

Atomistic Study of the Bandgap Engineering of Two-Dimensional Silicon Carbide by Hydrogenation

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Cite This: *ACS Omega* 2023, 8, 25424–25431



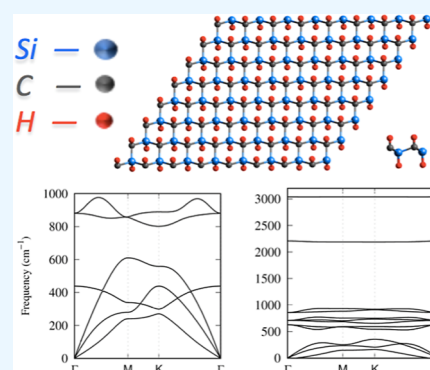
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ABSTRACT: This work studied hydrogen adsorption by a two-dimensional silicon carbide using a combined molecular dynamics and density functional theory approach. The geometrical properties of partially and fully hydrogenated structures were investigated, considering the effect of zero-point energy. The preferred hydrogen atom location is on top of silicon atoms. The hydrogen interaction energies were obtained for the first time as the attractive force. For fully hydrogenated 2D SiC, the chair-like conformer is the most stable configuration, and the next is the boat-like conformer, while the table-like structure is not stable. The coverage and arrangement of the adsorbed hydrogen atoms significantly influence the values of the direct/indirect bandgaps of the considered systems, increasing the bandgap to 4.07, 3.64, and 4.41 eV for chair-like, table-like, and boat-like, respectively. Their dynamical stability was investigated by phonon dispersion calculations. The obtained results can serve as a guide for the application of hydrogenated two-dimensional silicon carbide in optoelectronic applications in manufacturing innovation.



1. INTRODUCTION

Because of its atomic size and unique electronic configuration, carbon forms a huge number of allotropes and compounds. In addition to the types of atoms forming the materials, their dimensionality significantly influences their physicochemical properties. With the advent of graphene,¹ the field of two-dimensional materials became one of the most prolific areas of research. While graphene continues to astonish the research community with recent discoveries, such as superconductivity and highly correlated electron physics in twisted bilayers² and trilayers,³ a plethora of other two-dimensional materials have emerged, covering a wide spectrum of electronic and optical properties.

One of these materials of significant recent interest is 2D SiC, which was predicted to have a stable hexagonal planar structure with a cohesive energy of 15.25 eV,⁴ strong second harmonic generation intensity spectrum,⁵ and large excitonic effects on the optical properties resulting from quantum confinement.⁶ Unlike graphene and silicene, which have zero bandgaps, 2D SiC is a semiconductor with a direct bandgap of about 2.5 eV,^{4,7} making it a promising material for logic gates. A density functional theory (DFT) study of strain engineering concluded that at lower stresses, 2D SiC transforms from a direct to an indirect bandgap semiconductor, and at higher stresses, it transforms to a metallic material.⁸ In addition to crystalline 2D SiC, amorphous 2D SiC has been of recent interest. Its detailed atomic structure has been studied by

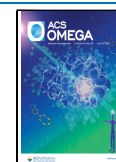
molecular dynamic (MD) simulations, where amorphous models were obtained by cooling from the melt.^{9,10} The synthesis of 2D SiC has challenged scientists for decades because, unlike graphitic carbon, bulk SiC is not a van der Waals-layered material and therefore is not convenient for exfoliation techniques. Additionally, bulk SiC exists in more than 250 polytypes, which further complicates the growth process. A successful production of 2D SiC using a top-down approach was reported in which wet exfoliation of bulk hexagonal SiC was performed in isopropyl alcohol or *N*-methyl-2-pyrrolidone solvents.¹¹ Also, a bottom-up synthesis of 2D SiC atop ultrathin transition metal carbide films on SiC substrates has recently been demonstrated.¹²

In addition to strain engineering, chemical modification of 2D materials has been used to tune their properties. To this end, for example, various graphene derivatives incorporating oxygen,¹³ nitrogen,¹⁴ as well as halogens¹⁵ have been considered. The saturation of the aromatic bonds of graphene with atoms of hydrogen leads to an extended 2D hydrocarbon (graphene),¹⁶ which transforms the highly conductive

Received: April 28, 2023

Accepted: June 15, 2023

Published: July 9, 2023



graphene into an insulator.¹⁷ This reaction with hydrogen is reversible, that is, upon annealing, the quantum Hall effect, lattice spacing, and metallic state of graphene are restored.¹⁷ Incomplete hydrogenation of graphene results in ferromagnetism¹⁸ as well as tunable bandgaps dependent on the extent of hydrogenation.¹⁹ In addition to graphene, other two-dimensional materials, such as group VA monolayers, also exhibit intriguing anisotropic electronic structures. These materials hold promise for utilization in field-effect transistors, showcasing their high saturation current in advanced electronic devices.^{19–22} Other potential applications of two-dimensional materials are in electrolysis technologies, which offer a promising way to create sustainable energy. Two usual approaches are CO₂ reduction^{23,24} and hydrogen reaction approach.²⁵ In both ways, the hydrogen adsorption energy is necessary to conclude about the hydrogen evolution reaction (HER), which can affect the CO₂ reduction rate, and directly affect hydrogen dissociation and recombination. Two-dimensional materials, like graphene, two-dimensional MoSe₂, and MoS₂ were also considered as alternative electrocatalysts to scarce and highly valuable Pt-based catalysts^{25,26} due to their high surface area.^{27–29}

Hydrogen atoms are proven to relax and fully adsorb on the hexagonal polytype 4H-SiC surface,³⁰ which suggests 2D-SiC is also capable of a fully hydrogen reaction. Semi-hydrogenated 2D SiC is a ferromagnetic semiconductor when carbon atoms are hydrogenated, while it is an antiferromagnetic semiconductor when silicon atoms are hydrogenated.³¹ The chair-like and boat-like conformers of a fully hydrogenated 2D SiC are found to be nonmagnetic semiconductors with direct band gaps of 3.84 and 4.29 eV, respectively.³² This makes 2D-SiC a promising electrocatalyst for electrolysis technologies and a base material for hydrogen storage applications due to its abundance, lightweight, and high durability. With full and partial hydrogen adsorption, the anisotropic electronic structures of two-dimensional SiC could also evolve to be more suitable for microelectronic applications.

In this work, partially and fully hydrogenated 2D SiC are carefully studied with the combination of the MD and DFT simulation methods. The MD simulation is used to find the most stable structure of 2D SiC, while the DFT simulations are used to find the hydrogenation ability of the SiC films as well as investigate their electronic and optical properties.

2. CALCULATION METHODS

The large-scale atomic/molecular massively parallel simulator (LAMMPS)³³ was used to generate the 2D SiC model with an area of $\sim 25885 \text{ \AA}^2$ (~ 3000 Si atoms and ~ 3000 C atoms) and with an initial bond length of $\sim 1.79 \text{ \AA}$.³⁴ The model was relaxed with 3×10^5 MD steps at room temperature using the NPT ensemble with two-body and three-body covalent interactions.^{9,35} The Vashishta potential and the periodic boundary conditions were used.³⁵ In Cartesian coordinates, along the y -axis, the armchair nanoribbon was obtained when the elastic reflection boundary condition was applied. The SiC nanoribbon was then relaxed with 3×10^5 steps at room temperature. To obtain the fully liquid-state SiC nanoribbon model, the system was heated up to 7000 K using the 10^{11} K/s heating rate and relaxed at 7000 K for 3×10^5 MD steps. The crystal SiC structure was formed when we cooled down the liquid SiC from 7000 to 300 K using the 10^{13} K/s cooling rate and relaxed the model for 3×10^5 steps. The bond length of 1.85 Å obtained from the radial distribution function of the

Si–C pairs, shown in Figure 1, is comparable to the bond length of 1.89 Å for the bulk SiC.³⁶ While silicone is

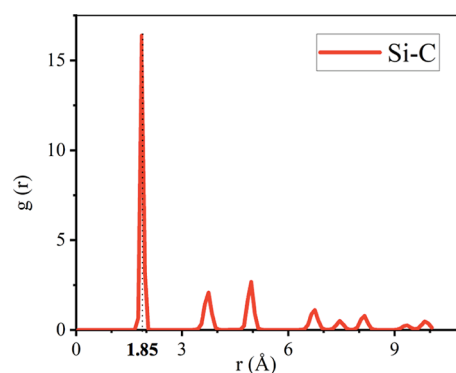


Figure 1. Radial distribution function $g(r)$ of the Si–C pair after relaxing the model at room temperature.

characterized by a slight out-of-plane buckling due to sp^3 hybridization of Si atoms, the planar structure of graphene and 2D SiC (see Figure 2) results from sp^2 hybridization.

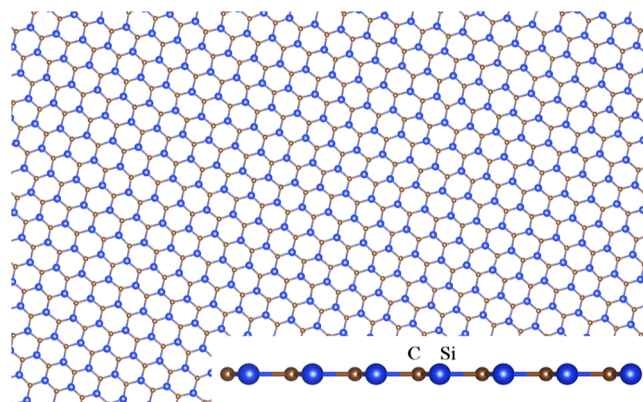


Figure 2. SiC model relaxed at 300 K by using the MD simulation; the inset shows the non-buckling side view.

To investigate the effects of hydrogenation, we employ the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) package.^{37,38} This is the combination of a self-consistent field loop, a norm-conserving pseudopotential, and plane-wave basis set. The generalized gradient approximation of the Perdew–Burke–Ernzerhof functional is applied for the exchange and correlation energy functionals. We used the double- ζ polarized basis set and the energy cutoff of 200 Ry. The periodic boundary conditions were used in the xy -plane, and the vacuum gap was 40 Å along the z -axis. The maximum stress component being less than 0.02 eV/Å was used as the criteria for exiting the geometry optimization loop.^{39–44}

After convergence testing of the k -point set, the $12 \times 12 \times 1$ Monkhorst–Pack scheme was used for calculation of the bandgap and the phonon spectrum.

From the 2D SiC model obtained by the MD simulations, an 8×8 supercell was used to avoid the size effects.⁴⁵ The stable sites for hydrogen atom adsorption were found to be on top of Si (T_{Si}) and on top of C (T_C) atoms.

In energy calculations, quantum zero-point energy (ZPE) is taken into account by assuming harmonic oscillations of the hydrogen atom along all three axes. The ZPE is calculated as

$$ZPE = \frac{h}{4\pi} \sqrt{\frac{k(m_{\text{H}} + m_{\text{Si/C}})}{m_{\text{H}}m_{\text{Si/C}}}}$$

where m_{H} is the mass of a hydrogen atom, $m_{\text{Si/C}}$ is the mass of a silicon/carbon atom, h is the Planck's constant, and k is the force constant (calculated via the least square method).

3. RESULTS AND DISCUSSIONS

3.1. Adsorption Energy Dependence on Hydrogen Coverage. To investigate the coverage-dependent adsorption energy of hydrogen on 2D SiC, we deposited one by one up to six hydrogen atoms on potential energy minima locations (top

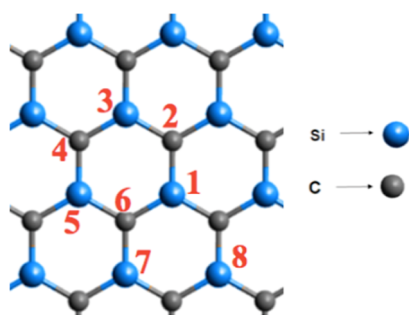


Figure 3. Hydrogen adsorption positions.

of Si and C sites), as shown in Figure 3. The hydrogen adsorption energy is calculated using the following equation

$$E_{\text{ads}} = E_{\text{SiC-}n_{\text{H}}\text{H}} - E_{\text{SiC}} - n_{\text{H}}(E_{\text{H}} + ZPE)$$

where E_{ads} is the hydrogen adsorption energy, $E_{\text{SiC-}n_{\text{H}}\text{H}}$ is the total energy of the SiC–H system with n_{H} hydrogen atoms, E_{SiC} is the total energy of bare 2D SiC, E_{H} is the energy of hydrogen atom, and ZPE is the zero point energy of hydrogen vibrations.

When hydrogen atoms are deposited on top of the Si atoms, the adsorption energy is linearly dependent on the number of hydrogen atoms, suggesting that the coverage dependence of the adsorption energy can be described by the Langmuir adsorption isotherm (Table 1, Figure 4a). However, in the

Table 1. Adsorption Energy (eV) of the Adsorbed Hydrogen Atoms on the Si Sites

number of hydrogen atoms	hydrogen adsorption sites	adsorption energy
1	1	−0.708
2	1, 3	−1.666
3	1, 5, 7	−2.501
4	1, 3, 5, 8	−3.419

realistic case when hydrogen atoms are adsorbed on top of both the Si and C atoms (see Table 2 and Figure 4b), the adsorption energy shows a deviation from linearity. This is due to the difference between the adsorption energies of hydrogen on the Si atom and the C atom. So, to describe the adsorption isotherm in experiments, it may need a coverage dependence correction.

3.2. Hydrogen Pair Interaction. To investigate the H–H interaction on the SiC surface, two hydrogen atoms were deposited on top of the nearest Si atoms as well as on top of the adjacent Si and C atoms. In the latter case, the interaction energy of these two adsorbed hydrogen atoms, H–H, on the SiC surface was calculated by

$$E_{\text{int}} = E_{\text{SiC-2H}} - E_{\text{SiC}} - 2E_{\text{H}} - E_{\text{ads}}(H_{\text{Si}}) - E_{\text{ads}}(H_{\text{C}})$$

where $E_{\text{SiC-2H}}$ is the total energy of the SiC system with two hydrogen atoms, $E_{\text{ads}}(H_{\text{Si}})$ and $E_{\text{ads}}(H_{\text{C}})$ are the adsorption energies of H_{Si} and H_{C} , respectively. The interaction energy in the case when both hydrogen atoms are adsorbed on top of the Si atoms is calculated in an analogous way. The results are displayed in Table 3. As the distance between the hydrogen atoms is in both cases greater than the bond length in the ground state of the hydrogen molecule, these interactions are attractive. The interaction between hydrogen atoms on top of carbon atoms is not listed in Table 3 as these are not equilibrium positions. During optimization, one of the hydrogen atoms moves on top of the silicon atom to form a $H_{\text{Si}} - H_{\text{C}}$ pair. This is also consistent with the obtained adsorption energy (shown in Tables 1 and 2), when the adsorption energy of H on Si (−0.708 eV) is almost twice that of the adsorption energy of H on C (−0.369 eV).

The attracted nature of hydrogen interaction on 2D-SiC enhanced the adsorption of hydrogen when the 2D-SiC surface already contained hydrogen. For both configurations, the adsorption energy increased (more negative) with more hydrogen atoms. In Table 1, considering only the Si site, the adsorption energy increased from −0.708 to −0.855 eV per hydrogen. When hydrogen adsorbed on both the top Si and C sites, the adsorption energy increased from −3.131 to −3.652 eV between one pair of hydrogen atoms and three pairs of hydrogen atoms (see Table 2). The adsorption energy is increasing with the number of hydrogen due to the attraction of hydrogen. Hydrogen is more likely to create a cluster of adsorbed hydrogen. In other words, it would likely populate the neighboring Si/C site more than spread uniformly on the Si site. As evident, the adsorption energy of two H atoms in the Si/C site is much bigger than that of two H atoms in the Si site, ranging from −3.131 to −1.666 eV (see Tables 1 and 2).

3.3. Full Hydrogenation of the SiC Surface. When depositing hydrogen atoms onto the entire SiC surface, three different structures were considered: chair-like, table-like, and boat-like (see Figure 5). In Figure 5a, the chair-like structure is shown, where the hydrogen atoms on top of Si are on the opposite side to those that are on top of C atoms. In a table-like configuration, Figure 5b, hydrogen atoms are attached to both C and Si atoms from the same side, while in the boat-like configuration (Figure 5c), hydrogen atoms are attached alternately on each side in pairs on top of C and Si atoms.

Table 4 shows the space groups, bond lengths, buckling, bond angles, binding energies, hydrogen Gibb's free energy difference, and bandgap energies. The binding energy is calculated using the formula

$$E_{\text{b}} = \frac{2}{n_{\text{H}}} (E_{\text{SiC-}n_{\text{H}}\text{H}} - E_{\text{SiC}} - n_{\text{H}}E_{\text{H}})$$

where E_{b} is the hydrogen binding energy per hydrogenated 2D SiC unit cell. The binding energy represents the stability of the structure, which is the combination of the adsorption energy

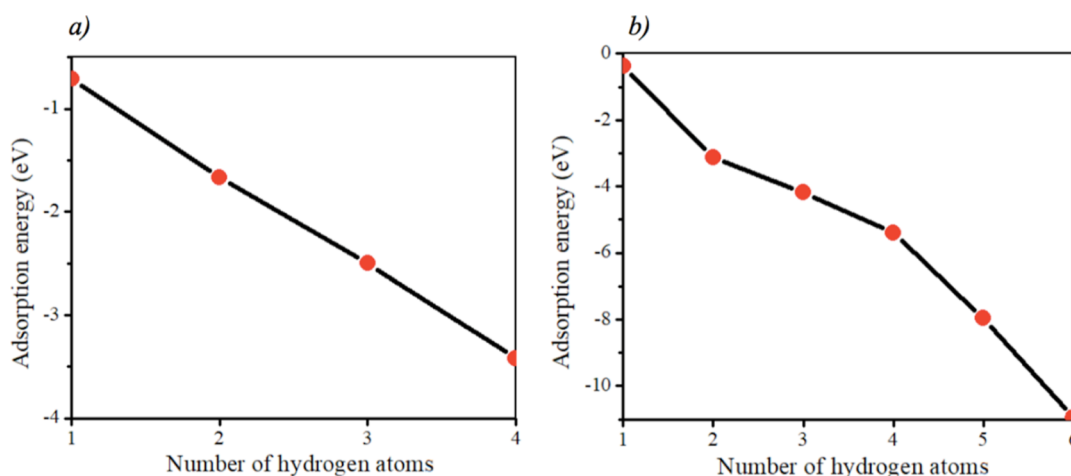


Figure 4. Dependence of adsorption energy on hydrogen coverage: (a) adsorbed hydrogen atoms on Si atoms and (b) adsorbed hydrogen atoms on both Si and C atoms.

Table 2. Adsorption Energy (eV) of the Adsorbed Hydrogen Atoms on Both Si and C Sites

number of hydrogen atoms	hydrogen adsorption sites	adsorption energy
1	2	-0.369
2	1, 2	-3.131
3	2, 3, 4	-4.168
4	1, 5, 6, 7	-5.391
5	1, 4, 5, 6, 7	-7.957
6	1, 2, 3, 4, 5, 6	-10.956

Table 3. H–H Interaction Energy (E_{int} , eV) on the SiC Surface

interaction pair	interaction energy
$H_{\text{T}_{\text{Si}}} - H_{\text{T}_{\text{Si}}}$	-0.196
$H_{\text{T}_{\text{Si}}} - H_{\text{T}_{\text{C}}}$	-1.994

and interaction energy of all the adsorbed hydrogen atoms on the surface of 2D SiC. The thermal stability of hydrogen in three configurations is further addressed as we calculate Gibb's free energy difference between hydrogen adsorbed on a 2D SiC unit cell versus hydrogen in the gas phase

$$\Delta G_{\text{H}} = E_{\text{b}} + \Delta E_{\text{ZPE}} - 2T\Delta S_{\text{H}}$$

where E_{b} is the binding energy, and ΔE_{ZPE} is difference in the vibrational energy of hydrogen in the adsorbed state compared to the gas state, calculated by the harmonic oscillations approximation mentioned above. While ΔS_{H} is the entropy difference, which we assume to be half of hydrogen molecule entropy, extracted from the thermochemical tables at a temperature of 298.15 K and a standardized pressure of 1 bar. The entropy of adsorbed H on SiC is neglectable compared with hydrogen in gas phase entropy because hydrogen on 2D-SiC vibrates much less than hydrogen in the gas phase.⁴⁴

The results show that the Si–C bond lengths of the considered structures are longer than the sp^2 bond length (~ 1.785 Å) of the 2D SiC surface.^{34,45} For the table-like conformation, the bond length ($d_{\text{Si-C}} \sim 1.867$ Å) is similar to the sp^3 bond length of 1.896 Å in bulk SiC.³⁶ However, the Si–C bond lengths of chair-like and boat-like structures are slightly longer due to hydrogen repulsion. This means that the

Si–C bonding is sp^3 -like only. This is also verified with the angles between bonds shown in Table 4. The angles H–C–Si, H–Si–C, C–Si–C, and Si–C–Si, of chair-like conformation, are 107, 107, 111, and 111°, respectively. These results are similar to the previously published results for SiC sheets and are slightly different from the result of bulk SiC at 109°. ³² These obtained bond angles again show that these C–H, Si–H, C–Si bonds are sp^3 -like rather than explicit sp^3 . For the C–H and Si–H bond lengths, the obtained values are similar to the values of hydrocarbon compounds ($d_{\text{C-H}} \sim 1.1$ Å) and hydro-silicon compounds ($d_{\text{Si-H}} \sim 1.5$ Å), respectively. The binding energies per H/SiC unit cell of the chair-like, the boat-like, and the table-like structures are -5.804, -5.696, and -4.284 eV, respectively. The obtained binding energy for the chair-like conformation is comparable to the previously published value of -5.821 eV.⁴⁶ Although the energy values are higher than the results of fully hydrogenated SiC from,³² the results are in the same order of stability as the models. This difference in energy can be attributed to the difference in bond lengths. The original structure in this study was obtained from MD simulation results for 6240 atoms. The difference in energy can be explained from the hydrogen interaction standpoint, while the chair-like conformer has the least $H_{\text{T}_{\text{Si}}} - H_{\text{T}_{\text{C}}}$ pair interaction and the table-like has the most. As shown in Table 3, the $H_{\text{T}_{\text{Si}}} - H_{\text{T}_{\text{C}}}$ pair has a stronger interaction, causing more instability in the system.

The bandgap values, listed in Table 4 (see also Figure 6), for the chair-like, boat-like, and table-like structures are 4.072, 4.412, and 3.639 eV, respectively. These values are significantly higher than the bandgap of 2.142 eV obtained for the pristine 2D SiC sheet. For the pristine SiC sheet, our result is lower than the values obtained in previous research.³⁴ This difference comes from parameters we obtained from the MD model relaxation at 300 K, in which Si–C bonding is 1.845 Å, which is longer than 1.79 Å in pure ab initio relaxation.⁴⁷ Nevertheless, our result shows a direct bandgap at the symmetric K point in the hexagonal Brillouin zone, implying the ability to tune the SiC bandgap by changing the Si–C bonding length, e.g., via strain, which can be of significance in optoelectronic applications such as light-emitting diodes and solar cells.⁴⁸ After full hydrogenation, the direct bandgap of the SiC sheet turns into the indirect bandgap and increases its width. This is similar to graphene, where after full hydro-

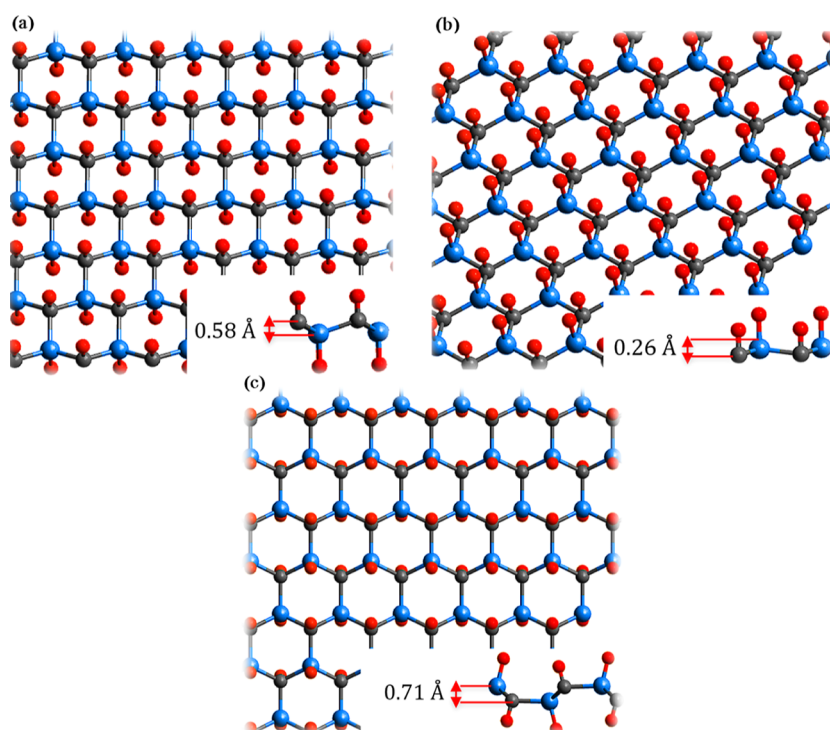


Figure 5. Three different structures of a fully hydrogenated SiC surface: (a) chair-like, (b) table-like, and (c) boat-like (hydrogen is marked in red).

Table 4. Relaxed Parameters, Binding Energy, Gibb's Free Energy Difference, and Bandgap for 2D SiC and Three Fully Hydrogenated configurations of 2D SiC

	2D SiC	table-like	chair-like	boat-like
space group	<i>P6M2</i>	<i>P3M1</i>	<i>P3M1</i>	<i>PMN21</i>
$d_{\text{Si-C}}$ (Å)	1.849	1.868 1.867 1.867	1.937 1.939 1.938	1.983 1.943 1.942
buckling (Å)		0.262	0.580	0.714 0.811
$d_{\text{C-H}}$ (Å)		1.119	1.112	1.113
$d_{\text{Si-H}}$ (Å)		1.534	1.505	1.509
$\theta_{\text{H-C-Si}}$ (deg)		82	108	106,104
$\theta_{\text{H-Si-C}}$ (deg)		98	107	105,107
$\theta_{\text{C-Si-C}}$ (deg)	120	118	111,112	113,111
$\theta_{\text{Si-C-Si}}$ (deg)	120	118	111,112	115,111
E_b (eV)		-4.284	-5.804	-5.696
ΔG_{H} (eV)		-3.871	-5.391	-5.283
E_g (eV)	2.142	3.639	4.072	4.412

genation the calculated bandgap increased from 0 to 3.5 eV.⁴⁹ The values of Gibb's free energy difference between hydrogen adsorbed on a 2D SiC unit cell versus hydrogen in the gas phase for the chair-like, boat-like, and table-like structures are 4.072, 4.412, and 3.639 eV, respectively. The negative results of ΔG_{H} suggest that all the fully hydrogenated reactions can happen at room temperature and standardized pressure, and the reaction is a spontaneous and exothermic process.

In graphene, hydrogenation leads to a change from sp^2 to sp^3 bonding, which in turn causes buckling and bandgap opening.¹⁶ Similarly, we find that hydrogenation in 2D SiC leads to buckling and bandgap widening. The tunable bandgap of 2D SiC is of significance for potential optoelectronics applications, such as light-emitting diodes, solar cells, and sensors.

The dynamic stability of the considered structures was investigated by calculating the phonon dispersion curves

(displayed in Figure 7). The three acoustic branches, which are longitudinal (LA), transverse (TA), and flexural (ZA) are observed for all the structures. Hydrogenation results in high-frequency modes. As in graphene, all phonon modes above 2000 cm^{-1} belong to H.⁵⁰ The vibration frequencies for H bond stretching are 2000 and 2900 cm^{-1} in the table-like case and 2100 and 3030 cm^{-1} for the chair-like and boat-like cases. While the two last conformers are stable, the negative frequency appears at the acoustic branch of the table-like conformer, causing instability. If 2D SiC is held by other base materials, the Si and C acoustic vibrations should be diminished so that, in that case, the table-like conformer could occur. The 2D SiC has achieved an H adsorption ratio of 1:1 and a hydrogen gravimetric capacity of 4.7 wt %.

4. CONCLUSIONS

We have performed MD simulations of the pristine and hydrogenated 2D SiC and have used the obtained structures as input into DFT calculations. The coverage dependence of hydrogen adsorbed on 2D SiC has been studied using the zero-point energy effect. The results show that the preferred hydrogen atom location is on top of silicon atoms. The adsorption energy increases linearly if H atoms are adsorbed only on Si and follow the Langmuir adsorption isotherm. If the less favorable C adsorption sites are taken into account, a coverage dependence correction is needed to describe the adsorption isotherm. The interaction between two hydrogen atoms adsorb adjacently on 2D SiC has been pointed out for the first time as the attractive force; the $H_{\text{Ts}_i} - H_{\text{Tc}}$ pair has stronger interaction energy than the $H_{\text{Tc}_i} - H_{\text{Tc}_i}$ pair. For fully hydrogenated 2D SiC, chair-like and boat-like conformers have been proven to be stable using DFT and phonon calculations, while the table-like structure is not stable. With this, the 2D SiC reaches a hydrogenation ratio of 1:1 and a gravimetric capacity of 4.7 wt %. The chair-like conformer is the most

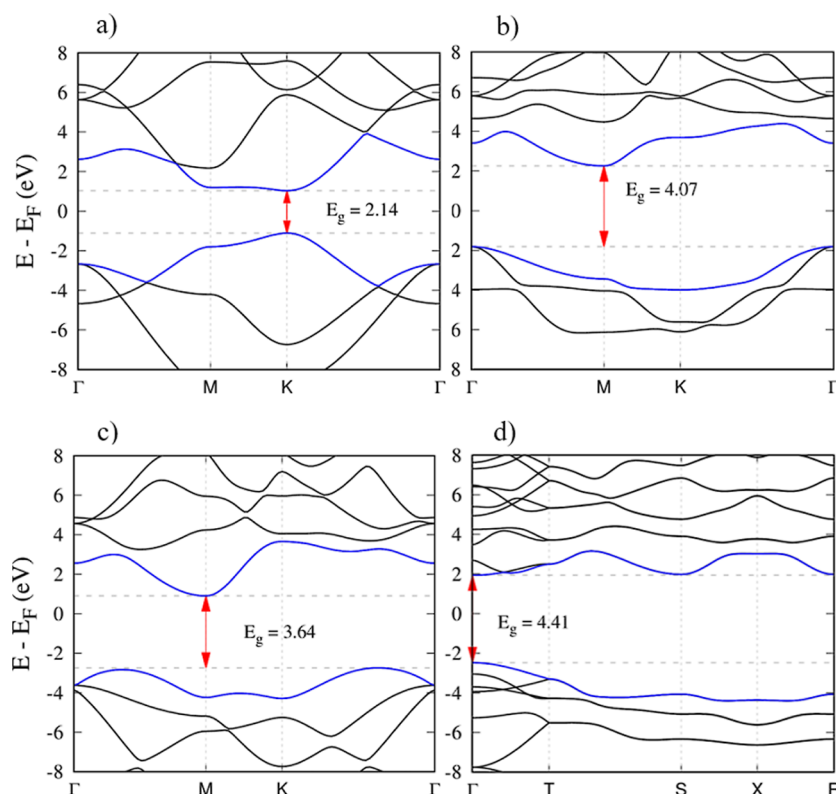


Figure 6. Band structure of (a) pure 2D SiC sheet and three fully hydrogenated SiC conformers: (b) chair-like, (c) table-like, and (d) boat-like.

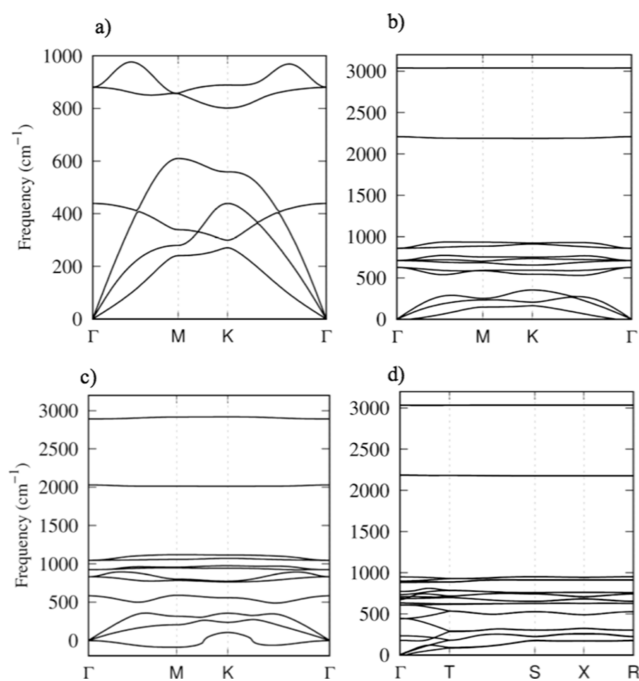


Figure 7. Phonon structure of (a) pure 2D SiC sheet and three fully hydrogenated SiC conformers: (b) chair-like, (c) table-like, and (d) boat-like.

stable configuration. The bandgap of the 2D SiC is tunable with the change of bond length and has increased drastically to 4.07, 3.64, and 4.41 eV for chair-like, table-like, and boat-like, respectively. These results show that 2D SiC has attractive properties for electronic and optical device applications.

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<https://pubs.acs.org/10.1021/acsomega.3c02914>

Author Contributions

H.T.T.T. conceived the idea of developing the research. P.M.N. conducted the simulation. H.T.T.T. and P.M.N. analyzed the data and wrote the manuscripts. All authors contributed to the review of the manuscript and approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge Ho Chi Minh City University of Technology (HCMUT) and the Vietnam National University, Ho Chi Minh City (VNU-HCM) for supporting this study. The authors would like to thank the New Zealand eScience Infrastructure (NeSI) for the use of supercomputing facilities. This research is funded by Vietnam National University Ho Chi Minh City (VNU-HCM) under grant number VL2022-20-02.

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