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Optimal approach site for Hydrogen Adsorption on Calcium-decorated Germanene surface

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Abstract: The lack of energy supplies worldwide has set the world for a search for an efficient substitute fossil fuel, the most used energy resource. A promising substitute is hydrogen fuel but as of now the development is still mainly focused on the inefficient storage media. The study focuses on a Ca-decorated Germanene that could serve as an effective storage media for hydrogen by means of physisorption. The germanene was modified by the addition of a Calcium decoration. The decoration should give a substantial effect on the interaction between hydrogen and the Germanene. The study was done using spin-polarized ground state density functional theory (DFT). The calculations for the experiment were done using the Vienna Ab Initio Simulation Package (VASP). DFT-D2 method of Grimme was activated for the Van der Waals correction. The Ca decorations preferred the hollow site with sufficient binding energy as found by the previous study. With the previous data as foundation, the configuration of the germanene substrate with the H_2 was made.For the adsorption of the hydrogen, various approach sites was considered. The relaxation calculation has shown that the H2 moves with a combination of translational and rotational movement. The optimal approach site which yields the largest hydrogen adsorption energy of 0.2748 was the bridge site when the H_2 came from a horizontal orientation. H2 Bond length elongation was found that suggest a weakening of bond. Approach site seems to have a great effect on the adsorption energy due to the some having more energy. There also seems to be potential barriers existing because H_2 don't necessarily migrate to lower potential sites.

Key Words: Hydrogen Storage; Germanene; Calcium Decoration; Adsorption

1. INTRODUCTION

Today, energy is an important factor that enables progress in the current society (Fatai et al., 2004; Chen et al., 2007). Unfortunately, the consumption of most energy resources (particularly fossil fuel) has some environmental consequences such as the production of carbon dioxide (Aspergis, 2009; Cox et al., 2000). To avoid the environmental impact of today's energy production, many have given efforts to develop renewable and clean energy resources. One of which is the hydrogen fuel.

Some of the advantage of using hydrogen fuel in contrast to fossil fuel first, is that it is present in high abundance and second, it has at least three time higher energy per mass density (Schlapbach & Züttle, 2001). Ideally, hydrogen fuel should serve as a better substitute however there are still some problems in the development of the industry. One is the cost for production of hydrogen dimers since hydrogen commonly exist as water so there is a need to transform it into its dimer form (Gaudernack, 1998). Another is the storage method for hydrogen which doesn't stand up to the efficiency and safety of liquid hydrocarbons' (common fuel) (Zhou, 2005). The significance of the storage is greater than the production particularly for mobile applications. Currently, the methods available for hydrogen are compression, physisorption, metal hydride via chemical reactions, carbon nanostructure and liquefaction. The study focuses on the physisorption method because it is lightweight which means it is ideal for mobile application. By physisorption, the hydrogen is adsorbed on the surface of the material (Züttle, 2003). The material that was investigated for the study was a Ca-decorated Germanene. A similar study was done on a K-decorated Germanene (Rojas & Arboleda, 2015).Germanene is a Germanium allotrope akin to graphene (Davila et al., 2014). In this study, the hydrogen is added at some distance on top of various adsorption sites. This is done to see any significance on the approach of the hydrogen adsorption. Also ideally, the adsorption energy of the hydrogen should not reach chemical bonds or should just be in the range of Van der Waals interaction. This is so that it won't cost too much energy to store and release the hydrogen for consumption.

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

The study employs a spin-polarized density functional theory (DFT) using the Vienna ab initio simulation package (VASP) code for the structural optimization and calculations (Kresse and Furthmuuller, 1996). The general gradient approximation (GGA) of the Perdew-Burke-Ernzerhof formula (PBE) was adopted for the exchange correlation potential. 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 7 x 7 x 1 Monkhorst-Pack Grid (Monkhorst and Pack, 1976). A convergence criterion 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). Van der Waals correction for hydrogen interaction was used in the calculation.

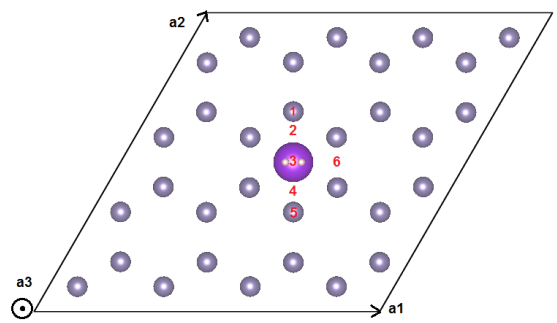

Fig. 1 Shows the supercell that contains the Hydrogen with a horizontal orientation on top of the K-Germanene material. Lattice vectors of the supercell are also define to be a1, a2, and a3. Also it shows the considered adsorption sites which are (1) top site, (2) Top to adatom site, (3) adatom site, (4) valley to adatom site, (5) valley site, and (6) bridge site.

The initial stage of this investigation involves finding the equilibrium geometry of the systems. The calculation was done with a multiple relaxed calculation. In the decoration stage, the preferred adsorption site of the Ca was to be determined. These stages were done in the previous study. The results found will be used as a foundation for this study (Rojas & Arboleda, 2015). In that previous study, the preferred site was found to be the hollow site at the center of the hexagon with a binding energy of 2.22 eV which is enough to overcome the cohesive energy of the adatom.

The hydrogen atom was introduced into the system by approaching it on top of six adsorption sites on the decorated material as labelled on fig. 1. Two types of orientations were considered for the initial state which is the horizontal and vertical orientation. It was then relaxed to see the optimized position and orientation of the hydrogen. The adsorption energy of the hydrogen on the Ca decorated germanene was calculated using Eq. 1.

$$E_{ads} = E(Ca/Ge) + E(H) - E(H/Ca/Ge) \qquad \text{(Eq. 1)}$$

where:
E(K/Ge) = Energy of relaxed Ca adsorbed on germanene
E(H) = Energy of H atom only
E(H/K/Ge) = Energy of relaxed H-Ca-Ge system

The orientation of the Hydrogen molecule was also defined in the study. Since polar and azimuthal rotations may occur there is a need to find the rotational movement. The azimuthal rotation is labelled by φ and it is the angular movement from the initial to the final states on the x, y plane. The angle of reference would differ between the two types of initial orientation. The reference for the initially horizontal orientation will be the x-axis while it is the y-axis for the initially vertical orientation. The movement on the polar rotation can be better described by the angle of incline labelled as θ since the inclination angle coming from the formerly flat orientation of the H_2 is more significant. The angle measurement only uses the H atom 1 from the two H atoms (see label on fig. 2) for generalization. The visualization for electronic and structural analysis (VESTA) was used to measure the angles. To better understand the angles, fig. 3 shows the diagram of the angles. Some changes in the adatom height was also considered and measured in reference to the furthest Ge atom of the substrate.

3. RESULTS AND DISCUSSION

The result of the structural relaxation and the corresponding adsorption energy of H_2 is presented in table I. The adatom height is defined as the distance between the z-component of the Ca and the furthest Ge atom. The relaxed adatom height was found to be in the range of 2.4 – 2.6 Å. The change of the adatom height has a maximum of 0.1 Å in magnitude where most have a decrease in height. An interesting result was that the top-horizontal approach which is the only one to yield an increase in height also has the minimum H_2 adsorption energy.

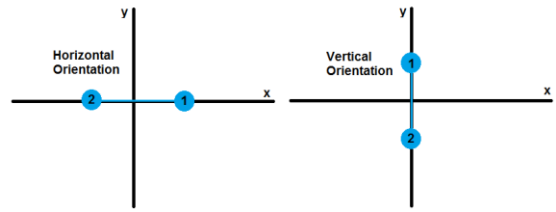

Fig. 2 shows the two types of initial orientation considered for every adsorption sites.

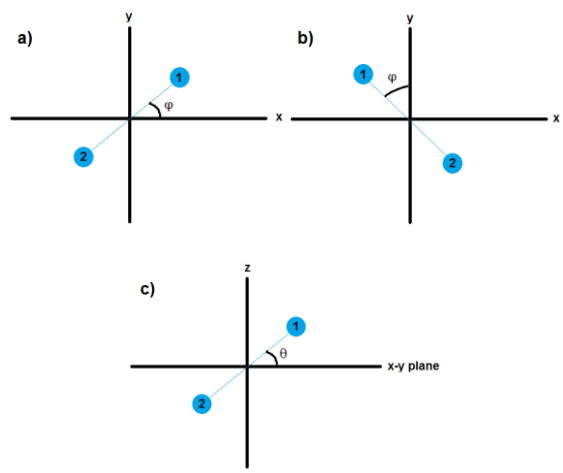

Fig. 3. (a) and (b)shows the measured φ in the case of the horizontal orientation and vertical orientation of H_2. (c) shows the angle of incline made by the H_2. Again all are measured using H atom 1 as labeled.

The H_2 height is defined as the difference between the z-component of the H_2 center of mass and the furthest Ge atom. In the relaxed state, the H_2 center of mass was situated with a H_2 height of 3.7 – 5.1 Å where the valley approach with a vertical orientation was found to be closest to the substrate in terms of height. The adsorption of the H_2 led to an elongation of the bond length of H_2 which may be a sign of a weakening bond. The least and the most affected bond length belongs to top-horizontal and bridge-horizontal approach, respectively. Another interesting look on the bond length is that there seems to be some correlation between bond length and adsorption energy. The trend is that the larger

Table I. Summary of results

Approach site	Initial Orientation	Final Adatom Height (A)	Change in Adatom Height (Å)	Final Height H2 (Å)	Change in Bond Length (Å)	ϕ	θ	Adsorption energy (eV)	Absolute Position delta (Å) Adatom a1	Adatom a2	Adatom a3	H2 Center of Mass a1	H2 Center of Mass a2	H2 Center of Mass a3
Adatom	Horizontal	2.4993	-0.0015	5.14	0.0057	0	0.0004	0.1864	-0.0089	0.0177	-0.0188	0.0114	-0.0228	-0.3768
	Vertical	2.4339	-0.0669	5.08	0.0060	0	1.9376	0.1893	0.0156	-0.0315	-0.0481	-0.0234	0.0469	-0.4031
Top	Horizontal	2.5929	0.0921	4.48	0.0002	0	0	0.1154	-0.0455	0.0909	0.0849	0.0392	-0.0784	-0.0144
	Vertical	2.4224	-0.0785	4.02	0.0227	-0.0032	-59.1283	0.2652	-0.0183	0.0355	-0.0487	0.2931	-0.5863	-0.4347
Bridge	Horizontal	2.4366	-0.0642	4.13	0.0246	-50.0633	-45.7657	0.2748	-0.0968	0.0425	-0.0085	-0.2330	-0.1052	-0.8561
	Vertical	2.4662	-0.0346	4.08	0.0226	39.75	46.1332	0.2715	-0.0615	0.0155	-0.0145	-0.1782	0.0166	-0.4435
Adatom to top	Horizontal	2.4499	-0.0510	4.88	0.0067	-1.7758	0.9328	0.1875	-0.0013	0.0161	-0.0499	0.0775	-0.1556	-0.3609
	Vertical	2.3998	-0.1010	4.33	0.0242	0.1586	-46.6898	0.2707	0.1044	-0.2179	-0.0340	-0.1143	0.2300	-0.8476
Adatom to valley	Horizontal	2.4348	-0.0661	4.46	0.0109	-0.0142	0.5148	0.2275	-0.0762	0.1583	-0.0670	0.1058	-0.2235	-0.3878
	Vertical	2.4029	-0.0979	4.65	0.0071	1.1106	34.9965	0.2038	-0.0305	0.0623	-0.0887	0.0346	-0.0646	-0.1876
Valley	Horizontal	2.4908	-0.0100	3.73	0.0171	0.1744	-0.0108	0.2540	-0.0182	0.0333	-0.0402	-0.1053	0.2091	0.0077
	Vertical	2.4602	-0.0406	3.71	0.0153	0.8356	66.8036	0.2485	0.0053	-0.0260	-0.0535	-0.0411	0.0803	0.0031

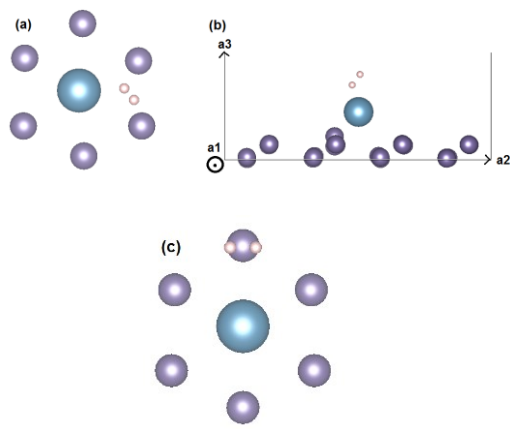

Fig. 4 (a) and (b) shows the relaxed configuration of the bridge-horizontal approach on a top and side view perspective, respectively. shows the two types of initial orientation considered for every adsorption sites. (c) shows the relaxed state of the top-horizontal approach on top view. This figure aims to show the relaxed configuration of the preferred site and initial orientation and that migration from lower adsorption site to larger does not necessarily happen for example the top-horizontal approach does not relaxed to a configuration similar to a relaxed bridge-horizontal approach.

the elongation of the H_2 bond length is the larger the adsorption energy.

As expected, after relaxation, some changes in the orientation were observed. The bridge-horizontal approach was found to have a significant change in angles on both the incline and azimuth. The valley-vertical on the other hand had the most change in the angle of incline. Most of the approach has successfully yield adsorption energy in the magnitude of Van der Waals interaction. The preferred site for H_2 adsorption is the bridge-horizontal approach with adsorption energy of 0.2748 eV (see Fig 4). The absolute position delta is defined as the absolute movement along the lattice vectors a1, a2, a3 as its components.

Although there are sites with higher adsorption energy than others, the H_2 doesn't necessarily migrate to other site of higher adsorption energy (see Fig. 4). This gives insight that within the structure of the system, there seems to be some potential barrier holding off migration to lower potential (higher adsorption energy) sites.

4. CONCLUSIONS AND RECOMMENDATION

The introduction of H_2 on the decorated germanene has made the adatom height decrease by a small amount. All approaches has experience H_2 bond length elongation after adsorption on the substrate. There is also an apparent direct correlation between the amount of elongation and H_2 adsorption energy. H_2 orientation was also seen to have some angular movements in both the incline and azimuthal angle and it's not particularly symmetric. Van der Waals interactions range of energy was achieved by most of the approach sites and bridge-horizontal approach has

the largest adsorption energy which means it's the preferred site and initial orientation. Migration of H_2 from an initial site to a site with higher adsorption site doesn't necessarily happen possibly due to the existence of some potential barriers in the system. For further studies it would be good to take the charge difference and forces present to have some data the might explain the mechanism behind the rotations of the orientation. Also more H_2 can be added to test the maximum limit for hydrogen adsorption.

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6. REFERENCES

Aspergis, N. & Payne, J. E. (2009). CO2 emmisions, energy usage, and output in Central America [Electronic version]. Energy Policy, 37, 3282-3286.

Blockl, P. E. (1994). Projector augmented-wave method [Electronic version]. Physical Review B, 50, 17953.

Chen, S. T., Kuo, H. I., & Chen C. C. (2007). The relationship between GDP and electricity consumption in 10 Asian countries [Electronic version]. Energy Policy, 35, 2611-2621.

Cox, P. M., Bretts, R. A., Jones, C. D., Spall, S. A., & Totterdell, I. J. (2000). Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model [Electronic version]. Nature, 408, 184-187

Davila, M. E., Xian, L., Cahangirov, S., Rubio, A., & Le Lay, G. (2014). Germanene: a two-dimensional germanium allotrope akin to graphene and silicone [Electronic version]. New Journal of Physical, 16, 095002..

Fatai, K., Oxley, L., & Scrimgeour F. G. (2004). Modelling the causal relationship between energy consumption and GDP in New Zealand, Australia, India, Indonesia, the Philippines and Thailand [Electronic version]. Mathematics and Computer in Simulation, 64, 431-445.

Kresse, G., & Furthmuller, J. (1996). Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set [Electronic version]. Computational Material Science, 6, 15-50.

Makov, G., & Payne, M. C. (1995). Periodic boundary conditions in ab initio calculations [Electronic version]. Physical Review B, 51, 4014.

Monkhorst, H. J., & Pack, J. D. (1976) Special points for Brillouin-zone integration [Electronic version]. Physical Review B, 13, 5188.

Rojas, K., & Jr, N. B. A. (2015). Hydrogen Adsorption on Calcium-decorated single-layer germanene: An ab initio study. In *33rd Physics Congress of the Samahang Pisika ng Pilipinas*.

Rojas, K., & Jr, N. B. A. (2015). Hydrogen Storage through Potassium adsorbed Germanene surface. In *DLSU Research Congress 2015* (Vol. 3, pp. 1–6).

Schlapback, L., & Zuttel A. (2001). Hydrogen-storage materials for mobile applications [Electronic version]. Nature, 414, 353-358.

Zhou, L. (2005). Progress and problems in hydrogen storage methods [Electronic version]. Renewable and Sustainable Energy Reviews, 9, 395-408.

Zuttel, A. (2003). Materials for Hydrogen Storage [Electronic version]. Materials Today, 6, 24-33.