Stable planar single-layer hexagonal silicene under tensile strain and its anomalous Poisson’s ratio

Baolin Wang, Jiangtao Wu, Xiaokun Gu, Hanqing Yin, Yujie Wei, Ronggui Yang, and Mildred Dresselhaus

View online: http://dx.doi.org/10.1063/1.4866415
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/104/8?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Internal-strain effect on the valence band of strained silicon and its correlation with the bond angles

Origin of anomalous strain effects on the molecular adsorption on boron-doped graphene
J. Chem. Phys. 139, 044709 (2013); 10.1063/1.4816365

Quantum mechanics based force field for carbon (QMFF-Cx) validated to reproduce the mechanical and thermodynamics properties of graphite

Carbon nanotube films change Poisson’s ratios from negative to positive
Appl. Phys. Lett. 97, 061909 (2010); 10.1063/1.3479393

Computational Protocols for Viscoelastic Material Property Characterizations without the Use of Poisson’s Ratios
Stable planar single-layer hexagonal silicene under tensile strain and its anomalous Poisson’s ratio

Baolin Wang,1 Jiangtao Wu,1 Xiaokun Gu,2 Hanqing Yin,1 Yujie Wei,1,a) Ronggui Yang,2,a) and Mildred Dresselhaus3

1LNM, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
2Department of Mechanical Engineering, University of Colorado, Boulder, Colorado 80309, USA
3Departments of Physics and Department of Electrical Engineering and Computer Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

(Received 17 November 2013; accepted 7 February 2014; published online 24 February 2014)

Here, we report the structural and mechanical properties of several two-dimensional (2-D) materials by using first-principles density functional theory calculations. We find that the buckled single-layer silicene could transit to planar hexagonal silicene at a critical tensile strain of 0.20. Phonon dispersion analysis suggests that the planar hexagonal silicene under tension is stable. The Poisson’s ratio of silicene and MoS2 shows strong anisotropy: it increases while stretched in the zigzag direction, but decreases when strained in the armchair direction. When stretched in the zigzag direction, the Poisson’s ratio of silicene could reach 0.62.

With the growing interest in the integration of 2-D materials,1–3 such as graphene and MoS2, with extraordinary properties for electronic applications, researchers find that the mechanical properties of such 2-D materials and their heterostructures are critical for their technical applications.4–6 Many typical single-layer 2-D materials, for example, graphene, hexagonal boron-nitride (h-BN), fluorographene, and MoS2, have been widely investigated. Although these 2-D materials all have a honeycomb arrangement, their properties can be very different. For example, h-BN is electrical insulating with a large band gap both within and across the layers, in contrast to graphene with no band gap and being a semi-metal. Fluorographene is a derivative of graphene and can serve as an insulation layer for graphene electronics with a band gap of about 3 eV.7 Single layer MoS2 is a direct band gap semiconductor with a band gap of 1.8 eV.8 The interest in silicene stems from the great success in silicon technology. As a corollary, we desire to know whether the great success in silicon is reproducible in its 2-D counterpart. Unlike graphene, silicene has a hexagonal atomic arrangement and a buckled configuration.9 Such structure difference calls for an in-depth investigation on whether silicene exhibits different mechanical behavior in contrast to graphene. The latter has been broadly recognized for its super-high strength4 and is regarded to have potential impact for composite materials.10,11 In this work, we perform close examination on the mechanical response of silicene by using first-principles density functional theory (DFT). For comparison, four typical other single layer 2-D materials including graphene, h-BN, fluorographene, and MoS2 are also investigated.

First-principles DFT calculations are performed to study the structural and mechanical properties of the five typical 2-D materials by using the Vienna Ab initio Simulation Package (VASP).12 The projector augmented wave (PAW) pseudopotentials13 and the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional14 are used. The kinetic-energy cut-off for the plane-wave basis set for silicene is 380 eV, and for graphene, h-BN, fluorographene and MoS2 the cutoff is 400 eV. For relaxation of the structures, 31 × 31 × 1 Monkhorst-Pack k-point mesh for graphene, h-BN and silicene, 16 × 16 × 1 mesh for fluorographene and 5 × 3 × 1 mesh for MoS2 are used. To eliminate the interactions between periodic images of single layer samples, a vacuum space of 20 Å was used. Periodic boundary conditions are applied to the in-plane directions in all the calculations conducted here. Here, we make the assumption that the periodic unit cell with several atoms may represent well the mechanical response of large area perfect samples. All structures (graphene, h-BN, fluorographene, MoS2, and silicene) are relaxed using a conjugate gradient (CG) algorithm until the atomic forces are converged to 0.01 eV/Å. The quasi-static displacement-controlled deformation is used by imposing the deformation with a small strain increment (a typical value of 0.01 is used for most calculations). The corresponding stress is obtained from the reaction force induced by the imposed strain divided by the current cross-sectional area (the current sample width times the sample thickness shown in Table I). So it is convenient to covert the stress-strain curves to force (per unit length) versus strain curves if the stress is multiplied by the sample thickness given in Table I. Phonon dispersion is analyzed by using the density functional perturbation theory (DFPT)15 implemented in the Quantum Espresso (QE) Package.16 We used the pseudopotentials Si.pz-hgh.UPF, S.pbe-mt_fhi.UPF, and Mo.pbe-mt_fhi.UPF from QE website. The kinetic energy cutoff was set to be 45 Ry for silicene and 70 Ry for MoS2.

Fig. 1(a) shows the stress versus strain curves of silicene in the armchair direction and in the zigzag direction. The mechanical behavior of silicene in the zigzag direction is substantially different from that in the armchair direction.
There exist two stress peaks in the stress-strain curves when stretched in the zigzag direction. The first one corresponds to the mechanical response of buckled hexagonal silicene (buckled h-Si) structure. After the buckled sample is completely flattened by tension, a small stress drop emerges, corresponding to point “d” keyed in Fig. 1(a) (the amplified region in the inset). Further stretching the planar hexagonal silicene (planar h-Si) may induce a transition to square lattice (s-Si), which however, is not a stable structure even under straining, as will be detailed in Fig. 2.

When strain is applied in the longitudinal direction, the samples are relaxed to ensure that the load in the transverse direction approaches zero. The degree of deformation in the transverse direction of the sample over that along the longitudinal direction is characterized by the Poisson’s ratio. It is well-known that the Poisson’s ratio is bounded in the range of \((\nu) \leq 0.5\) in isotropic materials.\(^{28,29}\) Materials with \(\nu > 0.5\)

<table>
<thead>
<tr>
<th>Name</th>
<th>(a) (nm) (DFT)</th>
<th>(a) (nm) (Exp.)</th>
<th>(c) (nm) (DFT)</th>
<th>(c) (nm) (Exp.)</th>
<th>(L_{x0})</th>
<th>(L_{y0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>0.247</td>
<td>0.245(^a)</td>
<td>0.33</td>
<td>0.33(^b)</td>
<td>0.2468</td>
<td>0.4271</td>
</tr>
<tr>
<td>h-BN</td>
<td>0.250</td>
<td>0.249(^c)</td>
<td>0.33</td>
<td>0.33(^d)</td>
<td>0.2504</td>
<td>0.4337</td>
</tr>
<tr>
<td>Fluorographene</td>
<td>0.254</td>
<td>0.248(^e)</td>
<td>0.62(^f)</td>
<td>0.62–0.87(^g)</td>
<td>0.2538</td>
<td>0.4415</td>
</tr>
<tr>
<td>MoS(_2)</td>
<td>0.318</td>
<td>0.315(^h)</td>
<td>0.614</td>
<td>0.675(^i)</td>
<td>0.6364</td>
<td>1.1022</td>
</tr>
<tr>
<td>Planar h-Si</td>
<td>0.3901</td>
<td>N/A</td>
<td>0.42</td>
<td>N/A</td>
<td>0.3901</td>
<td>0.6757</td>
</tr>
<tr>
<td>Buckled h-Si</td>
<td>0.3867</td>
<td>0.38(^j)</td>
<td>0.42(^k)</td>
<td>N/A</td>
<td>0.3867</td>
<td>0.6698</td>
</tr>
</tbody>
</table>

\(^a\)Reference 17.  
\(^b\)Reference 18.  
\(^c\)Reference 19.  
\(^d\)Reference 20.  
\(^e\)Reference 21.  
\(^f\)Reference 22.  
\(^g\)Reference 23.  
\(^h\)Reference 24.  
\(^i\)Reference 25.  
\(^j\)Reference 26.  
\(^k\)Reference 27.
will counter-intuitively undergo “stretch densifying,” which might find various applications. Following the original definition for the Poisson’s ratio \( \nu \), we have

\[
\nu = -\varepsilon_y / \varepsilon_x = -(L_y - L_{y0})L_{x0}/L_y(L_x - L_{x0}),
\]

where \( \varepsilon_x \) and \( \varepsilon_y \) are the engineering strains in the loading and the transverse directions, respectively, \( L_{x0} \) and \( L_{y0} \) are the initial lengths of the sample in the loading (longitudinal) direction and in the transverse direction, respectively, and \( L_x \) and \( L_y \) are the respective deformed dimensions. Following mechanical convention, the Poisson’s ratio defined above is called as the engineering Poisson’s ratio. For comparison, we also give the true Poisson’s ratio by calculating \( \nu \) at the deformed configuration, i.e.,

\[
\nu = -(L_y(t + dt) - L_{y0})L_{x0}(t)/L_y(t)L_x(t + dt) - L_{x0}(t),
\]

where the dimensions at time \( t \) and subsequent time step \( t + dt \) are used. From both the true and the engineering Poisson’s ratio versus strain curves shown in Fig. 1(b), we see that although \( \nu \) keeps decreasing with increasing strain in the armchair direction, it increases with straining in the zigzag direction. The engineering Poisson’s ratio of silicene indeed breaks the conventional upper bound at strains from 0.19 to 0.24 and is anomalously greater than 0.5. Figure 1(c) shows the height of the buckled layer as a function of strains in both the armchair and zigzag directions, which demonstrates the transition from buckled b-Si to planar h-Si. The energy as a function of strains (Fig. 1(d)) also shows an apparent kink at the point where the structure changes. We also find that the buckled h-Si state is most stable when the strain is less than 0.20, which is consistent with experimental observations. The structure becomes the planar h-Si structure in the strain range of 0.20–0.24.

While the structure transition seen in Fig. 1—from both buckled h-Si to planar h-Si—seems intriguing, it remains unclear whether such intermediate configuration is stable. We use the DFPT to perform phonon calculations. The obtained phonon dispersion could be used to determine the stability of 2-D structures, with negative frequencies suggesting structural instability. Figure 2(a) shows the phonon dispersions of buckled silicene at 0% strain; as a comparison, that for planar silicene without straining is given in Fig. 2(b). The negative frequency for the planar silicene without straining suggests the instability of this structure, which is consistent with previous analysis. Figure 2(c) gives the phonon dispersions of the buckled silicene at 20% tensile strain, where it becomes planar. At 20% strain, the structure is still stable. When further straining is applied, we see emergence of negative frequency for buckled silicene at 36% (now the structure changes to square silicene, and one-atom unit cell was used to calculate the phonon dispersion). Those phonon dispersion curves shown in Fig. 2 indicate that silicene is structurally stable even during the stress softening region while we apply strain to the buckled silicene.

As a comparison, we also explored the stress-strain response of MoS\(_2\). Figure 3(a) shows evolutions of both the Poisson’s ratio and the stress as a function of strain in single layer MoS\(_2\) stretched in both the armchair direction and the zigzag direction. The Poisson’s ratio in MoS\(_2\) increases with the applied strain when stretched in the zigzag direction, but decreases when the strain is applied in the armchair direction. Figures 3(b)–3(d) show in turn the bond configurations (both in plane and transverse projections) at different stage of deformation. By comparing both the stress-strain curve and the bond configurations, we see that the first peak occurs at a strain of 0.22 corresponding to the maximum stress achievable in the hexagonal-close packed (hcp) MoS\(_2\), but the second one at the strain of 0.55 may be due to the transition of hcp MoS\(_2\) to body-centered tetragonal (bct) MoS\(_2\). Results of phonon dispersion analysis shown in Figs. 3(e) and 3(f), at the strain of 0.0 and 0.4, suggest that the (bct) MoS\(_2\) is not stable. For completeness, we further explore the mechanical behaviors of three other 2-D materials, graphene, h-BN, and fluorographene. The results are shown in Fig. 4. The mechanical responses of these three materials are strikingly different from that of MoS\(_2\) and silicene. The Poisson’s ratio decreases monotonically with strains in graphene, h-BN, and fluorographene when stretched in the zigzag direction.

In summary, we report the structural and mechanical properties of several 2-D materials by using first-principles
require us to pay extra attention while designing poisson's ratio effect observed in those 2-dimensional may
required to flatten buckled silicene. furthermore, the distinct
and the silicene is able to overcome the strain energy
range, so that the interfacial energy between the substrate
2-dimensional materials. it also shows possibility that we may syn-
mechanism could be utilized in making composites based on
bendable and extensible to become in-plane bonds. such
than other 2-dimensional as their out-of-plane bonds are both
phene when stretched in the zigzag direction. the stability of
armchair direction. in contrast, the poisson's ratio
buckled planar silicene to planar silicene at a critical tensile
dft calculations. we show an abrupt structure transition in
buckled planar silicene under tension is stable, and sili-
strain of 0.20. phonon dispersion analysis suggests that the
image. the poisson's ratio of silicene shows strong
size transition in: (a) graphene; (b) h-bn; and (c) fluorographene.
DFT calculations. we show an abrupt structure transition in
buckled planar silicene under tension is stable, and silici-
effect in different layers could
different layers could
heterostructures where mechanical deformation presents:
Y.W. acknowledges the support from Chinese Academy of Sciences (CAS), National Natural Science Foundation of China (NSFC) (Nos. 11021262 and 11272327), and MOST 973 of China (No. 2012CB937500). computation is supported by the computation center of CAS. R.Y. acknowledges the support from NSF and AFOSR. M.S.D. acknowledges the support of NSF/dmr-10-04147.

FIG. 4. The engineering poisson’s ratio (left) and stress (right) as a function of strain until the failure strain in both the armchair and the zigzag directions in: (a) Graphene; (b) h-BN; and (c) Fluorographene.

heterostructures where mechanical deformation presents:

1l. Britnell, R. V. Gorbachev, R. Jail, B. D. Bello, F. Schedin, A.
Mishchenko, T. Georgiou, M. I. Katsnelson, L. Eaves, S. V. Morozov, N.
M. R. Peres, J. Leist, A. K. Geim, K. S. Novoselov, and L. A.
2m. P. Levandov, C. J. Kim, L. Brown, P. Y. Huang, R. W. Havenner, D. A.
3h. Yang, J. Heo, S. Park, H. J. Song, D. H. Seo, K.-E. Byun, P. Kim, H.-J.
5s. P. Koenig, N. G. Boddeti, M. L. Dunn, and J. S. Bunch, Nat.
 Nanotechnol. 6, 543 (2011).
6n. N. Klimov, S. Jung, S. Zhu, T. Li, C. A. Wright, S. D. Solares, D. B.
7r. R. Nair, W. C. Ren, R. Jail, I. Riaz, V. G. Kravets, L. Britnell, P. Blake, F.
Schedin, A. S. Mayorov, S. Yuan, M. I. Katsnelson, H. M. Cheng, W.
Strupinski, L. G. Bulusheva, A. V. Okotrub, I. V. Grigorieva, A. N.
Grigorenko, K. S. Novoselov, and A. K. Geim, Small 6, 2877 (2010).
8k. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105,
136805 (2010).
9b. Lalmi, H. Oughaddou, H. Enriquez, A. Kara, S. Vizzini, B. Ealet, and
10s. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhass, E. J.
11t. Ramanathan, A. A. Abdala, S. Stankovich, D. A. Dikin, M. Herrera-
Ruoff, S. T. Nguyen, I. A. Akasy, R. K. Prud’Homme, and L. C. Brinson,
ibid. 59, 1758 (1999).
14j. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865
(1996); 78, 1396 (1997).
Phys. 73, 515 (2001).
16p. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D.
Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de
Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C.
Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F.
Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia,
S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and
19n. Alem, R. Erni, C. Kisielowski, M. Rosselli, W. Gannett, and A. Zettl,
K. Zhang, H. Li, Z.-Y. Juang, M. S. Dresselhaus, L.-J. Li, and J. Kong,
21k. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V.
22s. Helveg, J. V. Lauritsen, E. Larsgaard, I. Stensgaard, J. K. Norskov, B.
S. Clausen, H. Topsøe, and F. Besenbacher, Phys. Rev. Lett. 84, 951
(2000).
23m. M. Benaimure, B. Radasavljevic, J. S. Hérion, S. Sahoo, H. Berger, and
24s. S. Han, T. H. Yu, B. V. Merinov, A. C. T. Van Duin, R. Yazami, and