

Cite this: *RSC Adv.*, 2018, 8, 39976Received 20th September 2018
Accepted 24th November 2018

DOI: 10.1039/c8ra07824f

rsc.li/rsc-advances

Hydrogenated derivatives of hexacoordinated metallic Cu₂Si monolayer†‡

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Herein, we carried out first-principles calculations based on density functional theory to investigate the effects of surface functionalization with hydrogen atoms on structural, dynamical and electronic properties of Cu₂Si monolayer. Pristine Cu₂Si, a metallic monolayer, has a planar hexacoordinate structure. Calculations revealed that the most favorable position of a single H atom on the Cu₂Si monolayer is at the top of a Si site. Derivatives of Cu₂Si monolayer with various H concentrations were investigated, and by performing phonon calculations, it was found that there are three stable hydrogenated structures. Specific heat of these monolayers was found to increase with the hydrogen concentration at temperatures higher than 100 K. Electronically, the hydrogenated derivatives of Cu₂Si monolayer preserve the metallic character.

1. Introduction

Following the successful isolation of graphene,¹ the family of two-dimensional (2D) materials has attracted great attention. This family has a large variety of members including monoatomic honeycomb structures (silicene,² germanene³), transition metal dichalcogenides (MoS₂,⁴ WS₂,⁵ ReS₂ (ref. 6)) and group III–V compounds (*h*-BN,⁷ *h*-AlN^{8,9}). Recently, Yang *et al.* proposed a new class of highly stable planar hypercoordinated materials, such as hexacoordinated Ni₂Ge,¹⁰ Cu₂Ge,¹¹ Cu₂As,¹² Au¹³ and Cu,¹⁴ which open up a new branch for the 2D materials. Those materials have attracted attention due to their structural and mechanical properties such as strong chemical bonding and in-plane stiffness.

One of these novel materials is the monolayer Cu₂Si¹⁵ with planar hexacoordinated Cu and Si motifs. It is a nonmagnetic metal with high stability stemming from the superposition of 4c–2e σ bonds extended within the 2D sheet. The metallicity of Cu₂Si has been known, Feng *et al.* verified Dirac nodal line fermions in Cu₂Si monolayer by using angle-resolved photo-emission spectroscopy and first-principles calculations.¹⁶ Nodal line semimetals,^{17,18} a type of topological semimetals, have symmetry-protected linear-band crossing points near the Fermi level and they have been intensively studied previously.¹⁹ These

materials are suitable candidates for the realization of high-speed, low-dissipation devices.¹⁶

Chemical functionalization of 2D materials is one of the most common methods to tune the structural,²⁰ electronic²¹ and magnetic²² properties of a material. For instance, H and F atoms are commonly used for the surface functionalization of the 2D materials. Following the theoretical prediction of hydrogenated graphene (graphene),²³ Elias *et al.* achieved the synthesis of the graphene and showed that the reversible hydrogenation process changes graphene into an insulator.²⁴ Moreover, Nair *et al.* achieved to synthesize fluorinated graphene (fluorographene) which possesses completely different electronic properties than that of graphene.²⁵ Although graphene is a highly conductive semimetal, fluorographene is an insulator with an optical gap of 3 eV. Recently, we reported that when the charge density wave (CDW) phase of single-layer TiSe₂ is fully hydrogenated, the structure transforms to a distorted T-phase (*T*_d).²⁶ In the mean time, hydrogenation is also used for the passivation of interfaces and contacts.^{27,28} For instance, electrical conductivity of metals can be changed through various manipulations such as binding foreign molecules or adatoms.²⁹ During experiments, the presence of the environmental interactions is inevitable; therefore, the passivation of such materials plays important role in achieving a stable electrical behavior. When the material is hydrogenated, the hydrogen layer acts as a protective layer against the external influences while preserving the electronic properties of the structure.

Even though there are several analyses on structural, chemical and electronic properties of the Cu₂Si, the effect of hydrogenation has not been studied thoroughly. Herein, we present an investigation of the feasibility of the hydrogenation of the Cu₂Si monolayer based on density-functional theory. Starting from single atom adsorption, structural, electronic and

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† PACS numbers: 71.15.Mb, 61.72.Ww, 63.20.Dj, 63.20.dk, 65.40.Ba, 73.22.-f.

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra07824f

vibrational properties of Cu₂Si covered with various concentrations of hydrogen are investigated. Three possible structures of hydrogenated Cu₂Si are found to be dynamically stable. As well as the pristine structure, hydrogenated derivatives of Cu₂Si monolayer exhibit metallic behavior. Moreover, it is found that the hydrogenation of Cu₂Si monolayer leads to an increase in its specific heat at temperatures higher than 100 K and it reduces the surface activity of the material against other foreign agents without effecting its metallic character and planar geometry.

The paper is organized as follows: detailed information about computational methodology is given in Sec. II. The structural, vibrational and electronic properties of pristine Cu₂Si, and also the adsorption and diffusion of a hydrogen atom on Cu₂Si are discussed in Sec. III. In Sec. IV, we present the structural, vibrational and electronic properties of the hydrogenated derivatives of Cu₂Si monolayer. Lastly, Sec. V is allocated for the conclusions.

II. Computational methods

In order to investigate surface functionalization of Cu₂Si monolayer, density functional theory (DFT)-based calculations were performed by using the Vienna ab initio Simulation Package (VASP).^{30,31} In order to describe the exchange and correlation energies, Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) functional was

adopted.³² DFT-D2 method of Grimme was used for the van der Waals (vdW) correction to the GGA functional.³³ Bader technique was used in order to determine the charge transfers in the structure.^{35,36}

Energy cutoff of the plane-wave basis set was chosen to be 500 eV. For the convergence criterion, the energy difference between successive electronic steps was taken to be 10^{−5} eV and the Hellmann–Feynman forces on each atom were reduced to a value of less than 10^{−4} eV Å^{−1}. A vacuum space of 12 Å was incorporated in order to avoid the interactions between the adjacent layers. 18 × 18 × 1 Γ -centered mesh was used for the Brillouin Zone (BZ) integration of the unit cell and the mesh is scaled accordingly for larger supercells.

Cohesive energy per atom (E_{coh}) was calculated for each structure, by using the following formula,

$$E_{\text{coh}} = \frac{1}{n_{\text{tot}}} \left[\sum_i n_i E_i - E_{\text{ML}} \right], \quad (1)$$

where i -index denotes the type of the atom. E_i and n_i are the single atom energy and the number of i atoms in the unit cell. n_{tot} and E_{ML} represent the total number of atoms in the unit cell and the total ground state energy of the related monolayer, respectively. The vibrational properties and the dynamical stability were calculated with the small displacement method as implemented in the PHON code.³⁴ Out-of-plane acoustic phonon modes in all structures were corrected by quadratic-fitting at the vicinity of the zone center.

III. Adsorption and diffusion of hydrogen on Cu₂Si

Cu₂Si monolayer has a planar structure that consists of a hexagonal sublattice of Cu atoms and a trigonal sublattice of Si atoms. The primitive unit cell of the structure includes two Cu atoms and one Si atom as seen from its optimized structure shown in Fig. 1(a). The calculated structural parameters are given in Table 1. It is found that the lattice constant of the Cu₂Si monolayer is 4.10 Å each Cu coordinates with three Si and three Cu atoms while each Si coordinates only with six Cu atoms. It is calculated that Cu–Si and Cu–Cu bond lengths are equal and 2.37 Å. Lattice parameter and bond length calculations are consistent with the values reported by Yang *et al.* ($a = b = 4.123$ Å, $d_{\text{Cu–Si}} = d_{\text{Cu–Cu}} = 2.38$ Å).¹⁵ According to Bader charge analysis, each Si atom donates 0.2 e to Cu atoms indicating the covalent character of Cu–Si bonds.

In order to investigate dynamical stability, phonon band dispersion of the Cu₂Si monolayer is calculated and is shown in Fig. 1(b). A 5 × 5 × 1 supercell is used for the phonon band structure calculations and it is found that the Cu₂Si monolayer is dynamically stable. As seen in the figure, the signature of a Kohn-type soft phonon mode appears at the M point in the BZ.³⁸ The highest-frequency modes, longitudinal optical (LO) modes, are mainly composed of the in-plane motions of Si atoms. The transverse optical (TO) modes that represent the out of phase vibrations of Cu atoms, have lower frequencies than that of the LO modes. Fig. 1(b) shows that Cu₂Si monolayer has

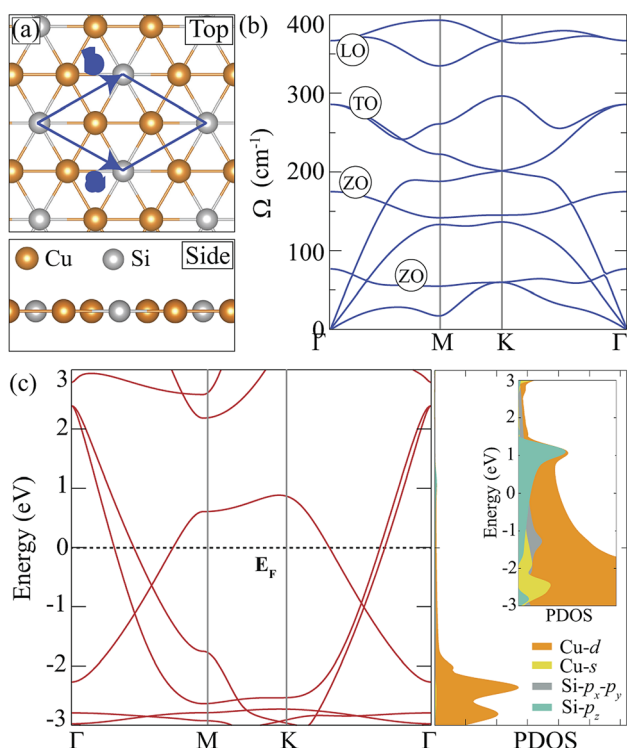


Fig. 1 (a) Top and side views of the pristine Cu₂Si monolayer. The blue rhombus represents the unit cell. (b) The phonon band dispersion of 5 × 5 × 1 supercell of Cu₂Si monolayer is displayed through the irreducible Brillouin zone. (c) The electronic band dispersion and partial density of states (PDOS) for the primitive unit cell of Cu₂Si monolayer. Fermi level (E_F) is set to zero.



Cu₂Si monolayer. Moreover, the nonmagnetic ground state of the material is not affected by the adsorption of the H atom.

For the hydrogenation process, it is essential to understand the interaction between the H adatoms. We investigate $3 \times 3 \times 1$ monolayer of Cu₂Si in which two H adatoms are bonded to the Si sites from (i) one side (single-sided) and (ii) both sides (double-sided) of the monolayer. Since the separation of the two nearest Si sites is equal to 4.10 Å, the coupling between two H adatoms is negligible. The binding energies of single-sided and double-sided structures are calculated to be -2.68 and -2.66 eV, respectively. The bond strength between the Si and H atoms in the H-adsorbed Cu₂Si is weaker than the one between two H atoms in the H₂ molecule (-4.54 eV). Thus, for the hydrogenation of the pristine monolayer, an extra energy is required to dissociate the hydrogen atoms of the H₂ molecule. In order to validate this discussion, adsorption of a H₂ molecule on Cu₂Si is also investigated and it is found that H₂ molecule is physisorbed ~ 4 Å above the pristine monolayer of Cu₂Si with a weak vdW interaction of -0.20 eV. For this reason the hydrogenation of Cu₂Si monolayer is only possible with the atomic hydrogen (which can be produced by hot wire chemical vapor deposition^{43,44}). Feasibility of the hydrogenation is possible with the atomic hydrogen processes by doing plasma hydrogenation; in particular, plasma hydrogenation is used in synthesis of graphene.⁴⁵

IV. Hydrogenated derivatives of Cu₂Si

In this section, we investigate the structural, vibrational and electronic properties of hydrogenated derivatives of Cu₂Si monolayer. We predict structures with various H coverage and analyze their stability by examining the vibrational spectra. Consistent with single atom adsorption calculations, surface coverage calculations show that H atoms do not prefer to bind on top of Cu atoms. It is found that the structures containing Cu–H bond are unable to generate the required restoring force against the atomic motions (see ref. 48). Here, we investigate three of the dynamically stable hydrogenated derivatives of Cu₂Si monolayer with the highest hydrogen concentration. For convenience, we label these structures according to their percentage of hydrogen coverage and their hydrogenated surfaces. Structure with a stoichiometry of Cu₄Si₂H, which is hydrogenated from double sides and has a hydrogenation atomic ratio of 16.7%, is labeled as low_H-d. For other two structures, the hydrogen concentration is 33.3% and stoichiometry is Cu₂SiH, but they differ in terms of the hydrogenated surfaces. Single-sided and double-sided Cu₂SiH structures are labeled as high_H-s and high_H-d, respectively. Various other hydrogenation scenarios were also considered but they all led to instabilities in the vibrational spectra.

A. Structural properties

Among the three hydrogenated derivatives, the monolayer low_H-d has the lowest amount of hydrogen. It has a unit cell containing 14 atoms and only the half of the Si atoms in the unit cell are hydrogenated. The hydrogenation leads to a 1.3%

contraction of in-plane lattice constant of the Cu₂Si monolayer. Although the *a* and *b* lattice parameters are found to be equal, its lattice structure is not a perfect hexagon since the angle between them is 58.4° . The bond lengths of Cu–Cu and Cu–Si are no longer equal to each other as is in the pristine structure and they vary from 2.33 to 2.46 Å. The bond distance between Si and H atoms is 1.51 Å. Bader charge analysis reveals that the average value of the total electron donation of each Si in low_H-d increases by $0.2e$ compared to the pristine monolayer.

For the monolayers high_H-s and high_H-d, the H concentration is doubled. The monolayers of high_H-s and high_H-d contain 4 and 16 atoms in their unit cells, respectively. Compared to the pristine monolayer, the lattice constants for both of the structures are found to increase less than 1%. Although the monolayer of high_H-s preserves its perfect hexagonal lattice structure, it is found that the monolayer of high_H-d is slightly distorted. Calculated bond lengths of Si–H for the monolayers of high_H-s and high_H-d, are 1.51 Å and 1.52 Å, respectively. For high_H-s and high_H-d structures, the average electron donation of Si atom to H atom is calculated to be same with a value of $0.6e$.

B. Vibrational properties

Here, we discuss how the vibrational properties of Cu₂Si monolayer change with surface hydrogenation. The calculated phonon spectra of the hydrogenated derivatives of Cu₂Si monolayer are demonstrated in Fig. 3(a)–(c). The vibrational analyses reveal that the monolayers of low_H-d, high_H-s and high_H-d have positive phonon branches through the whole BZ indicating the dynamical stability of the structures at $T = 0$ K.

Since the unit cells of the pristine Cu₂Si and high_H-s are similar, their phonon band diagrams can be directly compared. Although there is a resemblance between their phonon band

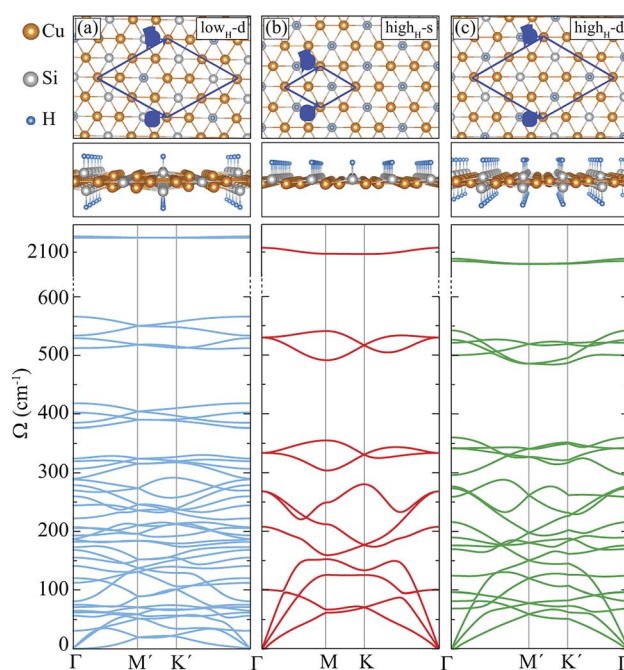


Fig. 3 Top and side views, and phonon band structures of the hydrogenated monolayers: (a) low_H-d, (b) high_H-s, and (c) high_H-d.



diagrams, LO and TO modes of pristine structure soften in the hydrogenated structure. Since Si atoms donate electron to the H atoms, the in-plane bonds of Si with Cu weaken and this leads to a decrease in the mode frequencies. On the other hand, ZO modes dominated by the Cu motions harden (which is discussed in Sec. IV C).

Furthermore, it is seen from the Fig. 3(a)–(c), the soft phonon mode previously seen at the M point of the phonon band diagram of Cu_2Si monolayer disappears when the material is hydrogenated. Differing from the pristine Cu_2Si , hydrogenated derivatives have high-frequency modes between 2000–2100 cm^{-1} (see Fig. 3) indicating the formation of strong Si–H bonds. H atoms are relatively much lighter than the Si and Cu atoms and thus, it is expected that the phonon modes that correspond to the Si–H bonds have much higher frequencies. These high-frequency modes have out-of plane character and include out-of-phase motions of Si and H atoms in all cases.

The effect of the hydrogenation on the constant-volume specific heat of the material is also investigated. The specific heat of structures as a function of phonon frequency, ω , is calculated as follows,⁴⁶

$$C_v = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 e^x}{(e^x - 1)^2}, \quad (2)$$

where $x = \hbar\omega/k_B T$. \hbar and k_B are Planck and Boltzmann constants, respectively and $D_p(\omega)$ denotes the phonon density of states (DOS).

Atom-projected partial phonon DOS of pristine and hydrogenated derivatives of Cu_2Si monolayer are presented in Fig. 4(a). At the low frequencies (*i.e.* $< 300 \text{ cm}^{-1}$), it is seen that the main contribution to the DOS comes from the Cu atoms, whereas the DOS of Si atoms dominate at relatively high frequencies (from 300 to 430 cm^{-1}) as expected from the masses of these atoms. In the highest frequency region (*i.e.* $> 500 \text{ cm}^{-1}$) contribution of the H atoms are dominant. The contribution of the Si atom in this region to the phonon DOS reveals the interaction of Si and H atoms.

Temperature dependent variation of the derivative of the phonon occupation functions are also illustrated in Fig. 4(a). These functions determine the contribution of vibrational modes to the specific heat of a material. It is evident that the hydrogen modes, which have very high frequency values, contribute more to the specific heat of the material at high temperatures. As a result of this, as the amount of hydrogenation increases, the higher temperature specific heat of the material also increases (see Fig. 4(b)). Moreover, it is well known that the hydrogenation of a material leads to decrease in its mass density which gives rise to an increase in its specific heat at high temperatures. As the temperature is lowered, the specific heat values of all these structures get close to each other, and at temperatures around 100 K, they merge to the same value. As the temperature is further lowered (around 20 K), the specific heat of pristine Cu_2Si becomes higher than those of the hydrogenated derivatives. A similar crossover in the specific heat values is also reported for graphite and diamond structures.⁴⁷ At room temperature specific heat values of Cu_2Si ,

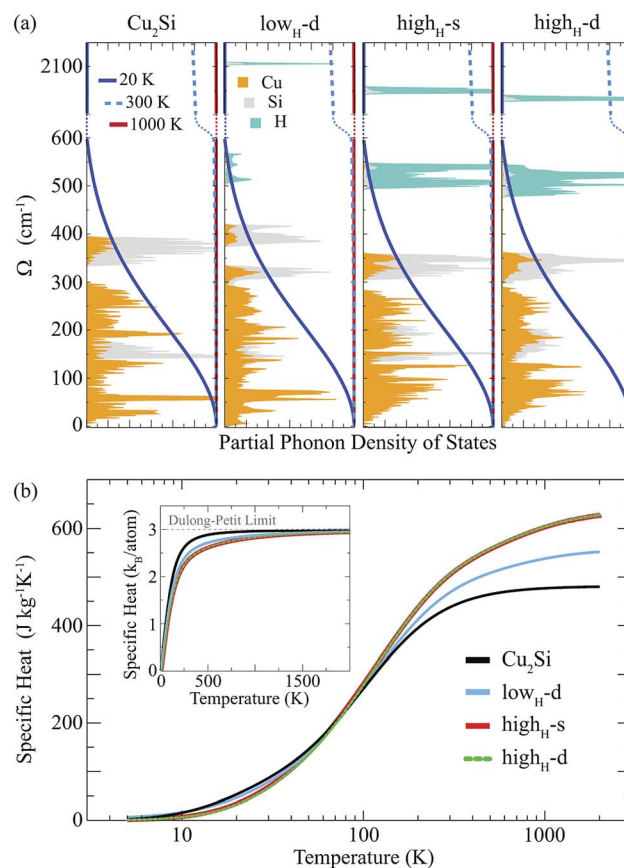


Fig. 4 (a) Phonon partial density of states and derivative of the phonon occupation functions of the Cu_2Si monolayer and its hydrogenated derivatives at various temperatures. Red, light and dark blue lines represent the functions calculated at 1000, 300, and 20 K. (b) For the Cu_2Si monolayer and its hydrogenated derivatives, constant volume specific heat per mass is demonstrated as a function of temperature in logarithmic scale.

$\text{low}_\text{H-d}$, $\text{high}_\text{H-s}$ and $\text{high}_\text{H-d}$ are calculated to be 438, 470, 507 and 508 $\text{J kg}^{-1} \text{K}^{-1}$, respectively. Moreover, in the inset of Fig. 4(b) the specific heat per atom of all the structures are also presented. As seen from the figure the pristine structure approaches the Dulong–Petit limit at much lower temperatures than the hydrogenated derivatives. Debye temperature values are calculated to be 429, 867, 1102, and 1078 K, for Cu_2Si , $\text{low}_\text{H-d}$, $\text{high}_\text{H-s}$ and $\text{high}_\text{H-d}$, respectively.

C. Electronic properties

Hydrogenation of a material is a common method to tune its electronic properties. It has been reported that while pristine graphene is a conductor, fully hydrogenated graphene is a semiconductor and half-hydrogenated graphene is a ferromagnetic, small band-gap material.^{24,37} In this section, hydrogen coverage dependency of the electronic structure of Cu_2Si monolayer is investigated.

As already mentioned in Sec. III, pristine Cu_2Si is a metal and possesses nodal lines in its electronic structure. Electronic band dispersion and PDOS of hydrogenated derivatives of Cu_2Si are



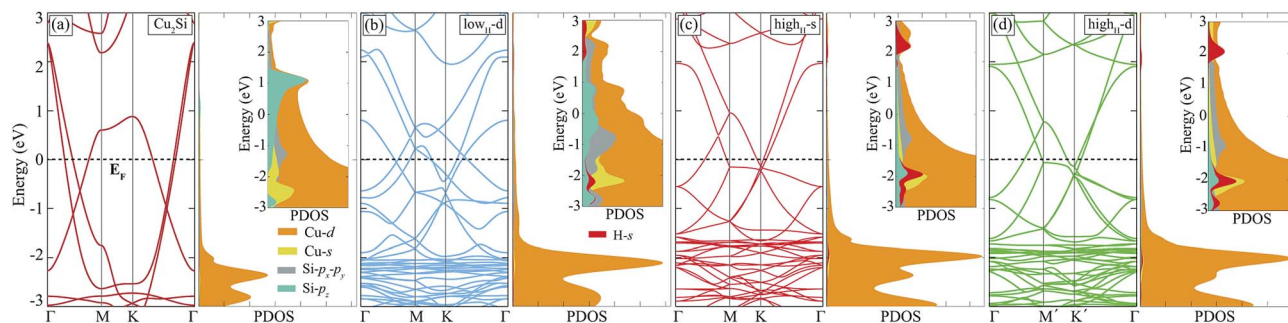


Fig. 5 Electronic band structure and PDOS are demonstrated for monolayers of (a) Cu_2Si , (b) $\text{low}_\text{H-d}$, (c) $\text{high}_\text{H-s}$, and (d) $\text{high}_\text{H-d}$. Fermi level, E_F , is set to zero. Inset figures of PDOS are rescaled with respect to the number of atoms per unit cell.

shown in Fig. 5. For the sake of comparison, the band structure of the pristine Cu_2Si is also added. As seen in the figure all of the hydrogenated derivatives preserve the metallic character as the pristine one. Although Cu_2Si monolayer possesses robust metallic character against hydrogenation, some deviations appear in the electronic structure as the hydrogen concentration increases. It is clearly seen that while the two nodal lines of pristine Cu_2Si reside between Γ and M points at 0.6 and 1.1 eV below the Fermi level, as the amount of hydrogen coverage increases, these nodal lines appear closer to the Fermi level (E_F) and at higher energies for $\text{low}_\text{H-d}$ and $\text{high}_\text{H-d}$, respectively. As seen in Fig. 5 (b) and (c), an energy gap occurs between the nodal lines which reside between Γ and M points.

To better understand the effect of H atoms on the electronic structure of Cu_2Si , we also analyze PDOS of the hydrogenated derivatives. As previously mentioned in Sec. III, the main contribution to the electronic structure around the Fermi level of the material originates from the Cu-d and Si-p orbitals. As seen in the Fig. 5 with increasing amount of hydrogen, the contribution from Si- p_z near the Fermi level decreases, and the hybridization between the orbitals of Si- p_z and Cu-d decreases. It is clearly seen from the PDOS diagrams of hydrogenated derivatives of the material peak positions and the shapes of the H-s and Si- p_z are overlapped which indicate the strong hybridization of these orbitals. As a result, the Si- p_z peak in PDOS of the pristine crystal dissolves and moves to lower energies when the structure is hydrogenated. Bonding states of Si-H reside about 2 eV below the E_F whereas the anti-bonding states of H-s are 2 eV above the E_F . The saturation of the dangling bonds of Si- p_z leads reduction of the surface activity of the Cu_2Si monolayer. In addition, the calculations reveal that hydrogenated derivatives of the material do not exhibit any net magnetic moment.

V. Conclusions

In this study, we investigated structures of hydrogenated derivatives of Cu_2Si monolayer by performing density functional theory-based calculations. The pristine monolayer of Cu_2Si composed of coplanar sublattices of hexagonal Cu and trigonal Si was found to be dynamically stable. Electronic structure calculations revealed that the monolayer Cu_2Si is a metal with a nonmagnetic ground state.

Adsorption of a single H atom on Cu_2Si monolayer was examined and the total energy calculations revealed that the most favorable adsorption site of H atom is Si site with a binding energy of -2.80 eV. Diffusion energy barrier and possible migration paths of a single H adsorbed on the structure were determined. Structural optimizations and phonon calculations revealed that there exists three dynamically stable hydrogenated monolayers of Cu_2Si . It was found that the planar geometry and the metallic electronic character of the material were not affected by different amounts of hydrogenation and the specific heat of the material at room temperature increases as the amount of hydrogenation increases. Cu_2Si monolayer with a planar geometry and robust electronic structure offers a new platform for nanoscale applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Computational resources were provided by TÜBİTAK ULAKBİM, High Performance and Grid Computing Center (TR-Grid e-Infrastructure). E. U. and R. T. S. acknowledge financial support from the TÜBİTAK through the project 117F131. H. S. acknowledges financial support from the TÜBİTAK through the project 117F095.

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- 48 See ESI† for the phonon spectra of dynamically unstable hydrogenated derivatives of Cu₂Si.

