Comparison of Properties of Silicon Nanoribbon Materials Adsorbed One and Two Lithium Atoms.

Dang Phuc Kien-Cuong and Tran Minh-Tien

February 20, 2024

Comparison of properties of silicon nanoribbon materials adsorbed one and two lithium atoms.

Kien-Cuong Dang Phuc [1]*, Minh-Tien Tran* [2]

(1) *Nam Ky Khoi Nghia High School, Tien Giang Province, Vietnam*
(2) *Applied Technology Institute, Thu Dau Mot University, Binh Duong Province, Vietnam*

Abstract: This paper presents the results of research on pristine armchair-side silicene nanoribbon (ASiNR) and zigzag (ZSiNR) systems, adsorption one (ASiNR-1Li, ZSiNR-1Li) and two Lithium atoms (ASiNR-2Li, ZSiNR-2Li). The adsorption site is placed at the optimal position as "hollow". The VASP (Vienna Ab Initio Simulation Package) quantum simulation program based on density functional theory (DFT) is used for the calculations. The basic structural parameters as the lengths of the sides of the hexagonal ring, and the buckling are investigated. Electronic properties such as electron band structure, density of state, charge density distribution, electron displacement were also investigated. The results have shown that there are change in the structure of the atomic system after adsorption. The ASiNR has a band gap of more than 0.2 eV. The contribution of Si-$3p_x3p_y$ orbitals is major compared to other orbitals. There is a mixed hybridization of sp2 and sp3 in some specific regions. There is an electron shift from one region to another, creating several holes and regions of greater electron density around the absorbing.

Key words: band structure, atomic adsorption, lithium, density of states, silicene nanoribbons.

1. Introduction

In recent years, research on low-dimensional materials is developing very strongly all over the world. Since 2D monolayer graphene was discovered and successfully created from graphite by the authors (A. Geim et al., 2004), a series of similar 2D materials have been focused on research such as silicene, germanene. , stanene, phosphorene. This is a group of materials known collectively as Xene (with X=graph, silicon, german, stan, and phosphor). Among these materials, silicene is a material with great potential for applications in the field of electronics, because the silicene structure is based on silicon atoms, which are the basic elements in today's electronic devices. Incorporating silicene would be more advantageous than other atom-based materials. Silicene has a hexagonal structure similar to graphene, but the surface has a certain buckling, which is not flat like graphene. However, the 2D silicene material has a limitation that the band gap is almost zero, so it is very limited in its application to electronic devices. Various methods to create a band gap for silicene have been studied such as application of a perpendicular electric field, chemical methods, defect generation, or atomic adsorption. A study by the authors (Z. Y. Ni et al., 2012) used a perpendicular electric field to create a static potential difference between two silicene sublattices, leading to the breaking of the inverse symmetry between the two sublattices, create a direct no-go zone at K-points in the Brilluoin region. The results are made when the electric field increases, from 0 V/Å, 0.51 V/Å, 1.03 V/Å, …, to 1.2 V/Å. The results have shown that when the electric field is increased, the width of the band gap increases, the highest can reach 0.15 eV when the electric field is 1.2 V/Å. Many studies using chemical methods to create a band gap for silicene have been performed such as hydrogenation or halogenation (J. Zhao et al., 2016; N Gao et al., 2012; M. Houssa et al., 2011). In the hydrogenation method, individual atoms or pairs of hydrogen atoms are arranged alternately above and below. Fully hydrogenated silicon is known as silicane. Studies using density functional theories (DFTs) show that hydrogenation also leads to significant structural changes of silicene, namely affecting buckling indices, bond length, bond angles and shows that buckling distance can increase from 0.42 Å to 0.72 Å. DFT calculations for the electronic band structure of silicene upon halogenation show that the band gap can be extended to values of 1.469 eV; 1,979 eV; 1,950 eV and 1.194 eV for F, Cl, Br and I, respectively. The effect of adsorption of B, N, Al, P atoms on the two-dimensional silicene surface has been studied in detail by the authors (J. Sivek et al., 2013). In this study, the authors performed initial principle calculations based on density functional theory (DFT). From here, some electronic, magnetic and phonon properties of this material are investigated. The preferred adsorption sites are also shown in this work, which are named “valley”, “bridge”, “hollow” and “top”. By molecular dynamics calculations, the authors show that the system is stable at a minimum temperature of 500 K. The results show that the silicene surface is very reactive. In addition, silicene adsorbed Au, Hg, Tl, and Pb atoms has also been investigated by DFT calculations by T. P. Kaloni et al. These results indicate that the atom adsorbent in the “hollow” position is the most optimal, and that Au, Tl and Pb adsorption achieves significantly lower adsorption energies than that of Hg (Kaloni et al., 2014). . Many studies on two-dimensional silicene properties on metal adsorption have been carried out (H. Liu et al., 2014; R. Quhe et al., 2013; H. Sahin et al., 2016). The adsorbed metal atoms can be alkaline, alkaline earth or transition metals. The following results were obtained: showing that the preferred position when silicene adsorbed Li is in the "hollow" or "valley" position; especially for alkaline earth metals (except Ca), the preferred position is “valley”; Ca adsorption can lead to destruction of silicene structure; or transition metals (except Ag, Au and Hg) interact more strongly with silicene than with alkali or alkaline earth metals. Research on silicene nanoribbons (SiNRs) and atomic adsorption of SiNRs have also received a lot of research interest. The authors Mehdi Aghaei, at. al conducted a study on the theoretical stability of the structure of edge hydrogenated and edge fluorinated SiNRs through initial principle calculations (Mehdi Aghaei et al. , 2016). Various edge forms of SiNRs including armchair, zigzag, and Klein edges have been considered. The results show that, the Klein edge SiNRs are completely fluorinated, where each Si atom is terminated by three fluorine atoms, which is the most structurally stable atom. The results also show that the Klein edge structure when hydrogenated by three hydrogen atoms, or the zigzag edge structure hydrogenated by two hydrogen atoms, increases the stability of SiNRs similar to the armchair case hydrogenated by two hydrogen atoms; structural form is considered the most stable. The authors (Long Xu et al., 2015) studied the influence of Ti adsorption on ZSiNRs on electronic, magnetic and thermodynamic properties.

In this study, silicene nanoribbon extended in one dimension, with two typical edge forms, armchair edge and zigzag. The structural and electronic properties were investigated when these atomic systems adsorbed 1 and 2 Lithium atoms in the 'hollow' position, respectively. This is the most stable, optimal adsorption site that has been shown in many previous studies, but the structural and electronic properties have not been clearly and specifically shown.

2. Models and calculation methods

The structural and electronic properties of the ASiNRs and ZSiNRs materials systems in this study are performed based on density functional theory, through the simulation program VASP (Vienna Ab Initio Simulation Package). The pristine ASiNR and ZSiNR system in a unit cell containing 12 Si atoms, made up of 6 dimer lines; The two edges are functionalized by H atoms. The PBE (Perdew-Perke-Ernzerhof) function is used for correlation and exchange energy calculations. The PAW pseudopotential is used for electron-ion interaction descriptions. The maximum cut-off energy is set at 500 eV. One-dimensional periodic material system in the Oz direction. The k-point grid in the Monkhorst-Pack diagram used for optimal computation is 1x5x16 and 1x5x100 for autocomposite calculations.

The model of the system of atoms is presented in Figures 1, 2, 3. From these models, the optimal structural parameters and electronic properties are investigated. The results are shown in the next sections.

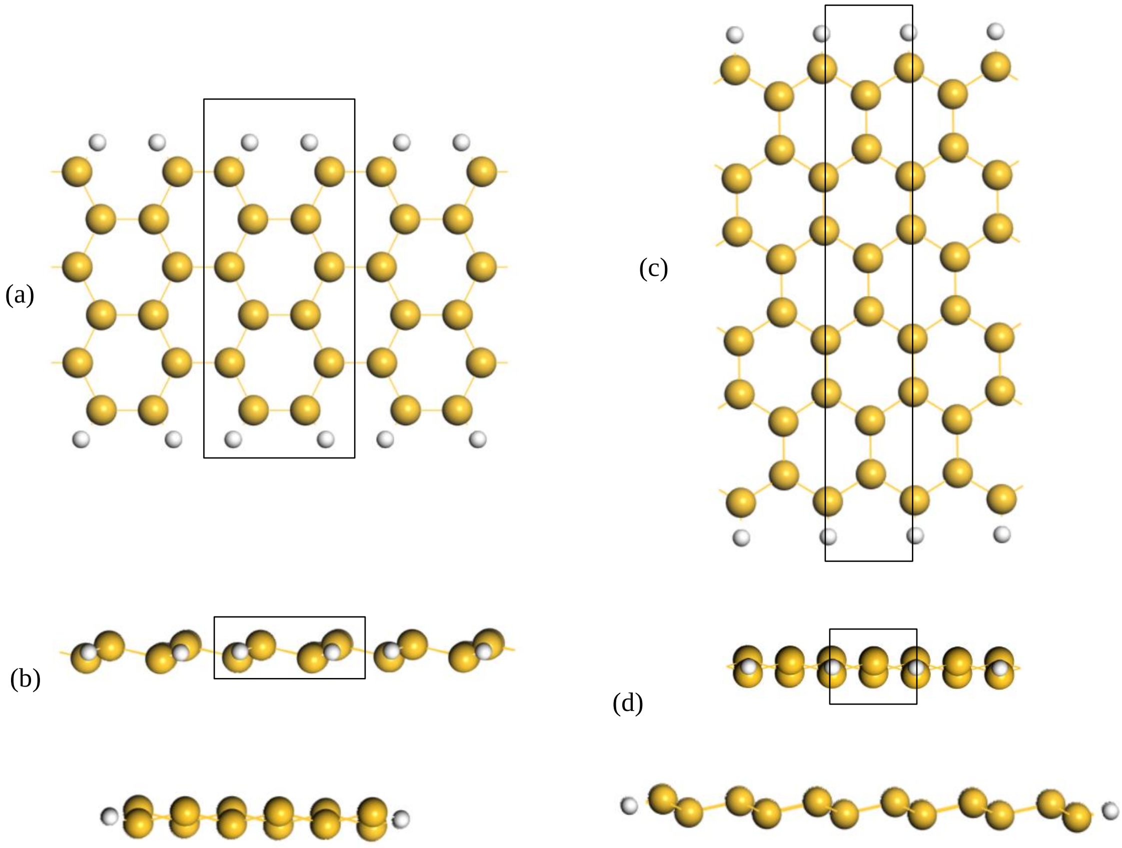


Fig 1. The structure of pristine ASiNR from top-down (1a) and side-by-side (1b); pristine ZSiNR in top down (1c) and side view (1d)

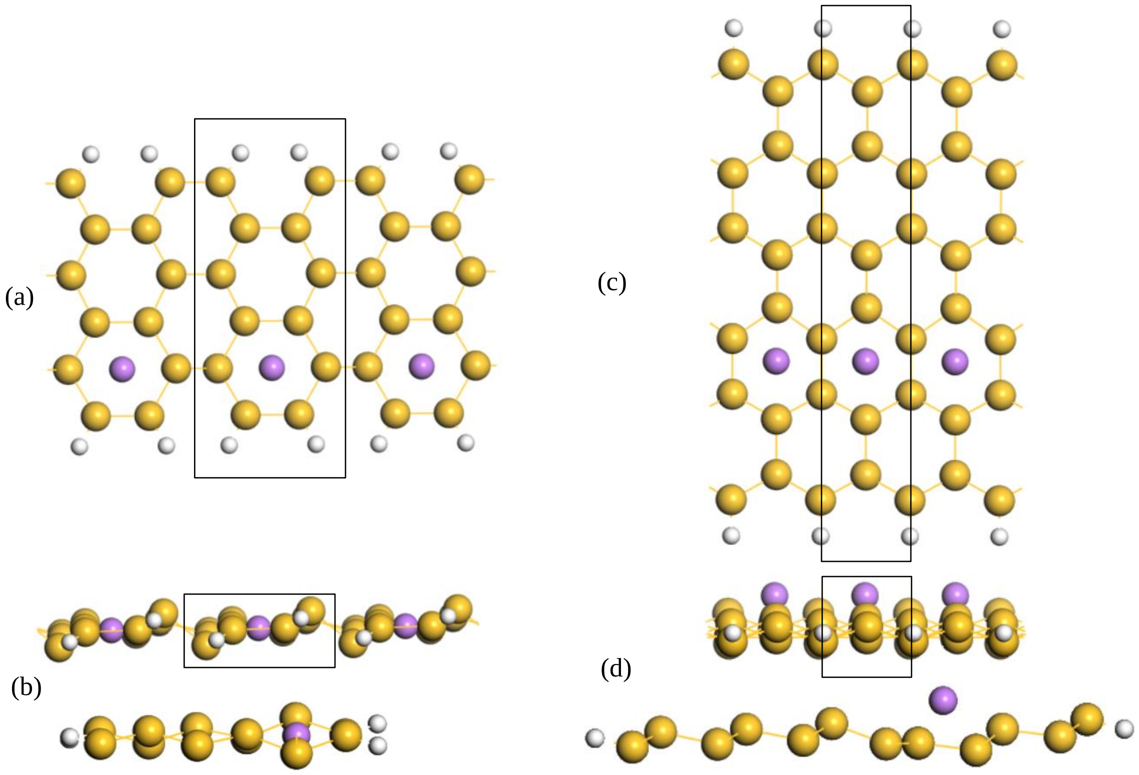


Fig 2. The structure of the ASiNR adsorbed one Si atom seen from the top (2a) and from the 2 sides (2b); ZSiNR adsorbed 1 Si viewed from the top (2c) and from the 2 sides (2d)

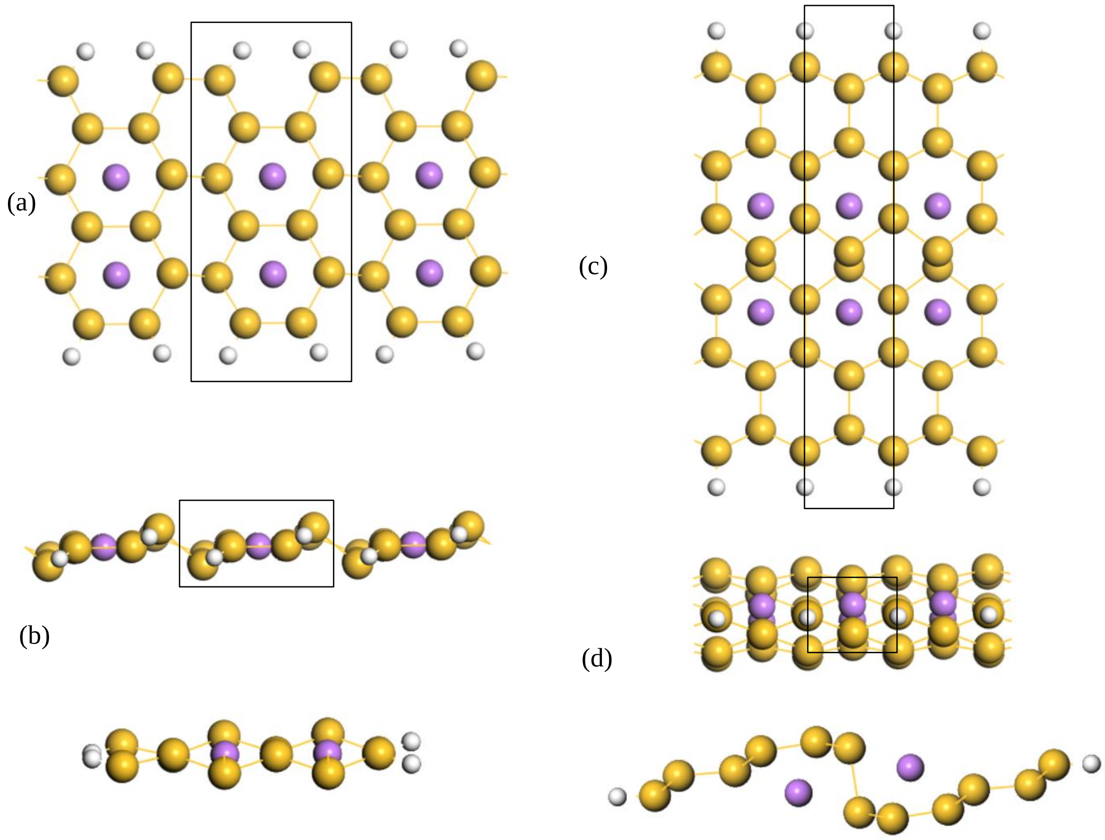


Fig 3. The structure of ASiNR absorbed 2 Si -top view (3a) and sides view (3b); absorbed 2 Si - top view (3c) and sides view (3d).

3. Results and discussion

3.1. The change of structure after adsorption

The structural parameters before and after adsorption are presented in table 1.

Tab 1. The bond length Si-Si 1st[Si-Si], 2nd[Si-Si] and buckling of ASiNR, ASiNR-1Li, ZSiNR-1Li, ASiNR-2Li, ZSiNR-2Li.

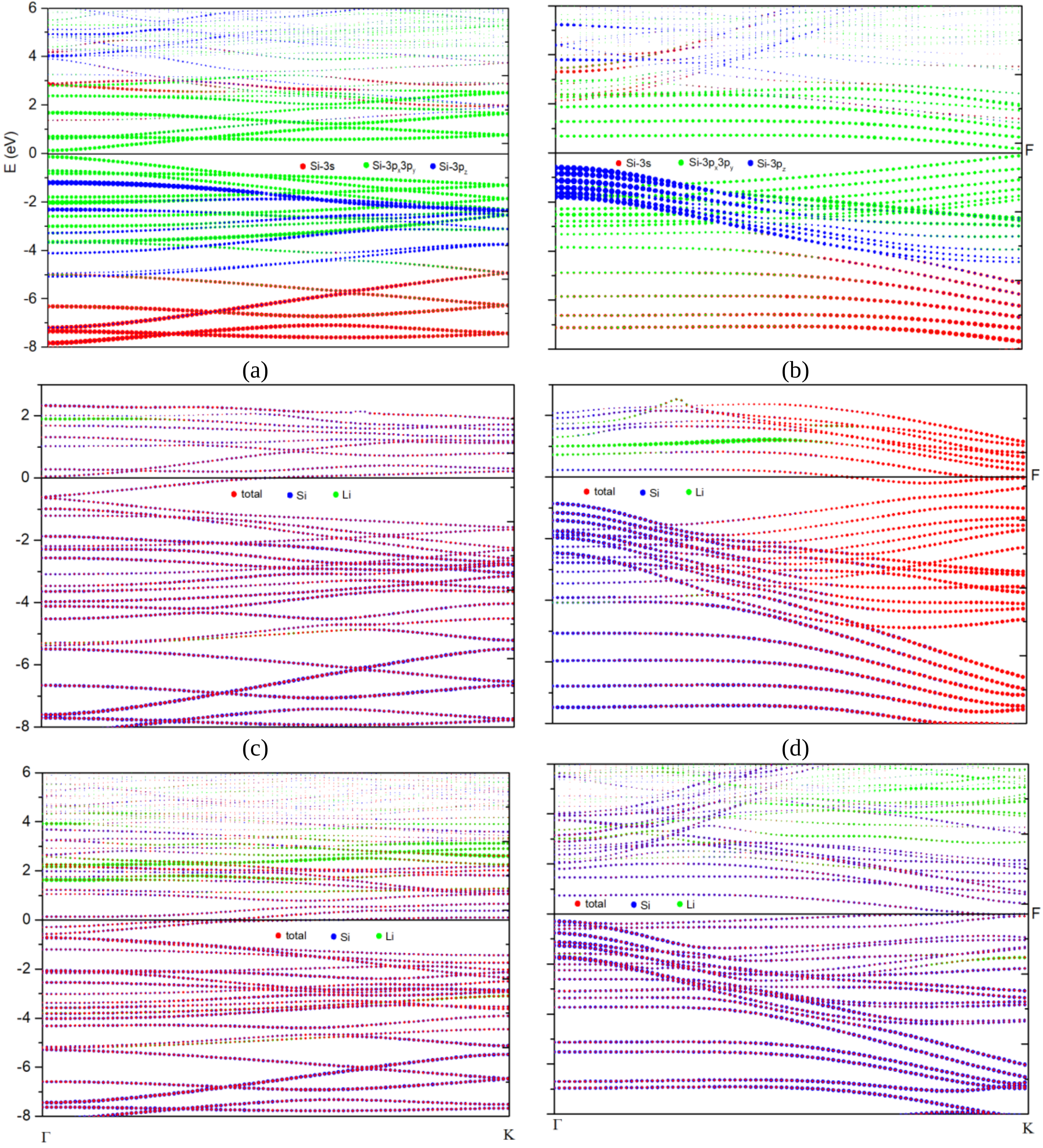
Configuration	**1st[Si-Si] (Å)**	**2nd[Si-Si] (Å)**	**δ (Å)**
ASiNR	2.20991	2.25821	0.55758
ZSiNR	2.23447	2.28723	0.63116
ASiNR-1Li	2.24830	2.36958	1.39498
ZSiNR-1Li	2.24537	2.27645	1.94559
ASiNR-2Li	2.25354	2.37227	1.48179
ZSiNR-2Li	2.23329	2.24655	3.05685

The results show that the conformational parameters change significantly after Li atom adsorption. Specifically, in the ASiNR structure, the Si-Si bond length at the proximal edge increased to 0.038 Å and 0.044 Å when adsorbing one and two Li atoms, respectively; for the second edge, the increments are 0.111 Å and 0.114 respectively. The buckling of ASiNR also has a significant change. Specifically, when adsorbing a Li atom, the structural irregularity increased by 0.837 Å; this increase is 0.924 Å after adsorption of two Li atoms. However, for the ZSiNR configuration, it is not always the case that the Si-Si bond length increases for the near and far edges. Specifically, for the first edge, the Si-Si bond length increased only to 0.011 Å but decreased by 0.001 Å after the adsorption of two Li atoms. For the second edge, the Si-Si bond length is also reduced by 0.011 Å for the case of single Li adsorption and by 0.041 for the case of two Li atoms. The buckling of ZSiNR is significantly changed. The increments are 1.314 Å and 2.426 Å respectively. From these results, it can be seen that with the ASiNR configuration, the hexagonal ring size is significantly changed by Si adsorption, but the structural irregularity has only a small change; while with the ZSiNR configuration, the ring size does not change much, but the bumpiness increases greatly, especially for the case of adsorption of two Si atoms into the "hollow" position in two consecutive hexagonal rings.

3.2. The electronic properties

3.2.1. The electron band structures

One of the factors determining the properties of materials belonging to the group of semiconductors or metals is based on the electronic band structure of the material system. The electronic band structures of ASiNR, ASiNR-1Li, ASiNR-2Li, ZSiNR, ZSiNR-1Li, ZSiNR-2Li are shown in figure 4, including the electron band structure separated according to the orbital contribution of ASiNR (a), ZSiNR (b), and atomically of ASiNR-1Li(c), ZSiNR-1Li(d), ASiNR-2Li(e), and ZSiNR-2Li(f). The results show that, for ASiNR, there is a band gap of about 0.262 eV open at point Γ.



(a)

(b)

(c)

(d)

(e)

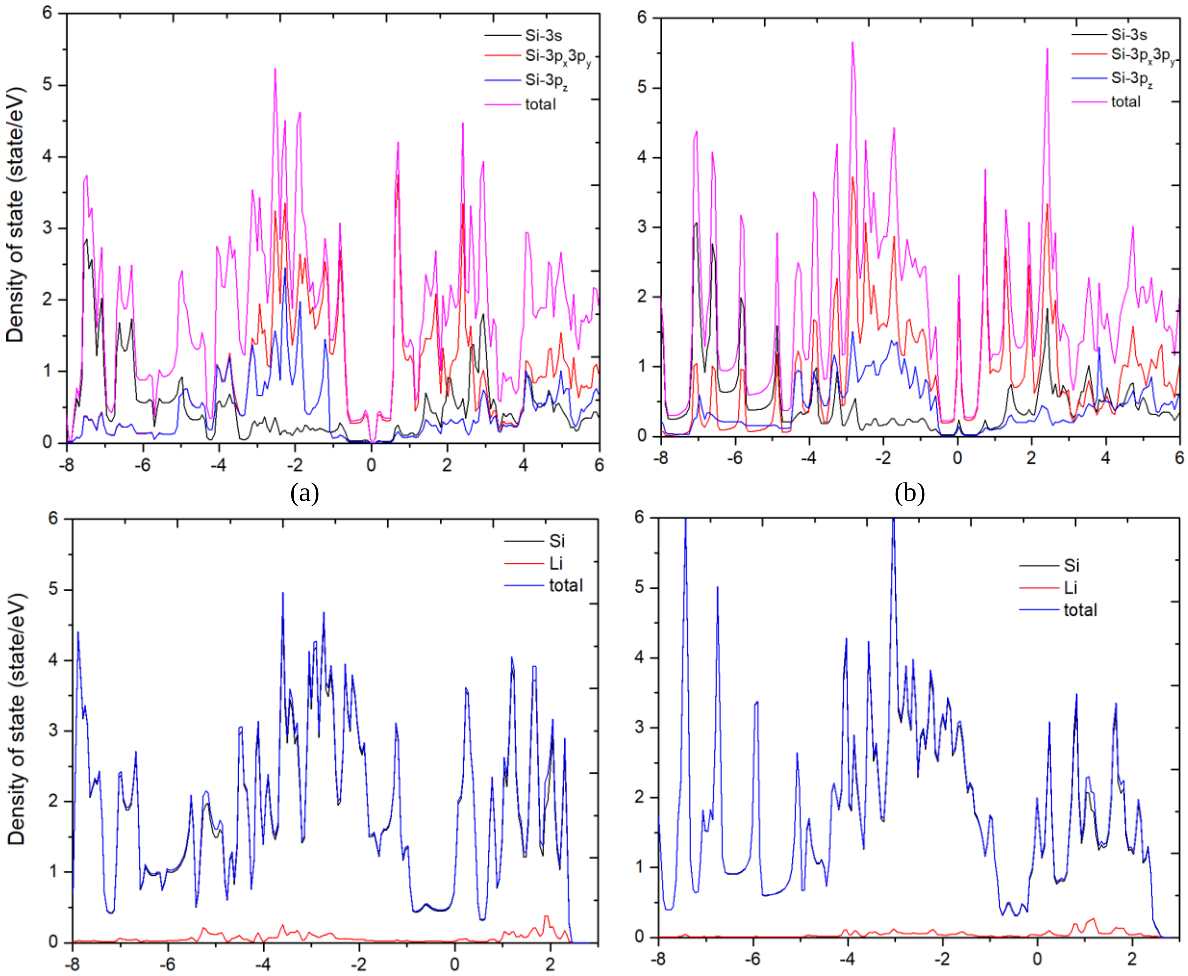
(f)

Fig 4. The electronic band structure is separated according to the orbital contribution of ASiNR (a), ZSiNR (b), ASiNR-1Li (c), ZSiNR-1Li (d), ASiNR-2Li (e), và ZSiNR-2Li (f)

This shows that ASiNR has semiconducting properties. Around the Fermi level, Si-$3p_x3p_y$ orbitals contribute mainly. The Si-$3p_z$ orbitals are concentrated mainly in the region below the Fermi level, while the Si-3s orbital contributes deeply in the valence band. When adsorbing a Li atom, the energy band is shifted downwards, creating some Fermi cut-off regions, which causes the band gap to be lost and no longer exhibits semiconductor properties. When adsorbing two Li atoms, the result is almost the same as when adsorbing one Si atom. In both cases, the contribution is mainly from Si, while Li contributes very little in the conduction and valence bands. In the ZSiNR structure, there is no band gap width. In the region around point K, some Si-$3p_x3p_y$ orbital energies cut the Fermi level, creating holes; so ZSiNR will behave like a metal. When adsorbing one or two Li atoms, more Fermi cut-off region is generated.

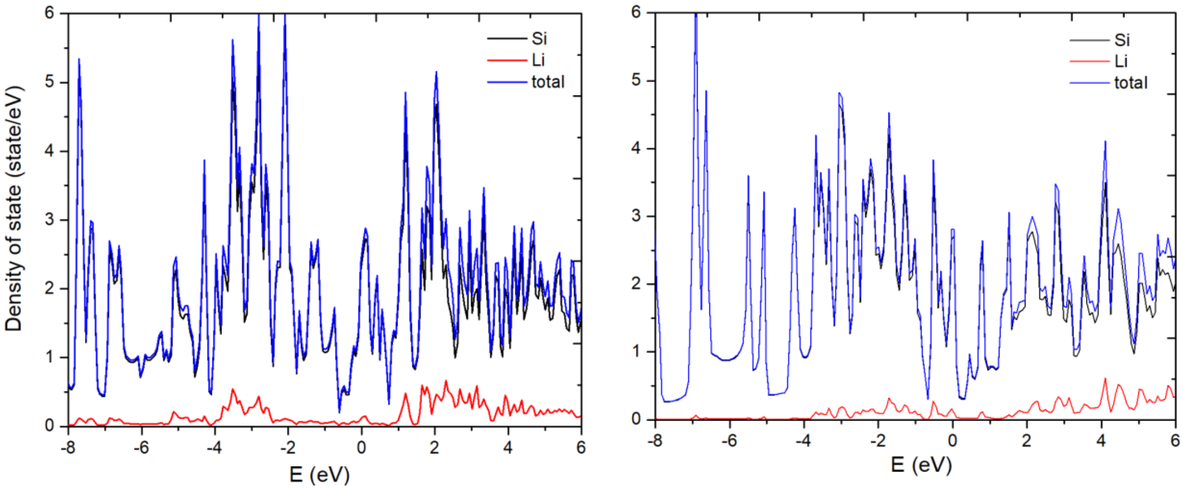
3.2.2. The density of states

The density of states will reveal more clearly the electronic properties. The figure 5 presents the electronic state densities separated by the orbital contributions of ASiNR(a), ZSiNR(b), and by atom of ASiNR-1Li(c), ZSiNR-1Li(d), ASiNR- 2Li(e), and ZSiNR-2Li(f).



(a) (b)

(c) (d)



(e) (f)

Fig 5. Density of separated electronic states according to the orbital contribution of ASiNR (a), ZSiNR (b), ASiNR-1Li (c), ZSiNR-1Li (d), ASiNR-2Li (e), và ZSiNR-2Li (f)

The results have shown that for ASiNR there is no electronic state in the vicinity of the Fermi level, which further reinforces the existence of a band gap energy for ASINR. The peaks represent the electronic state density of the Si-3p$_x$3p$_y$ orbital that is dominant over other orbitals, indicating that the contribution of this orbital is the largest, concentrated mainly in the lower and upper regions near the Fermi level. In these two regions there is a superposition of Si-3p$_x$3p$_y$ and Si-3p$_z$ peaks, indicating a possibility of sp$_2$ and sp$_3$ hybridization. The peaks representing the state density of Si-3s orbitals are concentrated in the low valence energy region, indicating that the Si-3s orbitals contribute mainly to this region only. For the ZSiNR atomic system, it can be seen that there exists an density of state at the level of Fermi, indicating that there is no energy band gap for such an atomic system. The contribution of the Si-3p$_x$3p$_y$ orbital is still predominant, centered in the around of Fermi; the contribution of the Si-3s orbital is also concentrated in the deep valence region as is the case with ASiNR. The electronic state densities for the cases of ASiNR-1Li, ZSiNR-1Li, ASiNR-2Li, and ZSiNR-2Li all show a superior contribution of Si over Li to the electronic properties of atomic systems.

3.2.3. The charge density distribution

The charge density distribution will indicate the strength of the chemical bonds between the atoms in the initial state and after adsorption, from which it is possible to evaluate the influence of the adsorption on the strength of the bonds. link in the system. Figure 6 shows the acquired charge density distributions of ASiNR(a), ZSiNR(b), ASiNR-1Li(c), ZSiNR-1Li(d), ASiNR-2Li(e), and ZSiNR-2Li(f).

The results show that with ASiNR, the bond strength created by Si-3s, Si-3p$_x$3p$_y$ orbitals is much stronger than the π bond, created by Si-3p$_z$. When adsorbing a Li atom, the σ bond strength between the Si atoms in the Li-containing ring is significantly reduced, while in the Si-Si bonds in the far Li ring, this change is negligible. When two Li atoms are adsorbed, the bond strength decreases. With ZSiNR, the results show almost the same; also showed a large change of Si-Si bond strength in the ring near the Si atom. These results show that the σ and π bonds of both ASiNR and ZSiNR configurations upon Li adsorption are strongly attenuated. The details of these changes need to be studied more clearly.

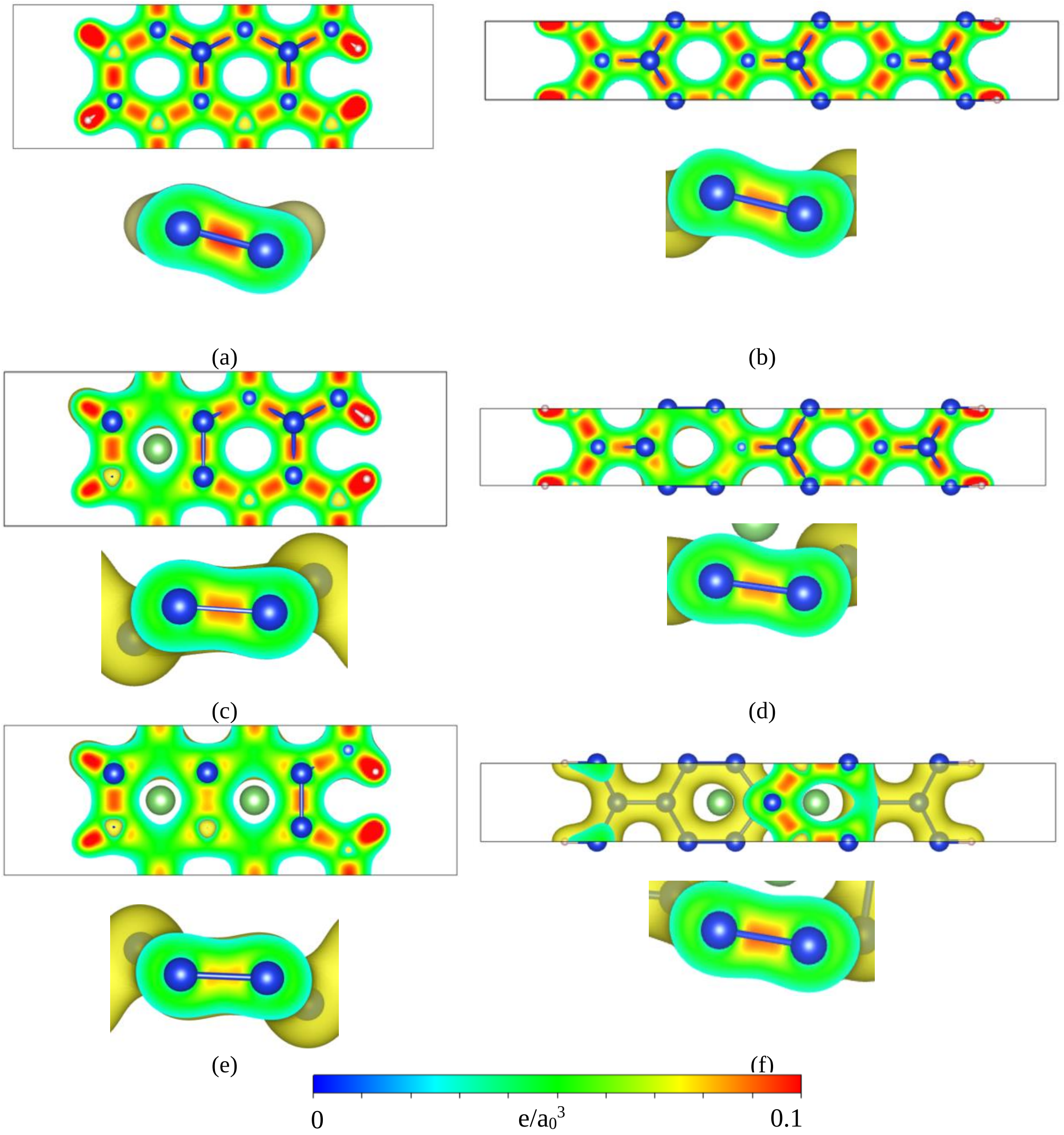


Fig 6. The charge density distribution of ASiNR (a), ZSiNR (b), ASiNR-1Li (c), ZSiNR-1Li (d), ASiNR-2Li (e), và ZSiNR-2Li (f)

3.2.4. Charge Density Difference

The charge density difference is the difference in charge density of the system after adsorption compared to the total charge density of the original system and of the adsorbed atom. The change in charge density of the ASiNR and ZSiNR systems is shown in Figure 7.

The results have shown that after the ASiNR and ZSiNR systems adsorb one or two Li atoms, there will be a significant charge shift, creating positively charged vacancy regions, some electron-concentrating regions creating electrons. negatively charged region. Specifically, with ASiNR-1Li, there was an increase in the positive charge density centered in the vicinity of two functionalized H atoms, and two Si atoms on either side of the Li atom, which indicates a shift in transfer electricity from two H atoms towards two Si atoms located near Li. In the region around the two Si atoms near the edge, there is an electron shift towards Li, creating two surrounding hole regions. Around the two Si atoms located on the common edge of the two hexagonal rings, there is a stronger charge displacement. With ASiNR-2Li, the electron shift is even more obvious.

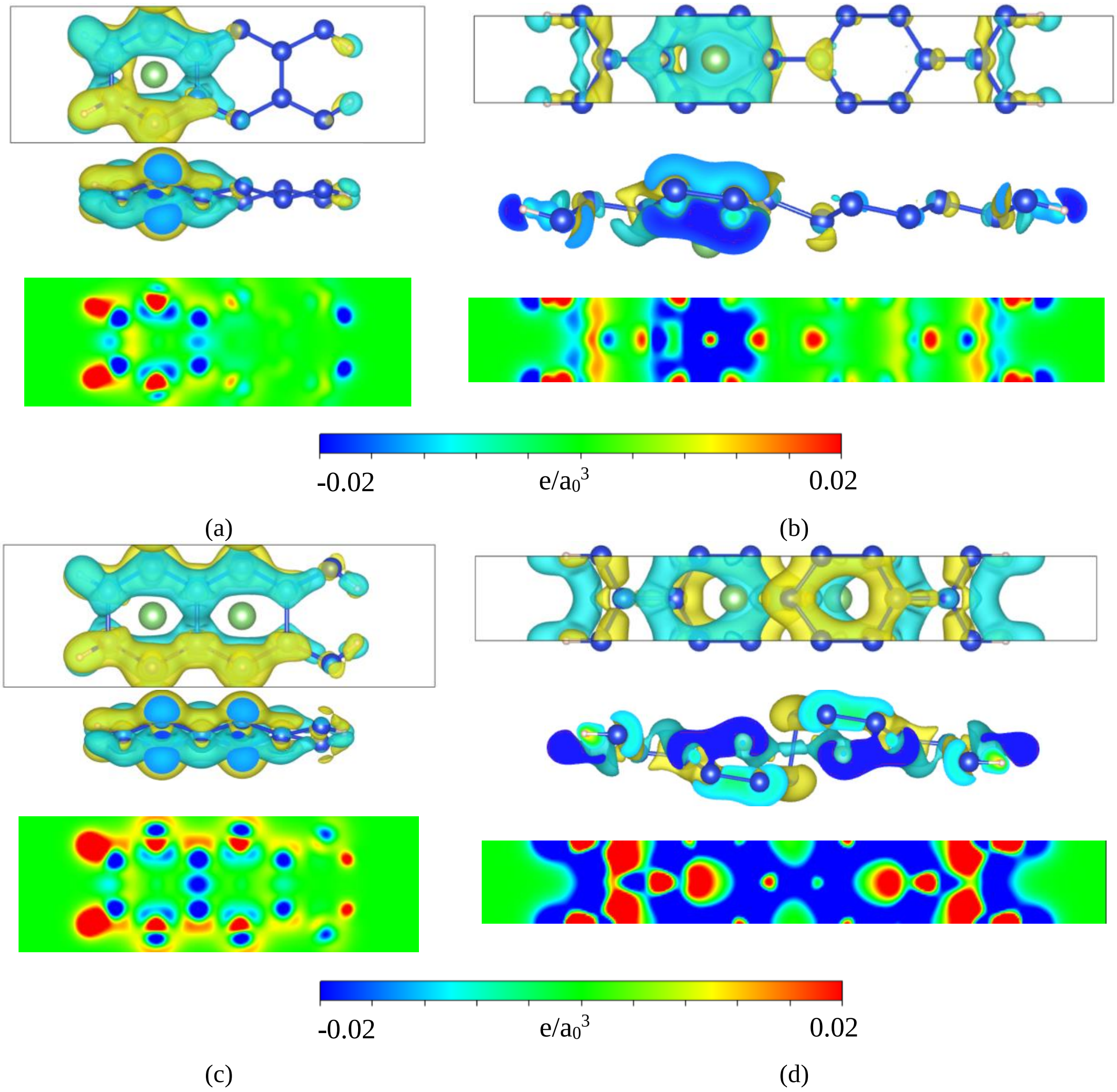


Fig 7. The charge density difference of ASiNR-1Si (a), ZSiNR-1Si (b), ASiNR-2Si (c), và ZSiNR-2Si (d)

The charge density varies in the maximum regions reaching more than 0.02 e/a03. For ZSiNR, it is also easy to see an increase in electron density in the vicinity of the adsorbed Li atom. As for the ZSiNR-2Li structure, because the post-adsorption structure is offset up and down symmetrically, the charge transfer is also symmetrical across the two intermediate Si-Si atoms. This is also the case that shows that the electron transfer occurs most strongly.

4. Conclusion

By using research methods based on density functional theory, using DFT simulation program and combining some other supporting programs in the field of nanomaterial simulation such as Vesta, Vaspkit, Materials studio, …; armchair and zigzag silicene nanoribbon atomic systems; pristine and when adsorbed one or two Li atoms in the "hollow" position are investigated. Structural parameters were evaluated, compared before and after adsorption. Essential electronic properties such as electron band structure, the density of state, charge density distribution, electron displacement were also investigated. The results have shown that only in ASiNR exists a band gap, while the remaining systems including ASiNR-1Li, ASiNR-2Li, ZSiNR, ZSiNR-1Li, ZSiNR-2Li exhibit metallic properties. . More conduction bands are generated when the Li atom is absorbed. These are shown to be potential conductive materials that can be applied in the field of electronics with high performance.

Acknowledgement

This study uses the resources of the high-performance computing cluster (HPCC) at Thu Dau Mot University.

References

[1]. H. Liu, N. Han, and J. Zhao, “Band gap opening in bilayer silicene by alkali metal intercalation. (2014), J. Phys. Condens. Matter, 26, 475303(1)

[2].H. Sahin and F. Peeters, (2013). “Adsorption of alkali, alkaline-earth, and 3d transition metal atoms on silicene.” Physical Review B, 87, 085423(1)

[3]. J. Zhao et al., “Rise of silicene: a competitive 2d material, (2016), Prog. Mater Sci., 83, 24

[4]. Kaloni, T. P., & Schwingenschlögl, U. (2014). Effects of heavy metal adsorption on silicene. *physica status solidi (RRL)–Rapid Research Letters*, *8*(8), 685-687.

[5]. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, (2004), Electric field effect in atomically thin carbon films, Science, 306, 666.

[6]. Long Xu, Wang, X. F., Zhou, L., & Yang, Z. Y. (2015). Adsorption of Ti atoms on zigzag silicene nanoribbons: influence on electric, magnetic, and thermoelectric properties. *Journal of Physics D: Applied Physics*, *48*(21), 215306.

[7]. M. Houssa, E. Scalise, K. Sankaran, G. Pourtois, V. V. Afanas’ev, and A. Stesmans, (2011), Electronic properties of hydrogenated silicene and germanene., Appl. Phys. Lett., 89, 223107(1)

[8].Mehdi Aghaei, S., Torres, I., & Calizo, I. (2016). Structural stability of functionalized silicene nanoribbons with normal, reconstructed, and hybrid edges. *Journal of Nanomaterials*. 42-4

[9]. N. Gao, W. T. Zheng, and Q. Jiang, “Density functional theory calculations for two-dimensional silicene with halogen functionalization, (2012), Phys. Chem. Chem. Phys., 14, 257

[10]. Ni, Z., Liu, Q., Tang, K., Zheng, J., Zhou, J., Qin, R., ... & Lu, J. (2012). Tunable bandgap in silicene and germanene. *Nano letters*, *12*(1), 113-118.

[11]. Sivek, J., Sahin, H., Partoens, B., & Peeters, F. M. (2013). Adsorption and absorption of boron, nitrogen, aluminum, and phosphorus on silicene: Stability and electronic and phonon properties. *Physical Review B*, *87*(8), 085444.

[12]. R. Quhe et al., (2012). “Tunable and sizable band gap in silicene by surface adsorption.” Sci. Rep., 2, 853