Magnetic properties of Ga-doped and As-doped hydrogenated silicene: Density Functional Theory (DFT) calculations

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Abstract. Computational studies of silicene, which is a two-dimensional silicon material with honeycomb structure, has been carried out using Density Functional Theory Calculation. This study was aimed to determine the effects of doping gallium (Ga) atom and arsenic (As) atom on the magnetic properties of hydrogenated silicene. The results showed that pure silicene has very small magnetic properties, can be considered as non-magnetic. The process of hydrogenation on silicene changes it to become a magnetic material. The effects of Ga/As dopant on the magnetic properties of hydrogenated silicene depends on positions of Ga/As atom. Silicene with As atom at hollow site has the highest magnetic moment of 0.0592 $\mu_B$. This value increases from the magnetic moment of hydrogenated silicene magnet by 104%.

1. Introduction
The discovery of graphene, as the first two dimension material successfully synthesized, has attracted considerable interest owing to its unique (e.g massless Dirac fermions and zero-gap) properties and superior properties (e.g high durability, strength, and conductivity)[1]. However, as silicon is still dominant in electronic components industries, compatibility to silicon layer must be considered. Silicene (2D silicon material) has the same structure as graphene, honeycomb [2]. Both are semi-metal materials without an energy gap [3]. The DFT and tight-binding approach performed provides a value of 7.9 meV for spin orbit coupling (SOC) silicon, which is 1000 times that of graphene [4]. Silicon also has properties that are compatible with semiconductor technology compared to graphene [5]. This silicon honeycomb structure therefore has a great opportunity to be favored in nanoelectronic devices over graphene [6].

The natural properties of silicene material can be improved by modifying the surface. In 2012, Zhang et al reported their studies regarding the effects of hydrogen atoms doping in pure silicene. The studies revealed changes from non-magnetic properties to ferromagnetic properties [7]. Similar studies have been reported by Majumdar, A. et al shows that silicene monovacancy is not magnetic. However, it is found that silicene divacancy has significant magnetic moment [8].

Among possible dopants, gallium and arsenic have been shown to enhance electronic and magnetic properties of other 2D materials. Previous studies have shown that gallium doping can increase the sensory capabilities of graphene [9]. It also has been reported that the arsenic adatom with stable energy can induce in magnetic moments the monolayer phosphorane [10]. Therefore this study investigated the effects of gallium and arsenic dopants on magnetic properties of silicene.
2. Method
This research work was performed Density Functional Theory (DFT) calculation implemented in the ABINIT software[11]. The approach used is the Generalized Gradient Approximation Pardew Bucke Erzhenhof (GGA-PBE)[12] approach. In this study, the 2x2 silicene structure was used with a cut-off energy of 25 Hartree. Silicon is 2D material, so vacuuming the z-axis is 15 Angstroms (Figure 1). The magnetic properties are known by calculating spin polarised density of states (DOS) and the difference of the energy produced.

3. Results and Discussion
This works was started with convergence test and minimization of energy by relaxation of the system to obtain a stable crystal state. Lattice constant of 3.89 Å was obtained for the pure silica which agree well with that reported by previous experimental works and calculation as shown in Table 1.

| Parameter | This work (Å) | Previous works Calculation (Å)[10] | Experiments (Å)[2] |
|-----------|--------------|-----------------------------------|--------------------|
| Silicene  | 3.89         | 3.91                              | 3.80               |

The magnetic properties of pure silica in Figure 1 show that the electron density in the energy of -13.905 eV to 7.864 eV is nearly symmetrical. It is generally said that this situation is composed of electrons with a paired orientation so that they cancel each other out, although it is still evident that there is very little asymmetry on the graph. This is evidenced by the calculation of the magnetic moment on 8 silicon atoms, which generates a magnetic moment of 0.0037 \( \mu_B \). This value is quite small, so it can be said that the magnetic moment of all pure silicon is close to zero. The above calculation results are confirmed by studies by Arnab Majumdar et.al dealing with the non-magnetic properties of monovacuum silicenes which was described as a result of the symmetrical Density of state.

![Figure 1. Spin polarised Density of State of pure silicene.](image-url)
The hydrogenation process in pure silicene leads to magnetic non-magnetic changes. This is shown in the Figure 2, which shows the hydrated silicon state at an energy of -13.88 eV - 7.89 eV with asymmetric geometry. This illustrates the arrangement of electrons in the crystal with different proportions of spin-up and spin-down. The graph shows the shift of the spin-down density to the right, indicating that the spin-up density has a single electron orientation. This is related to the addition of hydrogen atoms, which only have an orientation upwards. This hydrogen atom generates a magnetic spin moment. This result is in agreement with obtained by Zhang and Yan. They reported that hydrogenated silicene (zigzagged hydrogen atoms on the side above the silicene surface) are ferromagnetic [13].

Based on the DOS graph in Figures 3, 4, and 5, it can be seen that the silicene spin polarised density of state of hydrogenated silicene with three possible -positions of Ga dopant has an asymmetrical spin-up and spin-down density of state which indicates ferromagnetic state.
Similarly, when hydrogenated silicene was doped with arsenic in three possible positions it showed a symmetrical electron state meeting (Figures 6, 7, and 8). So the doping of gallium and arsenic atoms shows makes silicene become ferromagnetic.
Figure 6. Spin polarised Density of State (DOS) of hydrogenated silicene with As atom at Bridge (B-site).

Figure 7. Spin polarised Density of State (DOS) of hydrogenated silicene with As atom at Hollow of silicene (H-site).

Figure 8. Spin polarised Density of State (DOS) of hydrogenated silicene with As atom above silicon atom (T-site).
Based on the calculation of magnetic moments it is known that there was an increase in magnetic moments in both hydrogenated silicene and after doping. The magnetic moment of hydrogenated silicene increased by 681% from pure silicene. While the increase in magnetic moment after doping with gallium on hydrogenated silicene was 62%, 73%, 98% for hollow, bridge and top positions respectively. The increase in magnetic moments was also seen in silicene hydrogenated doping arsenic against hydrogenated silicene by 52.8%, 104%, and 24.9% for bridge, hollow and top positions respectively. This increase in magnetic moment can be seen in Figures 9 and Figure 10.

![Figure 9. Magnetic moments of silicene with different positions of Ga atom.](image1)

![Figure 10. Magnetic moments of silicene with different positions of As atom.](image2)

The magnetic properties of a material can be analyzed by the energy difference generated by ferromagnetic and anti-ferromagnetic systems. The difference in the energy produced shows the dominance of the material over the generated magnetic properties. When the energy of the system is positive, it shows more anti-ferromagnetic properties. Conversely, if the total energy is negative, the
more dominant ferromagnetic properties occur. Based on Table 2, pure silicene is anti-ferromagnetic, while hydrogenated silicic and hydrogenated silicic materials doping gallium and arsenic exhibit ferromagnetic properties. The magnetic property data generated from the energy difference calculation agrees with the results of the magnetic property analysis using the state parameter (DOS).

Table 2. Energy different between Feromagenntic state and Anti Feromagentic state.

| Material                        | Energy of FM (eV) | Energy of AFM (eV) | Energy difference (eV) |
|---------------------------------|-------------------|--------------------|------------------------|
| Pure Silicene                   | -852.56           | -852.56            | 0.002                  |
| Hydrogenated Silicene           | -971.45           | -971.13            | -0.317                 |
| As-doped hydrogenated Silicene  | Bridge            | -1133.48           | -1132.69               | -0.799                 |
|                                 | Hollow            | -1140.41           | -1139.80               | -0.614                 |
|                                 | Top               | -1128.68           | -1128.12               | -0.557                 |
| Ga-doped hydrogenated Silicene  | Bridge            | -2763.24           | -2762.80               | -0.534                 |
|                                 | Hollow            | -2772.48           | -2771.07               | -1.407                 |
|                                 | Top               | -2760.40           | -2759.62               | -0.780                 |

4. Conclusion
The calculation of the magnetic properties of hydrogenated silicates using the density functional theory method leads to changes in the non-magnetic properties of pure silicium to ferromagnetic properties with a magnetic moment value of 0.0289 μB. The surface modification by doping of gallium and arsenic in hydrogenated silicium exhibits ferromagnetic properties and leads to an increase in the value of the magnetic moments of hydrogenated silicene. Based on the research data, the collection of arsenic in hollow position gave the largest increase of the magnetic moment corresponding to 104% with the magnitude of the magnetic moment 0.0592 μB. While the gallium at the topmost position produces the highest magnetic moment with a 98% increase, this is 0.0574 μB. The calculation of the energy difference leads to data that corresponds to the situation. It was therefore concluded that surface modification by doping gallium atoms and arsenic increases the magnetic properties of hydrogenated silicene.

5. References
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