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FIRST PRINCIPLE CALCULATION ON ELECTRONIC AND MAGNETIC PROPERTIES OF HYDROGENATED GERMANENE

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ABSTRACT

First principle calculation has been performed to explore the structural, electronic, and magnetic properties of hydrogenated germanene (germanium analogue of graphene). Similar to silicene (silicon analogue of graphene), buckled pristine germanene (BL) also has more stable condition than pristine germanene in planar configuration (PL). Metallic properties can be found in planar structure, and semi-metal (with zero band gap) properties can be found in buckled structure, which are comparable to other works. As the most stable structure, buckled pristine germanene is performed with hydrogen atoms with several configurations. From five configurations that have been investigated, stable structure is only able to be found in chairlike obtuse and boatlike obtuse configuration. We found that both of them are semiconductor. Nevertheless, only in chairlike obtuse configuration, the system has non-zero magnetic moment. Overall, compared with 100 percent hydrogenated silicene and graphene, 100 percent hydrogenated germanene has the smallest band gap energy.

Keyword: density functional theory, first principle calculation, hydrogenated germanene, pristine germanene.

INTRODUCTION

Since graphene, which is the synthesis of single atomic plane graphite with two dimension honeycomb structure, was discovered in 2004, a lot of researchers have been attracted to investigate its properties and its application development. It is found that Graphene uniqueness offers promising potentials for various applications, especially in nano electronic devices. However, carbon based technology has compatibility problem when it incorporated with silicon based technology. Since silicon based technology has been widely used in electronic industry [1], numerous researchers have been attempting to find opportunity from other group IV elements, like silicon and germanium [2].

Recently, the investigation about electronic properties of two-dimensional honeycomb structure of silicon has not only been theoretically studied [4,5], but also has successfully grown over Ag in experimental studies [6]. Contrary to graphene, silicene structure in buckled configuration is more stable than in planar one. Considering this potentials, researchers put a lot of efforts to explore the advantages of silicene for varied applications: new silicone based devices, hydrogen storage, solar cell, or gas sensor [7]. As a part of group IV elements, germanene (germanium analogue to graphene) appears as an interesting subject to be examined in this present work.

Inspired by hydrogenated graphene which demonstrated significant changes in band gaps [8], it is predicted that hydrogenated germanene will give similar response although it is still called for further investigations. Therefore, in order to obtain its characteristics, the structural and physical properties of germanene are going to be investigated by using density functional theory based first principle calculation. The effect of the hydrogenation in hydrogen-germanene system is also checked in order to see the change in its band structure and density of state.

COMPUTATIONAL DETAILS

First principle calculation, implemented in PHASE which is provided by the member of Theory Group of Joint Research Center for Atom Technology (JR-CAR) [3], was used to perform structural optimization and property analysis calculations of germanene and hydrogenated germanene. Furthermore, the calculation process was carried out under QC Cluster in Department of Physics, Institut Teknologi Bandung, Indonesia. In this study, germanene was constructed by using one unit cell with two germanium atoms. As an exchange correlation functional, we used Local Density Approximation (LDA) and Generalized-Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) parameterization. Then, as a preparation part of calculation process, k-point mesh for Brillouin zone integration and cut-off wave function were checked in order to get better accuracy. We used 6 × 6 × 1 k-point mesh and 22 Rydberg for cut-off wave function.

Considering interactions among layers, large enough gap was chosen for *c*-vector. For structural optimizations, 0.001 Hartree per Angstrom was used as maximum force convergence. Self-consistent force should be performed until the convergence is fulfilled. For density of state and band structure calculations, 15 × 15 × 1 *k*-point mesh was used in order to get smooth results.

Table-1. Structure parameters of germanene.

Parameter	Our calculation		Other works	
	LDA	GGA	LDA	GGA
PL lattice constant (in Å)	4.000	4.125	4.034 [2] 4.020 [9]	4.126 [2]
BL lattice constant (in Å)	3.940	4.000	3.970 [4,5]	-
BL buckling height (in Å)	0.608	0.690	0.640 [4,5]	0.695 [10]

RESULTS AND DISCUSSIONS

To begin the structural investigation of germanene, firstly we need to find the lattice constant. Lattice constant was varied from 3.5-4.6 Å and it was found that germanene has planar (PL) and buckled (BL) arrangements. PL is a honeycomb germanene structure like a flat plane or sheet, whereas BL is like zigzag plane because some atoms move up. Figure-1 and Figure-2 showed that BL (in low buckling configuration) germanene has more stable structure than PL, both using LDA and GGA exchange correlation functional. It is similar to silicene which indicates that the hybridization has a tendency to turn to sp^3-hybridization.

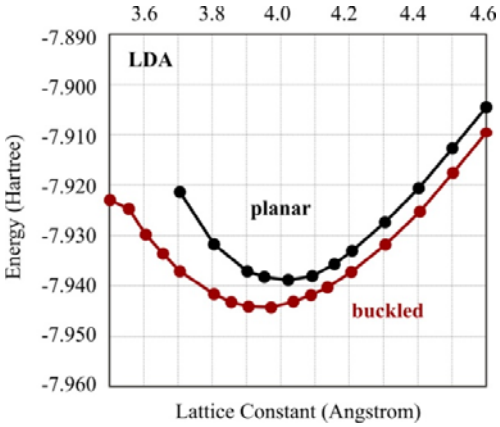

Figure-1. Lattice constant germanene using LDA.

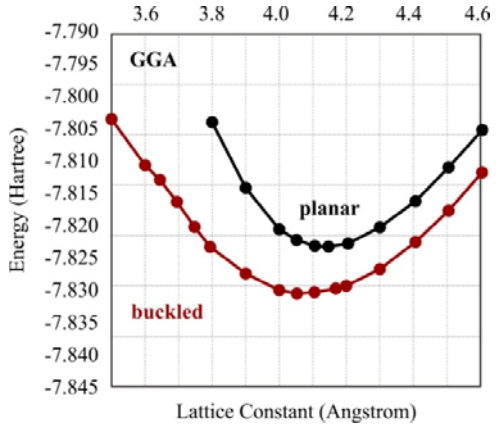

Figure-2. Lattice constant germanene using GGA.

Structure parameter of germanene from our calculation showed good agreement compares to other researches (Table-1). Since calculation using GGA gave better result, then we were going to use it for the next calculations. Electronic properties of pristine germanene were determined by calculating the density of state (DOS) and band structure of the system. As shown in Figure-3, overlapping between valence band and conduction band in K-band indicated that PL germanene has metallic properties. For BL germanene, DOS and band structure showed that the system has semi-metal properties with zero band gap.

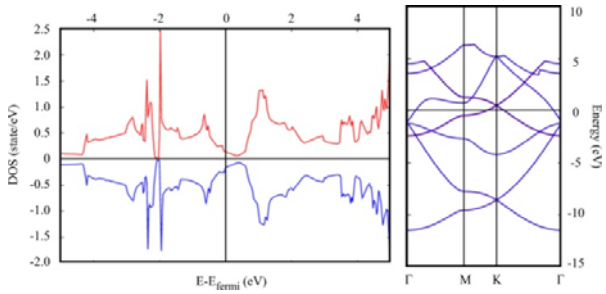

Figure-3. Density of state (left) and band structure (right) of PL germanene.

Table-2. Magnetic moment of pristine germanene.

Structure	Magnetic moment
PL	0.05694268
BL	0.11110852

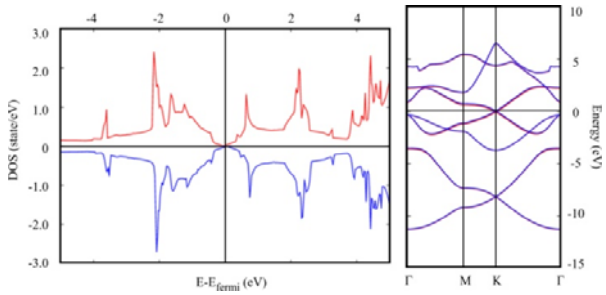

Figure-4. Density of state (left) and band structure (right) of BL germanene.

Magnetic properties both for PL and LB were determined as well. As shown in Table-2, both PL and LB had no significant magnetic moment. It means that both of them have zero magnetic moment in the normal condition.

Analyzing the effect of hydrogenation, five configurations of hydrogenated germanene system were checked in the current work (Figures 5-9). Generally, the system was divided into 2 classifications: 50 percent and 100 percent hydrogenated germanene. For 50 percent hydrogenated germanene, 50-obtuse configuration was more stable than 50-acute configuration. The distance of the second germanium became a reason why the configuration of 50-acute was unstable. Second germanium still had unpaired p_z-orbital. Therefore, it has possibility to bind with *s*-orbital of hydrogen. This situation affected the stability of the system. After structure optimization, electronic properties of 50-acute turning to metallic, whereas the electronic properties of 50-obtuse turning to semiconductor with direct band gap (1.1973 eV).

For 100 percent hydrogenated germanene, 3 types configuration were checked: 100-acute, 100-obtuse, and top configuration. Compare to others, 100-acute configuration was the most unstable configuration. This instability came from the same reason of instability in the 50-acute configuration. During relaxation, 100-acute turned to the 100-obtuse configuration (see Figure-8). Therefore, generally, there are 2 possible configurations: top and 100-obtuse (or boatlike hydrogenated germanene) configuration.

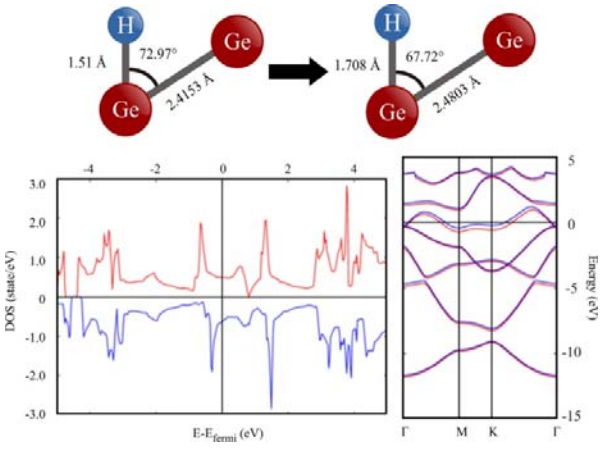

Figure-5. 50-acute configuration: (top) structural optimization, (bottom) DOS and band structure.

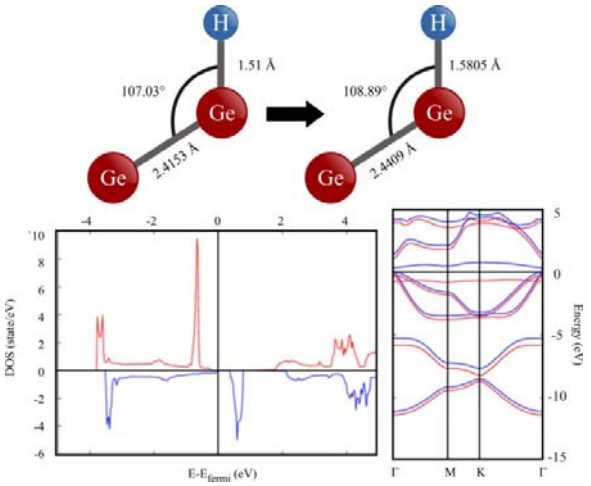

Figure-6. 50-obtuse configuration: (top) structural optimization, (bottom) DOS and band structure.

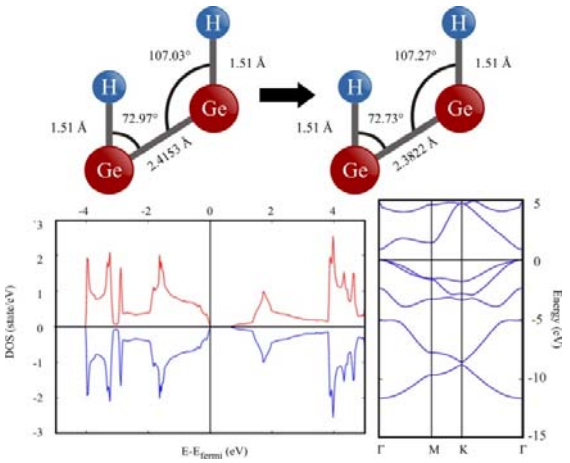

Figure-7. Top configuration: (top) structural optimization, (bottom) DOS and band structure.

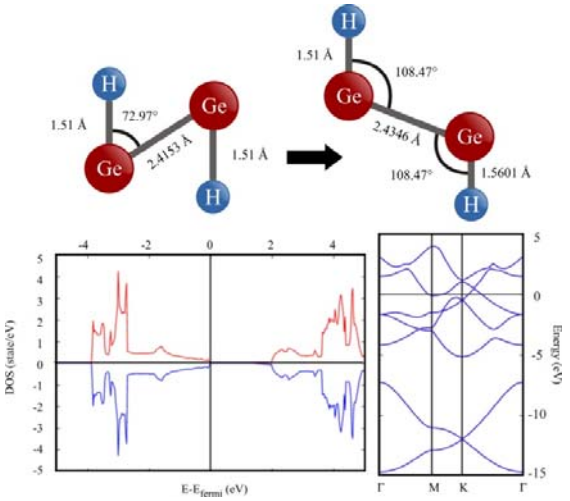

Figure-8. 100-acute configuration: (top) structural optimization, (bottom) DOS and band structure.

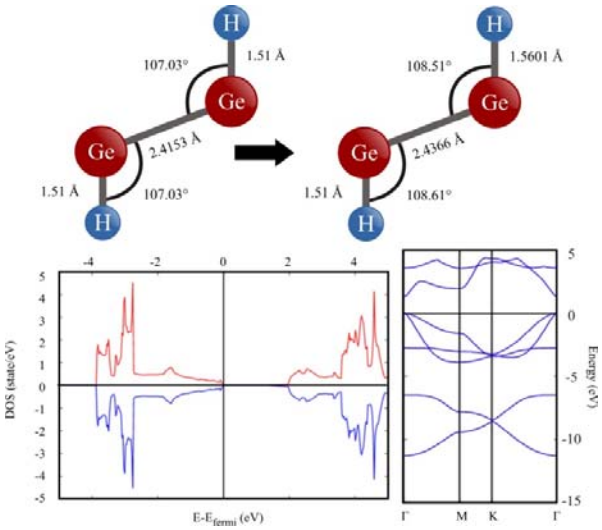

Figure-9. 100-obtuse configuration: (top) structural optimization, (bottom) DOS and band structure.

According to DOS and band structure calculations in Figure-9, boatlike hydrogenated germanene had semiconductor properties. The presence of hydrogen limits the motion of electrons. It make the (direct) band gap is opened at 1.279 eV. Comparing with 100 hydrogenated silicene (1.60 eV [9]) and hydrogenated graphene (4.66 eV [11]); hydrogenated germanene has the smallest band gap energy. Its band gap energy comes from turning hybridization of germanene from sp^2 to sp^3. Contrary to 50-obtuse configuration, the second germanium atom in boatlike configuration and the second hydrogen are bounded. This interaction adds more binding energy of the system. Furthermore, the distance of the first hydrogen is far enough from the second germanium. Thus, it is difficult to interrupt the stability of the system. For top configuration, one hydrogen atom make acute angle relative with two Germanium atoms. It caused instability of the system and made this configuration become unfavorable configuration.

As the most two stable structure configuration, magnetic properties of 50-obtuse and boatlike configuration was determined. Non-zero magnetic moment (μ=1.0) only comes from the 50-obtuse configuration. Free electron from this configuration becomes the origin of it.

SUMMARY

Hydrogenated germanene was investigated and the outcome implies that there are two kinds of stable structure: 50-obtuse configuration for 50 persent hydrogenated germanene system and boatlike configuration for 100 percent one. Both of these configurations are semiconductor, but only 50-obtuse that has non zero magnetic moment. Comparing to 100 percent hydrogenated silicone and grapheme, hydrogenated germanene has the smallest bandgap energy.

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