Himalayan Journal of Science and Technology, Vol 7. (2023) ,18-25

Himalayan Journal of Science and Technology

Original Article

doi: FOR PEER REVIEW

ADSORPTION OF HYDROGEN MOLECULES IN NICKEL DECORATED SILICENE

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Abstract

First-principles simulations based on density functional theory (DFT) have been used to study the structural, electronic and magnetic properties of pristine and Ni decorated silicene sheets. Generalized Gradient Approximation (GGA) based exchange correlation functionals are used under software package Quantum ESPRESSO (QE), 6.5 versions. We have reconstructed the optimized unit cell of silicene, which has a face centered cubic (fcc) structure with two silicon atoms having lattice parameters a = b = 3.8 Å. The distance between two nearest silicene monolayers is found to be 20.5 Å which is large enough to neglect the interlayer interactions between 4×4 supercells of silicene monolayers. The atoms in the prepared supercell are fully relaxed under Bloyden-Fletcher-Goldfarb-Shanno (BFGS) scheme prior to the self-consistent, band structure and density of state (DoS) calculations. The pristine silicene is semi-metallic in nature possessing a Dirac-cone as in graphene. The h-site adsorption is found to be the most stable adsorption site of nickel in silicene with the binding energy of 4.69 *eV*. The addition of nickel atom completely distorts the hexagonal structure of silicene destroying the Dirac cone and the system becomes slightly insulating from its semi-metallic nature. We then construct a 4×4 nickel dimer silicene which further destroys the hexagonal silicene structure with further opening of the band gap. The charge transfer analysis in the Ni decorated systems shows the charge transfers of 0.163e and 0.294e in Ni adatom silicene and Ni dimer silicene respectively showing that the nickel atoms are adsorbed by weak van der Waals forces in both of the systems. We then proceed to hydrogen molecule adsorption in these prepared 4×4 silicene systems: pristine, Ni adatom and Ni dimer silicene systems. The adsorption energy of hydrogen in the Ni adatom silicene is found to be the largest making it the most effective system for hydrogen storage.

Article Info

Article history:

Received date:30 August 2023
Accepted date: 9 December 2023

Keywords:
Density functional theory,
Silicene,
Quantum ESPRESSO

1. Introduction

Two-dimensional nanomaterials have gained more attention because of their rich and enhanced properties. The discovery of graphene, a single layer of graphite, in 2004 by Novoselov, Geim, and coworkers can be considered as a giant leap in the research and development of 2D-material systems (Novoselov et al., 2004). This preliminary 2D material has lured the scientific society with its unusual electronic and mechanical properties towards scientific research for its potential applications. However, the challenges like optimizing cost-effective manufacturing processes for single layer graphene, absence of band-gap, integration of graphene into Si-based electronic technology, etc. have stimulated interests in the investigations of atomic layers of other materials. The discovery of graphene provides the breakthrough for the advancement in the field of research and stimulates a strong effort to search theoretically and experimentally for similar 2D materials. Silicene, the Si counterpart of graphene with its enhanced advantage of easy integration in the Si-based electronic technology was first theoretically put forward by Takeda and Shiraishi in 1994 (Takeda and Shiraishi, 1994). This 2D material of silicon was then re-investigated by Guzman-Verri et al. in 2007, who coined its name as silicene (Guzman-Verri and Lew Yan Voon, 2007). After that thousands of works based on simulations and experiments have been performed on silicene.

The low buckled structures of silicene where two silicene sub layers were separated by a small vertical distance (Δz) of 0.44 Å were confirmed in 2009 through first principles calculations and was also found to be a stable system (Cahangirov et al., 2009). This low-buckled structure of silicene due to larger Si-Si bond length was supposed to have numerous advantages over flat graphene due to smaller C-C bond length such as stronger spin-orbit coupling, better tun-ability of band gap, easier valley polarization and more suitability of valleytronics (Houssa et al., 2010). Such larger bond lengths between the silicon atoms prevent the atoms to be purely hybridized and as a result form π- bonds (Jose and Datta, 2014) which lead to mixed sp2−sp3 hybridization. The calculated parameters of silicene based of DFT are a=b= 3.87 Å, α = β = 900 and γ = 1200 and Si-Si bond length is found to be about 2.28 Å (Houssa et al., 2010). As in graphene, the band structure of silicene possesses a Dirac cone at K-point of the first Brillouin zone (Cahangirov et al., 2009). The availability of any sorts of energy sources in a nation affects directly in the economic development. The limitations in the supplies of fossil fuels and their bad impacts on environment have led to various efforts to find the reliable and renewable sources of energy which are also environment friendly. In this course, many scientists have claimed that in the future hydrogen fuel cells will overcome these problems from non-renewable sources of energy (Lamichhane et al., 2021). Hydrogen fuel is the green and eco-friendly source of energy with the dominant advantage of hydrogen abundance. In spite of this superiority, there is the main drawback of lack of proper procedure for hydrogen storage. Due to the costly process of hydrogen liquefaction and the problem of leakage in liquid hydrogen, there is a big problem to store hydrogen in liquid state. Thus, at present context the problem in the storage of hydrogen constraints the usability and application of hydrogen fuel cells (Ross, 2006). One way to physically store hydrogen gas in any materials is to store the gas through adsorption process in these materials. Adsorption is the adhesion of ions, atoms or molecules from the gas or liquid to a surface of liquid or solid phase in comparison to bulk, it is different from absorption. The process of adsorption forms a thin flim of adsorbate on the surface of adsorbent. The adsorption process can be classified into two types depending on the forces of attraction between adsorbent and adsorbate. These two types are: physisorption (when the attractive force is weak van der Waals force) and chemisorption (when th attractive force is strong covalent bond). Some of the earlier works include the storage of hydrogen in CNTs, graphene and other 2D hexagonal materials. For instance: the work done by Lamichhane et al for the storage of H2 gas in palladium metal decorated graphene found the positive result in which a number of hydrogen molecules are effectively adsorbed in the Pd added graphene system. Moreover, the various computational studies of adsorption of small gas molecules on 2D nanosheets were performed in our laboratory such as the studies of N. Pantha et al. on methane adsorption on graphene (Pantha et al., 2020a), and defected h-BN (Pantha et al., 2020b) and phosphorene sheets (Pantha et al., 2020c) which motivated us towards the further investigation of hydrogen adsorption on silicene sheet.

The inert 2D nanomaterials are investigated for the hydrogen storage due to its large surface area. In graphene, the major problem we face is metal clustering as the binding energy of metal in graphene is smaller than the cohesive energy of the bulk counterpart of the metal. Thus, we choose our host 2D system to be silicene. Further, the effectiveness of storing process can be enhanced by adding more adsorption sites on the surface of the 2D materials as done by Lamichhane et al by the decoration of graphene by Pd metal atoms. The addition of transition metals (TM) allows the storage of H2 molecules via Kubas-type interactions between the added TM atoms and H2 molecules (Xiang et al., 2019). Among the transition metals (Fe, Co and Ni), nickel atom has the largest binding energy in silicene. These arguments inspired us to investigate about the efficiency of hydrogen storage in nickel decorated silicene system.

2. Computational Method

We have performed the ab-initio calculations to investigate the structural, the electronic and magnetic properties of pristine silicene and Ni metal adatom and dimer silicene within the framework of density functional theory with van der Waals (vdW) interactions using QE code (Giannozzi et al., 2009). In order to include the electronic exchange and correlation effect in our system, the generalized gradient approximation (GGA) (Perdew et al., 1996) was utilized.

We made the use of the Kresse-Joubert (KJ) projector augmented wave (PAW) pseudopotential from the QE official website to take into account the complicated effects of the motion of an atom's core (*i.e.*, non-valence) electrons with an effective potential, which allows only the chemically active valence electrons to play vital role in our overall calculations. At first step, the structure is allowed to relax under BFGS (Pfrommer et al., 1997) scheme until the total energy change is less than 10^{-4} Ry (1 Ry = 13.6 eV) between two consecutive self-consistent field (scf) steps and each component of force acting is less than 10^{-3} $Ry/Bohrs$ to get geometrically optimized structure. Following the relax calculations, we carried out a self-consistent total energy calculation in which the Brillouin zone of silicene is sampled in K-space using the Monkhorst-Pack method with an appropriate number of mesh of K-points established after the convergence test.

3. Results and Discussion

3.1 Geometry and formation energy of Ni doped silicene

The hole site adsorption of nickel atom is found to be the most stable site for the metal adsorption. Due to the addition of Ni atom, the perfect hexagonal structure of pristine silicene gets disturbed as Si-Si bond lengths and Si-Si-Si bond angles become unequal. The distance between the Si atoms enclosing the honey-comb structure at the center of which a Ni atom is introduced becomes irregularly distorted from originally equal distancing between Si-Si atoms of 2.28 Å. The distances between the Si atoms of the particular honey-comb structure become unequal with the new nearest distance being about 2.20 Å between the Si atoms. The introduction of Ni atom also unevenly changes the fairly regular bond angle of 120^0 between Si-Si-Si atoms due to which the hexagonal silicon structure surrounding Ni atom appears narrower than others. Further, the equal distancing between two sub-layers in the pristine silicene monolayer also becomes irregular with the new buckling heights ranging from 0.08 Å to 0.89 Å which can be clearly seen. Also the nickel atom is positioned at a distance 0.27 Å above the silicene sheet.

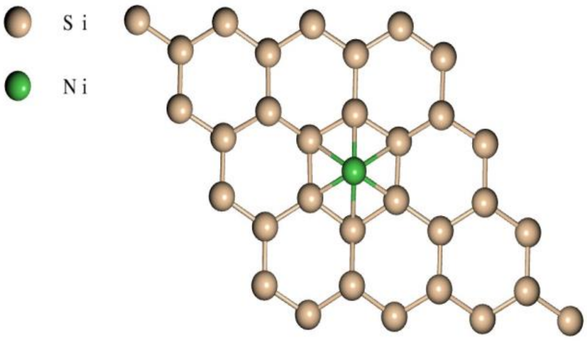


Figure 1: Top view of relaxed Ni adatom Silicene at h-site.

After the addition of Ni dimer in h-sites configuration, the perfect hexagonal structure of pristine silicene becomes distorted as Si-Si bond lengths and bond angles become unequal. The distance between the Si atoms enclosing the honey-comb structures in each of which a Ni atom is added becomes irregularly distorted from originally equal distancing of 2.28 Å with the new nearest distance being 2.618 Å. The distance between two nickel atoms at h-sites is found to be 3.77 Å. The introduction of Ni atom also changes the fairly regular bond angle between Si-Si-Si atoms. Further, the equal distancing between two sub-layers in the pristine silicene mono layer also becomes irregular with the new buckling heights ranging from 0.01 Å to 0.91 Å. Also the nickel atoms are positioned such that the left Ni atom lies at a distance 0.15 Å above the silicene sheet while the right Ni lies at a distance 0.14 Å above the sheet.

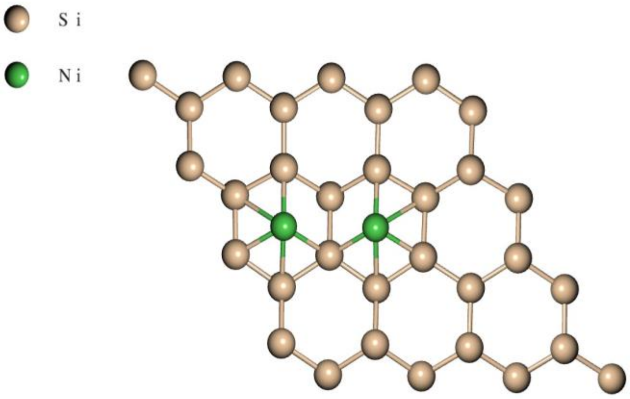


Figure 2: Top view of relaxed Ni dimer Silicene at h-sites.

The binding energy (B.E.) of each Ni atom in our Ni decorated silicene systems is given by,

$$E_{binding} = (n\,E_{Ni} + E_{pristinesilicene} - E_{NiSilicene})\,/\,n \qquad (1)$$

where n is the number of added nickel atoms where, E_{Ni} is the energy of an isolated Ni atom, $E_{pristinesilicene}$ is the energy of pristine silicene system and $E_{NiSilicene}$ is the energy of Ni decorated silicene system.

The B.E. per Ni atom in Ni adatom and Ni dimer silicene systems are found to be 4.690 *eV* and 4.598 eV respectively.

3.2 *Electronic properties*

In this section we discuss the electronic structures of pristine silicene, Ni doped silicene and Ni dimer silicene on the basis of spin polarized band structure calculations and the density of states calculation. The band structure of pristine silicene as shown in figure 3 suggests the silicene to be a semi metal as it exhibits as a zero band gap semiconductor. Clearly, the Dirac cone occurs as the K-point of the first Brillouin zone (BZ) as observed in graphene. At this point, the π and $\pi*$ bands of silicene cross linearly at the Fermi level causing the formation of mass less Dirac fermions at the point.

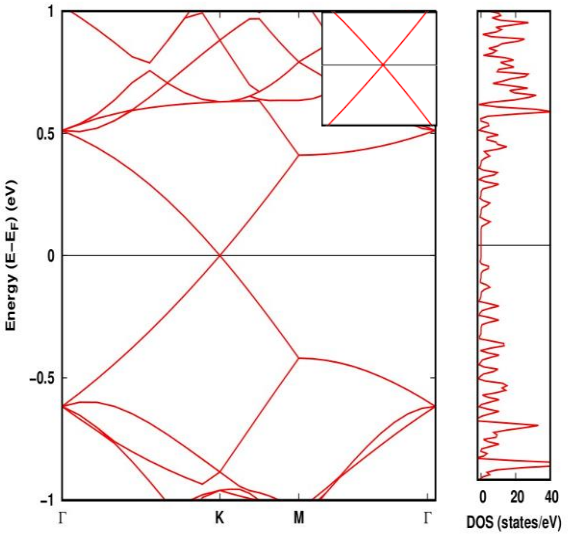


Figure 3: Band structure of 4×4 supercell of pristine silicene where the energies are shifted relative to the Fermi energy (E_F) = -2.930 *eV*.

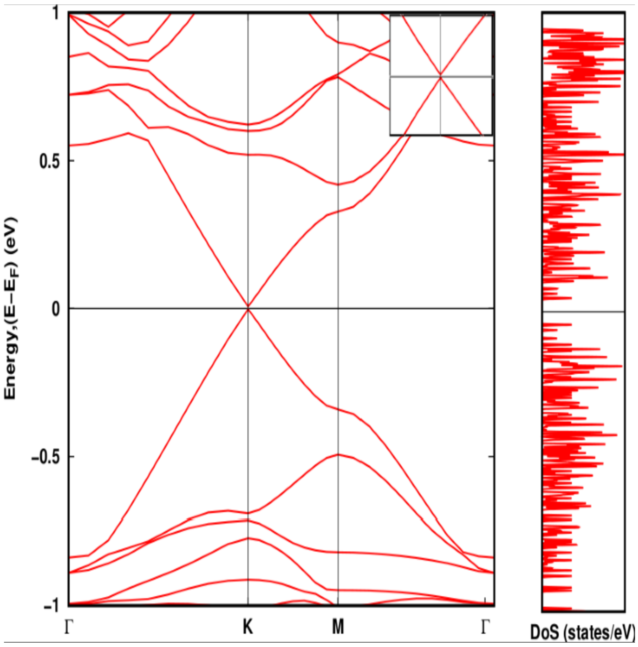


Figure 4: Band structure of 4×4 Ni adatom supercell of silicene where the energies are shifted relative to the Fermi energy (E_F) = -2.820 *eV*. [Band gap = 6.8 *meV*]

The band structure in figure 4 shows that the addition of Ni atom at hole site of pristine silicene system brings some notable changes in the electronic properties of the system. Clearly, the Fermi energy of the system increases after Ni addition and a small band gap is formed at the K-point destroying the initial Dirac cone structure at the point. A small band gap of about 6.8 *meV* is formed which comes in a close agreement with the band gap of about 8.7 *meV* observed by Kent et al (McGee et al., 2013). Thus, the system slightly moves towards semiconductor type behavior deviating from its semi metallic behavior after Ni decoration.

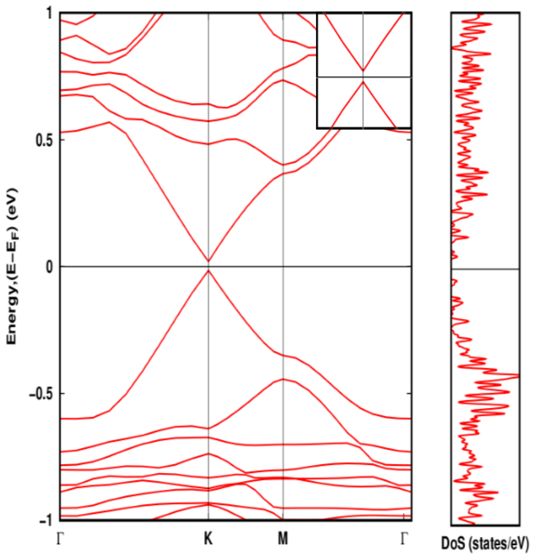


Figure 5: Band structure of 4×4 Ni dimer supercell of silicene where the energies are shifted relative to the Fermi energy (E_F) = -2.77 *eV*. [Band gap = 34.2 *meV*]

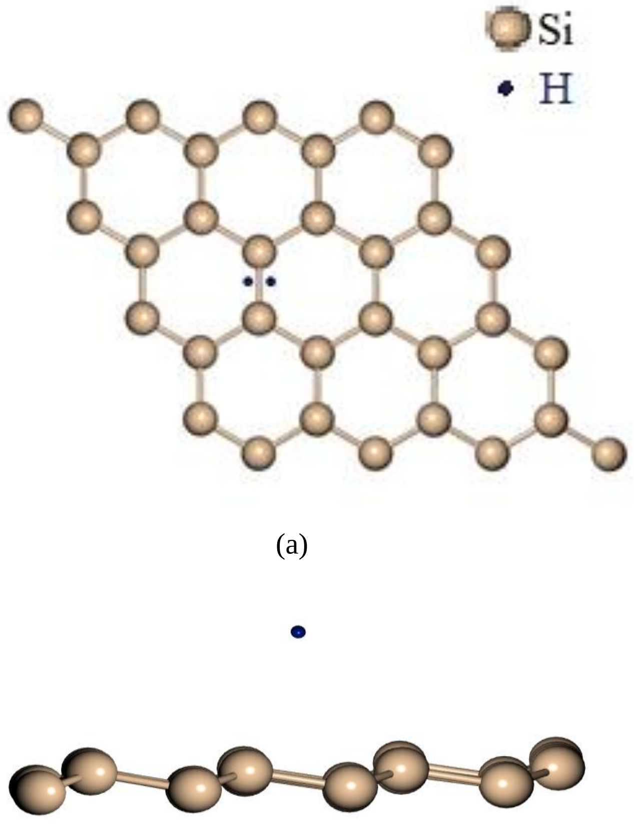
The band structure in figure 5 reveals that the opening of band gap becomes more significant when Ni dimer are added at hole sites than the addition of Ni adatom in the silicene sheet. The Ni dimer silicene system has the band gap of about 34.2 *meV* such that the Dirac cone in the pristine silicene completely disappears. Such small band gaps can be very important for micro-electronic devices.

Hydrogen Adsorbed Silicene Systems

Finally, we move on to the main motive which is to adsorb hydrogen gas in different prepared silicene systems. We place a hydrogen molecule above the 4×4 pristine, Ni adatom and Ni dimer silicene sheets and allow the system to relax using pw.x calculations. We consider two different orientations of hydrogen molecule viz. horizontal to the silicene sheet and vertical to the silicene sheet. We find that the horizontal orientation of the hydrogen molecule to be more stable than the vertical orientation when adsorbed over all types of prepared silicene systems. The different views of relaxed hydrogen adsorbed pristine, Ni adatom and Ni dimer silicene systems when placed horizontally to the silicene sheet. Further, the adsorption energy of hydrogen in these silicene systems is given as,

$$E_{ad} = E_{gas} + E_{system} - E_{gas+system} \tag{2}$$

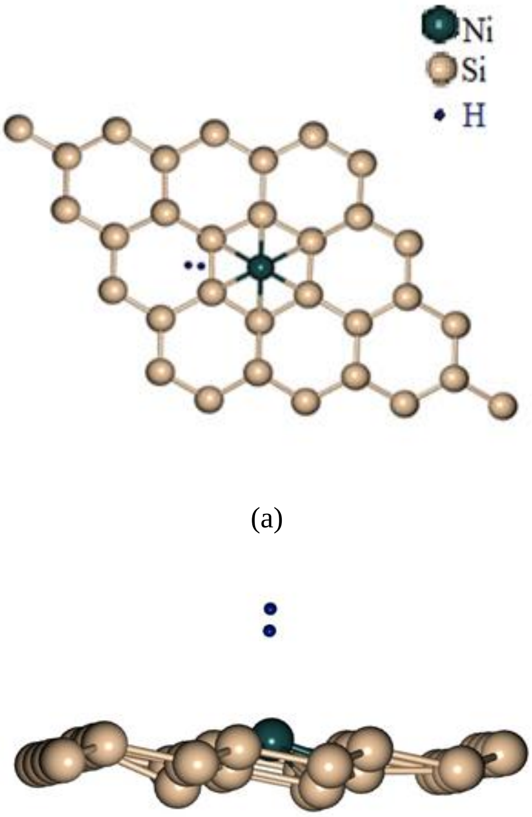
Where, E_{gas} is energy of H_2 molecule, E_{system} is the energy of system before gas adsorption and $E_{gas+system}$ is the energy of system after gas adsorption.



(a)

(b)

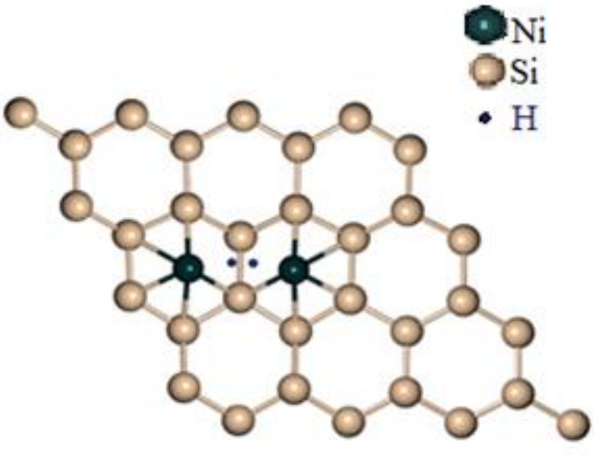
Figure 6: (a) Top and (b) Side views of a hydrogen molecule adsorbed 4×4 pristine silicene.



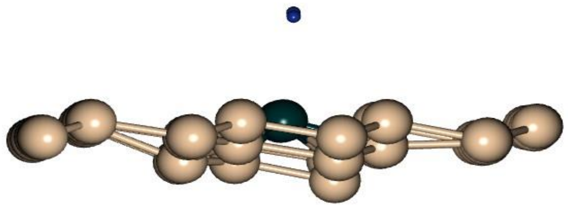
(a)

(b)

Figure 7: (a) Top and (b) Side views of a hydrogen molecule adsorbed 4×4 Ni adatom silicene.



(a)



(b)

Figure 8: (a) Top and (b) Side views of a hydrogen molecule adsorbed 4×4 Ni dimer silicene.

Table 1: Adsorption energies for pristine and Ni metal decorated silicene systems of 4×4 silicene supercell after hydrogen molecule adsorption hydrogen gas in all the systems

System	Distance	Adsorption Energy (E_{ad})
Pristine Silicene	3.44 Å	284.83 *meV*
Ni adatom Silicene	2.97 Å	317.14 *meV*
Ni dimer Silicene	2.80 Å	34.27 *meV*

We have attempted to adsorb one hydrogen molecule near the midpoint of two nearest silicon atoms each of sublayer A and B. In table 1, ‘distance’ refers to the height above different systems of silicene mono layer where the hydrogen molecule lies after adsorption. The hydrogen molecule is adsorbed more close to the silicene sheet in Ni dimer silicene system. In pristine and Ni dimer silicene systems, the hydrogen molecule is adsorbed symmetrically between the two Si atoms and is placed parallel to the silicene surface as shown in figure, in Ni adatom system the adsorbed hydrogen molecule is situated on the left of these Si atoms and is slightly tilted on the surface of surface of silicene as shown in figure. The adsorption energy column shows that the Ni adatom silicene is more favorable for hydrogen adsorption than the pristine and the Ni dimer silicene systems. The positive values of the adsorption energies in all the systems indicate the spontaneous adsorptions of hydrogen gas in all the systems. However, the adsorption energy is the largest in Ni adatom system which makes it more reliable for hydrogen adsorption than other silicene systems. The hydrogen bond lengths in Ni decorated silicene systems after its adsorption remain to be unchanged which indicates the absence of Kubas interaction between the transition metal and hydrogen molecule. It may be because we have considered the valley site as the adsorption site for hydrogen molecule where the effect of Ni doped at hole site may be very small. The Kubas interaction may be prominent if we have considered adsorbing hydrogen molecule directly above the Ni atom. The slight increase in the adsorption energy in Ni adatom system than that in the pristine system may be because of slight increase in the adsorption area after nickel doping. However, the adsorption energy decreases in Ni dimer silicene which may be because of the repulsive interaction of between two doped Ni atoms hampering the effective adsorption of hydrogen gas.

4. Conclusion

We performed first-principles calculations to study the structural stability, electronic, and magnetic properties of pristine silicene, Ni adatom silicene, and Ni dimer silicene and also investigated about the hydrogen gas adsorption in these silicene systems. The pristine silicine system exhibited semimetallic behavior with the presence of Dirac cone in its band structure as expected. We found out the hole site adsorption of nickel in pristine silicene sheet to be the most stable site with the highest binding energy of 4.69 *eV*. We then prepared Ni dimer silicene system by doping two Ni atoms at h-sites of two consecutive honey-comb structures in 4×4 silicene system. After examining the structural details of Ni decorated systems, we found that the addition of nickel atom(s) completely destroy the hexagonal structure of the pristine system with the changes in bond lengths, bond angles and buckling heights. The band structures of these metal decorated systems showed the destruction of Dirac cone. The systems after Ni decoration still remained to be non-magnetic as the pristine system. We also studied about the charge transfers utilizing Bader charge analysis in Ni decorated silicene systems and found that the charge transfer from Si atoms per Ni atom is smaller in Ni adatom system than that in Ni dimer silicene.

The adsorption energy of hydrogen molecule was found to be the largest in Ni adatom system making it the most reliable media for hydrogen storage among these three considered silicene systems. The band structures and density of state plots of the silicene systems remains almost unchanged after hydrogen adsorption which means that there is no any significant charge transfers taking place between the hydrogen and silicene systems and the gas molecule is adsorbed by weak van der Waals force.

Acknowledgments

We acknowledge the computational facility provided by Office of Research Directorate, Rector Office, Tribhuwan University through the Natronal priority project ‘TU-NPAR-077/078-ErG14’. We also acknowledge the useful scientific discussions with Prof. Dr. Narayan Prasad Adhikari.

Conflicts of Interest

The authors declare that there is no conflict of interest.

Funding

The partial financial support was provided to Mr. Prajwal Shrestha by University Grants Commission for the completion of his thesis work..

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