

## ENERGY BARRIERS OF N<sub>2</sub> ADSORPTION ON SiNR USING NUDGED ELASTIC BAND METHOD

Alvanh Alem G. Pido

Faculty, Department of Physics Mindanao State University - Main Campus  
9700 Marawi City, Philippines  
alvanhalem.pido@msumain.edu.ph

### ABSTRACT

Silicene is a very fascinating 2D material that is expected to infill the obstacles encountered in Graphene. Due to its remarkable properties, there has been an intensive immersion of research to synthesize more on its capabilities. As known, the adsorption of atoms and molecules on Silicene are very promising that reveals many applications in the field of nanotechnology. In this work, we adsorb molecular nitrogen (N<sub>2</sub>) molecule on silicene nanoribbon (SiNR) and calculated the minimum energy paths using the Nudged Elastic Band Method. We considered three adsorption sites for the simulation such as hollow site, top site and bridge site of the SiNR. The results revealed that the hollow site is the best site for adsorption, followed by the top site and the bridge site, respectively. Further, by employing the Langmuir – Hinshelwood mechanism, it was shown that N<sub>2</sub> is more stable compared to the individual N Atoms. These results serve as reference for the firmness of N<sub>2</sub> on SiNR which could open future works about the nature of their interaction.

**Keywords:** *Silicene, graphene, nanotechnology, nitrogen, nudged elastic band method, adsorption*

### INTRODUCTION

Due to the scarcity of controllable resources for electronic devices, studies about two-dimensional (2D) [11-12] materials in the past decade have been done. One of these materials is graphene. Graphene is a monolayer two-dimensional planar structure of carbon atoms which has attracted great attentions due to its remarkable properties [2, 6, 9,10]. Due to the intrinsic demand for energy, the scientific world focuses on finding a suitable material for gas reservoir. The fact that silicon has similar properties as carbon, theoretical calculations have motivated the study of a graphene-like material called silicene. Silicene is a two-dimensional honeycomb structure of silicon atoms with an sp<sup>2</sup>-sp<sup>3</sup> hybridization and a slightly buckled geometry [2]. This buckled structure makes it undeniably different from graphene despite their similarities [6]. Curiosity about these hidden differences in properties with graphene is still poorly answered.

**On one hand, Nitrogen, like many other chemical elements has catenation ability [3]. The N-N bond is significantly smaller than for carbons. While some of the studies about these 2D materials focus mainly on the interaction of the common gases on silicene nanoribbon (SiNR), only few considered N<sub>2</sub>. In this study, we adsorbed a single N<sub>2</sub> molecule on silicene nanoribbon (SiNR) using molecular dynamics (MD) [5] simulations in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [13].**

### COMPUTATIONAL DETAILS

We performed a molecular dynamics (MD) [5] simulations for our system using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [13]. The silicene nanoribbon (SiNR) was constructed with 416 Si atoms that lie flat on the simulation box with a dimension of 50 Å × 50 Å. The N<sub>2</sub> molecule was placed at Z = 5.000 Å above the SiNR particularly at the bridge, hollow and top sites.

To model the interactions between the Si atoms we make use of the modified Tersoff potential [15]. Further, we employed the Lennard-Jones potential [8] and GaN Tersoff potential for the N–Si interaction and N–N bond, respectively, and calculated the energy barriers for the formation and diffusion of  $N_2$  on the SiNR. The energy barriers for the formation and diffusion of  $N_2$  on the surface of SiNR have been then calculated using the Nudged-elastic band method (NEB) [4, 14] for finding the minimum energy path (MEP) of  $N_2$  on SiNR. For the formation of  $N_2$  on SiNR, we employ the Langmuir-Hinshelwood Mechanism [7].

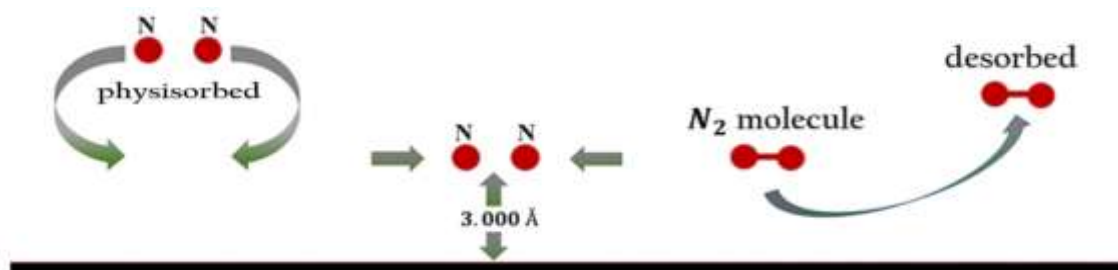


Figure 1. Illustration for the Langmuir-Hinshelwood Mechanism.

## RESULTS AND DISCUSSIONS

In this work, we calculated the energy barriers for the diffusion and formation of  $N_2$  on SiNR to find out which of the adsorption sites are most stable for  $N_2$  adsorption. The results are as follows.

### *Diffusion of $N_2$ on SiNR*

We first calculate the energy barriers for the diffusion of  $N_2$  adsorbed on SiNR. Figure 2 shows the reaction pathway of  $N_2$  on SiNR showing the forward and reverse energy barriers. Here, the forward energy barrier is the energy needed for the reaction to occur from its initial state to the final state. Comparably, the reverse barrier is the energy needed for the reaction to occur from the final state to the initial state.

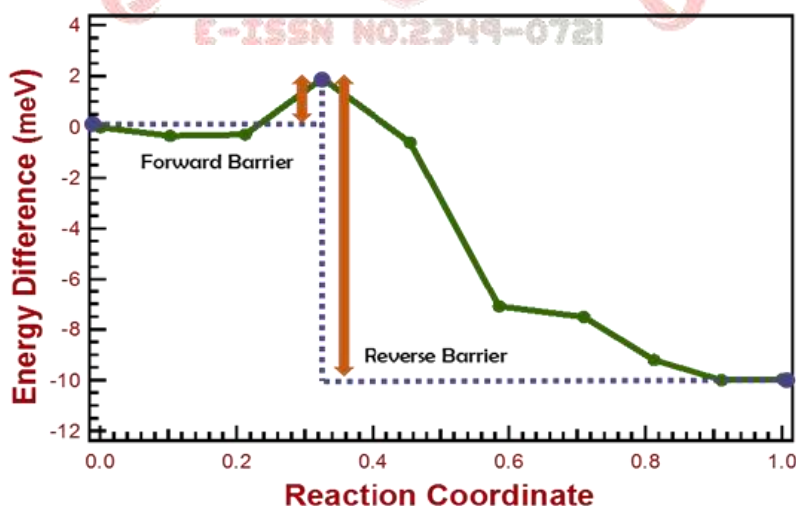


Figure 2. Plot of the reaction pathway of  $N_2$  on SiNR showing the forward and reverse energy barriers.

Figure 3 depicts the different adsorption sites for the diffusion of an  $N_2$  molecule on SiNR where B, H and T stand for the bridge site, hollow site, and top site respectively.

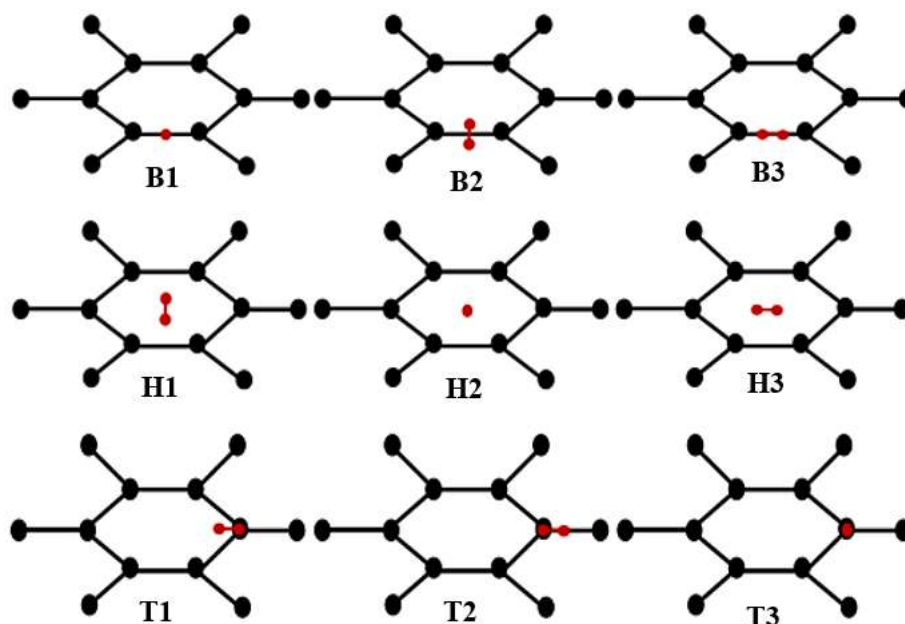
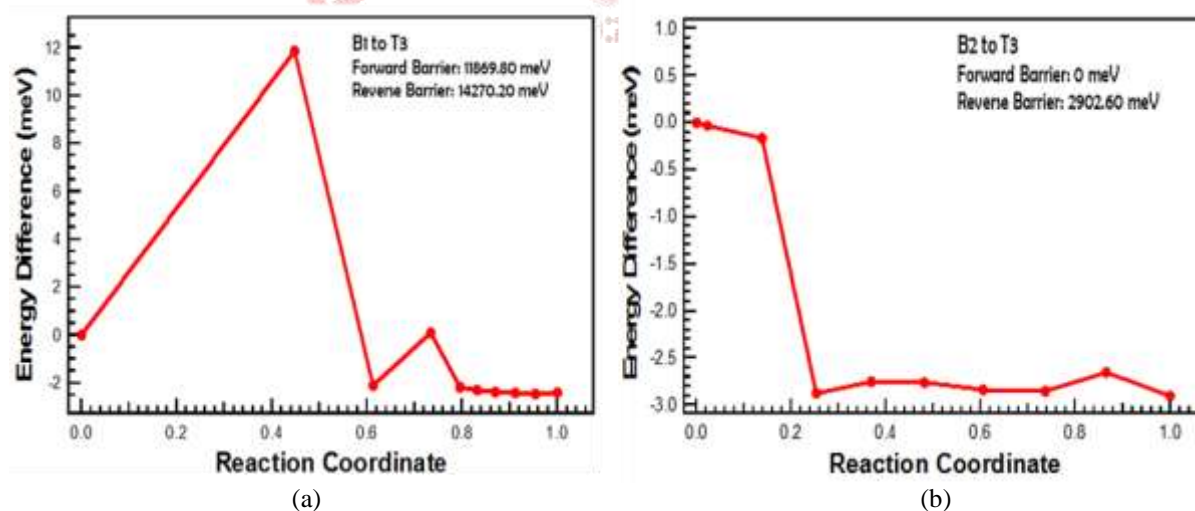
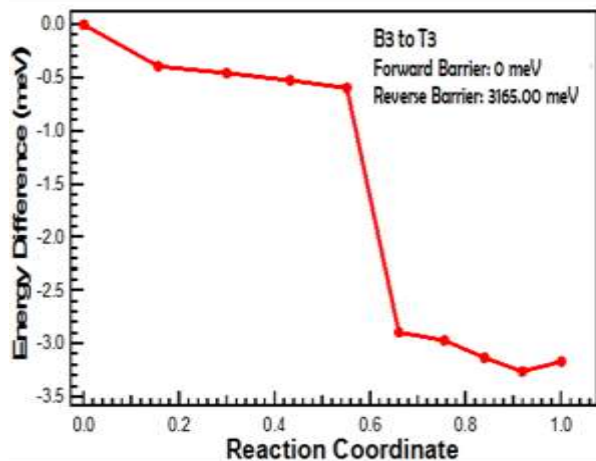


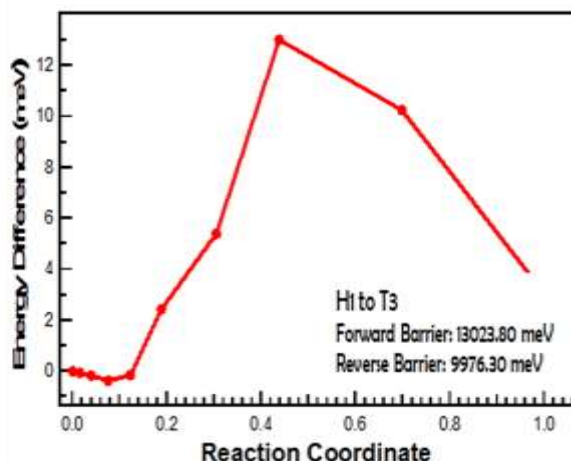
Figure 3. Nine adsorption sites for the diffusion of  $N_2$  molecule on SiNR where B, H, and T stand for the bridge site, hollow site, and top site, respectively.

The results of the simulation and the calculated energy barriers are shown in Figure 4. We explored different adsorption sites for the diffusion of  $N_2$  on SiNR. In Figure 4a to Figure 4c, we moved the  $N_2$  from the bridge sites B1, B2, and B3 to the Top site T3. As observed, the reverse energy barriers are larger than the forward energy barriers, indicating that the top site is more stable than the bridge sites. In Figure 4d to Figure 4f, we explored the stability of the  $N_2$  on the hollow site as compared to the top site. As depicted in the graphs for the energy barriers, the hollow site is clearly more stable than the top site. Finally, by comparing the different top adsorption sites (see Figure 4g and Figure 4h), it was observed that T1 is more stable than T3.

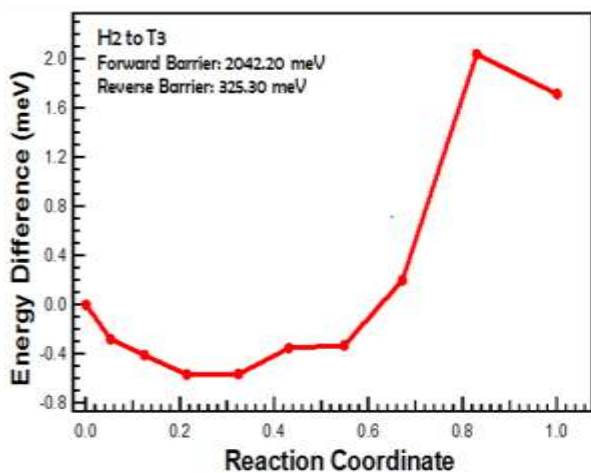




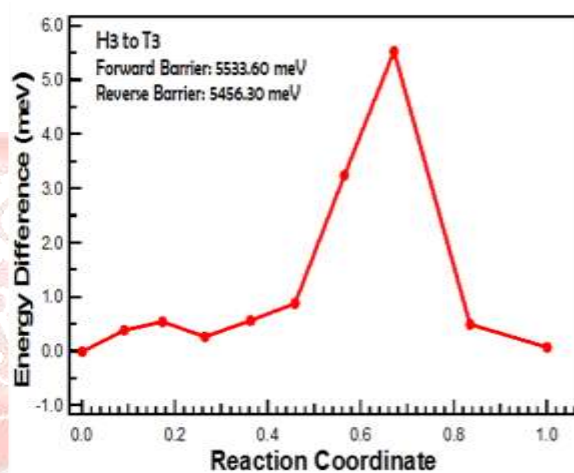
(b)



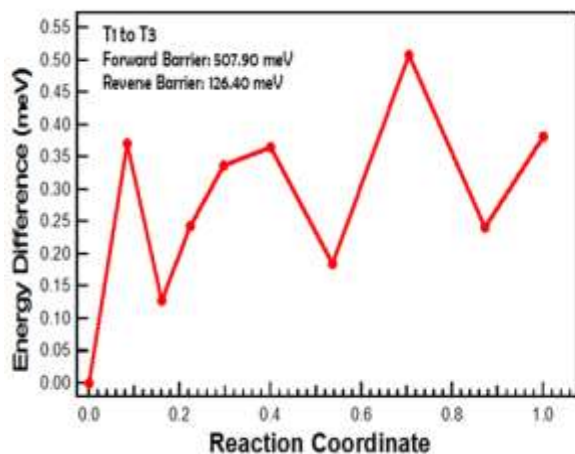
(d)



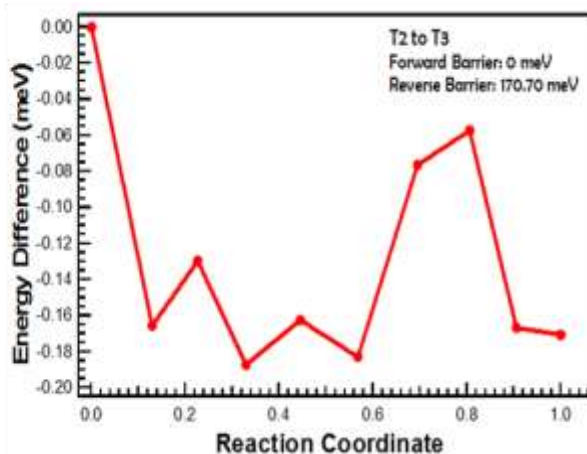
(e)



(f)



(g)



(h)

Figure 4. NEB results for the diffusion of N<sub>2</sub> on SiNR from one adsorption site to another.

Figure 4 generally show that the  $N_2$  molecule stabilizes more on the hollow site than the other adsorption sites and it requires up to 13023.00 meV diffusion energy barrier. It should be noted that the energy acts non-monotonically for all configurations which implies that  $N_2$  diffusion on SiNR takes place via a saddle point [4]. Table 1 shows the tabulated energy barriers for the diffusion of  $N_2$  on SiNR from one site to another.

Table 1. Forward and reverse barrier of the diffusion of  $N_2$  on SiNR from one site to another.

Configuration		$N_2$ on SiNR	
Initial	Final	Forward Barrier (meV)	Reverse Barrier (meV)
B1	B2	10	100
B2	H3	0	2749.80
B3	T1	0	3321.60
H1	B2	3570.70	208.60
H1	H3	296.10	0
H1	T1	2819.50	2552.80
H2	B2	1983.10	0
H2	H3	1585.50	0
H2	T1	1806.30	1744.20
H3	B2	3376.20	172.40
H3	H1	531.80	300.00
H3	T1	3434.60	0
T1	B2	2915.60	53.30
T2	H3	10330.20	12430.40
T3	T1	2374.90	12190.70

### Formation of $N_2$ on SiNR

By making use of the Langmuir – Hinshelwood mechanism (Figure 1), we considered the calculation of the energy barriers for the formation of two (2) N atoms into  $N_2$  molecule through the Nudged Elastic Band (NEB) method [4,14]. Figure 5 are the considered sites for the simulation.

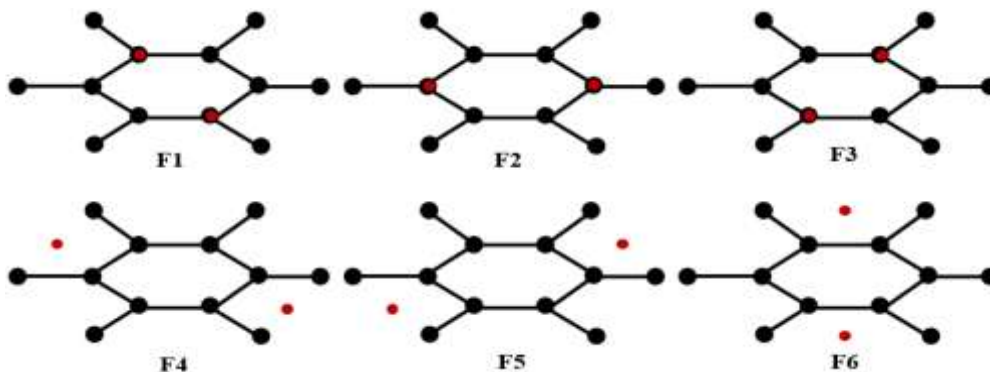
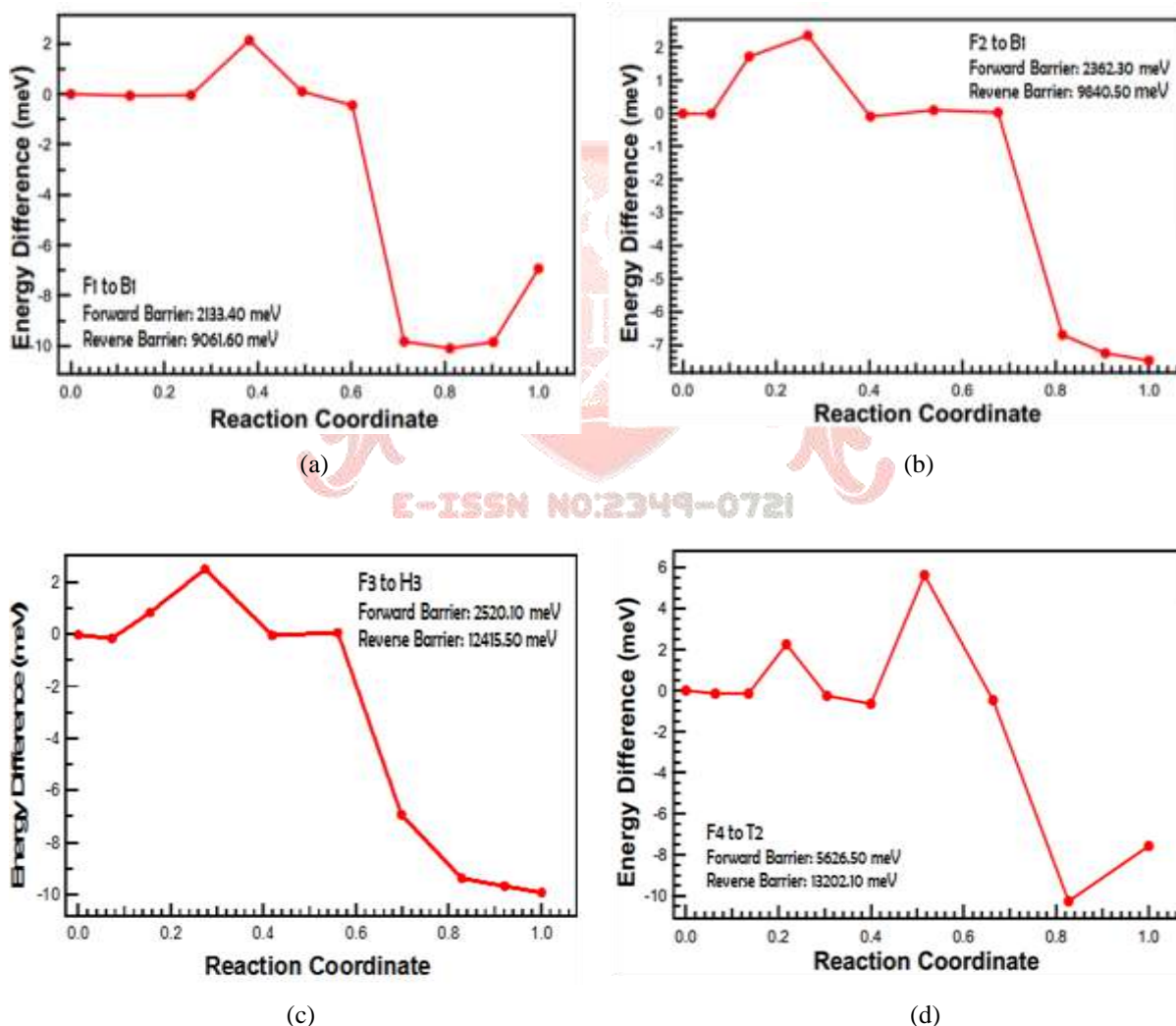


Figure 5. Initial sites for the formation of N<sub>2</sub> (red) on SiNR (black).

The first three (3) initial sites, F1 to F3, are para while the other three (3), F4 to F6 are the nearest neighbors. The energy barriers for the formation of an N<sub>2</sub> molecule on SiNR are shown in Figure 6. The initial replica represents the individual N atoms while the final replica is the N<sub>2</sub> molecule.



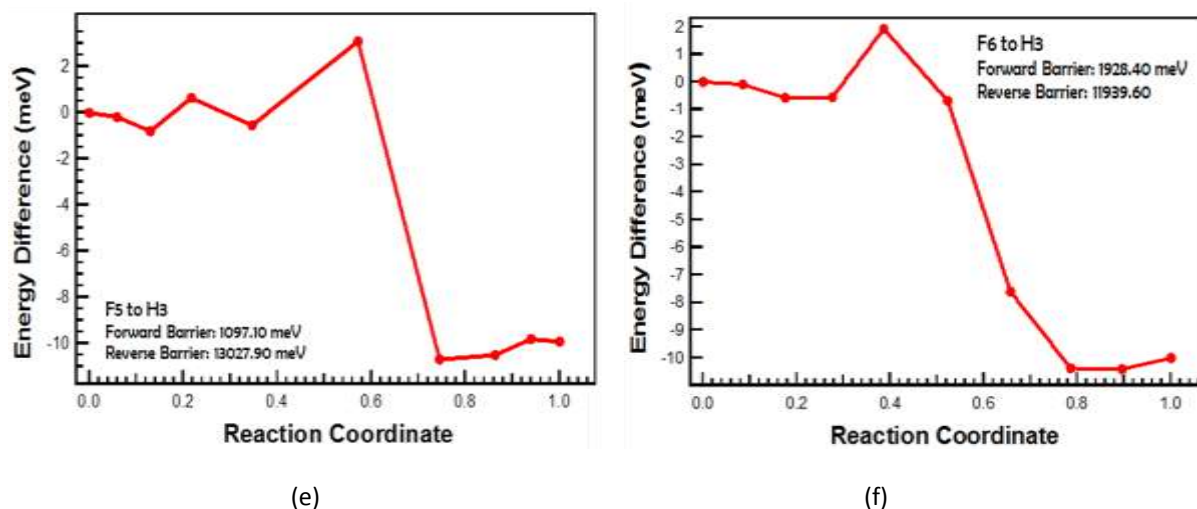


Figure 6. NEB results for the formation of Nitrogen on SiNR from one individual N atoms to a  $N_2$ .

By looking on the following graphs, the stability of  $N_2$  on SiNR has been lucidly observed where the reverse energy barriers are greater than the forward energy barriers. Evidently, nitrogen molecule stabilizes on SiNR in molecular form. Table 2 shows the energy barriers of  $N_2$ .

Table 2. Forward and reverse barrier of the formation of Nitrogen on SiNR from one individual N atoms to a  $N_2$ .

Configuration		Nitrogen on SiNR	
Initial	Final	Forward Barrier (meV)	Reverse Barrier (meV)
F1	H3	2771.80	12262.10
F2	H3	2520.10	12415.50
F3	H3	2520.10	12415.50
F4	H1	1920.80	11869.90
F4	H3	1928.40	11939.60
F5	H1	2797.40	13217.90
F5	H3	3097.10	13027.90
F6	H1	1900.90	11826.40
F6	H3	1928.40	11939.60
F6	B1	1719.50	8992.80
F6	B3	2459.70	12670.50

The spasmodic structure of silicene could be of great contribution to the disproportionate energy barriers for both the diffusion and formation of  $N_2$  on SiNR. Obviously, the graphs and/or the calculated energy barriers could be attributed on the buckled structure of silicene. This disproportionality may be due to the Pseudo Jahn – Teller effect [1].

## SUMMARY AND CONCLUSIONS

Silicene has been touted to be a two-dimensional material that could go beyond graphene. This is because it is predicted to easily generate a band gap opening because of the periodic puckering in its surface. The fact that silicene is still on the process to characterizing some of its properties, many studies about its interaction to many elements have been conducted. Also, due to the scarcity of available and genial energy, finding a suitable gas reservoir for alternative energies are very important. Thus, the interaction of an  $N_2$  molecule on silicene nanoribbon (SiNR) has been conducted. The study focused on the calculation of the diffusion and formation energy barriers for the interaction of the  $N_2$  on the SiNR. The nudged elastic band method has been used as a basis for the calculation of energy barriers for both the diffusion and formation.

For the diffusion, the results of the simulation have shown the stability of  $N_2$  on SiNR. This could be verified by the graphs. The calculated barriers have been tabulated and it has been observed that the reverse barriers for the diffusion from a hollow adsorption site to another adsorption site are greater than the forward barriers. This suggests that of all the considered adsorption sites (bridge site, hollow site and top site),  $N_2$  stabilizes most on the hollow site.

For the formation, the Nitrogen molecule has been split into individual Nitrogen atoms, adsorbed onto the surface, and then diffused, to confirm find out whether it prefers to stabilize more in atomic or molecular form. A fundamental mechanism like the Langmuir – Hinshelwood mechanism has been used. The calculated energy barriers confirm the steadiness of nitrogen on SiNR in molecular form.

For both the diffusion and formation, we observed that the energy behaves non-monotonically, revealing that the movement of Nitrogen from one adsorption site to the other takes place via a saddle point. This study serves as a reference to some possible future applications of silicene such as gas sensing and gas reservoir.

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