silicene phases and band structure

3×3/4×4   √7×√7/√13×√13   √7×√7/2√3×2√3

Si (top)
Si (bottom)
Ag

2.0nm

e silicene transistor

epitaxy

silicene
Ag
mica

encapsulation

Al$_2$O$_3$

delamination

Ag
silicene
Al$_2$O$_3$

device integration

f stanene: atomic structure

A
B

Sn-A   Sn-B   Te

491

492
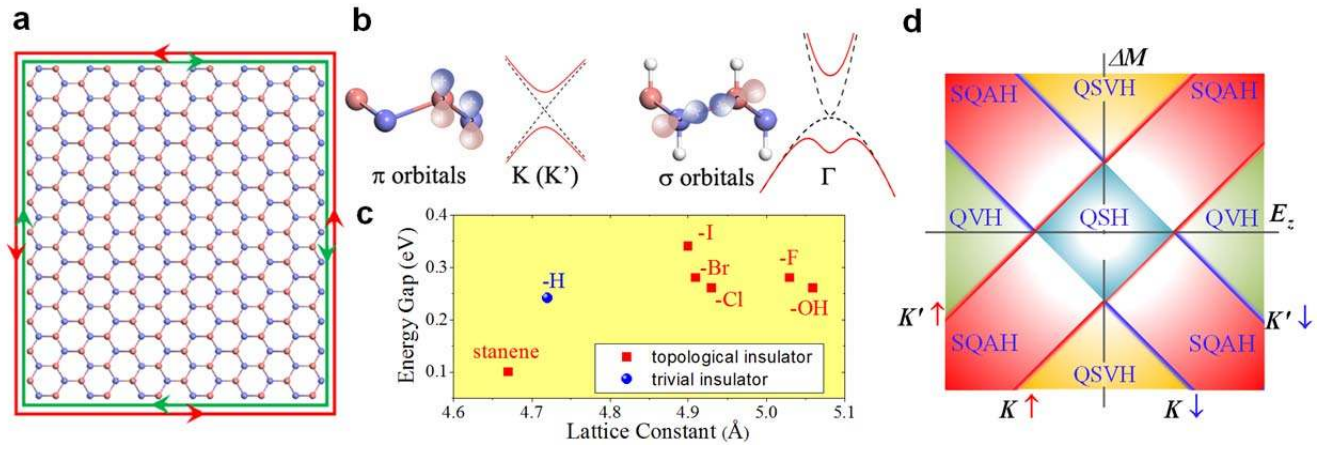
493

494

Figure 1

495

496

497

Figure 2

504
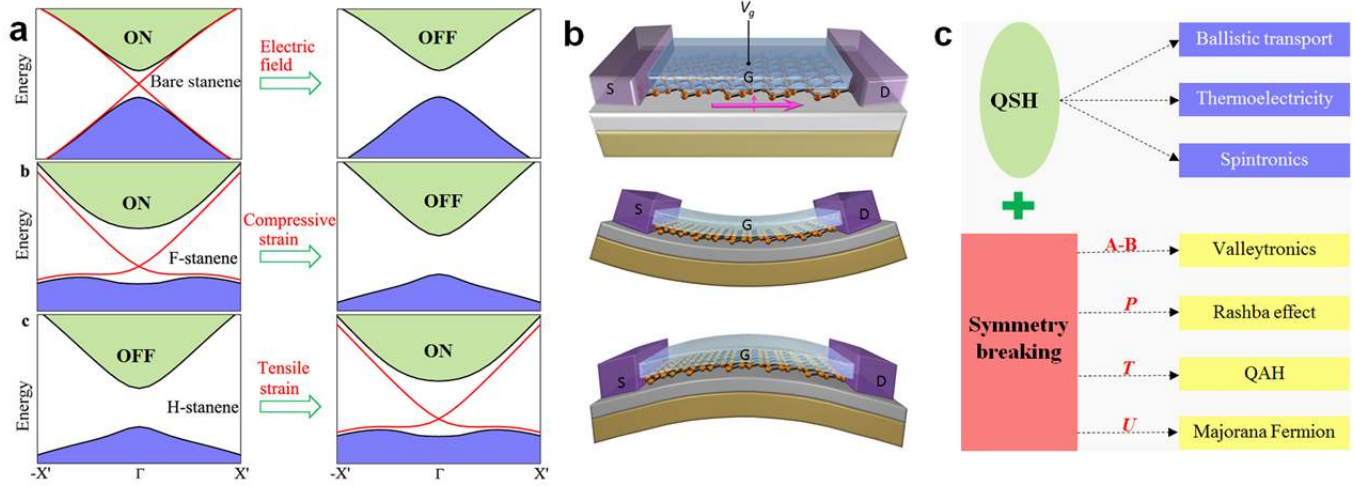
505

506

507

508

509

510

Figure 3

511

512

513

514

515

516

517

518

519

520

521

522

523

List of References
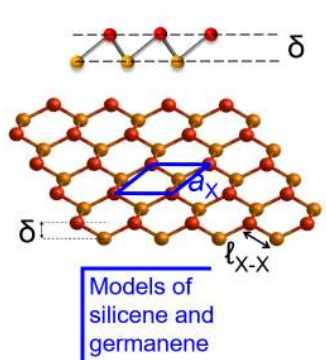
1   G Fiori, F Bonaccorso, G Iannaccone, T Palacios, D Neumaier, A Seabaugh, SK Banerjee, and L Colombo, Nature Nanotechnology **9** (10), 768 (2014).

2   AC Ferrari, F Bonaccorso, V Fal'ko, KS Novoselov, S Roche, P Boggild, S Borini, FHL Koppens, V Palermo, N Pugno, JA Garrido, R Sordan, A Bianco, L Ballerini, M Prato, E Lidorikis, J Kivioja, C Marinelli, T Ryhanen, A Morpurgo, JN Coleman, V Nicolosi, L Colombo, A Fert, M Garcia-Hernandez, A Bachtold, GF Schneider, F Guinea, C Dekker, M Barbone, ZP Sun, C Galiotis, AN Grigorenko, G Konstantatos, A Kis, M Katsnelson, L Vandersypen, A Loiseau, V Morandi, D Neumaier, E Treossi, V Pellegrini, M Polini, A Tredicucci, GM Williams, BH Hong, JH Ahn, JM Kim, H Zirath, BJ van Wees, H van der Zant, L Occhipinti, A Di Matteo, IA Kinloch, T Seyller, E Quesnel, XL Feng, K Teo, N Rupesinghe, P Hakonen, SRT Neil, Q Tannock, T Lofwandera, and J Kinaret, Nanoscale **7** (11), 4598 (2015).

3   Akinwande D, Tao L, Yu Q, Lou X, Peng P, and Kuzum D, IEEE Nanotechnology Magazine **9**, 6 (2015).

4   S Balendhran, S Walia, H Nili, S Sriram, and M Bhaskaran, Small **11**, 640 (2015).

5   K Takaeda and K Shiraishi, Physical Review B **50**, 14916 (1994).

6   S Cahangirov, M Topsakal, E Akturk, H Sahin, and S Ciraci, Physical Review Letters **102**, 236804 (2009).

7   GG Guzman-Verri and LCLY Voon, Physical Review B **76**, 075131 (2007).

8   Carlo Grazianetti, Eugenio Cinquanta, and Alessandro Molle, 2d Materials **3** (1) (2016).

9   CC Liu, WX Feng, and YG Yao, Physical Review Letters **107** (7), 076802 (2011).

10   CL Kane and EJ Mele, Physical Review Letters **95**, 146802 (2005).

11   M Houssa, A Dimoulas, and A Molle, Journal of Physics-Condensed Matter **27**, 253002 (2015).

12   Y Xu, BH Yan, HJ Zhang, J Wang, G Xu, PZ Tang, WH Duan, and SC Zhang, Physical Review Letters **111**, 136804 (2013).

13   B van den Broek, M Houssa, E Scalise, G Pourtois, VV Afanas'ev, and A Stesmans, 2D Materials **1**, 021004 (2014).

14   P Vogt, P De Padova, C Quaresima, J Avila, E Frantzeskakis, MC Asensio, A Resta, B Ealet, and G Le Lay, Physical Review Letters **108**, 155501 (2012).

15   CL Lin, R Arafune, K Kawahara, N Tsukahara, E Minamitani, Y Kim, N Takagi, and M Kawai, Applied Physics Express **5**, 045802 (2012).

16   BJ Feng, ZJ Ding, S Meng, YG Yao, XY He, P Cheng, L Chen, and KH Wu, Nano Letters **12**, 3507 (2012).

17   Daniele Chiappe, Carlo Grazianetti, Grazia Tallarida, Marco Fanciulli, and Alessandro Molle, Advanced Materials **24**, 5088 (2012).

18   L Meng, YL Wang, LZ Zhang, SX Du, RT Wu, LF Li, Y Zhang, G Li, HT Zhou, WA Hofer, and HJ Gao, Nano Letters **13**, 685 (2013).

19   A Fleurence, R Friedlein, T Ozaki, H Kawai, Y Wang, and Y Yamada-Takamura, Physical Review Letters **108**, 245501 (2012).

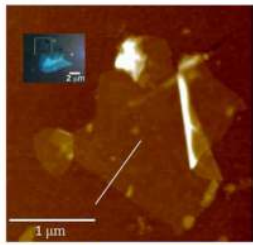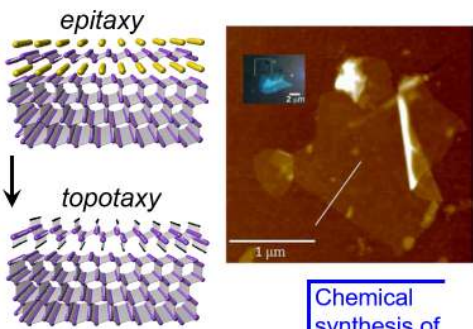| 569	20	E Scalise, E Cinquanta, M Houssa, B van den Broek, D Chiappe, C Grazianetti, G
570		Pourtois, B Ealet, A Molle, M Fanciulli, VV Afanas'ev, and A Stesmans, Applied
571		Surface Science **291**, 113 (2014).
572	21	Tsoutsou D, Xenogiannopoulou E, Golias E, Tsipas P, and Dimoulas A, Applied
573		Physics Letters **103**, 231604 (2013).
574	22	ME Davila, L Xian, S Cahangirov, A Rubio, and G Le Lay, New Journal of
575		Physics **16**, 095002 (2014).
576	23	LF Li, SZ Lu, JB Pan, ZH Qin, YQ Wang, YL Wang, GY Cao, SX Du, and HJ
577		Gao, Advanced Materials **26**, 4820 (2014).
578	24	M Derivaz, D Dentel, R Stephan, MC Hanf, A Mehdaoui, P Sonnet, and C Pirri,
579		Nano Letters **15**, 2510 (2015).
580	25	P Bampoulis, L Zhang, A Safaei, R van Gastel, B Poelsema, and HJW Zandvliet,
581		Journal of Physics-Condensed Matter **26**, 442001 (2014).
582	26	F D'Acapito, S Torrengo, E Xenogiannopoulou, P Tsipas, J Marquez Velasco, D
583		Tsoutsou, and A Dimoulas, Journal of Physics - Condensed Matter (2016).
584	27	FF Zhu, WJ Chen, Y Xu, CL Gao, DD Guan, CH Liu, D Qian, SC Zhang, and JF
585		Jia, Nature Materials **14**, 1020 (2015).
586	28	AJ Mannix, XF Zhou, B Kiraly, JD Wood, D Alducin, BD Myers, XL Liu, BL
587		Fisher, U Santiago, JR Guest, MJ Yacaman, A Ponce, AR Oganov, MC Hersam,
588		and NP Guisinger, Science **350** (6267), 1513 (2015).
589	29	Baojie Feng, Jin Zhang, Qing Zhong, Wenbin Li, Shuai Li, Hui Li, Peng Cheng,
590		Sheng Meng, Lan Chen, and Kehui Wu, Nat Chem **advance online publication**
591		(2016).
592	30	Jia Lin Zhang, Songtao Zhao, Cheng Han, Zhunzhun Wang, Shu Zhong, Shuo
593		Sun, Rui Guo, Xiong Zhou, Cheng Ding Gu, Kai Di Yuan, Zhenyu Li, and Wei
594		Chen, Nano Letters (2016).
595	31	Elisabeth Bianco, Sheneve Butler, Shishi Jiang, Oscar D. Restrepo, Wolfgang
596		Windl, and Joshua E. Goldberger, Acs Nano **7**, 4414 (2013).
597	32	Shishi Jiang, Maxx Q. Arguilla, Nicholas D. Cultrara, and Joshua E. Goldberger,
598		Accounts of Chemical Research **48** (1), 144 (2015).
599	33	F. Wohler, Justus Liebigs Annalen der Chemie **127** (3), 257 (1863).
600	34	Shishi Jiang, Sheneve Butler, Elisabeth Bianco, Oscar D. Restrepo, Wolfgang
601		Windl, and Joshua E. Goldberger, Nature Communications **5**, 3389 (2014).
602	35	Hideyuki Nakano, Mitsuru Nakano, Koji Nakanishi, Daiki Tanaka, Yusuke
603		Sugiyama, Takashi Ikuno, Hirotaka Okamoto, and Toshiaki Ohta, Journal of the
604		American Chemical Society **134** (12), 5452 (2012).
605	36	XH Liang, QH Zhang, MD Lay, and JL Stickney, Journal of the American
606		Chemical Society **133** (21), 8199 (2011).
607	37	Qiu J, Fu X, Xu Y, Zhou Q, Meng S, Li H, Chen L, and Wu K, (ACS Nano,
608		2015), Vol. 9, pp. 11192.
609	38	Hongbin Yu, Lauren J. Webb, Santiago D. Solares, Peigen Cao, William A.
610		Goddard, III, James R. Heath, and Nathan S. Lewis, Journal of Physical
611		Chemistry B **110**, 23898 (2006).
612	39	CG van de Walle and JE Northrup, Physical Review Letters **70**, 1116 (1993).
613	40	Y Xu, PZ Tang, and SC Zhang, Physical Review B **92**, 081112 (2015).

41   D Chiappe, E Scalise, E Cinquanta, C Grazianetti, B van den Broek, M Fanciulli, M Houssa, and A Molle, Advanced Materials **26** (13), 2096 (2014).

42   L. Zhang, P. Bampoulis, A. N Rudenko, Q. Yao, A. van Houselt, B. Poelsema, M. I Katsnelson, and H. J W Zandvliet, Physical Review Letters **116** (25), 256804 (2016).

43   A Molle, C Grazianetti, D Chiappe, E Cinquanta, E Cianci, G Tallarida, and M Fanciulli, Advanced Functional Materials **23** (35), 4340 (2013).

44   L Tao, E Cinquanta, D Chiappe, C Grazianetti, M Fanciulli, M Dubey, A Molle, and D Akinwande, Nature Nanotechnology **10** (3), 227 (2015).

45   M Ezawa, Physical Review Letters **109**, 055502 (2012).

46   BA Bernevig, TL Hughes, and SC Zhang, Science **314**, 1757 (2006).

47   M Konig, S Wiedmann, C Brune, A Roth, H Buhmann, LW Molenkamp, XL Qi, and SC Zhang, Science **318**, 766 (2007).

48   C Si, JW Liu, Y Xu, J Wu, BL Gu, and WH Duan, Physical Review B **89**, 115429 (2014).

49   PZ Tang, PC Chen, WD Cao, HQ Huang, S Cahangirov, LD Xian, Y Xu, SC Zhang, WH Duan, and A Rubio, Physical Review B **90** (12) (2014).

50   Motohiko Ezawa, Journal of the Physical Society of Japan **84** (12), 121003 (2015).

51   M Ezawa, Physical Review B **87**, 155415 (2013).

52   J Wang, Y Xu, and SC Zhang, Physical Review B **90**, 054503 (2014).

53   M Ezawa, Applied Physics Letters **102**, 172103 (2013).

54   WG Vandenberghe and MV Fischetti, Journal of Applied Physics **116**, 173707 (2014).

55   Y Xu, ZX Gan, and SC Zhang, Physical Review Letters **112**, 226801 (2014).

56   S Rachel and M Ezawa, Physical Review B **89**, 195303 (2014).

57   SC Wu, GC Shan, and BH Yan, Physical Review Letters **113**, 256401 (2014).

58   J Wintterlin and ML Bocquet, Surface Science **603** (10-12), 1841 (2009).

59   E Scalise, M Houssa, G Pourtois, B van den Broek, V Afanas'ev, and A Stesmans, Nano Research **6** (1), 19 (2013).

	Free-standing Xenes (predicted)					**Epitaxial Xenes (Xene-on-substrate)**					
	a_X (Å)	$\ell_{X\text{-}X}$ (Å)	δ (Å)	E_g	Ref.	substrate	phase	a_X (Å)	$\ell_{X\text{-}X}$ (Å)	δ (Å)	Ref.
Graphene	2.47	1.42	0	~1 µeV		metals		2.47	1.42	0	58
Silicene	3.87	2.28	0.44	1.5-2 meV	59	Ag(111)	3×3/4×4	11.78	2.34-2.39	0.71-0.79	14,15,16,17
							√7×√7/√13×√13	10.60	2.31-2.36	0.77-0.79	
							√7×√7/2√3×2√3	10.20	2.28-2.37	1.10	
						Ir(111)	√3×√3/√7×√7	7.20	2.10	0.83	18
						ZrB$_2$	√3×√3/2×2	6.72-6.78	2.24-2.26	0.90-1.35	19
						MoS$_2$	1×1/1×1	3.17	2.61	1.90	41
Germanene	4.06	2.44	0.69	23.9-30.0 meV	59	Au(111)	√3×√3/√7×√7	7.65	2.55	0.47	22
						Pt(111)	3×3/√19×√19	12.0	~2.31	0.60	23
						Al(111)	2×2/3×3	8.50	2.58	1.23	24
						MoS$_2$	1×1/1×1	3.82	2.20	0.86	42
						hex-AlN	3×3/4×4	12.31	2.37	0.70	26
Stanene	4.68	2.83	0.85	0.1 eV	12	Bi$_2$Te$_3$	1×1/1×1	4.38	2.80	1.20	27

a free-standing 2D-Xenes

δ

a_X

δ

ℓ_{X-X}

Models of silicene and germanene

c exfoliation of germanane

epitaxy

topotaxy

2 µm

1 µm

Chemical synthesis of germanane

d germanene: atomic structure

top

top

Ge
Al

Epitaxy of germanene

Epitaxy of borophene

Silicene transistor

Phosphorene transistor

Epitaxy of phosphorene

1994 2009 2012 2013 2014 2015 2016

Epitaxy of silicene

Epitaxy of stanene

b silicene phases and band structure

$3\times3/4\times4$ $\sqrt{7}\times\sqrt{7}/\sqrt{13}\times\sqrt{13}$ $\sqrt{7}\times\sqrt{7}/2\sqrt{3}\times2\sqrt{3}$

2.0 nm

Si (top)
Si (bottom)
Ag

e silicene transistor

epitaxy

silicene
Ag
mica

encapsulation

Al_2O_3

delamination

Ag
silicene
Al_2O_3

device integration

f stanene: atomic structure

A
B

Sn-A Sn-B Te

a

b

π orbitals   K (K')   σ orbitals   Γ

c

Energy Gap (eV)

-I
-H
-Br
-F
-Cl
-OH
stanene

■ topological insulator
● trivial insulator

Lattice Constant (Å)

d

ΔM

SQAH   QSVH   SQAH

QVH   QSH   QVH E_z

K'↑   K'↓

SQAH   QSVH   SQAH

K↑   K↓