

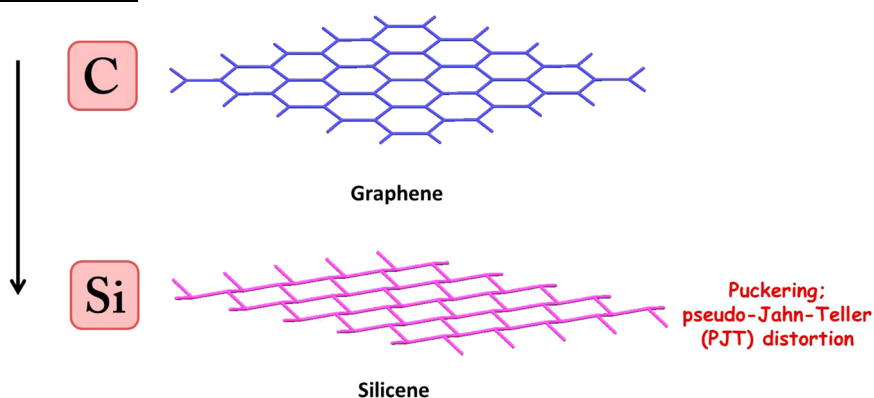
Structures and Chemical Properties of Silicene: Unlike Graphene

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CONSPECTUS



The discovery of graphene and its remarkable and exotic properties have aroused interest in other elements and molecules that form 2D atomic layers, such as metal chalcogenides, transition metal oxides, boron nitride, silicon, and germanium. Silicene and germanene, the Si and Ge counterparts of graphene, have interesting fundamental physical properties with potential applications in technology. For example, researchers expect that silicene will be relatively easy to incorporate within existing silicon-based electronics.

In this Account, we summarize the challenges and progress in the field of silicene research. Theoretical calculations have predicted that silicene possesses graphene-like properties such as massless Dirac fermions that carry charge and the quantum spin Hall effect. Researchers are actively exploring the physical and chemical properties of silicene and tailoring it for wide variety of applications.

The symmetric buckling in each of the six-membered rings of silicene differentiates it from graphene and imparts a variety of interesting properties with potential technological applications. The pseudo-Jahn–Teller (PJT) distortion breaks the symmetry and leads to the buckling in silicenes. In graphene, the two sublattice structures are equivalent, which does not allow for the opening of the band gap by an external electric field. However, in silicene where the neighboring Si atoms are displaced alternatively perpendicular to the plane, the intrinsic buckling permits a band gap opening in silicene in the presence of external electric field. Silicene's stronger spin orbit coupling than graphene has far reaching applications in spintronic devices. Because silicon prefers sp^3 hybridization over sp^2 , hydrogenation is much easier in silicene. The hydrogenation of silicene to form silicane opens the band gap and increases the puckering angle. Lithiation can suppress the pseudo-Jahn–Teller distortion in silicene and hence can flatten silicene's structure while opening the band gap.

So far, chemists have not successfully synthesized and characterized a free-standing silicene. But recently chemists have successfully produced silicene sheets and nanoribbons over various substrates such as silver, diboride thin films, and iridium. The supporting substrate critically controls the electronic properties of silicene, and the match of the appropriate support and its use is critical in applications of silicene.

I. Introduction

The discovery of graphene, a single layer of graphite, in 2004 by Novoselov, Geim, and co-workers can be considered as a breakthrough in the research and development of stable, truly 2D material systems.¹ This prototype 2D material

with its unusual electronic and mechanical properties has attracted the scientific community as a material of basic scientific research as well as potential applications. However, the challenges, like optimizing cost-effective manufacturing processes for single layer graphene, absence of a band gap,

integration of graphene into Si based technology, etc., have stimulated interest in the investigation of atomic layers of several other materials with new properties and novel applications. The various possibilities for creating and understanding the underlying physics of new 2D crystals with novel, exotic, and unanticipated properties open up a fertile area of research and can lead to exciting technological applications in next generation nanoelectronic devices.²

The representative examples for 2D materials other than graphene for which the preliminary work has already come out are monolayers of BN, MoS₂, NbSe₂, Bi₂Sr₂CaCu₂O_x, and Si.³ Silicene, the Si counterpart of graphene with its added advantage of easy integration in the existing Si based electronics industry has progressed from theoretical prediction to experimental observations recently. Theoretical calculations predict a buckled honeycomb structure for silicene. This buckled structure makes it strikingly different from graphene despite the similar electronic properties.⁴ The intrinsic buckling in silicene provides the opportunities for manipulating the dispersion of electrons and opening up the band gap. Though the experimental investigation of silicene is still in its infancy, the recent reports of formation of buckled silicene over silver substrate, diboride thin film, and iridium substrate are encouraging to researchers.^{5–8} This review attempts to summarize the major progress, findings, and challenges in the field of silicene.

II. Unsaturated Compounds of Silicon

The ease with which carbon forms multiple bonds with itself and other elements makes it special and adds to the diversity of organic chemistry. Compared with carbon, the succeeding element in the family, silicon, is a little reluctant to form unsaturated compounds. Though the unsaturated silicon chemistry is not as rich as that of carbon, silicon does form multiply bonded compounds. Brook et al. isolated a double bonded silicon compound (silaethene) in the year 1981.⁹ West and co-workers in the same year synthesized stable tetramesityldisilene containing a Si–Si double bond, opening a new chapter in silicon chemistry.¹⁰ Since then, the field has progressed remarkably with more examples of low coordinate silicon compounds like disilenes, trisilaallenes, and tetrasilabutadienes and also extensive theoretical calculations on the nature of bonding in these compounds.¹¹ The synthesis of a stable disilyne containing a Si–Si triple bond, a molybdenum–silylydyne complex with a Mo–Si triple bond, cyclic disilenes, etc., are significant achievements in the area organosilicon chemistry.^{12,13}

A landmark achievement in this field promising to the researchers working on silicene is the recent report of

synthesis of an isomer of hexasilabenzene by Abersfelder et al.¹⁴ Si₆H₆ being the smallest repeating unit of silicene and a Si analogue of benzene has been of great interest in the silicene community and a subject of extensive theoretical investigations. Though the *ab initio* calculations by Nagase and colleagues at HF level predicted that planar *D*_{6h} Si₆H₆ is a minimum energy structure, they proposed a chair like *D*_{3d} structure for Si₆H₆ based on calculations that include electron correlation.¹⁵ Further studies by various research groups using DFT and higher level calculations where electron correlation is taken into account validated the instability of *D*_{6h} Si₆H₆ and stability of chair-like *D*_{3d} structure over the *D*_{6h} geometry.^{16,17} The instability of *D*_{6h} Si₆H₆ is attributed to pseudo-Jahn–Teller effect, which will be discussed in detail later in this Account.^{16,17} Abersfelder et al. synthesized the dark green crystals of an isomer of Si₆H₆ by the reduction of unsymmetrically substituted trichlorocyclotrisilane. It has a chair-like conformation in accordance with the theoretical results.^{16,17} Authors propose the term dismutational aromaticity to explain the bonding pattern of this molecule.^{12,14}

III. Effect of Substitution of C by Si in Benzene

The structure and aromaticity of silabenzenes and Si₆H₆ have been investigated extensively.^{16,17} The calculations of Baldrige et al. on the silabenzene series suggest that the ionic contribution to the bonding is significant in stabilizing these systems.¹⁶

In an earlier work from our group, the effect of Si substitution on the planarity of the benzene ring has been investigated. The calculations at B3LYP/6-31+G(d) level revealed that benzene maintains its planarity until two of its carbon atoms are substituted by silicon. With the increase in the number of Si atoms, the planar hexagonal ring starts to pucker. It has been also suggested that silabenzenes form more stable complexes with transition metals than their organic counterpart. Among the full-sandwich complexes of silabenzenes with Cr ((C_nSi_mH₆)₂Cr), the complexes in which Si atoms are adjacent to each other are found to be more stable than the other isomers. Si₆H₆ is puckered in the complex too. The half-sandwich complexes ((C_nSi_mH₆)Cr(CO)₃) with enhanced metal to ligand backbonding due to the carbonyl groups are found to be more stable than full-sandwich complexes for the same degree of substitution. Representative examples for full-sandwich and half-sandwich complexes and the variation in the binding energies (in kcal/mol) with sequential substitution of C by Si in full- and half-sandwich complexes is shown in Figure 1.²⁰

In a recent theoretical work, Ivanov and Boldyrev have systematically investigated the structural transition from

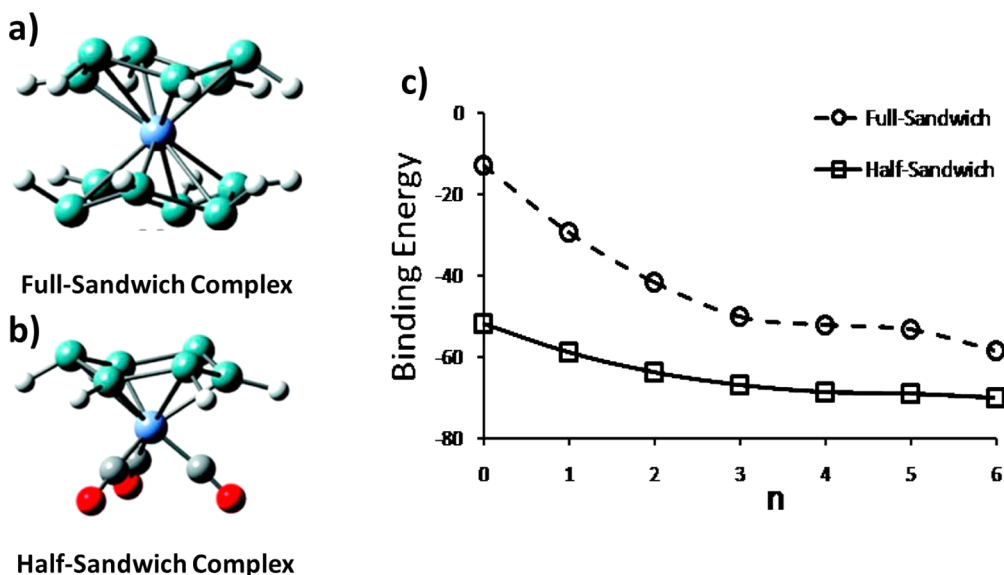


FIGURE 1. Minimum energy structure of (a) full-sandwich complex ($\text{Si}_6\text{H}_6)_2\text{Cr}$ and (b) half-sandwich complex $\text{Si}_6\text{H}_6\text{CrCO}_3$ and (c) the variation in the binding energies (in kcal/mol) with sequential substitution of C by Si in full- and half-sandwich complexes. Reproduced with permission from ref 20. Copyright 2010 American Chemical Society.

nonplanar three-dimensional structures to planar benzene-like structures in $\text{Si}_{6-n}\text{C}_n\text{H}_6$ ($n = 0-6$) series. Figure 2 shows the representative optimized isomers of each species in the $\text{Si}_{6-n}\text{C}_n\text{H}_6$ ($n = 0-6$) series and the relative energies of these with respect to global minimum structure at CCSD(T)/CBS//B3LYP/6-311++G** level of theory. The most stable isomer of Si_6H_6 is nonplanar with C_{2v} symmetry (I.1 in Figure 2). They found a planar global minimum structure only for SiC_5H_6 ($n = 5$ in the $\text{Si}_{6-n}\text{C}_n\text{H}_6$ ($n = 0-6$) series).¹⁸

IV. Theoretical Investigations on Nanostructures of Silicene

The significance of aromaticity and the versatile applications of aromatic compounds urged researchers to explore it beyond the realm of organic chemistry. Though carbon exists in many allotropic forms, only the diamond like structure of Si is known to exist in nature, and its small clusters have compact 3D structure. The first principle total energy calculations by Takeda and Shiraishi in 1994 predicted a corrugated aromatic stage for Si and Ge, unlike C. The band structure is found to be similar to that of graphene with Dirac cone and linear electronic dispersion around the K point.²¹ Using the first-principles tight-binding-like total-energy method, Fuentes-Cabrera and co-workers investigated the stability of the aromatic phase of two-dimensional monolayers of BN, C, SiC, Si, and GaAs. They found that BN, C, and SiC form the flat aromatic phase and Si and GaAs corrugate resulting in a structure with D_{3d} and C_{3v} symmetry, respectively, and the energy needed to flatten a corrugate structure is much less.²²

In a comparative study between the hypothetical Si nanotube and C nanotube, Fagan et al. have shown that the cohesive energies for Si nanotubes are only 82% of the cohesive energy for the Si bulk in the diamond structure whereas C nanotubes have about 99% of bulk cohesive energy, which explains the difficulty in synthesizing it.⁴ The calculations by Zhang et al. have validated the viability of puckered Si nanotubes if the dangling bonds are properly terminated.²³ By using first-principles pseudopotential plane wave method and finite temperature *ab initio* molecular dynamics calculations, Durgun et al. have shown that (*n*,0) zigzag and (*n*,*n*) armchair nanotubes of silicon having $n \geq 6$ are stable.²⁴

Chahngirov et al. have done extensive first principle calculations to understand the structure and properties of silicene and germanene. They considered the planar (PL), low-buckled (LB), and high-buckled (HB) honeycomb configuration in their study. The phonon mode analysis revealed that the PL honeycomb structure of both Si and Ge have an imaginary frequency in the Brillouin zone. The HB structure showed a tendency to cluster during the structure optimization on a 2×2 supercell. The variation of binding energy as a function of lattice constant for PL, LB, and HB honeycomb silicene and germanene and their respective band structure is shown in Figure 3.²⁵ The phonon analysis of Ding and Ni is also in agreement with the previous results with no soft modes for the buckled silicene.⁴

The reactivity of the silicene surface has been investigated by Houssa and colleagues. The weak π -bonds in silicene have made its surface very reactive, and hence it

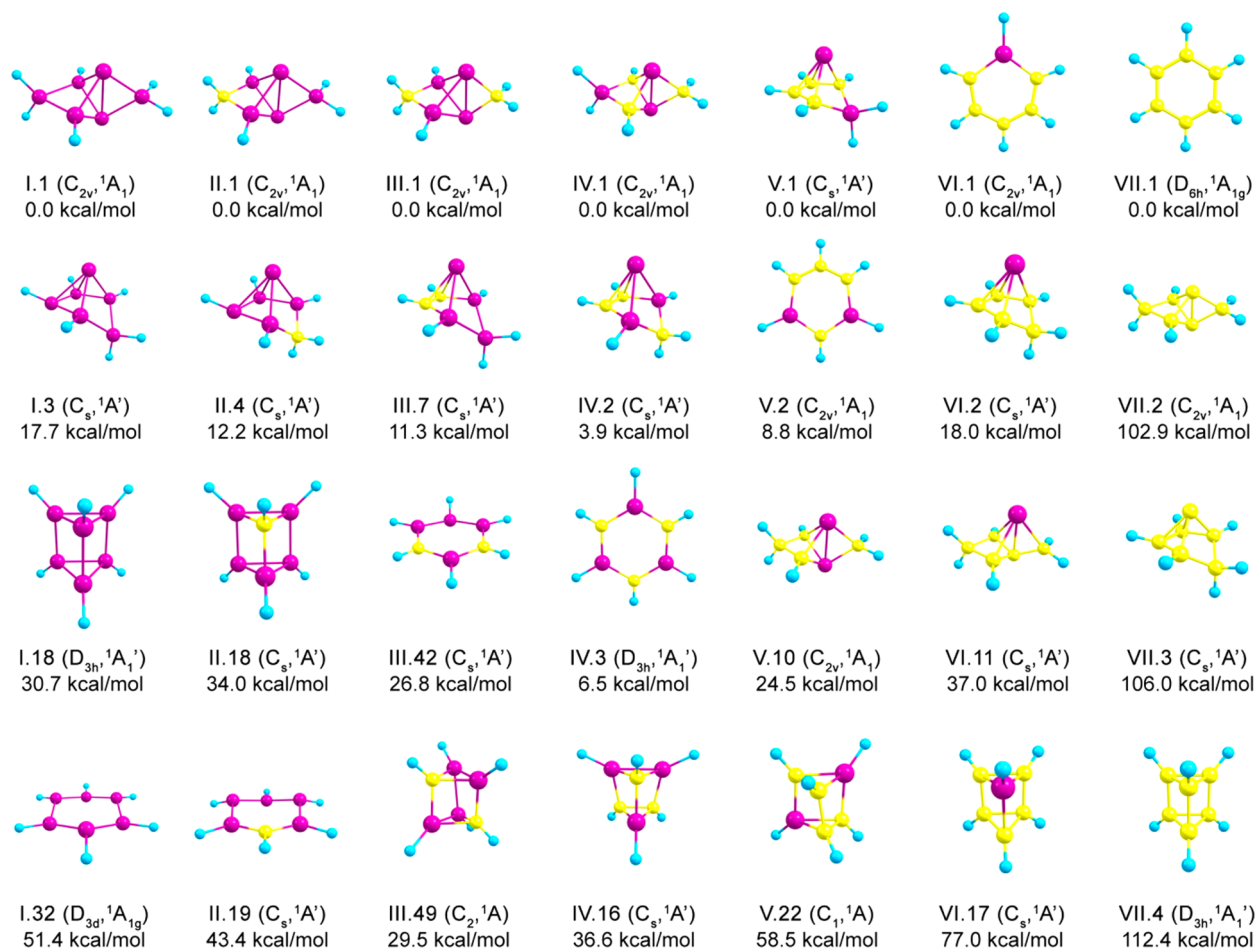


FIGURE 2. Representative optimized isomers of each species in the $Si_{6-n}C_nH_6$ ($n = 0-6$) series, ZPE (B3LYP/6-311++G**) corrected relative energies (CCSD(T)/CBS//B3LYP/6-311++G**). The yellow, violet, and blue spheres represent carbon, silicon, and hydrogen atoms, respectively. Reproduced with permission from ref 18. Copyright 2012 American Chemical Society.

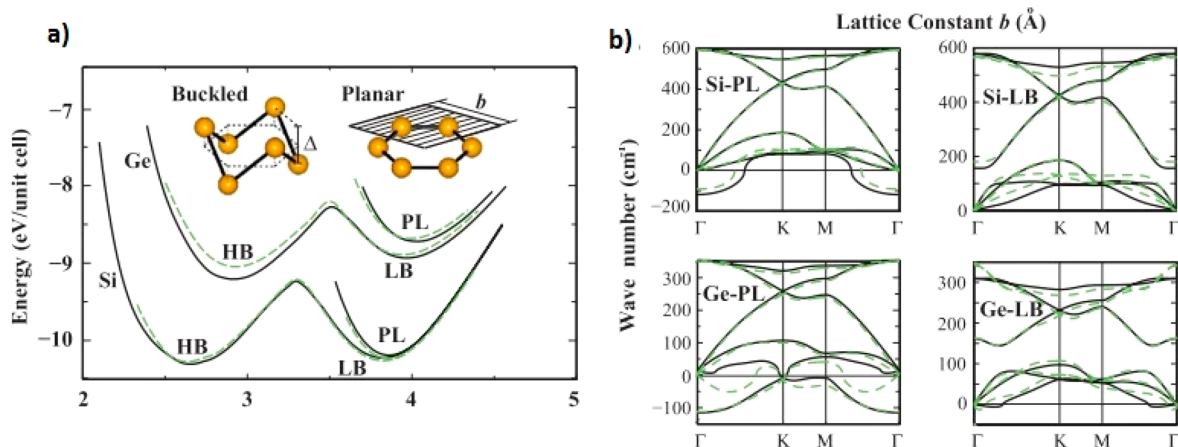


FIGURE 3. (a) The variation of binding energy as a function of lattice constant for PL, LB, and HB honeycomb silicene and germanene and (b) the band structures of PL and LB silicene and germanene. Reproduced with permission from ref 25. Copyright 2009 American Physical Society.

can readily adsorb chemical species forming chemical bonds with them.⁴ By the modification of the silicene surface with transition metals, Dzade et al. have designed new systems

with interesting properties. The puckered silicene becomes planar in the presence of Ti and Ta. $NbSi_2$ possesses the largest mechanical stiffness, and $CrSi_2$ turns into a two-dimensional

piezomagnet.²⁶ It has been also found that doping has a pronounced effect on the lattice structure and electronic properties of silicene. The lattice parameter and buckling in silicene is found to be strongly influenced by the carrier concentration.⁴

We have done extensive DFT calculations on 2D silicene clusters for a detailed understanding of the structure and electronic properties and potential applications. We considered the smallest silicene cluster Si_6H_6 to a 25 ring cluster, $\text{Si}_{70}\text{H}_{22}$ with valency of terminal Si atoms satisfied by H atoms. The C_3 puckering distortion is found to be preserved with varying size of silicene clusters. Though the energy gain upon puckering is only 1.64 kcal/mol for Si_6H_6 at B3PW91/TZVP level, it is noted to be significant for large silicene sheets. All these clusters are found to have favorable binding energies. With increase in the size of silicene fragments, the HOMO–LUMO gap decreases with a corresponding increase in its polarizability. The decrease in the reorganization energy values of the silicene fragment with increase in its size is predicted to be interesting for applications in electronics.

We have also investigated the hydrogenation of all these silicene fragments and found that the reaction is more exothermic than that with the corresponding carbon analogues. The preference of Si to be in an sp^3 environment makes hydrogenation much easier in silicene. The puckering angle of silicene increases during hydrogenation. The weight percent of hydrogen for various silicenes ranges from 6.6% to 4.5%. More interesting is the opening of band gap of these clusters on saturation with hydrogen, converting them into wide gap semiconductors. The calculations on the dimers of these clusters showed that a covalent Si–Si bond stabilizes the interlayer bonding unlike the π -stacking interactions in the carbon world and hence explains the nonexistence of a graphitic form for Si.²⁷

Having an electronic structure similar to graphene, silicene is expected to possess all the remarkable and fascinating properties of graphene. Liu and co-workers predicted a detectable quantum spin Hall effect in silicene with a spin orbit band gap of 1.55 meV in the accessible temperature regime, and also the gap can be increased by pressure strain.²⁸ The band gap and effective masses of electrons and holes in silicene are predicted to increase linearly with the electric field strength.²⁹ Osborn et al. with the aid of DFT calculations and MD simulations have described tuning the band of silicene with appropriate hydrogenation ratio to obtain silicene of desired characteristics.³⁰ Halogen functionalization and lithiation has also been shown to induce a band gap in silicene.^{31,32} The weak SiH/π interaction between silicene and its hydrogenated phase has also been proven

to be strong enough to open a band gap in silicene without any effect on its carrier mobility.³³ Recently Drummond et al. have also reported the stability and electronic structure of silicene in an external electric field perpendicular to its plane. At low field, silicene is found to undergo a transition between a topological and a simple band insulator, whereas at high field, it becomes a semimetal.³⁴ Motohiko Ezawa has predicted the coexistence of topological insulating, band insulating, and metallic regions in the same silicene sheet by the application of an inhomogeneous electric field.³⁵ It has been also proposed that application of electric field can induce a quantum spin Hall effect in silicene even if it has a weak spin orbit coupling.³⁶ This weak spin orbit interaction makes silicene an ideal candidate to explore the spin and valley physics. Tahir and Schwingenschlogl have established valley polarized quantum Hall effect and topological insulator phase transitions in silicene.³⁷

V. Origin of Buckling Distortions in Silicene

Contrary to graphene, free-standing silicene is predicted to have a buckled structure. The buckling in silicene is significant and promising since it provides a way to tune silicene's band gap by the application of external electric field without any chemical modification. The puckering angle for the minimum energy structure of D_{3d} Si_6H_6 and $\text{Si}_{70}\text{H}_{22}$ silicene clusters at the B3PW91/TZVP level of theory is 33.7° and 35.6°, respectively. For a silicene sheet optimized using periodic calculations, the puckering angle was about 36.8°. Hence the puckering in silicene is conserved and is symmetric for a large silicene sheet. The consistency of the buckling angle from the lowest silicene cluster to the extended silicene sheet is shown in Figure 4.

We have recently performed a detailed analysis of puckering distortion in silicene using DFT calculation. In harmony with the previous results, D_{6h} benzene-like planar structure of Si_6H_6 is a first order saddle point. As discussed before the instability of D_{6h} Si_6H_6 is caused by pseudo-Jahn–Teller distortion, which is the coupling between nondegenerate electronic states of proper symmetry leading to nonsymmetric vibrations. The strong vibronic coupling of unoccupied molecular orbitals (UMOs) and occupied molecular orbitals (OMOs) orbitals that are sufficiently close in energy causes distortion in high symmetry configurations.³⁸ The instability of high symmetry geometries of various molecular systems due to PJT effect has been studied and methods have been proposed to suppress it.^{39,40}

The vibronic coupling of HOMO (e_{1g}) and LUMO + 2 (e_{2g}) results in the instability along the b_{2g} mode in the case of

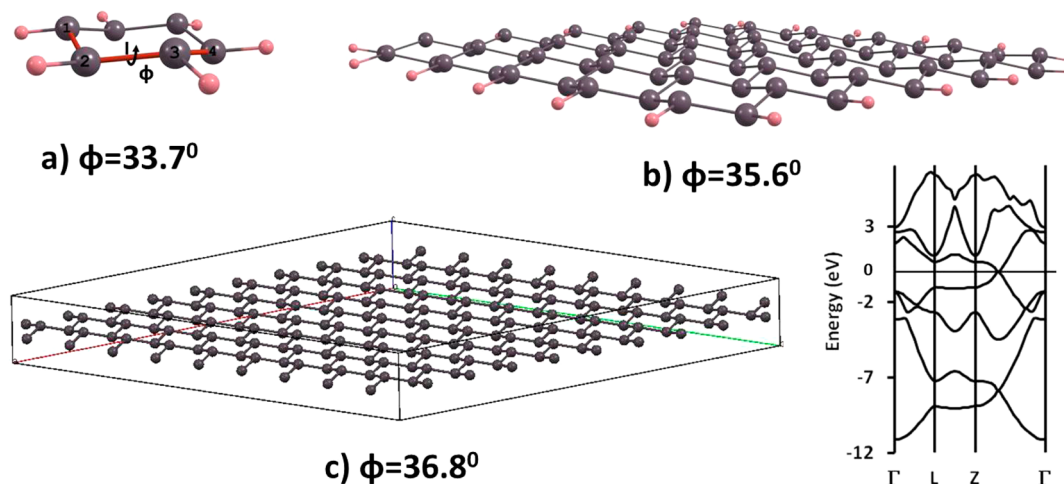


FIGURE 4. Puckering angle ϕ for (a) Si_6H_6 , (b) $\text{Si}_{70}\text{H}_{22}$, and (c) a silicene sheet with its band structure. Reproduced with permission from ref 17. Copyright 2012 American Chemical Society.

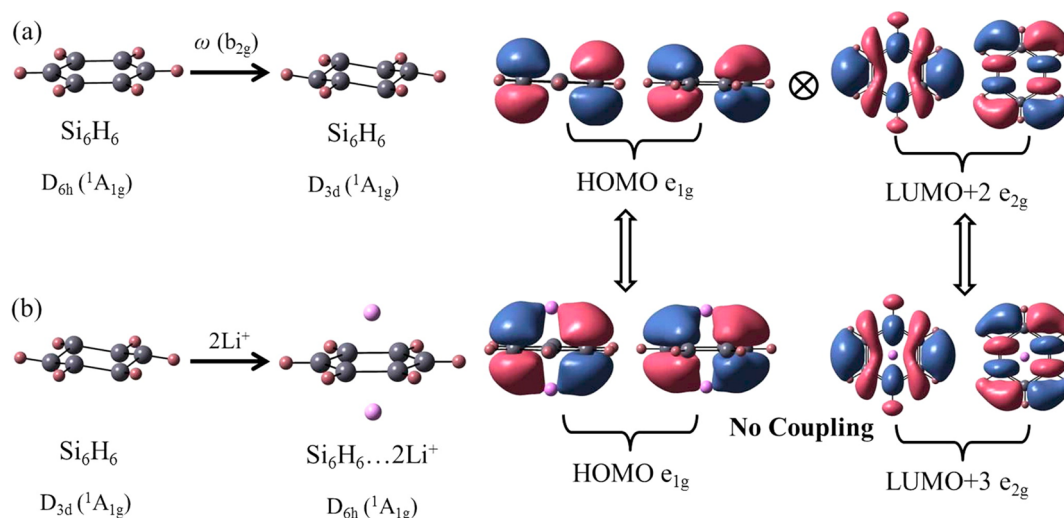


FIGURE 5. (a) Onset of puckering from $D_{6h} \rightarrow D_{3d}$ via b_{2g} distortion in Si_6H_6 . The corresponding OMO and UMO involved in this vibronic mixing associated PJT are also shown. (b) Suppression of distortion in $\text{Si}_6\text{H}_6 \cdots 2\text{Li}^+$. The 1:1 correspondence between the OMO and UMO is shown with respect to the undoped Si_6H_6 . Reproduced with permission from ref 17. Copyright 2012 American Chemical Society.

D_{6h} Si_6H_6 . The product of symmetries of HOMO and LUMO + 2 contains the symmetry of the unstable mode (b_{2g}). The energy gap between this OMO–UMO pair is 6.83 eV at M05-2X/6-31+G(d,p) level of theory¹⁷ and 9.78 eV at HF/cc-pVTZ//B3LYP/6-311++G** level.¹⁸ The PJT effect can be suppressed by increasing the energy gap between the interacting OMO–UMO pair, as it was shown by Sergeeva and Boldyrev.¹⁹ The puckered Si_6 ring of Si_6H_6 becomes planar in the presence of Li^+ ion to form a stable C_{6v} $\text{Si}_6\text{H}_6 \cdots \text{Li}^+$ complex with binding energy -45.3 kcal/mol as shown in Figure 5.

We have also done σ – π separation analyses for Si_6H_6 and benzene with respect to the puckering angle. While the σ -backbone gets stabilized, the π -backbone is destabilized

due to buckling for both of them. For benzene, the σ energy gain on puckering is negligible compared with destabilization associated with π energy. In contrast, the σ energy is stabilizing over the π energy by about 1.3 kcal/mol on puckering in Si_6H_6 . The puckering distortion allows σ – π mixing and Si_6H_6 gains substantial stability as revealed by NBO analysis. The adsorption of Li^+ ion over the surface of Si_6H_6 reverses the situation, and the π energy overwhelms the σ energy, thus flattening the puckered Si_6H_6 . Our periodic calculations on an extended silicene sheet have also revealed that presence of Li^+ suppresses the PJT effect and hence flattens the puckered silicene with the opening of the band gap as shown in Figure 6.¹⁷

We then explored the intrinsic buckling in various silicene fragments by capturing its signature in Raman spectra and

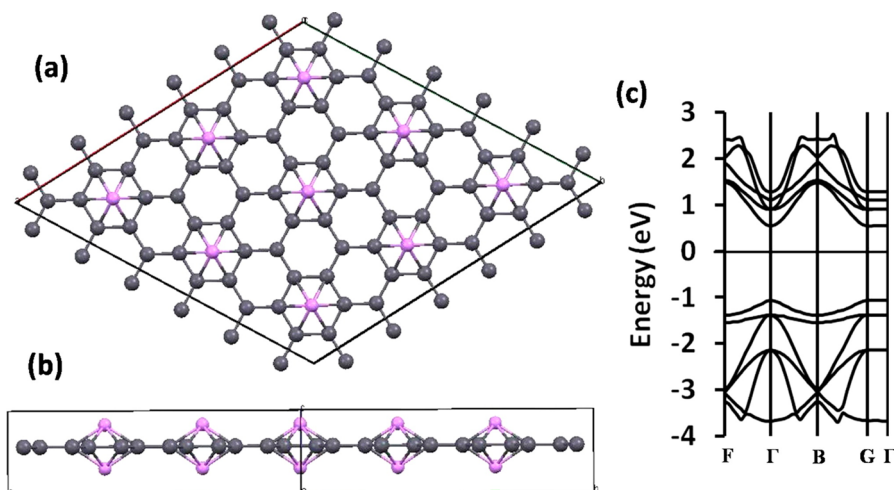


FIGURE 6. (a) Transverse view and (b) lateral view of optimized Li^+ decorated silicene sheet and (c) its band structure (at the GGA/PBE level with plane wave basis). Reproduced with permission from ref 17. Copyright 2012 American Chemical Society.

enhancing the intensity of this particular mode using metal clusters. The calculated Raman buckling frequencies of these clusters in the range $100\text{--}200\text{ cm}^{-1}$ and the buckling mode is IR inactive as expected. Tip enhanced Raman spectroscopy with its externally tunable hot spot STM tip is an efficient technique to enhance the intensity of Raman signals and investigate the surface properties. We model the STM tip using the clusters of Ag and Au and found that in their presence the intensity of Raman peaks get enhanced with a red shift in the buckling frequency. We considered the M_2 , M_4 , and M_{20} clusters of Ag and Au, and Figure 7 shows the adsorption of these clusters over the silicene clusters under study. The enhancement is found to increase with increase in the size of the metal cluster, and in the case of Ag cluster, the enhancement increases from 3 times to 17 times as the size of the cluster increases from 2 to 20.

The substantial binding energy for silicene and metal clusters points out that the metal clusters are chemisorbed over the silicene surface leading to chemical enhancement of the Raman peaks. NBO analysis and ESP maps further confirm the chemisorption of metal clusters over the silicene surface. The presence of metal clusters over the silicene surface also leads to the appearance of new Raman peaks and also the disappearance of some Raman peaks of bare silicene. We suggest that a properly designed metal cluster can be used as the tip of STM to capture the buckling distortions in silicene.⁴⁰

VI. Experimental Investigations on Silicene

The experimental synthesis of one atom thick silicene sheets is challenging despite the synthesis of nanotubes

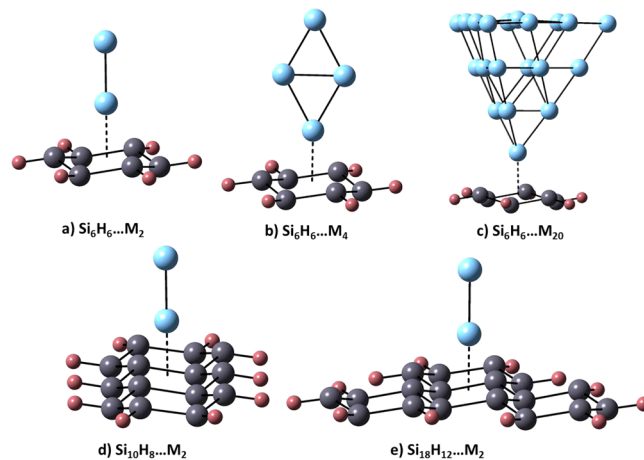


FIGURE 7. Silicene fragments with metal clusters adsorbed over the surface ($M = \text{Au, Ag}$). Reproduced with permission from ref 40. Copyright 2013 Royal Society of Chemistry.

and nanostructures of Si by various research groups.⁴ Since the interlayer Si–Si bond in bulk Si is covalent in nature and the graphitic form of Si is not known to exist, one cannot use exfoliation techniques to extract silicene as in the case of graphene. The STM analysis of the self-aligned nanoribbons on the Ag(110) surface by Aufray et al. revealed that it possesses a honeycomb graphene-like atomic structure. De Padova and co-workers could identify silicon nanoribbons as a 1D honeycomb material on Ag(110) surface.⁴¹

In 2012, Vogt et al. provided experimental evidence for monolayer large area silicene sheets on a Ag(111) surface. By angular-resolved photoelectron spectroscopy (ARPES) studies, they demonstrated a downward dispersing conical branch of the honeycomb Si bands. Based on STM and low-energy electron diffraction (LEED) results together with DFT

calculations the authors conclude that a (4×4) 2D Si adlayer on Ag(111) is a real 2D silicene sheet.⁷ Lin and co-workers observed 4×4 and $\sqrt{13} \times \sqrt{13}$ R13.9° superstructures with honeycomb lattices of Si on a Ag(111) surface.⁴² Using molecular beam epitaxy experiments and spatially resolved tunneling spectroscopy, Chiappe et al. have explored the thermodynamic phase diagram of Si monolayers grown on Ag(111) and characterized the density of states of Si layers *in situ* for various silicene phases.⁴³ Feng et al. have demonstrated the evolution of different monolayer superstructures of silicon on Ag(111), depending on the silicon coverage and substrate temperature.⁵ Jamgotchian and colleagues could observe (4×4) , $(2\sqrt{3} \times 2\sqrt{3})$ R30° and $(\sqrt{13} \times \sqrt{13})$ R13.9° superstructures of silicene with honeycomb lattice on a Ag(111) surface by varying the temperature of Ag substrate. They have also predicted the possibility of a $(\sqrt{7} \times \sqrt{7})$ R19.1° superstructure for silicene on the Ag(111) surface.⁴⁴ Fleurence et al. have recently reported the presence of buckled epitaxial silicene on the diboride surface. They noticed that the buckling induced by epitaxial strain results in a direct π -electronic band gap at the Γ point contrary to the free-standing silicene.⁶ The electronic structure of a (3×3) silicene phase on Ag(111) surfaces has been investigated extensively in a recent study by Avila et al. using LEED, core level X-ray photoelectron spectroscopy (CLs), and ARPES data. They found a silicene-derived band with a band gap of ~ 0.3 eV at the Γ symmetry point of a (3×3) phase at several Brillouin zones, with a band velocity of $\sim 1.3 \times 10^6$ ms⁻¹. Figure 8 shows the experimental valence band electronic structure of a (3×3) silicene film on (111) Ag surfaces at the Γ point of (3×3) supercell Brillouin zones (SBZ).⁴⁵ Another example for silicene formation on a substrate apart from Ag(111) is the formation of a $(\sqrt{7} \times \sqrt{7})$ superstructure of silicene on the Ir(111) surface as reported by Meng et al. The different silicon atoms are found to be positioned in different chemical environments with respect to the substrate revealing the buckling in silicene.⁸

Inspired from the experimental results, numerous theoretical investigations have been reported exploring the structural evolution of silicene on various substrate. Gao and Zhao have modeled the initial phase of the growth of silicene on a substrate by investigating the structures and stabilities of Si_N clusters on a Ag(111) surface. Silicene over the substrate is found to be less buckled than free-standing silicene.⁴⁶ The first principle calculations by Kaltsas and Tsetseris shows that $\sqrt{3} \times \sqrt{3}$ reconstructed silicene geometry over group-IV semiconductors is more stable than the honeycomb lattice.⁴⁷

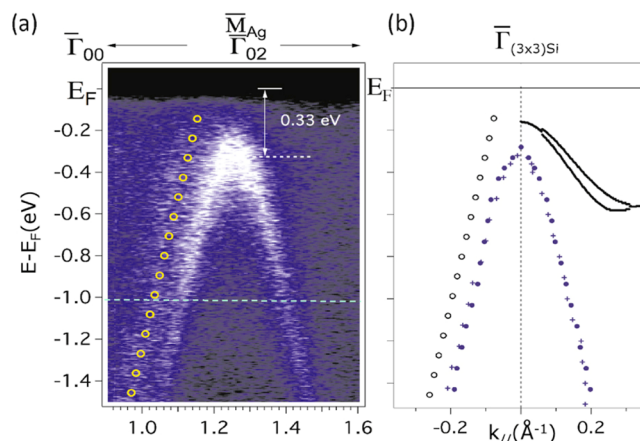


FIGURE 8. (a) ARPES spectrum measured at the Γ_{02} point of the (3×3) lattice with empty yellow dots denoting the unaffected “sp” silver substrate band. (b) A discrete representation of the ARPES spectra measured at the Γ_{00} points (blue dots) and at the Γ_{02} points (blue crosses) of the (3×3) lattice. Reproduced with permission from ref 45. Copyright 2013 IOP Publishing.

Lin et al. have found that the electronic properties of silicene vary drastically when it is adsorbed on a Ag(111) surface for it no longer exhibits Dirac fermion characteristics due to substrate-induced symmetry breaking. The band structure has also been modified due the interaction between Si and the Ag surface.⁴⁸ However, the first principle calculation by Cahangirov et al. on (3×3) reconstructed silicene on (4×4) Ag(111) demonstrated that new states emerge due to the strong hybridization between silicene and Ag. They could differentiate these new states from the states originating from the Dirac cone of a free-standing silicene or from the sp bands of bulk Ag and assign their contribution toward the linearly dispersing band observed in experimental photoemission spectra.⁴⁹ The first principle simulations by Huang and co-workers found that the band structure of silicene is sensitive toward the buckling in silicene. The silicene structures proposed by recent experiments were calculated to have finite band gap, unlike the planar or low buckled silicene.⁵⁰ The calculations by Liu et al. suggests that insulating substrates like hexagonal boron nitride, hydrogenated Si terminated SiC, etc. can preserve the Dirac cone characteristic of free-standing silicene even after its adsorption over the substrate.⁵¹

VII. Conclusions

The research in the field of 2D monolayer silicon has advanced drastically with the experimental accomplishment of silicene over various substrates. The pseudo-Jahn–Teller distortion, the only source of instability of high symmetry geometries of molecular systems, is significant for

low dimensional systems also. The intrinsic buckling in the 2D silicene sheet is attributed to the pseudo-Jahn–Teller effect. Though free-standing silicene has not yet been synthesized, the experimental and theoretical results are promising. Theoretical calculations have shown that substrate has a pronounced effect on the electronic properties of silicene. Hence the choice of substrate is very essential for the effective use of the predicted remarkable properties of silicene. The intrinsic buckling in silicene is interesting because it enables one to tune the band gap of silicene using an external electric field without any chemical modification. The tunable quantum Hall effect, valley quantum Hall effect, and topological insulating states using an external electric field makes it an ideal candidate for spintronic devices.

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BIOGRAPHICAL INFORMATION

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FOOTNOTES

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