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,7,8 and stanene,9,10 have been recently proposed as a potentially powerful alternative11–17 (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 lattice parameter (a) and buckling (δ) are shown in Table I.

<table>
<thead>
<tr>
<th>Material</th>
<th>a (Å)</th>
<th>δ (Å)</th>
<th>Band gap (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3.83</td>
<td>0.44</td>
<td>1.5</td>
</tr>
<tr>
<td>Ge</td>
<td>3.97</td>
<td>0.64</td>
<td>23.9</td>
</tr>
<tr>
<td>Sn</td>
<td>4.62</td>
<td>0.85</td>
<td>100</td>
</tr>
</tbody>
</table>

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),38–39 where the lattice mismatch is 0.94 Å. Later, it was also synthesized through a similar process on Ru(0001)39 and Ir(111)40 surfaces, or via segregation on top of ZrB2 thick films grown on a Si(111) substrate.41–44 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 Ag-Ge alloy on the surface.45–48 Therefore, following the considerations above regarding substrate selection, germanene was first synthesized on Au(111)44 and Pt(111)45 and later on Al(111).46 More recently, germanene has been also successfully synthesized on semimetallic Sb(111).47 When it comes to stanene, ultrathin—i.e., “nonbuckled”—stanene has been grown on Cu(111)48 and on Ag(111).49 The study reported in Ref. 49 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,50 with Ca50 and Pb51 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.45–50 In addition, conductive substrates jeopardize integration into microelectronic devices as they do not allow modulating the 2D material’s Fermi level by electric gating. For this reason, and because of their instability in air, there are presently only a few reports on electric devices based on this class of materials. The only example so far of FET with a single layer of silicene as the channel was fabricated in 2015 and showed Dirac-like ambipolar charge transport at room temperature in ambient conditions.52 Despite its short lifetime, the realization of this device represents a milestone in the research field, as it demonstrated the feasibility of fabricating working devices with group-IV X-enes, and their potential to overcome graphene’s limitations. The carrier mobility was \( \sim 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) and, more importantly, the opening of a small bandgap was discussed. Later, FETs based on less air-sensitive multilayer silicene were reported as well,53 providing an interesting pathway to stabilize the quickly degradable single-layer silicene-FET.54 In this scenario, it is also worth noting that silicene and germanene, differently from graphene and other classes of 2D materials, offer the prospect of full compatibility with the existing semiconductor technology. Therefore, if high performance devices were to be realized, the existing technology infrastructure, based almost entirely on the processing of Si and to a lesser extent of Ge, could easily be applied. Nevertheless, the study on X-enes is still in its infancy, and if there are only a few studies on silicene-based devices, the ones on germanene or stanene are even more rare.54

Therefore, growing X-enes on nonmetal and inert substrates is of paramount importance in order to (i) gain more insights into their intrinsic electronic properties and (ii) make easier the realization of electronic devices. At this aim, the first important issue becomes to identify the properties that such inert substrates should possess to enable successful growth of X-enes. With these premises, here we first review the state of the art of the recent progress achieved in the deposition of Si, Ge, and Sn on nonmetal substrates, with special attention to the most compelling experimental findings that are supported by atomic-scale structural characterization of the grown 2D sheet. In particular, we start focusing on hexagonal layered surfaces. These are very promising growth substrates because their surface terminates with no dangling bonds, and they are therefore expected to interact only weakly with the ad-layer on top (i.e., van der Waals epitaxy).55–58 In addition, some of them have considerable band gaps (1–6 eV), which would enable direct realization of electrical devices without the need of a postgrowth transfer step. As we will see however, layered substrates bring many challenges, mainly due to possible intercalation of group-IV atoms under the substrate top layer(s) during deposition. This has led to an interesting yet unsettled debate, and to publications showing similar results but with different interpretations. Next, we discuss those nonmetal substrates that, although not layered, are still expected to interact weakly with the growing 2D overlayer. Examples of this class of materials are calcium difluoride (CaF2), lanthanum aluminate oxide (LaAlO3, LAO), and sapphire (Al2O3). Theoretical predictions involving these substrates have been already reported, and some promising preliminary experiments have been carried out as well. Yet, convincing and thorough characterization of the structural and electronic properties of the grown 2D layers is still missing. In addition, we also look at an alternative yet promising route for the synthesis of X-enes via chemical modification of X-ene-based composites.

II. RECENT PROGRESS

A. Si and Ge on MoS2

Molybdenum disulfide (MoS2) is a semiconducting layered material and probably the most noted compound among the family of transition metal dichalcogenides.59,60 It has also been one of the first substrates used to grow silicene,54 because, despite a smaller lattice parameter (3.16 Å), it fulfills the requirement of hexagonal symmetry and lack of dangling bonds on the surface that would be required to preserve silicene electronic properties.61–63 MoS2 in its bulk form is composed of stable S-Mo-S layers interacting with each other via van der Waals forces. A first experimental result on silicene epitaxy on a MoS2 substrate was reported by Chiappe et al.,64 where Si was deposited through molecular beam epitaxy (MBE) at 200 °C. Figure 2 summarizes the main findings of that study. In particular, scanning tunneling microscopy (STM) data revealed that Si atoms are indeed arranged in graphene-like nanodomains with threefold symmetry. Surprisingly, despite a mismatch as large as 20% between free-standing silicene and MoS2 and the expected weak interaction between the substrate and ad-layer in the van der Waals epitaxy growth mode, the authors claim to observe Si domains having the same lattice constant of the MoS2 underneath. Density functional theory (DFT) calculations were used to supplement the experimental results, and revealed a remarkable buckling of the Si layer of about 2 Å, which is indeed in good agreement with line profiles extracted from the STM data. Such a value, quite large compared to those previously experimentally measured64 and theoretically predicted5 for low-buckled silicene structures,
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 back-shift of threshold voltage at Vds values and an extra bias modulation. Looking more into details, from the linear Ig–Vg curve emerged a double threshold. The physical meaning of this last feature is elucidated by the transconductance (gm) 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. found experimental STM results similar to those previously reported by Chiappe et al. but the interpretations given in the two works are completely different. Indeed, the former's 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. From the experimental considerations above, van Bremen et al. concluded that Si atoms intercalated between the 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. 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, 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$_2$, 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 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

![Fig. 3. Valence band structure of (a) bare MoS$_2$ and (b) MoS$_2$ after Si deposition at 200 °C collected with a photon energy $h\nu = 100$ eV along the K-$\Gamma$-K reciprocal lattice direction. (c) Bottom: Comparative line profiles of the valence band plots taken at the $\Gamma$ point for bare MoS$_2$ (black line) and after the growth of Si nanosheets (circles). Top: Line profile in the vicinity of the Fermi level taken at the $\Gamma$ point (left) and at $k_z = 0.72$ Å$^{-1}$ (right). (d) Schematic diagram of the electronic bands at the Si/MoS$_2$ interface. (e) Sketch of the fabrication process of the Si/MoS$_2$ FET. (f) Admittance response of the Si/MoS$_2$ FET. The capacitance-voltage (black line) and conductance-voltage (gray circles) curves are shown. (g) Comparative transconductance $g_m$ plot as a function of gate bias derived at a source-drain voltage of 0.2 V. Gray lines are from the Si/MoS$_2$ FET, while the black line from MoS$_2$ FET. Reproduced with permission from Molle et al., Adv. Mater. Interfaces 3, 1500619 (2016). Copyright 2016 John Wiley and Sons.](image-url)
coverage, the lattice parameter of the Ge sheet still does not match that of the MoS₂ 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 MoS₂ 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) p-bands close to the K point, and (ii) two parabolic σ bands close to Γ point. Unfortunately, the observed large buckling of germanene leads to σ-π 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 [Figs. 5(a)—5(c)] 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 ± 0.1 Å, while the inner one has a larger parameter, of 4.1 ± 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 germanene sheet.
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 $(3 \times 3)R30^\circ$ 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 particles and creation of defects induced by Ar$^+$ bombardment.

Shortly after the publication of Ref. 72, a new interesting analysis based on Raman spectroscopy supports instead the formation of silicene on HOPG as concluded in Ref. 69. As shown in Fig. 6, ex-situ Raman measurements collected on uncapped silicene/HOPG samples feature a peak at 542.5 cm$^{-1}$. Such a Raman peak is different from that of all known Si configurations and therefore recognized as an intrinsic mode of silicene. The reason why silicene's Raman features can be observed even though the sample has been exposed to air, i.e., the reason why silicene is not oxidized, might be the fact that silicene does not form on top of the graphite surface, but between its layers. Indeed, in Ref. 76 Kupchak et al. have recently demonstrated that Si intercalates under the topmost graphitic layer of HOPG. This was proposed after analyzing height profiles taken over bright-contrast areas in the STM images. In the case of silicene patch grown on top of the HOPG substrate, a step-like behavior of the line profile in conjunction with the silicene patch's borders is expected. Instead, the STM images reveal a smoother change in profiles, as the height gradually degrades around the highest spot in the curve. This interpretation probably resolves the doubts aroused in Ref. 72. High magnification STM images show the coexistence of Si cluster and bubbles. Theoretical calculations have shown that the presence of defects in the graphene layer lowers the energy barrier for Si penetration, allowing the Si-C atom exchange mechanism also at room temperature. To better understand the nature of these bubbles, i.e., protrusions with an almost flat top, Raman measurements were performed [Fig. 6(c)]. The spectrum related to the pristine HOPG shows the characteristic D and G Raman modes. After deposition of 1 ML of Si, the Raman spectrum presents a predominant feature at 517 cm$^{-1}$, consistent with sp$^3$ hybridized Si nanoclusters. Additionally, a small feature arises around 538 cm$^{-1}$. This resonance is close to the one previously reported by Castrucci et al. at 542.5 cm$^{-1}$ and recognized as a silicene nanosheet mode on top of HOPG. In contrast with what reported by Castrucci et al., the dramatic changes in D and G modes of HOPG are observed in this study. The D and G resonances indeed widen after the deposition of Si, as they are the result of different contributions. In particular, the G band presents components toward lower wavenumbers, while the D band intensity now dominates over that of the G band. In order to understand these observations, Kupchak et al. performed ab initio calculations. The theoretical model is in agreement with the experimental STM images and the Raman measurements, by considering the insertion of Si atoms arranged as silicene underneath the outmost graphitic layer. By modeling the tensile strain distribution of the C atoms, the percentage varies between 0 and 4% of the bond length in free-standing graphene. These strain values largely affect the vibrations of the atoms and consequently also the Raman spectrum. Indeed, the strain induces a longer lattice parameter and consequentially a shift of the G band toward lower wavenumbers.

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, Bi$_2$Te$_3$, 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) and where the authors studied the growth modes and phase transitions of Sn 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 Sb-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 Sn conduction band states. Nevertheless, the bandgap of 0.44 eV measured for single-layer stanene makes the system stanene/InSb(111) promising for quantum spin 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 Bi$_2$Te$_3$(111). The substrate, either bulk single crystal or thin film, was kept at RT during deposition of Sn via MBE. Figures 7(a)–7(c) 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 ± 0.02 nm. The ARPES measurements [Figs. 7(d)–7(k)] showed that the valence band of Bi$_2$Te$_3$ 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.\textsuperscript{82,83}

Besides the studies on InSb and Bi\textsubscript{2}Te\textsubscript{3} surfaces, stanene has also been successfully fabricated on PbTe(111)/Bi\textsubscript{2}Te\textsubscript{3} substrates via MBE.\textsuperscript{84} The quality of the film was monitored by RHEED and confirmed via STM characterization. Very interestingly, while bulk \textit{\alpha}-tin is not superconductive, this study demonstrates that few-layer stanene is indeed a superconductor.\textsuperscript{85} Figure 8(a) displays a sketch of the structure of the system with trilayer Sn deposited on top of PbTe/ Bi\textsubscript{2}Te\textsubscript{3}/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 ($T_c$) increases with the number of Sn layers [Figs. 8(b) and 8(c)], as already found for other ultrathin film systems.\textsuperscript{86,87} Besides, $T_c$ also depends strongly on the thickness of the PbTe buffer layer [Fig. 8(d)]. While it

FIG. 6. (a) Raman spectroscopy of three different regions of a HOPG sample after deposition of 1 ML of Si from Ref. 81: The black line shows the standard Raman modes of bare graphite, while the red line shows the Raman modes at 510 cm$^{-1}$, relative to silicon nanoclusters and at 520 cm$^{-1}$ relative to bulk silicon. The green line shows the Raman resonance at 520 cm$^{-1}$. (b) Blow-up around 520 cm$^{-1}$. The arrow shows the Raman mode at 542.5 cm$^{-1}$ due to the silicene nanosheets on top of HOPG. (c) Raman spectra of the clean HOPG surface (red curve) and the HOPG surface after 1 ML Si deposition at room temperature (green curve) from Ref. 82. The resonance of 3D silicon is located at 517 cm$^{-1}$ and a new peak is located at 538 cm$^{-1}$, which is ascribed to silicene intercalated under the first graphitic layer. The G and D bands of HOPG are different from the ones of clean HOPG due to strain experienced by the outermost graphitic layer after silicene nanosheet intercalation and the presence of graphite edges. (d) STM image of the HOPG surface after the deposition of 1 ML of Si at room temperature. Lower panel: Height profile of the bubble taken along the yellow line in the above image ($V = 0.3 \text{ V}, I = 0.4 \text{nA}$). (e) Theoretical height of the outermost graphitic layer over the silicene nanostructure. Panels (a) and (b) reproduced with permission from Castrucci et al., Nano Res. 11, 5879 (2018). Copyright 2018 Springer Nature. Panel (c)–(e) reproduced with permission from Kupchak et al., Nanoscale 11, 6145 (2019). Copyright 2019 Royal Society of Chemistry.
FIG. 7. (a)–(c) Model of the atomic structure of 2D stanene on the Bi $_2$Te$_3$ (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 Bi $_2$Te$_3$ (111) (d) and stanene on Bi $_2$Te$_3$ (e) along the K–C–K direction. The orange dashed lines define the bulk band dispersions of Bi $_2$Te$_3$. The blue dotted lines define the valence bands of stanene. “SS” marks the surface state and “CB” marks the conduction band of Bi $_2$Te$_3$, 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 Bi $_2$Te$_3$. (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 Bi $_2$Te$_3$ (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 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 $k_z$.

This remarkable study hence opens to the possibility of integration of topological insulator and superconductor in the same material owing to the delicate dependence of $T_c$ and $N_{\text{Sn}}$.

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 $10^6$ cm$^2$/Vs$^{-1}$ 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. CaF₂

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 and for fabrication of ionic superconducting materials. Among the diverse industrial applications, CaF₂ is especially important in the production of hydrofluoric acid (HF), because fluorite, i.e., the mineral form of CaF₂, is the most important source in this process. In the production of HF, fluorite needs to be separated from the surrounding minerals through a flotation 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 CaF₂ surface. It is expected, however, that CaF₂ could also be a suitable substrate for the growth of silicene. Indeed, because of its electrostatic properties, the cleaved CaF₂(111) surface terminates with a F⁻ layer, with the F⁻ ions arranged in a triangular pattern with spacing of 3.88 Å. This provides a lattice mismatch of only 0.3% with silicon. 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 CaF₂(111) surface inert and a good candidate as a substrate for van der Waals epitaxy of ad-layers.

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. LaAlO₃

Oxide lanthanum aluminate, LaAlO₃ (LAO), is a notable example. It has a high value of dielectric constant (ε = 24), is thermodynamically stable, and hence does not intermix with, for instance, silicon. 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° 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. 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 500 °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 adlayer 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.
mined its optical conductivity \( r \) through transmittance \( T(\omega) \) knowing the refraction index of the substrate and measuring the optical properties of the deposited Si indeed grows in a 2D fashion. Although in the early around 3 eV up to the ultraviolet range. The same features are 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 \textit{ab initio} calculations for I and II interband transitions in free-standing silicene.\(^{108}\) 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,\(^ {52}\) 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)].\(^ {105}\) Hence, the absence of a peak related to silicene, which should be at higher wavelengths, around 540 cm\(^{-1}\),\(^{75,76}\) might in fact cast doubt on the successful synthesis of 2D silicene on Al\(_2\)O\(_3\)(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 \textit{in situ} “noncontact” atomic force microscopy (on uncapped samples) or a surface-sensitive diffraction technique, is highly desired.

2. Al\(_2\)O\(_3\)(0001)

A very recent work reports on the optical conductivity of ultrathin Si nanosheets grown on Al\(_2\)O\(_3\)(0001).\(^ {106}\) 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.\(^ {107}\) Furthermore, theoretical calculations show that silicene on Al\(_2\)O\(_3\)(0001) has a low-buckled structure.\(^ {105}\) 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 \textit{in situ} XPS experiments, whereas the thickness was measured by \textit{ex-situ} AFM measurements after the samples had been capped with a 5 nm thick layer of amorphous Al\(_2\)O\(_3\) in order to prevent air-induced oxidation [Fig. 11(a)]. By knowing the refraction index of the substrate and measuring the optical transmittance \( T(\omega) \) of the samples, the authors eventually determined its optical conductivity \( \sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) \) 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) \( \sigma_1(\omega) \) 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 \textit{ab initio} calculations for I and II interband transitions in free-standing silicene.\(^ {108}\) 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,\(^ {52}\) the observation of Dirac-like optical conductivity might

D. Epitaxial graphene/SiC

As the passivation of SiC surfaces due to the epitaxial growth of graphene has been intensively studied,\(^ {111,112}\) and the Dirac cone feature of silicene and germanene on graphene surface is predicted to be maintained,\(^ {113}\) the G/SiC system may also be an adequate substrate to grow group-IV X-enes. This possibility has been theoretically studied by Matsusalem and coworkers,\(^ {116}\) 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(f)–12(h)]. 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.

CaGe₂, instead of a puckered Si layer intercalated by Ca layers (Fig. 13), shows 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, 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...
effectively protected from degradation in air, as Ref. 76 reports for the could actually represent an interesting opportunity worth investigating. Indeed, being formed under a coating layer, the X-enes could be effectively protected from degradation in air, as Ref. 76 reports for the case of silicene intercalated under the topmost graphitic layer of HOPG. This growth process somewhat recalls the migration-enhanced encapsulated growth technique that allowed stabilizing 2D GaN under a graphene layer.123

Another insulating substrate that we have discussed is calcium difluoride. 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. 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.

Finally, we have also presented an alternative route to epitaxy on solid surfaces. It consists instead of chemical modification of X-ene-based composites, and we have reported examples of synthesis of silicene and germanene.

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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