



## Hydrogen Storage through Potassium adsorbed Germanene surface

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**Abstract:** Renewable energy is one of the most promising solution to the energy issues concerning the limited supply of energy and the environmental impact of the current energy industry. Hydrogen fuel is one possible source of renewable energy, and much research and interest has been directed to this. The key issue regarding the hydrogen fuel system was that there is inefficiency in the storage system. The perspective or approach of this paper in contributing to the hydrogen fuel industry is by finding more efficient hydrogen storage through hydrogen adsorption also known as materials-based hydrogen storage. In this paper, the capability of the potassium-decorated germanene, a germanium allotrope akin to graphene, as a hydrogen storage was investigated. The interaction between the hydrogen molecules and potassium-decorated Germanene was studied using spin-polarized ground state density functional theory (DFT) calculations. The calculations were performed using the Vienna Ab Initio Simulation Package (VASP), a plane wave-based code. The potential was described using the projector-augmented wave (PAW) method. The general gradient approximation (GGA) of Perdew-Burke-Ernzerhof formula (PBE) was adopted as the exchange correlation potential. The k points were gamma-centered and automatically generated using the Monkhorst-Pack Scheme. The energy cutoff, number of k points, vacuum spacing, germanene lattice constant, and germanene buckling height were determined using multiple convergence tests. The potassium atom was used as the decoration. Relaxation and static calculations to determine the most stable adsorption site for the decoration is currently in progress.

**Key Words:** Hydrogen Storage; Germanene; Potassium Decoration, Adsorption

### 1. INTRODUCTION

Energy is seen to be a very important enabling factor for most industries and countries up to date. It has been deemed that energy gives potential for economic growth and thus energy consumption can be related to the economic progress of countries and industries (Fatai et al. 2004; Chen et al. 2007). It is inevitable to say that energy is also important to the improvement of human

lifestyle. However, although energy's importance is deemed necessary for economic and technological progress, we have had always been in need of more energy and with that, more and more power plants are erected to sustain the needs of our society. Most of these power plants use fossil fuel to produce energy which would be converted to electricity (World Energy Council, 2013). Fossil fuel power plants are indeed efficient and well implemented in society; however the consumption of fossil fuel results to the



emission of carbon dioxide (Aspergis, 2009). The increase of the concentration of carbon dioxide is expected to significantly affect the climate and induce global warming or climate change as popularly known (Cox et al., 2000). Climate change, the most prominent environmental issue of recent times, is predicted to progress as the CO<sub>2</sub> emission continues to increase. An alternative method for energy production is the renewable energy, more popularly known as clean or green energy. A significant characteristic of renewable energy is that in producing energy, these power plants produce low carbon emission, significantly lower than in fossil fuel plants. Renewable energy not only reduces carbon dioxide emission but also enables rural areas, which are mostly inaccessible, to have access to electricity (Panuly, 2001). Some of the most popular sources of renewable energy are hydropower, geothermal, solar and wind (World Energy Council, 2013).

Another renewable energy is the hydrogen fuel. It should be an ideal substitute for fossil or gasoline fuel, because it is lightweight, present in high abundance and its discharge consumption by oxidation is water which is benign to the environment (Schlapback, 2001). Hydrogen is considered as the cleanest fuel. Although hydrogen is an ideal fuel there are some hurdles it must pass through to be realized today. One of these is the cost of hydrogen production which is at least 3 times the cost of natural gas production (Gaudernack, 1998). However, the bottleneck problem for hydrogen fuel is the hydrogen storage (Zhou, 2005). The storage methods that exist today are compression, physisorption, metal hydrides *via* chemical reactions, carbon nanostructures and liquefaction. This study intends to contribute to the physisorption study of hydrogen gas on germanene sheet. Physisorption is a method where the gas (hydrogen) has an attractive interaction with the surface of the material (K adsorbed germanene sheet) that leads further into the adsorption of the gas onto the surface. An advantage to this method was that the store-release mechanism was relatively easy and reversible (Zuttel, 2003). The challenge in Physisorption is to find the efficient and safe material for hydrogen storage that would yield high gravimetric and volumetric density.

Graphene, a 2-dimensional carbon allotrope with a honeycomb structure material (Novoselov et al., 2004), has garnered significant interest in exploring its properties (electronic, optical and mechanical) (Peres et al., 2006; Guinea et al., 2007; Xu et al., 2014; Falkovsky, 2008) and ways on functionalizing graphene for possible applications through adatom

adsorption (Novoselov, 2011; Shi et al., 2014; Gallouze et al., 2013; Gkikas et al., 2014; Lee et al., 2011). The unique honeycomb network of pi-orbital in graphene gives it the “peculiar” electronic structure (Lin and Ni, 2012). Silicene is a honeycomb material that exists today and often related with graphene. Carbon, silicon and germanium belong to the same group IV in the periodic table and have similar valence electron configuration. Although diamond and Silicon Bulk have the same crystal structure (diamond), Germanium bulk has a different one (face-centered cubic). A pure germanium bulk behaves as a semiconductor. In terms of atomic radii, Germanium has the largest compared to Silicon and Carbon. In comparing the electronegativity of these three elements, Silicon has the smallest and carbon has the largest while germanium lies between. Pure germanium is a semiconductor which has a band gap much smaller than in diamond and silicon and is regarded well in the transistor industry. Germanene, a 2-dimensional germanium allotrope with a honeycomb structure, does not exist naturally in nature and cannot be exfoliated from the bulk (Dimoulas, 2014), but it was recently synthesized for the first time by epitaxially growing it on a gold (111) surface (Davila et al., 2014). Compared to graphene and silicene, germanene has a larger hexagon and is more buckled than silicene. Similar to silicene, Germanene also prefers sp<sup>3</sup> hybridization than sp<sup>2</sup> hybridization in grapheme (Trivedi et al., 2014). germanene may be similar to graphene and silicene but due to the structural difference, it is clear that germanene will present a different circumstance for the surface-adatom interaction. In this work we have investigated the structural and energetic properties of pristine and K decorated germanene using first principle calculation. Aside from the previous system, a hydrogen was approached on the K decorated germanene to see the reaction of the system.

This paper is organized as follows. In §2, the text presents the ideas, crucial equations and the methods done in the study. In §3, the calculation results are presented and discussed. Finally, §3 summarizes the analysis of the results in the calculations.

## 2. METHODOLOGY

In our work, we employed spin-polarized density functional theory (DFT) using the Vienna ab initio simulation package (VASP) code for the structural optimization and calculations (Kresse and Furthmuller, 1996). The general gradient approximation (GGA) of the Perdew-Burke-Ernzerhof

formula (PBE) was adopted as the exchange correlation potential (Perdew et al., 1997). The projector augmented wave (PAW) potentials (Blochl, 1994; Kresse Joubert, 1999) were used and a mesh cut off of 450 eV was found to be sufficient for the convergence of the plane. The hexagonal 'c' vector was kept large 15 Å to accommodate a large vacuum between the planes thus removing any inter layer interactions. For the germanene unit cell, a Brillouin Zone (BZ) sampling is done with a 11x11x1 Monkhorst-Pack Grid (Monkhorst and Pack, 1976). A convergence criteria for energy  $10^{-4}$  was used and all atomic position were relaxed until the force on each atom is less than 0.02 eV/Å. A dipole correction was implemented on the VASP code in the cases of ionic bindings (Makov and Payne, 1995).

The initial stage of this investigation involves finding the equilibrium geometry of the systems. The calculation was done with a multiple relaxed calculation. In this stage, the lattice constant 'a' was varied manually while the atomic position was allowed to move to its equilibrium position. Through the multiple data that was recorded, the one with the lowest energy was taken as the optimized geometric structure.

We investigated three adsorption sites to see the most energetically favored site: the hollow (H) site above the center of the hexagon, the Valley (V) site above the Ge atom of the sublattice A (lower Ge atom), and the top (T) site above the Ge atom of the sublattice B (upper Ge atom) (see Fig. 1). Setting the K on the bridge site would only result in the migration of the K atom to the valley (V) site after relaxation and with that the bridge site was not considered further. The binding energies ( $E_B$ ) of K for the three adsorption sites were calculated using Equation 1 and compared. The site that contains the largest binding energy was considered as the most favourable site. The K adatom height was defined as the z-coordinate difference between the K atom and the nearest top Ge atom.

$$E_B = E(Ge) + E(K) - E(K/Ge) \quad (\text{Eq. 1})$$

where:

$E(Ge)$  = energy of pristine germanene system

$E(K)$  = energy of K atom only

$E(K/Ge)$  = energy of relaxed K adsorbed on germanene system

The hydrogen atom was introduced into the investigation by approaching it on top of the K atom

on the most favored site. It was then relaxed to see the optimized position. The adsorption energy of the hydrogen on the K decorated germanene was calculated using Eq. 2.

$$E_{ads} = E(K/Ge) + E(H) - E(H/K/Ge) \quad (\text{Eq. 2})$$

where:

$E(K/Ge)$  = Energy of relaxed K adsorbed on germanene system

$E(H)$  = Energy of H atom only

$E(H/K/Ge)$  = Energy of relaxed H-K-Ge system

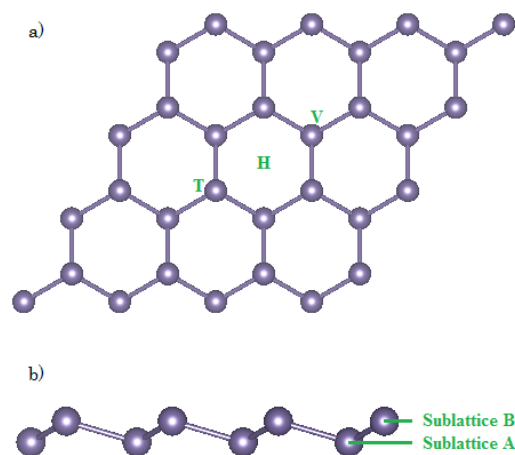


Fig. 1. (a) System of pristine germanene. The different adsorption sites for the K adatom are indicated correspondingly. (b) Division of the pristine germanene into two sublattices indicating the lower and the upper atoms.

### 3. RESULTS AND DISCUSSION

The structural configuration differ greatly compared to graphene but is quite similar to the silicene. The lattice constant 'a' of the relaxed pristine germanene supercell was found to be 4.06 Å which is 3.87 Å and 2.47 Å for silicene and graphene, respectively (Lin and Ni, 2012; Chan et. al., 2008). The buckling height between sublattices A and B was 0.689 Å. The shortest distance between two Ge atoms was found to be 2.44 Å which was also considered as the Ge-Ge bond length (see Fig. 2.). The geometric calculations are in close agreement with previous calculations (Trivedi et. al., 2014; Li et. al., 2014).

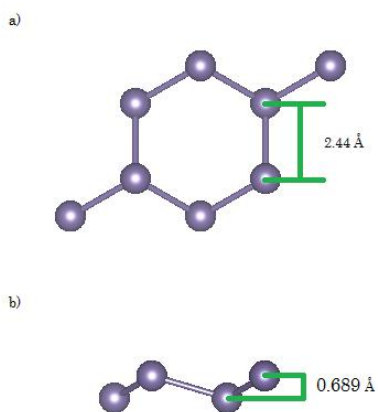


Fig. 2. (a) The bond length between two Ge atoms in the pristine germanene system. (b) The buckling height between the sublattices A and B plane.

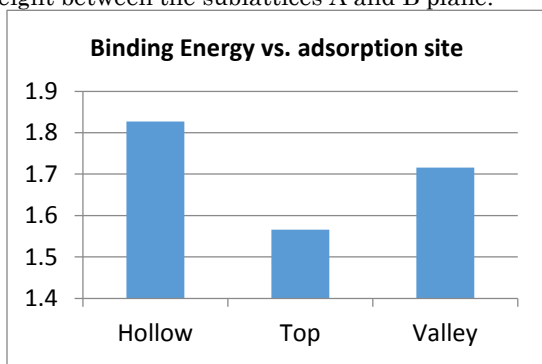


Fig. 3. Binding energies of K on germanene at different adsorption sites, indicating that the hollow site is the most favored site with the largest binding energy.

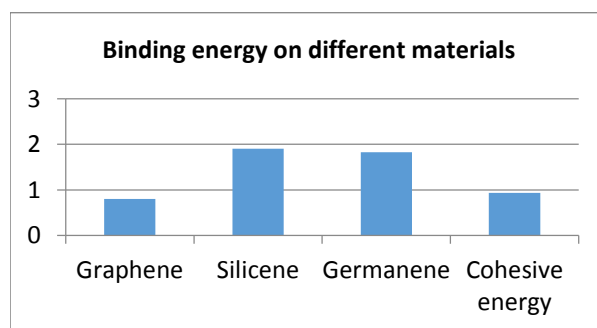


Fig. 4. Comparison of the Cohesive energy of K and the binding energies of K on different materials such as graphene, silicene, and germanene (Lin and Ni, 2012). The K atom on graphene would likely form a cluster.

A structural relaxation was done on the K-SEE-II-016

germanene system from different adsorption sites. Through comparing the different binding energies for their respective site, it was found that the Hollow site was the most favored site amongst the other two at 1.83 eV (see Fig. 3). The binding energy of K on germanene sheet was found to be larger than the cohesive energy which can mean that the K on the germanene material would less likely form a cluster. This scenario was similar to when a silicene was used and was different when a graphene was used as material (see Fig. 4).

The result of the calculations on the structural configuration shows that germanene is larger and more buckled compared to graphene and silicene, and agrees well on previous germanene studies.

The calculation for the binding energies concludes that the Hollow site was the most favored among the different sites. This was due to its binding energy which was the largest. A notable analysis on the binding energy was that by comparing it with the cohesive energy, it became apparent that K would most likely stay isolated and less likely to form clusters or bulk.

A hydrogen molecule (H<sub>2</sub>) was allowed to relax on top of the K decorated germanene. A H-K distance was found to be 3 Å. A height of 2.98 Å which was defined to be the difference between the z coordinates of the hydrogen and potassium atom. The adsorption energy of the H<sub>2</sub> molecule on the K/germanene material was calculated using the Eq. 2 and was found to be 0.05 eV.

## 4. CONCLUSIONS AND RECOMMENDATION

The calculated results on the structural parameters of the stable pristine germanene were found to be in close agreement with previous pristine germanene studies. K adsorption on the pristine germanene was done to possibly functionalize the germanene to be good hydrogen storage. The binding energy of the K atom was found to be greater than its cohesive energy which means that an isolated K can be achieved in the system which is ideal for functionalizing. A hydrogen molecule was allowed to relax on the system. By calculating for the adsorption energy, it was confirmed that the hydrogen was adsorbed on the material. This suggests that a K decorated germanene has a potential for hydrogen storage.

However, further studies should be done in order to conclude that K decorated germanene can be efficient hydrogen storage. Further studies are recommended to focus on the addition of more H<sub>2</sub>

molecules and the calculation for the gravimetric and volumetric capability of the material.

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