

Structural, Electronic and Magnetic Properties of Silicene Functionalized with 4d TM Atoms

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Abstract

The experimental realization of silicene has ignited a great deal of interest in researching its properties for utilization in device applications. Silicene is composed of a lattice of silicon. As a result, it can be integrated with contemporary circuitry structures, which are predominantly silicon-based. Therefore, investigating its characteristics, especially those of the bandgap, is pivotal. In the present work, the density functional theory approach is employed to examine the structural, electronic and magnetic characteristics of free-standing silicene doped with 4d Transition Metal (TM) atoms. Modelling is done for a 4x4 silicene supercell with a single vacancy. The resulting structure is, thus, doped with 4d transition metal atoms. Doping results in lattice distortion, as evidenced by the variance in Si-TM bond length relative to Si-Si bond length. The shortest bond length is noticed in the instance of Ru doping, thus demonstrating its strongest bonding with Si atoms. Doping causes the structure to become increasingly deformed, as proved by the elevation in buckling height as well. Except for Zr, Ru and Pd, which exhibit semiconductor behaviour, the 4d TM doping in silicene results in metallic characteristics as the bands cross the Fermi level in the majority of the configurations discussed here. A narrow band gap with a range of 2.1 to 252 meV is produced by doping silicene with Zr, Ru, and Pd. Magnetism is demonstrated by Nb, Mo, Tc, and Rh-doped structures, whereas the other structures are nonmagnetic. The presence of magnetism in these structures is primarily due to contributions from Si-3p, TM-4d/5s orbitals, and their hybridization.

Keywords: Band Gap, Silicene, 4d Transition Metal Atoms

1.0 Introduction

Silicene has emerged as a promising alternative to graphene for the fabrication of nanoelectronic devices since its synthesis on Ag (111)¹. Graphene, being a carbon allotrope, is incompatible with silicon-based electronic devices. This magnifies the attention given to silicene, which, being composed of Si atoms, is more compatible with silicon technology. It has a 2-dimensional honeycomb structure with low buckling caused by the 3p_z orbital of the Si-Si bond which assists in opening the bandgap in

silicene to apply it. As with graphene, the pristine silicene is a zero-bandgap semimetal with a Dirac cone. Silicene is predicted to have extraordinarily high carrier mobility given the almost massless Dirac fermion character². As a result, silicene is a good choice for high-speed electronics. To employ silicene in electronic devices, it is crucial to investigate it for electronic properties, particularly those related to the bandgap. A variety of techniques have been used to modulate the band gap, including impurity doping³, defect creation^{4,5}, and the application of an electric field^{6,7}. 3d TM-doped silicene has been the

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subject of numerous investigations. The 3d TM-doped silicene sheet shows metallic behaviour with crossing bands at the Fermi level⁸. Earlier studies on Ti-doped silicene⁹ showed a direct bandgap of 221 meV. Recently, it was demonstrated that among the 3d TM-Si systems they explored, Ti-Si became an indirect semiconductor, whereas Cr-Si and Mn-Si systems transformed into full metals¹⁰. The choice of pseudopotentials employed for interactions can be attributed to the variations in 3d TM-doped silicene findings reported by various studies. Further research on 4d TM doped¹¹, however, reveals that a 2d buckled structure doped with 4d doping is capable of creating a bandgap as well.

To the best of our knowledge, no comprehensive study of the properties of 4d TM-doped silicene has been conducted. We focused on the effects of doping 4d TM atoms on the structural, electronic, and magnetic properties of silicene in this study. It should be noted that a 4x4 supercell of silicene with 32 atoms has been considered here. A single silicon atom is replaced with a 4d TM atom to produce doped silicene. As a result, the TM atom concentration in doped silicene is approximately 3.2%. A total of nine configurations are investigated, including pristine and 4d TM (Y, Zr, Nb, Mo, Tc, Ru, Rh, and Pd) doped silicene.

2.0 Computational Method

In this study, we have adopted a Density Functional Theory (DFT) approach with a plane wave basis. A 4x4 silicene monolayer is modelled with 32 atoms. A vacuum higher than 20 Å is established between the slabs to avert erroneous interactions between periodic cells. Kohn-Sham equations are resolved using the Perdew-Burke-Ernzerhof (PBE) subfunctional in conjunction with the Generalised Gradient Approximation (GGA) functional. The SIESTA code¹² has been used to optimise all of the geometries. Localized pseudo-atomic orbitals with a Double-Polarized (DZP) basis set are used to define the valence electrons. A simple wave basis with a cutoff energy of 300 eV and a 6x6x1 Gamma Monkhost Pack K-point grid is used to sample the Brillouin zone. The atomic positions are relaxed and optimized using the conjugate gradient approach until a maximum force on any atom of 0.04 eV/Å is achieved.

3.0 Results and Discussion

3.1 Structural Properties

To assess the viability of these structures, we first calculate the formation energy using the equation:

$$E_f = (E_{\text{doped}} + E_{\text{Si}}) - (E_{\text{pristine}} + E_{\text{TM}})$$

Here, E_{doped} and E_{pristine} represent the total energies of optimized doped and pristine silicene respectively. The energy of isolated Si and TM atoms is depicted by E_{Si} and E_{TM} , respectively.

The calculated formation energies range between -5.49 eV and -0.39 eV. This demonstrates that all the configurations considered here are thermodynamically stable. It is found that Rh-doped silicene has the lowest formation energy (-0.39 eV), while Mo-doped silicene has the highest. This implies that the most stable configuration is Mo-doped silicene. The relaxed structures of 4d TM doped and pristine silicene are shown in Figure 1.

According to our calculations, the optimized Si-Si bond length and buckling height for pristine silicene is 2.30 Å and 0.45 Å. It is to be noted that our findings for pristine silicene are consistent with the previous results¹³⁻¹⁸. The structural characteristics of the optimized

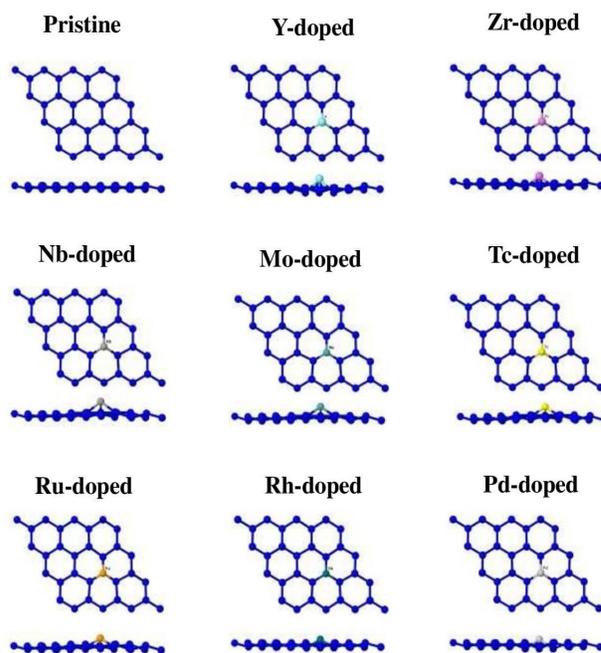


Figure 1. Top and side view of pristine and TM-doped structures.

Table 1. Bond length (Å), buckling height (Å), Si-TM-Si bond angles and magnetic moment of optimized structures

Silicene configurations	Bond Length (Å)		Buckling Height (Å)	Si-TM-Si Bond Angle	Magnetic Moment (μ_B)
	Si-Si	Si-TM			
Pristine	2.30	-	0.45	-	0
Y-doped	2.28	2.75	1.73	85°	0
Zr-doped	2.32	2.58	1.45	91.8°	0
Nb-doped	2.29	2.51	2.01	93.1°	1.85
Mo-doped	2.34	2.36	1.77	97.5°	1.99
Tc-doped	2.31	2.30	1.81	99.6°	0.44
Ru-doped	2.31	2.29	1.48	100.6°	0
Rh-doped	2.31	2.32	1.07	100.5°	0.78
Pd-doped	2.32	2.42	1.20	97.4°	0

pristine and doped configurations are displayed in Table 1.

In comparison to Si-Si bond length, the estimated values of Si-TM bond lengths have greater values. We find that in doped configurations, the Si-TM bond length reduces up to Ru as the atomic radius lowers¹⁹. In the case of Ru doping, a minimum Si-TM bond length is observed, indicating the strongest bonding between Ru and Si atoms. Beyond Ru, the Si-TM bond length increases slightly. Ru has the shortest bond length (2.29 Å) and Y has the longest (2.75 Å). The bond length varies due to interatomic interactions and the subsequent lattice deformation caused by doping. In pristine silicene, the Si-Si-Si bond angle is 116.2°. However, the bond angle lowers with TM doping. The largest and smallest Si-TM-Si bond angle values are 85° and 100.6° for Y and Ru doped silicene, respectively. As can be seen in Table 1, the buckling height increases in doped configurations as these angles approach sp^3 hybridization¹⁹.

3.2 Electronic Properties

The band diagrams of 4d TM-doped silicene and pristine silicene are shown in Figure 2. The outcomes show that, depending on the types of doped atoms, the substitution of TM atoms considerably alters the silicene's electronic structure and leads to metallic or semiconductor behaviour. It is known that doping of TM atoms results in the introduction of novel states and modifications to the host's band diagram. For nanoelectronic applications, a gap at the Fermi energy (E_F) is more significant than

the gaps at the other energy levels. This is due to the ability of the E_F bandgap to control electron flow. The Y, Nb, Mo, Tc, and Rh-doped structures out of the eight doped configurations covered here exhibit metallic characteristics as their valence bands and conduction bands cross the Fermi level. Zr, Ru and Pd-doped silicene exhibit semiconductor behaviour. However, Zr and Pd-doped have direct band gaps of 200 meV and 179 meV, respectively, and Ru-doped exhibits an indirect bandgap of 252 meV. This gap is caused by the sublattice symmetry breaking due to a vertical electric field inside the body and the Jahn-Teller distortion. The symmetry of the two sublattices of silicene is broken when an impurity atom is substituted for a Si atom, and this has a significant effect on the electronic properties of silicene.

The Si-TM bond lengths, which are related to the electronic structure, are altered by this displacement. Earlier studies⁹ have shown a direct bandgap of 221 meV for Ti-doped silicene. These investigations imply that the electronic behaviours of silicene monolayer can be effectively tuned through the substitution of transition metals. These band-gap gaps in TM-silicene demonstrate the advantages of using silicene-based materials in the design of nanoelectronic devices.

3.3 Magnetic Properties

The variations in the spin magnetic moments of 4d TM-doped silicene are shown in Figure 3. On the one hand, magnetism is shown in Nb, Mo, Tc, and Rh-doped materials. Y, Zr, Ru, and Pd-doped, on the other hand,

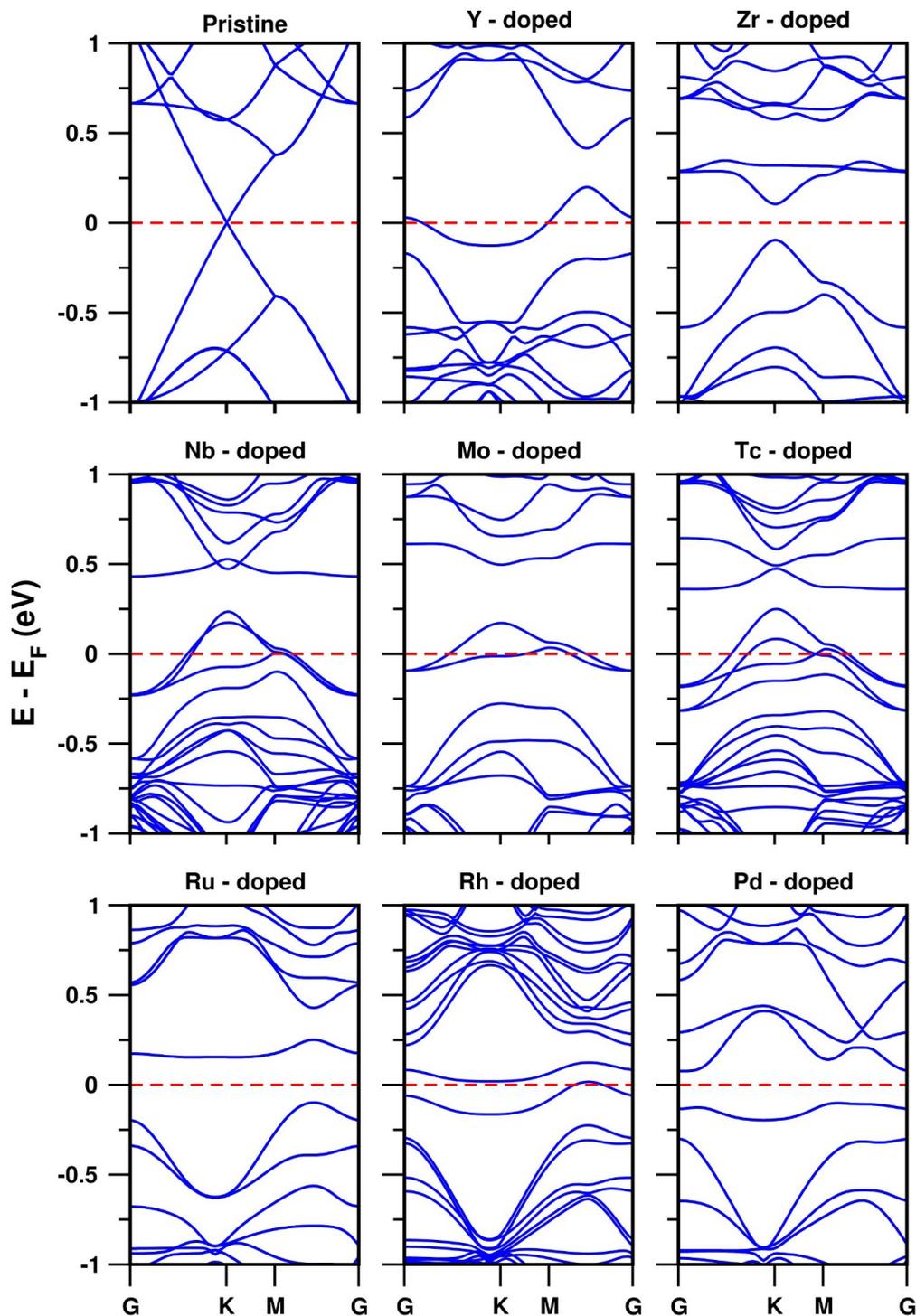


Figure 2. Band diagrams of pristine and TM-doped silicene structures.

continue to be nonmagnetic like pristine silicene. According to Hund's rule, isolated TM atoms have enormous spin magnetic moments. However, the electron

delocalization in TM-doped silicene manifests in the form of a reduced spin magnetic moment. The values of the spin magnetic moments for Nb, Mo, Tc, and Rh-doped

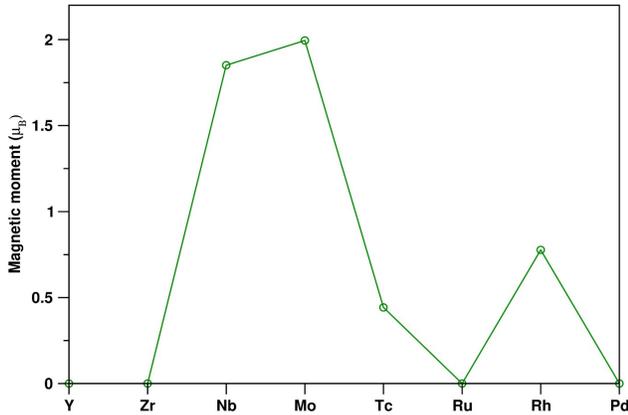


Figure 3. Magnetic moments of TM-doped silicene structures.

silicene are 1.85, 1.99, 0.44, and 0.78, respectively, as shown in Table 1. By computing the difference in the values of the spin-up and spin-down PDOS of Nb, Mo, Tc, and Rh-doped silicene, as depicted in Figure 4, we have further analysed the origin of magnetism. We know that an asymmetric PDOS distribution is produced by magnetic systems. Si-3p and Nb/Mo-4d make the most asymmetric contributions to Nb, Mo-doped configurations. However, Tc-5s, in addition to the two orbitals that have already been discussed, also contribute significantly to Tc-doped silicene. Si-3p and Rh-5s orbitals make up the majority of the contribution in the case of Rh-doped materials.

In all the structures, the orbital hybridization is visible. The spin-polarized Projected Density of States

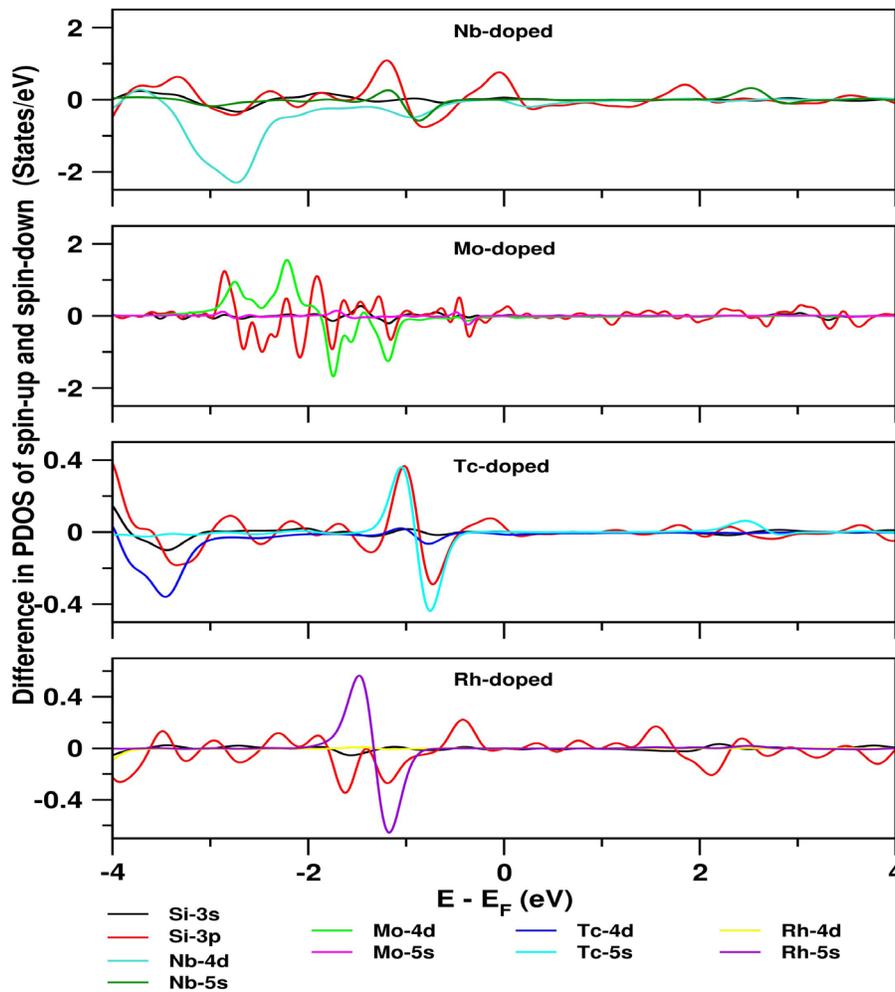


Figure 4. Difference in the PDOS of spin-up and spin-down for Nb, Mo, Tc and Rh-doped silicene structures.

(PDOS) of Nb, Mo, Tc, and Rh-doped silicene prove that the magnetism is due to the presence of TM impurities.

4.0 Conclusion

The structural, electronic and magnetic properties of silicene with a 4d TM atom substitution are examined using DFT calculations. Lattice distortion due to doping is demonstrated by the variation in Si-TM bond length in comparison to Si-Si bond length. In the case of Ru doping, the shortest bond length is observed, thus exhibiting that its bond with Si atoms is the strongest. The distortion in the structure increases with doping, as shown by the rise in buckling height as well. Similar to an electric field or metal adsorption, doping opens a gap in Zr, Ru, and Pd-doped silicene. Additionally, silicene that has been doped with Y, Nb, Mo, Tc, and Rh displays metallic behaviour. The metallicity of these structures is due to the emergence of electronic bands crossing the Fermi level. Nb, Mo, Tc, and Rh-doped structures exhibit magnetism. However, the other structures continue to be nonmagnetic, like pristine silicene. Si-3p, TM-4d/5s orbitals, and their hybridization are principally responsible for the magnetism present in these configurations. The investigation of silicene properties by TM doping is, therefore, an important area of research. This can prove to be vital in the modulation of structural, electronic and magnetic properties for a wide range of applications.

5.0 References

- Vogt P, De Padova P, Quaresima C, Avila J, Frantzeskakis E, Asensio MC, Resta A, Ealet B, Lay GL. Silicene: compelling experimental evidence for graphene-like two-dimensional silicon. *Phys Rev Lett.* 2012; 108(1):155501. <https://doi.org/10.1103/PhysRevLett.108.155501> PMID:22587265
- Chen L, Liu CC, Feng B, He X, Cheng P, Ding Z, Meng S, Yao Y, Wu K. Evidence for Dirac Fermions in a Honeycomb Lattice Based on Silicon. *Phys Rev Lett.* 2012; 109:056804. <https://doi.org/10.1103/PhysRevLett.109.056804> PMID:23006197
- Dávila ME, Marele A, De Padova P, Montero, I, Hennies, F, Pietzsch, A, Shariati, MN, Gómez-Rodríguez, JM, Le Lay, G. Comparative structural and electronic studies of hydrogen interaction with isolated versus ordered silicon nanoribbons grown on Ag(110). *Nanotechnology.* 2012; 23:385703. <https://doi.org/10.1088/0957-4484/23/38/385703> PMID:22947695
- Gao N, Zheng WT, Jiang Q. Density functional theory calculations for two-dimensional silicene with halogen functionalization. *Phys Chem Chem Phys.* 2012; 14:257-61. <https://doi.org/10.1039/C1CP22719J> PMID:22083171
- Gao J, Zhang J, Liu, H, Zhang Q, Zhao J. Structures, mobilities, electronic and magnetic properties of point defects in silicene. *Nanoscale.* 2013; 5:9785. <https://doi.org/10.1039/c3nr02826g> PMID:23963524
- Tsai WF, Huang CY, Chang TR, Lin H, Jeng HT, Bansil A. Gated silicene as a tunable source of nearly 100% spin-polarized electrons. *Nat Commun.* 2013; 4:1500. <https://doi.org/10.1038/ncomms2525> PMID:23422668
- Ni Z, Liu Q, Tang K, Zheng J, Zhou J, Qin R, Gao Z, Yu D, Lu J. Tunable bandgap in silicene and germanene. *Nano Lett.* 2013; 2:113-8. <https://doi.org/10.1021/nl203065e> PMID:22050667
- Gheshlagh ZHT, Beheshtian J, Mansouri S. The electronic and optical properties of 3d transition metals doped silicene sheet. A DFT study. *Mater Res Express.* 2019; 6:126326. <https://doi.org/10.1088/2053-1591/ab6541>
- Youngbin L, Kyung-Han Y, Sung Beom C, Yong-Chae C. Electronic Properties of Transition-Metal-Decorated Silicene. *Chem Phys Chem.* 2014; 15(18):4095-9. <https://doi.org/10.1002/cphc.201402613> PMID:25303061
- Kalwar BA, Fangzong W, Saeed MH, Bhutto AA, Tunio MA, Bhagat KJ. Geometric, spintronic, and optoelectronic properties of 3d transition metals doped silicene: An ab initio study. *Chin Chem Soc.* 2022; 69:1706-18. <https://doi.org/10.1002/jccs.202200234>
- Wang D, Gao H, Xiang Y, Jiang L. Tuning the structural and electronic properties of single-layer stanene through doping 4d transition metals (Mo, Nb, Rh and Ru): A DFT study. *Synthetic Metals.* 2020; 264:116399. <https://doi.org/10.1016/j.synthmet.2020.116399>
- Soler JM, Artacho E, Gale JD, Gracia A, Junquera J, Ordejon P, Sánchez-Portal D. The Siesta method for ab initio order-N materials simulation. *J Phys:Condens Matter.* 2002; 14(11):2745-79. <https://doi.org/10.1088/0953-8984/14/11/302>
- Behera H, Mukhopadhyay G. Structural and Electronic Properties of Graphene and Silicene: An FP-(L) APW+lo Study. *AIP Conf Proc.* 2010; 1313:152-5. <https://doi.org/10.1063/1.3530474>
- Cahangirov S, Topsakal M, Aktürk E, Şahin H, Ciraci S. Two- and one-dimensional honeycomb structures of silicon and germanium. *Phys Rev Lett.* 2009; 102:236804.

- <https://doi.org/10.1103/PhysRevLett.102.236804>
PMid:19658958
15. Houssa M, Pourtois G, Afanas'ev VV, Stesmans A. Can silicon behave like graphene? A first-principles study. *Appl Phys Lett*. 2010; 97:112106. <https://doi.org/10.1063/1.3489937>
 16. Lebégue S, Eriksson O. Electronic structure of two-dimensional crystals from ab initio theory. *Phys Rev B*. 2009; 79:115409. <https://doi.org/10.1103/PhysRevB.79.115409>
 17. Şahin H, Cahangirov S, Topsakal M, Bekaroglu E, Akturk E, Senger RT, Ciraci S. Honeycomb structures of group-IV elements and III-V binary compounds: First-principles calculations. *Phys Rev B*. 2009; 80:155453. <https://doi.org/10.1103/PhysRevB.80.155453>
 18. Wang S. Studies of Physical and Chemical Properties of Two-Dimensional Hexagonal Crystals by First-Principles Calculation. *J Phys Soc of Jpn*. 2010; 79:064602. <https://doi.org/10.1143/JPSJ.79.064602>
 19. Slater JC. Atomic radii in crystals. *J Chem Phys*. 1964; 41:3199-204. <https://doi.org/10.1063/1.1725697>