

FE, CO AND NI ADATOMS ADSORBED ON SILICENE: A DFT STUDY

KENT GANG

*Illinois Mathematics and Science Academy
Aurora, Illinois 60506, USA
Email: kgang@imsa.edu*

SIVA GANGAVARAPU

*Illinois Mathematics and Science Academy
Aurora, Illinois 60506, USA
Email: sgangavarapu@imsa.edu*

MATTHEW DENG

*Illinois Mathematics and Science Academy
Aurora, Illinois 60506, USA
Email: mdeng@imsa.edu*

MAX MCGEE

*Illinois Mathematics and Science Academy
Aurora, Illinois 60506, USA
Email: maxmcgee@imsa.edu*

RON HURLBUT

*Illinois Mathematics and Science Academy
Aurora, Illinois 60506, USA
Email: rshurl@imsa.edu*

MICHAEL LEE DAO KANG

*National Junior College, 37 Hillcrest Road,
Singapore 288913, Singapore
Email: ldaokang@gmail.com*

SEAN NG PENG NAM

*National Junior College, 37 Hillcrest Road,
Singapore 288913, Singapore
Email: sean_npn@hotmail.com*

HARMAN JOHLL

*National Junior College, 37 Hillcrest Road,
Singapore 288913, Singapore*

TOK ENG SOON

*Department of Physics, National University of Singapore,
2 Science Drive 3, Singapore 117551, Singapore*

Two-dimensional materials have attracted much research attention given their intriguing properties. The latest member of this class of materials is silicene. In this work, we investigate the adsorption of Fe, Co and Ni adatoms on silicene using plane-wave density functional theory calculations within the Perdew-Burke-Ernzerhof parameterization of the generalized gradient approximation for the exchange-correlation potential. In particular, we calculate the binding energy, magnetization, and projected electronic configurations of these adatoms adsorbed at different sites on the silicene. Our calculations show that the hole site (i.e. in the centre of a hexagonal-like arrangement of Si atoms) is the most stable configuration for all three elements. The Fe, Co and Ni adatoms were found to bind very strongly to the silicene, between 4-6 times stronger compared to their binding strength when adsorbed on graphene. Like graphene, we find that the Ni adatom binds strongest. We also find that the binding strength is inversely proportional to the distance between the metal adatom and a Si atom in the silicene sheet. Our work suggests that these adatoms are stable on silicene and have potential to be used in applications such as spintronics and topological insulators.

1. INTRODUCTION

Two-dimensional materials have garnered much attention since of their rich properties. For example, graphene¹⁰, a flat monolayer of carbon atoms tightly packed into a two dimensional honeycomb lattice honeycomb¹⁸, has a unique sp² hybridization, a wide range of thermal, chemical and electronic properties, and potential for many novel applications. Since 2004 when graphene nanoribbons were shown to be able to be separated from bulk graphite²³, graphene has been applied for various functional uses, such as the growth of semiconductors. Superposition of graphene and other carbon atoms can form many other structures, including graphite, nanotubes, or fullerenes. This makes graphene a flexible material for use in industrial applications. Furthermore, graphene is classified as a zero-gap semiconductor, although only for a maximum of two carbon layers¹⁰.

Silicon resides in the same group in the periodic table as carbon and shares several similar characteristics to it, such the number of valence electrons. However, silicon has additional properties that carbon does not exhibit, and carbon based nanomaterials are not compatible with modern silicon based electronics.² Since it is unlikely that the electronics industry would reconfigure and base their technology on carbon, there has been strong theoretical interest in investigating the properties of the Si analogue of graphene, silicene^{1,30-31}

Silicene does not occur naturally, and also there does not seem to be a Si equivalent of graphite that occurs naturally in nature; hence, pure 2D silicene layers cannot be achieved by extrapolation methods which were previously used to synthesize graphene.

Silicene has been shown to be produced through epitaxial growth of silicon atoms on Ag(111), although they can be partially grown on Ag(110) and Ag(001) as well.¹⁸ This notation describes the lattice structure of the metal using its Miller indices, so that the integers (hkl) represent a plane orthogonal to the three given components.¹⁷ However, this can only occur under special conditions, such as the use of a powerful vacuum and the relatively weak interaction between the metal and silicon atoms, which allows bonds to form between silicon instead of the other metal.¹⁸ Silicon structures such as silicene nanoribbons have also been achieved through the use of such method¹, and more efforts are now channeled to synthesizing larger structures of silicene with different configurations.

The band structure of silicene has also been a subject of several studies. For example, the band gap of silicene can be placed under direct control by an external electric field. An external electric field can break the inversion symmetry at the Fermi level in silicene, which would expand the band gap at that point.³

Comparisons between silicene and graphene also give rise to several interesting conclusions; for example, Lalmi et al. demonstrated that the band structure of silicene is analogous to graphene's own unique band structure composed of Dirac cones (2010). Specifically, the presence of Dirac cones around the K and K' crossing points of both silicene and graphene allows the electrons in this area to behave as Dirac fermions, which are massless. Near these K points, the pi bands are two-fold degenerate and weaker in silicene, meaning that quantum tunneling is less common than in graphene. Interestingly, this result was calculated using density functional theory, which will be the prime tool in this investigation.¹² Graphene also presents some limitations that silicene overcomes: for example, silicene does not exhibit a zero band gap and weak spin orbit interaction, which presents a big problem when studying graphene and its applications.²⁹

Other theoretical results from experiments include the possible modulation of the electronic and the magnetic properties of silicene using a single C-chain²⁸, modulation of the energies of spin-polarized edge states with perpendicular electric fields¹⁹, the existence of the quantum anomalous Hall (QAH) phase in silicene through control of the electric field in the silicene sheet⁷, and the varying hybridisation states of the silicene structure.¹ This shows the versatility of silicene as a new material, and its possible diverse applications in electronics. Recently, some studies discuss the possibility of silicene as a possible spintronics material.^{24,31} which was logical as graphene already shows spintronics properties.¹⁴ Furthermore, silicene is classified as a topological insulator, which means its interior behaves as an insulator while the surface can conduct electricity like a superconductor. When an electric field is applied to silicene, it undergoes a topological phase transition. At this phase transition point, the presence of a band inversion allows the silicene to be in the topological insulator phase, or another band insulator phase.⁵ These properties all allow silicene to be a viable component of spintronic devices, which gives it an advantage over graphene in the modern-day electric components.

Several scientific techniques and instruments are crucial in the study of these nano-materials as well. This includes density functional theory (DFT), which has been used commercially in research of insulators, semiconductors, and other bulk materials such as metals. However, it is especially useful in the study of other materials, such as silicene and even proteins. DFT generalizes the many factors involved concerning electrons in a solid state system to simply electron density through the Hohenberg-Kohn theorem and the Kohn-Sham method, which models electrons that do not interact. In general, the many different Hohenberg-Kohn theorems incorporate the movement of electrons due to a force provided by any external potential, and relate it to electron density; one theorem in particular states that ground state density of a system is that which minimizes total energy of the system.⁴ Another theorem, the Hellman-Feynman theorem, simplifies the energies of multiple electron systems into single-electron based calculations. The plane wave variety of this process is useful in the study of material in the solid state such as silicene or graphene. Density functional theory also incorporates several other theorems and equations in its calculations. Most importantly, it incorporates all the electrons interactions through modeling coulomb interaction, and then provides asymmetrical solutions to the many-electron Schrodinger equation. However, the near impossible many-electron Schrodinger equation is solved by the DFT because it maps the entire system onto an approximation of a singular particle, which gives a highly accurate approximation. In order to consolidate the many mathematical

principles and achieve the single electron equations, DFT finally incorporates what is known as the variation principle.²²

The purpose of this investigation is to determine the effect of adding adatoms of iron, nickel, and cobalt on a single layer of silicene lattice through the use of a computation program that incorporates Density Functional Theory (DFT). Specifically, the project aimed to determine the most energetically favorable bonding configurations, as well as to study various electrical and magnetic properties of these configurations. These calculations can provide the basis for future research, and may also have novel applications in semiconductors, spintronic devices, and other electronic devices.

2. METHODOLOGY

The plane-wave based density functional theory program PWSCF (ESPRESSO Version 5.0.1)²⁷ was used to perform all calculations. The Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) ultrasoft pseudopotential was used for all species. In the case of all the atoms, only the valence electrons were considered. The Perdew-Burke-Ernzerhof (PBE)¹⁵ generalized gradient approximation (GGA) correction formalism was employed for the exchange-correlation functional. All pseudopotentials were obtained from the PWSCF pseudopotential online reference²⁷. Moroni et al.⁵ reported that GGA-type calculations are poor in predicting the ground state electronic structure of free atoms (4s2 3dn-2) because of the inadequate treatment of exchange-correlation in the functionals used. This is due to preference of d occupancy over s occupancy, and the adsorption energies calculated may be underestimated. Though, with use of a RRKJ ultrasoft pseudopotential, it has been shown that the magnetic moments calculated for a Fe atom on graphene, obeyed Hund's rule¹⁶, hence, the calculations are of sufficient reliability.

Each periodic supercell in our calculations consisted of 32 Si atoms (in the silicene sheet) and 1 metal adatom. Our supercell dimensions are 15.36Å x 15.36Å x 15.36Å in each of the unit cell vectors. We made use of the Marzari-Vanderbilt method²¹, and smearing was used to aid convergence with a small Gaussian spread of 0.001 Ry (0.013 eV). Local states and populations were calculated by projecting the plane-wave onto specific orbitals. All k-points generated in our calculations were based on the Monkhorst-Pack algorithm¹³. Convergence with respect to cutoff energies for both the wave function and the electron density, and the number of k-points, was checked by calculating the binding energy of the a single Fe atom adsorbed at the hole site of the silicene sheet.

A cutoff energy of 40 Ry for the planewave and 480 Ry for the energy density, with a Monkhorst-Pack grid of $4 \times 4 \times 1$ (equivalent to 10 k-points in the Brillouin Zone for the symmetry of our supercell) was found to be sufficient to achieve convergence in the context of calculating relative energies, specifically the adsorption energy of Fe above a hole site in silicene. There was no significant difference (i.e. more than 0.01 eV) when using a $(6 \times 6 \times 1)$ or a $(8 \times 8 \times 1)$ Monkhorst-Pack grid was used. In calibrating these energies, we utilized the Monkhorst-Pack grid without any Brillouin Zone shift and a force convergence threshold of 10^{-3} a.u. An excess of at least 10 bands was used in each of our calculations.

3. RESULTS AND DISCUSSION

In this work we calculated the binding energy, magnetization, projected electronic configurations, band structures and density of states for Fe, Co and Ni adsorbed at four different sites on silicene. These four sites are represented in Figure 1.

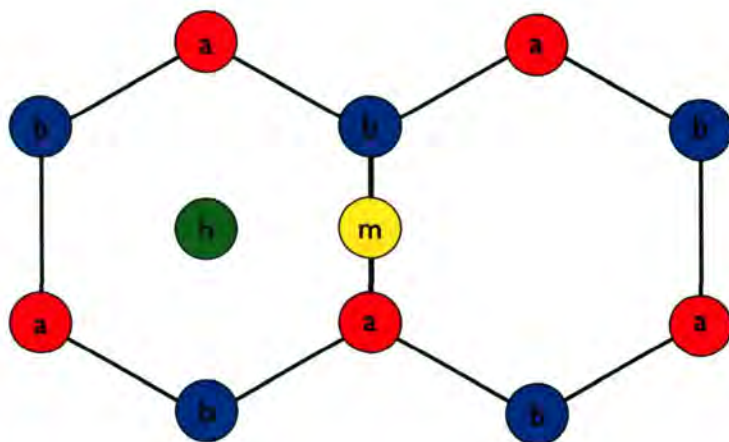


Fig. 1. The four adatom adsorption sites studied in this work. The Si atom in silicene at an *a*-site (red) is above the average plane of silicene. The Si atom at the *b*-site (blue) is below the average plane of silicene. For the 'a' and 'b' sites, the Fe, Co and Ni adatoms are adsorbed vertically above those points. The hole site (*h*-site, green) and middle-of-SiSi bond (*m*-site, yellow) site correspond to Fe, Co and Ni adatoms adsorbed vertically above those points.

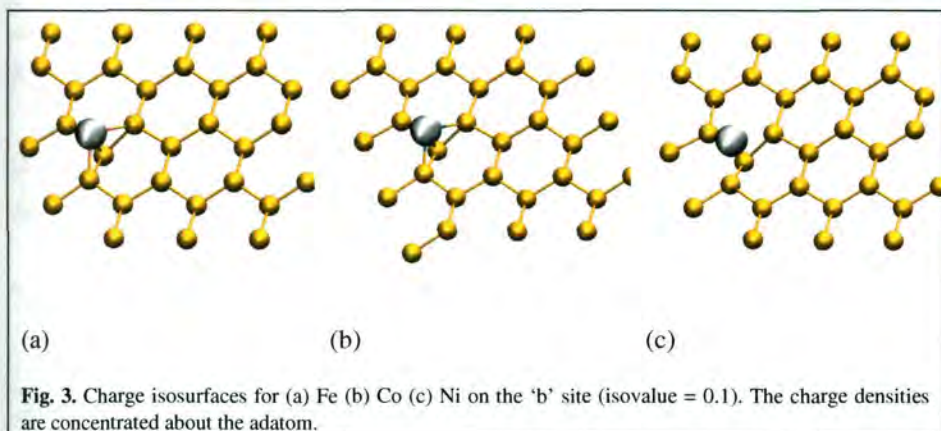
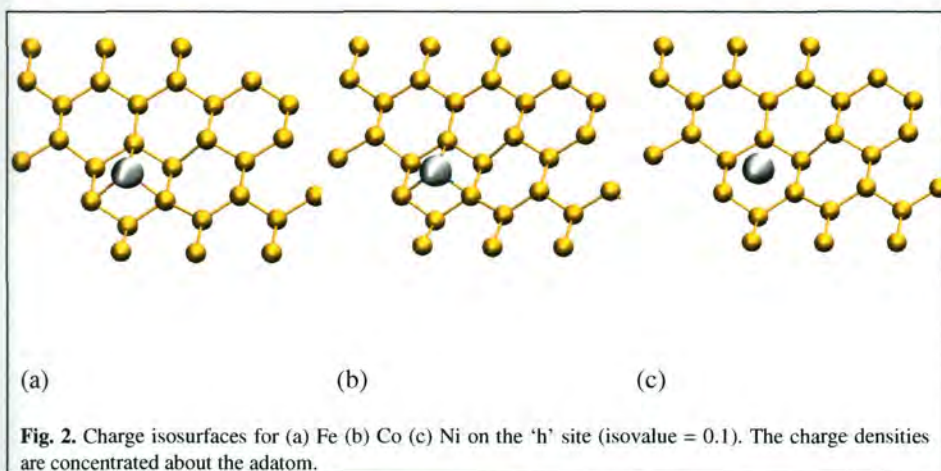
Table 1. The binding energy (B.E.), the metal adatom electronic configuration when adsorbed (Ad.E.C), and magnetization (Mag.) of the Fe, Co and Ni adatoms adsorbed at each of the four sites. The hole site configuration for all species was found to bind strongest to silicene. The magnetic moments for each adsorbed adatom is $2 \mu_B$ lower compared to the free atom magnetization.

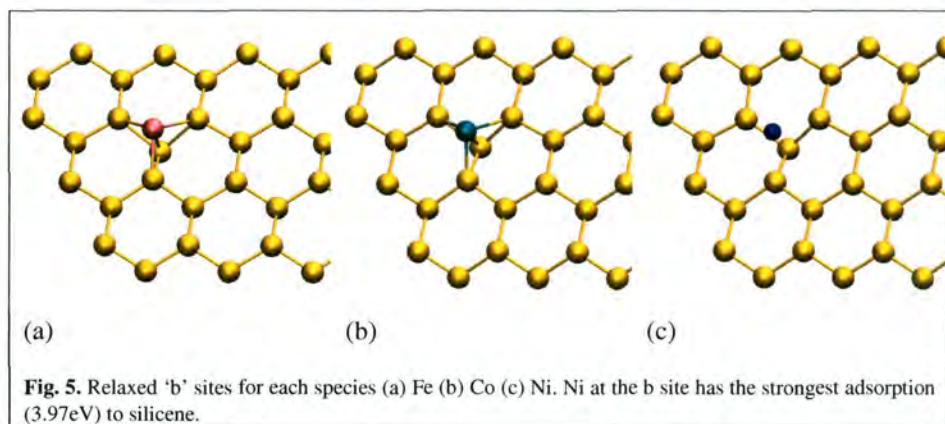
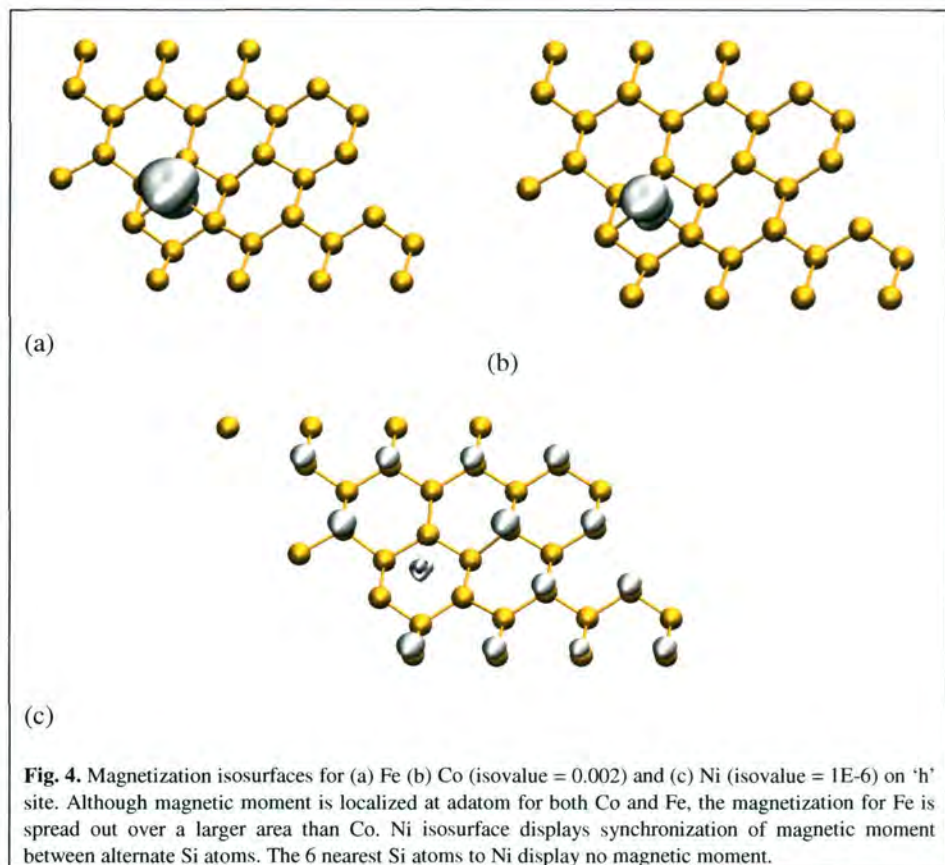
Metal	Ad. Site	B.E. (eV)	Ad.E.C.	Mag. (μ_B)
Fe	h	3.51	$3d^{7.06}4s^{0.37}$	2.0
	a	2.99	$3d^{7.11}4s^{0.41}$	2.0
	b	3.15	$3d^{7.12}4s^{0.41}$	2.0
Co	h	3.88	$3d^{8.25}4s^{0.38}$	1.0
	a	3.34	$3d^{8.21}4s^{0.43}$	1.0
	b	3.46	$3d^{8.21}4s^{0.42}$	1.0
Ni	h	4.58	$3d^{9.09}4s^{0.40}$	0.0
	a	3.77	$3d^{9.06}4s^{0.44}$	0.0
	b	3.97	$3d^{9.08}4s^{0.42}$	0.0

Fe, Co and Ni adatoms adsorbed at the h-site are the most stable relative to other adsorption sites for each species. The binding energy of each species at the h-site is at least 0.4 eV higher than at the next most stable site. The binding energy of all three species on silicene (at the h-site) is at least four times higher compared to their corresponding adsorption site on graphene. Fe, Co and Ni bind 6.1, 4.0 and 3.3 times more strongly (0.58 eV, 0.97 eV and 1.37 eV for Fe, Co and Ni respective; Johll 2009) to silicene at the h-site than to graphene at a similar h-site as well. The magnetization of each metal adatom is reduced by $2 \mu_B$ when adsorbed compared to the free-atom magnetization.

The electron configurations for each metal adatom differs little when adsorbed at different sites. The Fe, Co and Ni adatoms have electron configurations of $3d^{7.1}4s^{0.4}$, $3d^{8.2}4s^{0.4}$, and $3d^{9.1}4s^{0.4}$, irrespective of the adsorbed site. The 3d electron population is very similar to the 3d electron population of the same species when adsorbed at the more stable hole-site on graphene. The difference in electron populations of these adatoms when adsorbed on silicene compared to graphene arises mainly in the 4s electron population. In silicene, the metal adatoms have about 0.4 electrons in the projected 4s state. In graphene this state is only populated with 0.15 (or 0.16) electrons. This implies that there are approximately 0.25 less electrons transferred to the silicene than to graphene. We hypothesize here that a greater amount of electrons is transferred to graphene than to silicene because of the low-lying π^* bands in the former. This would also explain the lower binding energy

of the adatom to graphene: populating the π^* states might imply breaking some π -bonds. Also, the sp^3 - sp^2 mix in silicene would imply that electron transfer to this material would be less pronounced. Instead, there might be a greater extent of covalent bonding between the metal adatom and the silicon atoms in its immediate environment. In this work, our pseudopotential for the Si atoms does not take into account the 3d states. Hence, all electron transfer from metal adatom to silicene would be constrained to the 3s and/or 3p states alone. This points us to consider the same set of calculations albeit using a pseudopotential that takes into account the 3d states in Si.





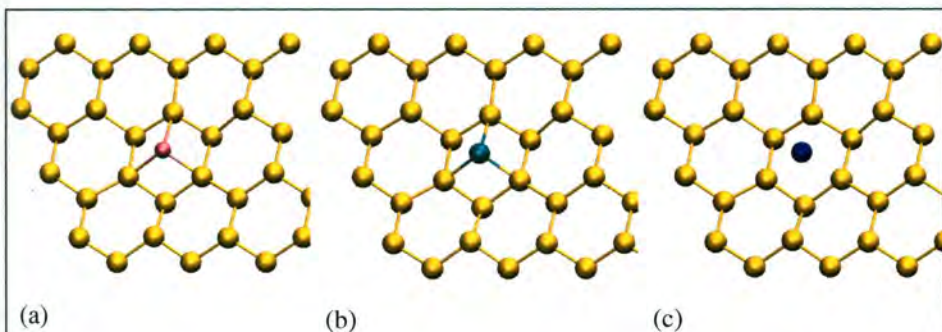


Fig. 6. Relaxed 'h' sites for each species (a) Fe (b) Co (c) Ni. Ni at the h site has the strongest adsorption (4.58eV) to silicene.

Adatoms in the 'h' and 'b' site were 2.3\AA from the nearest silicon atom, with the exception of Fe-h (2.2\AA).

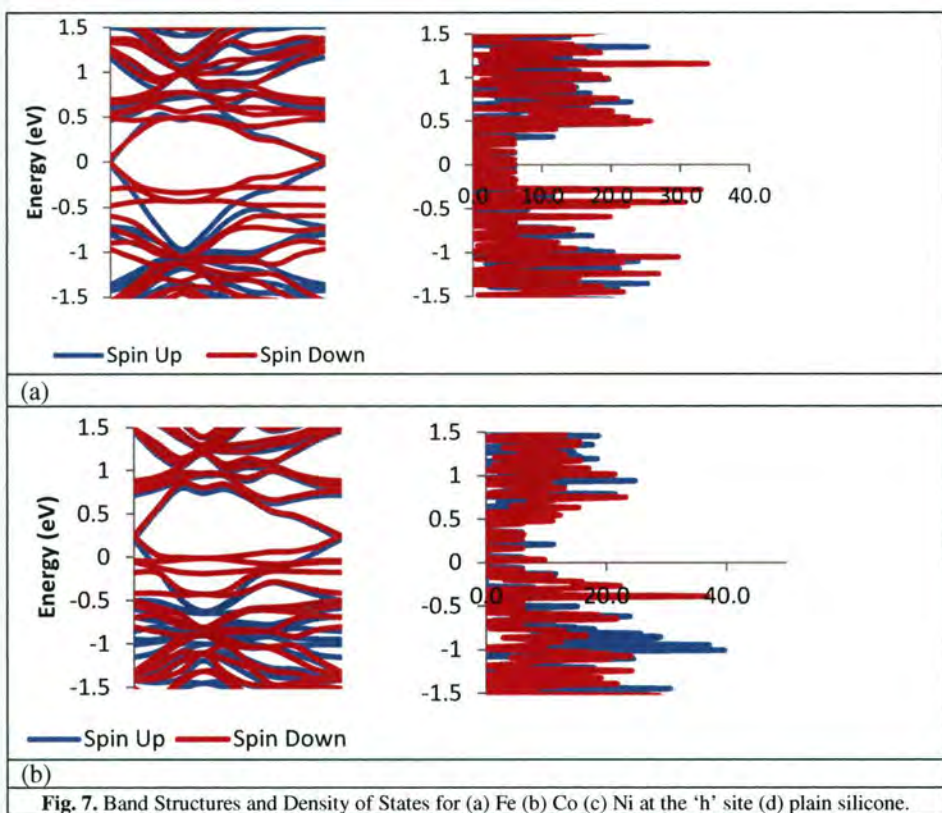


Fig. 7. Band Structures and Density of States for (a) Fe (b) Co (c) Ni at the 'h' site (d) plain silicene.

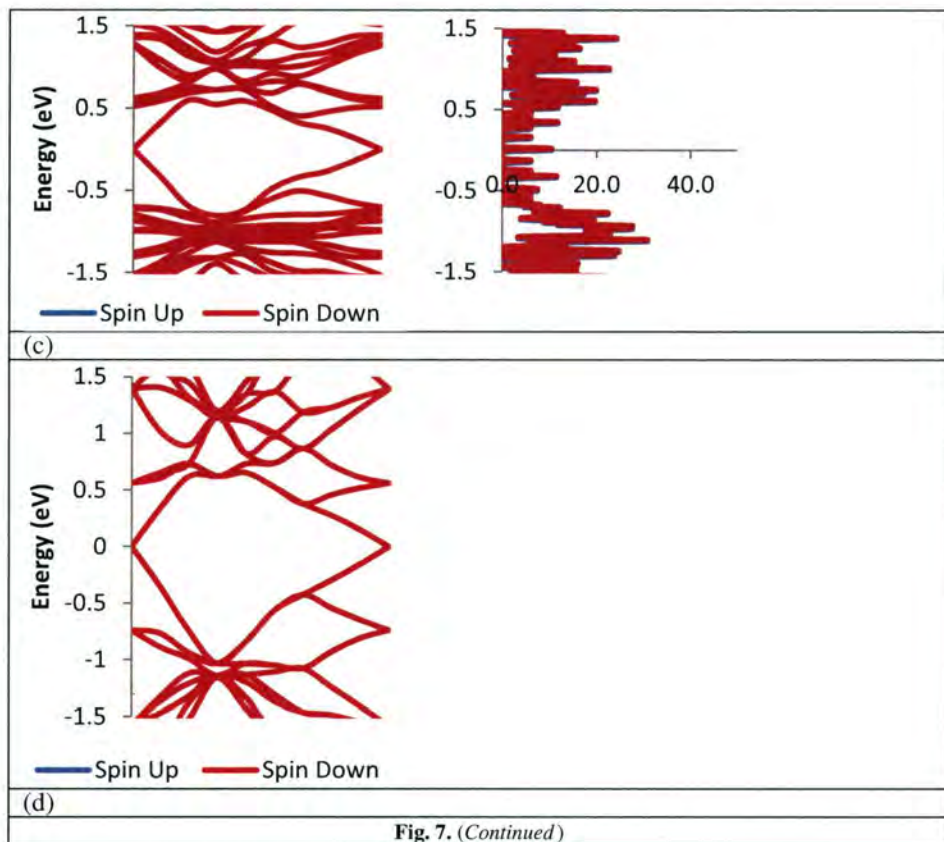


Table 2. Spin-up and Spin-down band gaps for metal species at the h site.

Metal	Site	Band Gap at K Point (eV)		
		Spin-up	Spin-down	Difference
Co		0.7028	0.2822	0.4206
Ni	h	0.0087	0.0087	0
Fe		0.0399	0.0594	-0.0195
Si	Plain	0.5621	0.5621	0

We studied the band structure for spin up and spin down electrons in each species in the h site. The difference in spin-up and spin-down band gaps in Co suggests the possibility of using it as a spintronics device with a higher energy barrier for spin-up current.

4. CONCLUSION

In this work, we used density functional theory to calculate the ground state electronic properties and geometries of Fe, Co and Ni adatoms adsorbed at four sites on silicene. We found that the h-site (i.e. hole site) configuration is the most stable. This site is at least 0.4 eV more stable than other adsorption sites for any given element. Fe, Co and Ni adatoms adsorbed by at least four times more strongly to silicene than to graphene. This might imply that the sticking coefficients and diffusion barriers of these adatoms are higher for silicene than for graphene. There are approximately 0.2 less electrons transferred to silicene than to graphene for the systems we studied here. We postulate that this is due to the lack of low-lying π^* bands in silicene. Finally, the direct spin-up/spin-down band gaps at the \mathbf{K} point for Fe, Co and Ni adsorbed at the h-site are x, 0.7028/0.2822 and 0.0087/0.0087 eV respectively.

References

1. Aufray, B., Kara, A., Vizzini, S., Oughaddou, H., Léandri, C., Ealet, B., & Le Lay, G. (2010). Graphene-like silicon nanoribbons on Ag(110): A possible formation of silicene. *Applied Physics Letters*, 96(18), 183102. doi:10.1063/1.3419932
2. Chiappe, D., Grazianetti, C., Tallarida, G., Fanciulli, M., & Molle, A. (2012). Local electronic properties of corrugated silicene phases. *Advanced materials* (Deerfield Beach, Fla.), 24(37), 5088–93. doi:10.1002/adma.201202100
3. Chinnathambi, K. (2012). Controlling Band Gap in Silicene Monolayer using external Electric field. Cornell University Library Condensed Matter. Retrieved from <http://arxiv.org/abs/1202.2636>.
4. Clark, S. J. *The Hohenberg-Kohn Theorems*. Durham University 2013.
5. E. G. Moroni, G. Kresse, J. Hafner, and J. Furthmüller, *Phys. Rev. B* 56, 15629 (1997).
6. Ezawa, M. Spin-Valley Optical Selection Rule and Strong Circular Dichroism in Silicene. Cornell University Library Condensed Matter 2013.
7. Ezawa, M. (n.d.). Valley-Polarized Metals and Quantum Anomalous Hall Effect in Silicene, 1(iii), 3–6.

8. F. Pulizzi, *Nature Materials* 11, 367 (2012)
9. Fujita, T., Jalil, M. B. a., Tan, S. G., & Murakami, S. (2011). Gauge fields in spintronics. *Journal of Applied Physics*, 110(12), 121301. doi:10.1063/1.3665219
10. Geim, a K., & Novoselov, K. S. (2007). The rise of graphene. *Nature materials*, 6(3), 183–91. doi:10.1038/nmat1849
11. Gong, S. J., Li, Z. Y., Yang, Z. Q., Gong, C., Duan, C.-G., & Chu, J. H. (2011). Spintronic properties of graphene films grown on Ni(111) substrate. *Journal of Applied Physics*, 110(4), 043704. doi:10.1063/1.3622618
12. Guzmán-Verri G. G., Lew Yan Voon L.C. *Electronic Structure of Silicon-Based Nanostructures*. American Physical Society *Physics Review B* 2013; 76.
13. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* 13, 5188 (1976).
14. Ilyasov, V. (2011). Materials for Spintronics: Magnetic and Transport Properties of Ultrathin (Monolayer Graphene)/MnO(001) and MnO(001) Films. *Journal of Modern Physics*, 02(10), 1120–1135. doi:10.4236/jmp.2011.210139
15. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 77, 3865 (1996).
16. Johll, H., & Kang, H. C. (2009). Density functional theory study of Fe, Co, and Ni adatoms and dimers adsorbed on graphene. *Physical Review B*, 79(24), 245416. doi:10.1103/PhysRevB.79.245416
17. Kittel, C. *Introduction to Solid State Physics*. New York: Wiley, 2004.
18. Lalmi, B., Oughaddou, H., Enriquez, H., Kara, A., Vizzini, S., Ealet, B., & Aufray, B. (2010). Epitaxial growth of a silicene sheet. *Applied Physics Letters*, 97(22), 223109. doi:10.1063/1.3524215
19. Liang, Y., Wang, V., Mizuseki, H., & Kawazoe, Y. (2012). Band gap engineering of silicene zigzag nanoribbons with perpendicular electric fields: a theoretical study, 455302. doi:10.1088/0953-8984/24/45/455302
20. Liu, F., Liu, C., Wu, K., Yang, F., & Yao, Y. (n.d.). d+id' Chiral Superconductivity in Bilayer Silicene, 1–11.
21. N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, *Phys. Rev. Lett.* 82, 3296 1999.
22. Narasimhan S. *Introduction to Density Functional Theory*. Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR).
23. Novoselov, K. S., Geim, a K., Morozov, S. V, Jiang, D., Zhang, Y., Dubonos, S. V, Grigorieva, I. V, et al. (2004). Electric field effect in atomically thin carbon films. *Science (New York, N.Y.)*, 306(5696), 666–9. doi:10.1126/science.1102896
24. Ran, Q., Zhang, C.-H., & Shen, J. (2012). Silicene-like beryllium encapsulated nanowires. *Chemical Physics*, 397, 42–47. doi:10.1016/j.chemphys.2011.12.012

25. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. vonMolnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, *Science* 294, 1488 (2001).
26. Şahin, H., Senger, R. T., & Ciraci, S. (2010). Spintronic properties of zigzag-edged triangular graphene flakes. *Journal of Applied Physics*, 108(7), 074301. doi:10.1063/1.3489919
27. S. Baroni, A. D. Corso, S. de Gironcoli, and P. Giannozzi, PWSCF pseudopotentials, 2008 <http://www.pwscf.org/pseudo.htm>
28. Song, Y.-L., Zhang, Y., Zhang, J.-M., Lu, D.-B., & Xu, K.-W. (2010). Modulation of the electronic and magnetic properties of the silicene nanoribbons by a single C chain. *The European Physical Journal B*, 79(2), 197–202. doi:10.1140/epjb/e2010-10627-5
29. Tahir M., *Schwingenschlögl. Polarized quantum Hall effect and topological insulator phase transitions in silicene. Scientific Reports* n.d.; 3.
30. Vogt, P., De Padova, P., Quaresima, C., Avila, J., Frantzeskakis, E., Asensio, M., Resta, A., et al. (2012). Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon. *Physical Review Letters*, 108(15), 1–5. doi:10.1103/PhysRevLett.108.155501
31. Zheng, F.-B., & Zhang, C.-W. (2012). The electronic and magnetic properties of functionalized silicene: a first-principles study. *Nanoscale research letters*, 7(1), 422. doi:10.1186/1556-276X-7-42