Group-IV 2D materials beyond graphene on nonmetal substrates: Challenges, recent progress, and future perspectives

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ABSTRACT

The family of two-dimensional materials has been expanding rapidly over the last few years. Within it, a special place is occupied by silicene, germanene, and stanene due to their inherent compatibility with the existing semiconductor technology (notably for the case of silicene and germanene). Although obtaining them is not trivial due to the lack of layered bulk counterparts from which they could be mechanically exfoliated, they have been recently synthesized on a number of metallic substrates. The remarkable interaction between metals and these puckered materials, however, strongly modifies their intrinsic electronic properties, and also jeopardizes their integration into functional devices. In this context, first experimental efforts are now being devoted to the synthesis of silicene, germanene, and stanene on nonmetal substrates. Here, we review these pioneering works, present the ongoing debate, analyze, and discuss the major technical challenges and finally suggest possible novel solutions worth exploring.

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I. INTRODUCTION

Since its isolation in 2004, graphene—a single atomic layer of carbon atoms bonded in a hexagonal lattice—has attracted enormous attention both in academia and industry owing to its outstanding properties.\(^1,2\) Notably, due to its superior charge carrier mobility and monoatomic thickness, graphene has been proposed as a viable option that could push performance of current information technology beyond its traditional boundaries.\(^3\) However, the lack of a bandgap is a significant problem that has so far hampered its integration in, for instance, digital logic devices. Indeed, field effect transistors (FETs) with a graphene-based channel exhibit poor switching capabilities or, in other words, a low on-off current ratio, which in turn gives rise to huge power consumption.\(^4\)

In this scenario, graphene-like elemental group-IV materials (also called group-IV X-enes), such as silicene,\(^5,6\) germanene,\(^5,7,8\) and stanene,\(^9,10\) have been recently proposed as a potentially powerful alternative\(^11-17\) (Fig. 1). Here, it is worth discussing from the onset the
fundamental difference between graphene and the other group-IV elemental two-dimensional (2D) materials. At ambient conditions (i.e., room temperature and pressure of 1 atm), the energetically most favorable structure for C is the honeycomb structure (i.e., graphene or graphite), where C atoms exhibit pure sp² hybridization. As a consequence, this structure is atomically flat. On the other hand, diamond, with C atoms showing a sp³ character, is thermodynamically stable only at very high pressures. When it comes to single layers of the other group-IV elements, completely planar structures are not stable, as they would suffer from imaginary phonon modes in a large part of the Brillouin zone. The larger Si-Si or Ge-Ge bond lengths indeed prevent Si or Ge to hybridize in a purely sp² fashion. As a consequence, in these single layers, Si or Ge has a mixed sp²-sp³ hybridization that leads to a small buckling—i.e., a displacement of the atoms in the out-of-plane direction. Theoretical calculations predict this buckling to be of about 0.44 Å, 0.64 Å, and 0.85 Å for free-standing silicene, germanene, and stanene, respectively, as reported in Table I.

Interestingly, the buckled structure and the enhanced spin–orbit coupling make this class of 2D materials topological insulators with energy gaps of approximately 1.5 meV, 23.9 meV, and 100 meV, respectively for silicene, germanene, and stanene. The presence of topologically nontrivial electronic states introduces a rich physics and would possibly allow devices based on these materials to preserve quantum information. Silicene-based spin-filters have also been suggested. Furthermore, their structural buckling enables the bandgap to be modulated when (i) applying an electric field perpendicular to the plane, (ii) changing the degree of buckling by tuning the interaction with the substrate, and (iii) introducing chemical or structural modifications (i.e., applying mechanical strain).

However, X-enes are much less stable in air than graphene and moreover do not have a bulk counterpart from which they can be mechanically exfoliated. Therefore, it is more challenging to fabricate them, and the major synthesis approach has been epitaxial growth on solid surfaces in ultrahigh vacuum (UHV) chambers. Suitable growth substrates will act as a template, and thus will generally satisfy two criteria, that is, hexagonal symmetry and a small lattice mismatch (Δa) with the 2D

| TABLE I. Predicted values of lattice parameter (a), buckling (δ), and bandgap for free-standing 2D low-buckled Si, Ge, and Sn. |
|---------------|--------|-----------------|
| Material | a (Å) | δ (Å) | Band gap (meV) |
| Si | 3.83 | 0.44 | 1.5 |
| Ge | 3.97 | 0.64 | 23.9 |
| Sn | 4.62 | 0.85 | 100 |

FIG. 1. Overview of graphene (left side) and group-IV X-enes (right side) main properties as reported in the text. Carrier mobility values are taken from Refs. 18–20.
overlayer. Thus far, the majority of experiments on the growth of group-IV X-enes have been performed on metallic substrates. For instance, silicene was first successfully synthesized by depositing silicon onto Ag(111), where the lattice mismatch is 0.94 Å. Later, it was also synthesized through a similar process on Ru(0001) and Ir(111) surfaces, or via segregation on top of ZrB₂ thin films grown on a Si(111) substrate.41,42 In the case of germanene, the condition of lattice match with Ag(111) does not hold anymore, and besides, it is known that Ge and Ag tend to form an Ag₆Ge alloy on the surface.43 Therefore, following the considerations above regarding substrate selection, germanene was first synthesized on Au(111) and Pt(111) and later on Al(111).44 More recently, germanene has been also successfully synthesized on semimetallic Sb(111).45 When it comes to stanene, ultraflat—i.e., “nonbuckled”—stanene has been grown on Cu(111)46 and on Ag(111).47 The study reported in Ref. 30 is particularly interesting, because it is an excellent example of how it is possible to modify X-enes’ electronic properties by tuning the interaction with the growth substrate. Indeed, when grown at room or higher temperature, stanene on copper exhibits a buckled structure; however, if deposited at low temperature, it grows as an ultraflat sheet that consequently modifies profoundly the electronic properties and gives rise to topological states.

Although metallic surfaces are normally used as growth substrates, the strong hybridization between metal’s and 2D layer’s electronic bands greatly affects both structural and electronic properties of the 2D overlayer. For instance, the Dirac cone predicted for free-standing X-enes is commonly absent when they are grown on metals, with Ca alloys and Pb substrates being theoretically predicted to be exceptions. More importantly, ruling out completely the formation of alloys between metals and Si/Ge/Sn is not trivial, and controversial reports indeed question the successful synthesis on metal substrates.48–50 In addition, conductive substrates jeopardize integration reports, the study in Ref. 30 is particularly interesting, because it is an excellent example of how it is possible to modify X-enes’ electronic properties by tuning the interaction with the growth substrate. Indeed, when grown at room or higher temperature, stanene on copper exhibits a buckled structure; however, if deposited at low temperature, it grows as an ultraflat sheet that consequently modifies profoundly the electronic properties and gives rise to topological states.

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might have been the result of the remarkable shrinking of the Si lattice induced by the substrate. Because the magnitude of buckling largely influences the electronic band structure of silicene, the authors performed scanning tunneling spectroscopy (STS) measurements to gain insights into the electronic properties of the highly strained silicene. Although some differences could be appreciated when STS was performed on bare MoS2 or on Si-coated MoS2, unfortunately STS experiments are very sensitive to tip-substrate interaction in the case of layered materials and thus compelling conclusions could not be drawn at that stage.61 To shed light onto the electronic properties of the system, the same group later carried out also in situ angle-resolved photoemission spectroscopy (ARPES) experiments [Figs. 3(a)–3(d)]. A comparison of the valence band structure along the high-symmetry K–Γ–K direction for the MoS2 substrate before and after Si deposition illustrates that the silicene/MoS2 system is metallic in character due to an accumulation of electrons at the interface.64 It is worth pointing out that the information gained by the ARPES data is relative to the topmost MoS2 layer because the inelastic mean free path of electrons with the photon energy used for the experiments (100 eV) was almost comparable to the thickness of a single MoS2 layer.

Further experimental efforts were devoted to the fabrication of a back-gated FET.64 A monolayer of silicon was deposited in vacuum onto few layers of MoS2 previously exfoliated on a SiO2/Si+ substrate and already contacted by Au/Ti electrodes. Afterward, a 5 nm-thick film of Al2O3 was used as a capping layer to protect the 2D Si nanosheets against oxidation [Fig. 3(e)]. To better characterize the device described above, its electrical behavior was compared with that of the MoS2 FET. First, the admittance was measured. From the data collected, the channel in the Si/MoS2 heterosheet FET started accumulating charges at lower bias with respect to the MoS2 FET taken as reference. Furthermore, the capacitance curves exhibited a bias-modulated stretch-out that could be explained as the interplay of the two active interfaces (i.e., Si/MoS2 and MoS2/SiO2). The electrical characteristics of the two devices are shown in Fig. 3(f). The two devices showed different back gate voltage (Vbg) dependence in the drain–source I-V (Ids-Vds) curves, indicating that the two devices had different threshold voltage. The heterosheet FET showed a rigid backshift of threshold voltage at Vds values and an extra bias modulation. Looking more into details, from the linear Ids-Vbg curve emerged a double threshold. The physical meaning of this last feature is elucidated by the transconductance (g_m) plot in Fig. 3(g). In the case of...
MoS$_2$ FET the $g_m$ curve exhibited one peak while for Si-MoS$_2$ FET the profile is double peaked. Thus, in agreement with the admittance response, the authors have concluded that two active channels are formed at MoS$_2$/SiO$_2$ and Si/MoS$_2$ interfaces. The conduction through the Si nanosheets is neglected as the transconductance peak is comparable with the MoS$_2$/SiO$_2$ channel and suggests a semiconducting behavior rather than the expected metallic one of the silicene layer. This can be due to the disconnection of different grains in the Si nanosheet surface that can compromise the overall electrical transport properties. It cannot be excluded that the Al$_2$O$_3$ capping has no influence on the mobility of the Si/MoS$_2$ interface, but the creation of a conductive channel at the Si/MoS$_2$ interface can be a direct consequence of the Si-induced band bending and suggests n-type doping due to the electron transfer in the topmost region of MoS$_2$ induced by the Si nanosheets. Silicene deposition has to be improved both in quality and size of layers in order to reach higher carrier mobility, but this framework is a relevant starting point for the optimization and tuning of van der Waals heterostructures for nano- and optoelectronic applications.

Interestingly, Van Bremen et al.\textsuperscript{65} found experimental STM results similar to those previously reported by Chiappe et al.\textsuperscript{61} but the interpretations given in the two works are completely different. Indeed, the former\textsuperscript{65} claimed that, upon low rate deposition at room temperature, Si intercalated between MoS$_2$ layers rather than growing silicene islands on top of the substrate. MoS$_2$ has also been experimentally investigated as a growth substrate for germanene.\textsuperscript{8} In this case, the deposition of Ge was performed while keeping the substrate at room temperature. Ge atoms diffuse onto the MoS$_2$ surface and use defects in the substrate, such as vacancies or lattice impurities,\textsuperscript{66,67} as nucleation points. At low coverage, the 2D Ge islands exhibit different shapes and sizes; yet they all show an interesting hexagonal shaped vacancy in their center (Fig. 4). Compared to what was observed in the case of 2D silicon nanosheets grown on MoS$_2$,\textsuperscript{61} here the lattice parameter of the Ge islands does not match that of the substrate, although is contracted of about 5% compared to that of for free-standing germanene (3.8 Å and 3.97 Å respectively). STS data collected at room temperature on bare MoS$_2$ areas showed the presence of a bandgap, whereas when acquired on the islands revealed a well-defined V shape around zero bias [Fig. 4(d)], which is characteristic of 2D Dirac systems. At full monolayer
coverage, the lattice parameter of the Ge sheet still does not match that of the MoS$_2$ underneath, and the two lattices are aligned. Furthermore, DFT calculations performed on islands laterally contracted by 5% were used to support the experimental observations. The shape of both germanene and MoS$_2$ calculated density of states (DOS) is found to be in very good agreement with the experiments, with the only difference being the position of the Fermi energy, which is shifted in the calculated DOS of $0.3$ eV toward higher energy, this implying $n$-type doping of the system. This discrepancy could be explained by the presence of doping impurities or unsaturated defects in the sample. The DFT calculations provided further details about the band structure of the system, and revealed the presence of (i) $\pi$-bands close to the $K$ point, and (ii) two parabolic $\sigma$ bands close to $\Gamma$ point. Unfortunately, the observed large buckling of germanene leads to $\sigma-\pi$ charge transfer, which would suppress the anomalous quantum Hall effect as well as the 2D Dirac transport properties.

### B. Si and Ge on Highly Oriented Pyrolytic Graphite (HOPG)

Owing to a hexagonal symmetry and a surface free of dangling bonds, highly oriented pyrolytic graphite (HOPG) is a promising candidate as a weakly interacting growth substrate for X-enes. Moreover, it is chemically inert and expected to form no alloy intermixing with either Si or Ge. In the past couple of years, the growth of silicene and germanene on HOPG has been studied intensively, and much interesting progress has very recently led to a stimulating debate.

In Ref. 69, silicon atoms were deposited on a HOPG kept at room temperature in UHV conditions. High-purity silicon was evaporated from a wafer at a nominal constant rate of 0.1 nm/min (0.04 ML/min). Atomic force microscopy (AFM) investigations showed the simultaneous presence on the sample of (i) 2D islands, (ii) areas of uncovered HOPG, and (iii) three-dimensional (3D) clusters.

Atomically resolved STM data were used to provide more insights into the structure of the obtained 2D islands, and showed that these exhibit a small buckling of 0.5 Å, in good agreement with the value expected for free-standing silicene. Furthermore, an analysis of the Fourier transform reveals two hexagons rotated by 30° with respect to each other. The outer hexagon is relative to HOPG, corresponding to a lattice parameter of 2.4 $\pm$ 0.1 Å, while the inner one has a larger parameter, of 4.1 $\pm$ 0.2 Å, which is close to the value of 3.83 Å, theoretically predicted for free-standing silicene. The fact that the values experimentally measured for the lattice parameter and the out-of-plane buckling are so close to the ones theoretically predicted for free-standing silicene implies that silicene on HOPG is unstrained. This is indeed expected for van der Waals epitaxy, and is the signature of a weak interaction between the substrate and the...
ad-layer. Under this condition, silicene on HOPG is supposed to display its intrinsic electronic properties. STS performed at room temperature on silicene areas indeed shows a metallic behavior with a finite density of states at the Fermi level [Fig. 5(f)].

Similarly, in Ref. 71 the synthesis of germanene islands on HOPG at room temperature is reported. Ge was deposited using an e-beam evaporator at a rate of 0.7 ML/min. STM measurements [Figs. 5(d) and 5(e)] showed a 2D layer with lattice parameter and buckling, respectively, of 4.2 ± 0.3 Å and 0.7 Å, values that closely match those theoretically predicted for free-standing germanene, that is 3.97 Å and 0.64 Å, respectively. As in the case of silicene on HOPG, also for the case of germanene on HOPG the ad-layer seems to grow unstrained, as expected with a substrate free of surface dangling bonds. Similar to the case of silicon deposited on HOPG, also in this case three-dimensional (3D) Ge clusters can be observed, suggesting a competition between 2D and 3D growth. The structural and electronic properties of the 2D Ge on HOPG obtained by DFT calculations are consistent with the experimental findings. In particular, the islands show the Dirac cone and a distinct charge transfer with the substrate that are predicted by simulations and experimentally observed in STS spectroscopy data [Fig. 5(g)].

The conclusions of Refs. 69 and 71 regarding the formation of unstrained silicene and germanene on HOPG have been recently rejected by another research group, after reproducing the same
experimental conditions. Notably, in Ref. 72 the authors proposed a completely different interpretation of the results obtained from STM measurements. The ($\sqrt{3} \times \sqrt{3}$)R30° honeycomb superstructure arising after the deposition of Si or Ge atoms was observed around step edges and Si/Ge clusters, while the majority of the atomically flat areas between clusters exhibited the triangular lattice of the HOPG surface. From the unconstructed HOPG areas to the honeycomb superstructure areas, the change in height (i.e., the slope of the line profile taken across an area with the superstructure and one without) appeared to be smooth and continuous, and not sharp and step-like as expected for the case of silicene/germanene islands grown on top of HOPG. The observed superstructures were always confined around step edges or clusters and involved a breakdown in the lattice periodicity of graphite. Therefore, the authors in Ref. 72 proposed that the observed superstructures result from a long-range perturbation of the charge density in HOPG due to electronic interferences between surface and scattered waves from defects or clusters. Similar conditions were found after deposition of Pt particles73 and creation of defects induced by Ar+ bombardment.74

Nevertheless, the controversy and the opposite interpretations highlight the need for more convincing results to shed light on the growth of X-enes on HOPG, and in general on layered substrates. Growing larger and more uniform silicene or germanene areas on HOPG, for instance by tuning the growth conditions (i.e., substrate temperature, evaporation rate), would be probably beneficial for resolving this debate.

C. Sn on InSb, Bi2Te3, and PbTe

Very few experimental studies have been reported thus far on the growth of stanene, and mostly are on metal surfaces such as Cu(111) and Ag(111). However, in the 1990s some MBE experiments might have led to the synthesis of stanene-like structures on InSb(111),11 where the authors studied the growth modes and phase transitions of Si on the substrate by means of reflection high-energy electron diffraction (RHEED) and Auger electron spectroscopy. However, no atomic-scale characterization was provided at that time. Much more recently, Xu and co-authors replicated that study by growing epitaxially stanene on the Sn-terminated InSb(111) surface, and by carrying out RHEED and ARPES experiments. Their findings show that while monolayer stanene on InSb(111) has a large bandgap of 0.44 eV, bilayer stanene is instead a semimetal, as the bandgap is filled in by InSb conduction band states. Nevertheless, the bandgap of 0.44 eV measured for single-layer stanene makes the system stanene/InSb(111) promising for spin quantum Hall applications even at room temperature, where the thermal energy $k_B T$ is 25 meV.

In Ref. 9, an interesting work reports on the growth of stanene on Bi2Te3(111). The substrate, either bulk single crystal or thin film, was kept at RT during deposition of Sn via MBE. Figures (7a)–(7c) display STM images and atomic model of the system. The deposition resulted in several layers of Sn with a constant spacing between layers of about $0.35 \pm 0.02$ nm. The ARPES measurements [Figs. 7(d)–7(k)] showed that the valence band of Bi2Te3 shifts to higher energy with the Sn deposition, indicating electron transfer from the ad-layer to the substrate. The lattice constant for the substrate is 4.383 Å, while for free-standing stanene it is expected to be 4.62 Å from DFT calculations. This means that the substrate should apply a compressive strain on stanene possibly leading to an increase in the buckling from 0.85 to 1.09 Å. Theoretical models for different binding sites of stanene give similar results concerning the geometry of the system, probably due to the weak interaction with the substrate. The experimental results obtained in Ref. 9 are in agreement with theoretical calculation. Indeed, the DFT model showed that the valence band shifts upward resulting in a transition from topological insulator to metal. Thus, it can be inferred that stanene under compressive strain remains metallic. Nevertheless, it could still be possible to open a bandgap via chemical functionalization of stanene.
which would then allow this system to host quantum spin Hall and quantum anomalous Hall states. 82,83

Besides the studies on InSb and Bi₂Te₃ surfaces, stanene has also been successfully fabricated on PbTe(111)/Bi₂Te₃ substrates via MBE. 84 The quality of the film was monitored by RHEED and confirmed via STM characterization. Very interestingly, while bulk α-tin is not superconductive, this study demonstrates that few-layer stanene is indeed a superconductor. 85 Figure 8(a) displays a sketch of the structure of the system with trilayer Sn deposited on top of PbTe/ Bi₂Te₃/Si(111), with hydrogen atoms passivating the surface. Figure 8(b) shows that superconductivity emerges starting from bilayer stanene, and the sample remains a superconductor even at a thickness of 20 Sn layers (NSn). It is also evident that the critical temperature (Tₖ) increases with the number of Sn layers [Figs. 8(b) and 8(c)], as already found for other ultrathin film systems. 86,87 Besides, Tₖ also depends strongly on the thickness of the PbTe buffer layer [Fig. 8(d)]. While it
FIG. 7. (a)–(c) Model of the atomic structure of 2D stanene on the Bi₂Te₃ (111). The green and orange balls represent the bottom and top Sn atoms, respectively. The gray balls represent the surface Te atoms of the substrate. (a) Top view of the top Sn atoms. (b) Top view of both the top and bottom Sn atoms. (c) Side view. (d) and (e) ARPES spectra of Bi₂Te₃ (111) (d) and stanene on Bi₂Te₃ (e) along the K–C–K direction. The orange dashed lines define the bulk band dispersions of Bi₂Te₃. The blue dotted lines define the valence bands of stanene. “SS” marks the surface state and “CB” marks the conduction band of Bi₂Te₃, respectively. (f) Fermi surface mapping in large momentum space. The red hexagons are the 2D Brillouin zones of stanene. (g) ARPES spectra along two momentum directions marked by yellow lines in (f). (h) Sketch of the two light polarizations used in the experiments. (i) and (j) ARPES spectra taken under p-polarization (i) and s-polarization (j). White dotted lines mark the valence bands of stanene. “VB” marks the valence band of Bi₂Te₃. (k) ARPES spectra along the C–M–C–K–M–K directions. Blue dotted lines represent the experimental electronic bands of stanene, while the green dashed lines the valence band of Bi₂Te₃ (111). Reproduced with permission from Zhu et al., Nat. Mater. 14, 1020 (2015). Copyright 2015 Springer Nature.
seems that there is no dependence of $T_c$ for stanene grown on less than 6 PbTe layers, $T_c$ doubles when the number of PbTe layers is larger than 8. The authors explain this finding as due to variation in the density of states, as observed from ARPES experiments, and the release of mechanical strain caused by the lattice mismatch with the substrate. Figure 8(e) indeed shows ARPES data of a trilayer stanene with increasing number of PbTe layers ($N_{\text{PbTe}}$), where two different valence bands can be identified. One parabolic band below the Fermi level, and one with linear dispersion with the two arms crossing the Fermi level. When $N_{\text{PbTe}}$ increases, the two valence bands downshift due to an enhancement in the electron transfer from PbTe buffer layer, and a third band becomes visible around the Fermi level. There is therefore a transformation of the trilayer stanene from a one-band to a two-band system when it is grown on 10-layer PbTe or thicker. Theoretical calculations supported the ARPES data and even showed an s-p band inversion at the $\Gamma$-point for trilayer stanene on the number of PbTe layers. Circles indicate the linearly dispersed valence band. Triangles indicate the width of the parabolic band around $k_1$.

Figure 8. (a) Sketch of the Sn/PbTe/Bi$_2$Te$_3$ structure and the stanene lattice. (b) Normalized resistance of stanene with varying the number of Sn layers grown on PbTe (15 layers). (c) $T_c$ as a function of the number of stanene layers ($N_{\text{Sn}}$). (d) $T_c$ as a function of PbTe layers ($N_{\text{PbTe}}$). The three data points of $T_c$ in a row represent the temperatures where the resistance drops to 1%, 50%, and 90% of the normal resistance ($R_n$). The $T_c$ in the bulk $\beta$-Sn is 3.7 K. (e) Dependence of the band structure around the $\Gamma$-point for trilayer stanene on the number of PbTe layers. Circles indicate the linearly dispersed valence band. Triangles indicate the width of the parabolic band around $k_1$. Reproduced with permission from Liao et al., Nat. Phys. 14, 344 (2018). Copyright 2018 Springer Nature.

III. OTHER POTENTIAL SUBSTRATES FOR GROUP-IV X-ENES GROWTH

In addition to the layered substrates discussed above, many other possible suitable candidates for epitaxial growth of X-enes have been discussed theoretically, and preliminary experimental data are also available in some cases, but no conclusive structural characterization of the grown 2D layer has been reported yet. Although these substrates are not yet sufficiently studied, we believe they could lead to interesting discoveries in the near future. Among those, the layered material InSe, the insulating calcium difluoride (CaF$_2$), the oxides LaAlO$_3$ and Al$_2$O$_3$ and graphene on SiC have received particular interest.

A. InSe

Similar to HOPG and MoS$_2$ mentioned earlier, InSe is a layered material with the consecutive layers interacting among each other through van der Waals forces; its bulk crystal is a direct bandgap semiconductor with anisotropic electronic properties and lattice constant of about 4 Å. The lack of dangling bonds, the hexagonal symmetry and a small lattice mismatch with silicene and germanene make it an interesting candidate as a growth substrate for 2D group-IV materials. First-principles calculations performed by Fan et al. show that both silicene and germanene can be indeed stably formed on InSe, and that their intrinsic electronic properties are largely preserved. Notably, silicene (germanene) on InSe would display a Dirac-cone-like dispersion with a bandgap of 141 meV (149 meV). A more interesting finding, though, is the ultrahigh carrier mobility on the order of $10^3$ cm$^2$ V$^{-1}$ s$^{-1}$ that makes them extremely appealing for the realization of novel electronic devices based on van der Waals heterostructures.

Since it has been recently reported that InSe thin films can be exfoliated from bulk crystals and deposited on substrates such as silicon oxides, glass, or mica, it is reasonable to foresee that the first attempts at growing silicene or germanene on it will soon appear.
B. CaF$_2$

Calcium difluoride is a ceramic widely used for the production of mineral and organic fluorine-based chemicals and glass. Recently, it has also been studied for growth of epitaxial thin films such as lithium fluoride$^{95}$ and for fabrication of ionic superconducting materials.$^{96}$ Among the diverse industrial applications, CaF$_2$ is especially important in the production of hydrofluoric acid (HF), because fluorite, i.e., the mineral form of CaF$_2$, is the most important source in this process. In the production of HF, fluorite needs to be separated from the surrounding minerals through a front-floating technique as removal of fluorite in flotation leads to the reduction of operating costs. This process is performed in an aqueous environment, and therefore, the characterization of fluorite surface in the presence of water is crucial for industries. For this reason, many surface science groups worldwide have been studying the CaF$_2$ surface.$^{97}$–$^{99}$ It is expected, however, that CaF$_2$ could also be a suitable substrate for the growth of silicene. Indeed, because of electrostatic reasons, the cleaved CaF$_2$(111) surface terminates with a F$^-$ layer,$^{100}$ with the F$^-$ ions arranged in a triangular pattern with spacing of 3.88 Å. This provides a lattice mismatch of only 0.5% with silicene. From theoretical calculations, such little mismatch and consequent small tensile strain do not affect the Dirac cone in silicene. Moreover, the completely filled valence shell makes the CaF$_2$(111) surface inert$^{101}$ and tensile strain do not affect the Dirac cone in silicene. Moreover, the large bandgap of the substrate would still lacking, yet highly desired. The large bandgap of the substrate would gate their electronic properties, and compare them to related theoretical calculations.

C. Oxides

As ideal growth substrates need to be inert in order to leave unaltered the 2D overlayer’s intrinsic electronic properties, oxides are of course an attractive choice.

1. LaAlO$_3$

Oxide lanthanum aluminate, LaAlO$_3$ (LAO), is a notable example. It has a high value of dielectric constant ($\varepsilon = 24$), is thermodynamically stable, and hence does not intermix with, for instance, silicon.$^{102}$ A promising study on epitaxial growth of Si on LAO substrates is reported in Ref. 103, where a single layer of Si is deposited via MBE onto a LAO(111)–(2,3 × 2,3)R30$^\circ$ reconstructed surface. The growth experiments were performed at different substrate temperatures (i.e., 300 °C and 500 °C) and followed using the RHEED technique. The RHEED pattern reported here in Figs. 10(a)–10(f) shows both Kikuchi lines, connecting the bright spots of the pattern, and integral streaks related to LAO(111) after deposition. The combination of those two elements suggests that the surface remains flat and that silicon grows as a two-dimensional layer. The complementary XPS analysis [Figs. 10(g)–10(n)] revealed no evolution in the spectra of O 1s and Al 2p peaks, suggesting that the LAO crystalline structure is not modified and does not intermix with Si, as expected due to the repulsion between Al and Si.$^{104}$ Therefore, it is expected that only weak interaction is present between the substrate and overlayer. Interestingly, the Si 2s core-level XPS peak shows a higher energy component at 153.2 eV and a lower one at 150.5 eV. The higher binding component is consistent with the formation of Si-O bonds and its energetic position does not shift when the substrate temperature changes, meaning that there is no formation of other silicate compounds. On the other end, the lower component is instead related to the formation of Si-Si bonds. This component increases in intensity with the growth temperature, suggesting a larger Si-Si formation on the LAO surface at 300 °C than at 300 °C. These studies on LAO hold much promise for growing 2D silicon layers on insulating surfaces. Nevertheless, further studies especially by means of scanning probe microscopy techniques that are able to probe the atomic structure of the grown ad-layer are required, since as of today the morphology of such samples is not known. If structural studies were to confirm the presence of 2D silicon sheets, it would be then extremely interesting to investigate their electronic properties, and compare them to related theoretical calculations.

![FIG. 9.](a) Sketch of silicene adsorbed on a clean CaF$_2$(111) surface. Si, Ca, and F atoms in blue, yellow, and red, respectively. (b) Calculated band structure of silicene adsorbed on CaF$_2$(111). The regions of the dense slab bands represent the projected bulk CaF$_2$ band structures. The silicene bands are indicated by black lines. The red-dashed horizontal line represents the Fermi level. Reproduced with permission from Kokott et al., J. Phys. Condens. Matter 26, 185002 (2014). Copyright 2014 Institute of Physics.)
2. Al2O3(0001)

A very recent work reports on the optical conductivity of ultrathin Si nanosheets grown on Al2O3(0001). This is an interesting choice of substrate because it exhibits a wide bandgap of 8.8 eV (Ref. 106) and the Dirac point of a silicene ad-layer is predicted to lie just in the middle of this gap. Furthermore, theoretical calculations show that silicene on Al2O3(0001) has a low-buckled structure. Two sets of samples were investigated. The first one had a variable thickness of the Si nanosheets ranging from 1.5 to 0.5 nm (VT), while the second one had a constant thickness of 0.5 nm (CT). The chemical status of as-grown Si nanosheets was characterized by in situ XPS experiments, whereas the thickness was measured by ex-situ AFM measurements after the samples had been capped with a 5 nm thick layer of amorphous Al2O3 in order to prevent air-induced oxidation [Fig. 11(a)]. By knowing the refraction index of the substrate and measuring the optical transmittance T(ω) of the samples, the authors eventually determined its optical conductivity σ(ω) = σ1(ω) + iσ2(ω) and observed a Dirac-like behavior in the infrared part of the conductivity spectra. Indeed, in the sample with a constant thickness of 0.5 nm (that is, a silicene monolayer) σ1(ω) displays a behavior consistent with that predicted for a 2D layer of Si. The optical behavior of these samples is summarized in Figs. 11(b)–11(e). Notably, the absorption spectra show a peak at 1.4 eV in the infrared range, peak that then raises linearly around 3 eV up to the ultraviolet range. The same features are predicted by ab initio calculations for I and II interband transitions in free-standing silicene. More interestingly, the conductance is quantized and depends on the layer thickness, which is for instance a characteristic of 2D Dirac fermions in graphene and thus suggests that the deposited Si indeed grows in a 2D fashion. Although in the early times the excitement about silicene was mainly due to the possibility of realizing high-performance electrical devices, like field-effect transistors, the observation of Dirac-like optical conductivity might trigger the interest toward a silicene-based photonics. Nonetheless, the Raman spectra of these samples feature only the mode related to 3D cubic silicon at 520.5 cm−1 [Fig. 11(f)]. Hence, the absence of a peak related to silicene, which should be at higher wavelengths, around 540 cm−1, might in fact cast doubt on the successful synthesis of 2D silicene on Al2O3(0001), which could be instead an ultrathin 3D silicon film. Therefore, a deeper characterization of the structural properties of the grown film, by means for instance of in situ “noncontact” atomic force microscopy (on uncapped samples) or a surface-sensitive diffraction technique, is highly desired.

D. Epitaxial graphene/SiC

As the passivation of SiC surfaces due to the epitaxial growth of graphene has been intensively studied and the Dirac cone feature of silicene and germanene on graphene surface is predicted to be maintained, the G/SlC/SlC system may also be an adequate substrate to grow group-IV X-enes. This possibility has been theoretically studied by Matusalem and coworkers, where the slab method is used to simulate the SiC substrate covered by graphene and silicene/germanene/stanene as ad-layers. Using first-principles calculations, the authors demonstrated that C-terminated SiC (000–1) covered by graphene could be used as a substrate to epitaxially grow X-enes in general with a low-buckled structure. The interaction between the overlayer and substrate is indeed weak, leading to the maintenance of the Dirac cone feature, even if small gaps are opened (96 meV, 116 meV, and 146 meV for silicene, germanene, and stanene, respectively). The presence of Dirac cones calls for an investigation of the topological nature of the overlayers. Graphene affects the topological behavior present in the free-standing group IV X-enes. For silicene, which is the most strongly bound to graphene among the three, the interaction is strong enough to destroy the topological character of the system. For germanene, the charge transfer is really small toward...
graphene and therefore, the topological properties are maintained. For stanene instead, contradicting features are present; thus, the appearance of topological behavior is still not clear.

Experimentally, however, Sone et al. attempted to grow 2D silicene on graphene previously deposited on 6H-SiC (0001) but could not succeed even if various substrate temperatures were employed. Instead, they found nanometer-thick flower-like dendritic islands of silicon when it was deposited with the substrate being in the temperature range 290–420 K. Higher temperatures would instead lead to formation of featureless clusters [Figs. 12(a)–12(e)].

On the other hand, it could be interesting to investigate the possibility of intercalating Si/Ge/Sn under graphene grown on a SiC substrate, as recently proposed for Si with graphene/Ru. In this way, the corresponding X-ene would be protected from oxidation upon reaction with air by the graphene top layer. Few studies go toward this direction, but it is worth considering the study reported by Visikovskiy et al., where interface modifications due to the successful intercalation of Si atoms between graphene and the underneath SiC substrate were indeed shown [Figs. 12(a)–12(b)]. Along the same line, Si/Ge/Sn could be intercalated under other 2D materials rather than graphene, as it was recently demonstrated for the case of Si intercalated under hexagonal boron nitride grown on ZrB₂. From an electronic structure perspective, no indication of interaction between the silicene layer and the hexagonal boron nitride coating was observed, and silicene was protected from oxidation upon exposure to air for a period of time of at least 1 h.

IV. ADDITIONAL SYNTHESIS ROUTES BEYOND EPITAXY

An alternative strategy for obtaining group-IV X-enes not necessarily deposited on metal surfaces is through modification of X-enes-based composites. Notable examples of such composites are the layered Zintl phases such as calcium disilicide (CaSi₂) and germanide (CaGe₂). CaSi₂ consists of a puckered Si layer intercalated by Ca layers (Fig. 13). ARPES maps of CaSi₂ show a massless Dirac-cone at the k-point in the Brillouin zone, which is however very far from the Fermi level due to charge transfer to the Si layer from the Ca counter ions. This strong effect of the external environment (i.e., the presence of the Ca layers) does not allow studying the intrinsic silicene properties, not so different from the case of silicene grown on metals. Therefore, to reduce the electrostatic interaction between Si and Ca layers, Yaokawa et al. intercalated F ions into the system in order to form ionic bonds between Ca and F. Through this process, the authors obtained patches of bilayer silicene structures with a 2D
translation symmetry and a wavy morphology, where Si atoms show tetrahedral coordination.

In a different study, Chen et al.\textsuperscript{54} used a two-step process to obtain germanene from CaGe\textsubscript{2}. First, CaGe\textsubscript{2} is turned into bulk germanane (i.e., hydrogenated germanene) following the topotactic deintercalation method in which H atoms replace Ca atoms, according to the chemical reaction CaGe\textsubscript{2} + 2HCl $\rightarrow$ 2GeH + CaCl\textsubscript{2}.\textsuperscript{124} In the second step, germanane flakes are mechanically exfoliated onto SiO\textsubscript{2} slabs and then turned into germanene by thermal annealing. Interestingly, while the germanane flakes show high resistance (sheet resistance above 10 M$\Omega$ at room temperature), the annealed germanene has a resistivity of $\sim$10$^{-7}$ $\Omega$m, which is orders of magnitude lower than any other allotrope of Ge. More interestingly, in the magneto transport measurements, the authors also observe evidence of weak antilocalization at low temperature and low magnetic fields, as the result of the strong spin–orbit coupling expected in germanene.

V. OUTLOOK AND CONCLUSIONS

Silicene, germanene, and stanene are examples of synthetic elemental 2D materials,\textsuperscript{125} meaning that there are no bulk analogs from
which they can be derived. Instead, they need to be synthesized via physical and/or chemical processes that often require highly technical skills and costly, specialized instrumentations. As a consequence, the rate of progress in these materials is much slower than that of other 2D materials, which can be instead exfoliated from layered bulk systems, like for instance graphene (from graphite), transition metal dichalcogenides, and hexagonal boron nitride. Furthermore, the investigation of their intrinsic electronic properties, crucial for further advancing the field, is hampered by the metals that are usually used as growth substrates, since they (i) strongly interact with the 2D ad-layer, and (ii) do not allow for direct integration in electronic devices. Besides, it is not trivial to exclude formation of surface alloys between Si/Ge/Sn and a given metal substrate, which has even led to doubt the formation of silicene and germanene on metals.126–131

In this context, successfully synthesizing these 2D materials on “nonmetals” would therefore represent a certain breakthrough in the field because these substrates are supposed to interact only weakly with the 2D ad-layer, hence preserving its intrinsic electronic properties. Therefore, in this review we have focused on the synthesis and characterization of silicene, germanene, and stanene on such materials.

The first class of possible nonmetal substrate candidates that we have considered is layered materials, such as MoS2, HOPG, Bi2Te3, InSe, PbTe, and graphene because of their hexagonal symmetry and lack of dangling bonds. They are ideal substrates for van der Waals epitaxy,126–131 moreover, MoS2, Bi2Te3 and InSe, being semiconductors, would enable direct fabrication of electronic devices. However, we also pointed out that the layered structure of this type of substrates can in

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FIG. 13. (a)–(c) Experimental (main panels) and simulated (insets) high-angle annular dark field scanning transmission electron micrographs of the bilayer silicene structure, denoted as w-BLSi. (a) The [01]w-BLSi and [11]w-BLSi incident directions ([1-10]CaF2), (b) the [10]w-BLSi and [11-2]Si and CaF2 directions and (c) the [13]w-BLSi and [11-2]Si and CaF2 directions. (d) Schematic illustration of the w-BLSi atomic structure. (e)–(h) Schematic structures projected in each direction along [01], [13], [11], and [10] directions respectively in (e), (f), (g), and (h). All scale bars 1 nm. Reproduced with permission from Yaokawa, et al., Nat. Commun. 7, 10657 (2016). Licensed under a Creative Commons Attribution (CC-BY_4.0) license.
effectively protected from degradation in air, as Ref. 76 reports for the formation of silicene, germanene, or stanene under another layered material. However, intercalation of Si, Ge, or Sn and possibly the consequent forming the interpretation of the results extremely difficult. On the other fact be a serious problem, as the deposited Si/Ge/Sn atoms may diffuse and although they show somewhat similar observations, the interpretation is often very different and the consequent debate is still unsettled. Some experimental studies have been reported, particularly fascinating is the possible observation of quantized optical conductance depending on the thickness for silicon deposited on Al2O3(0001). Yet, as we commented on the text, conclusive and decisive proofs of successful growth are still unavailable.

Another insulating substrate that we have discussed is calcium fluoride. It forms with silicene an almost lattice-matched system and does not affect silicene’s Dirac cone; however, no experimental study has been reported yet.

The last class of substrates that we have considered is oxides. Indeed, owing to their large band gaps, they might be ideal substrates as they would enable direct fabrication of electronic devices. As of today, however, very few studies have focused on this class of substrates and only preliminary results have been reported. In conclusion, as we show in this review, it is clear that the topic is still in a truly early stage. Some experimental studies have been reported, and although they show somewhat similar observations, the interpretation is often very different and the consequent debate is still unsettled. Therefore, more efforts need to be devoted to realizing X-enes on non-metal substrates with higher structural quality, and on a larger scale.

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