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Carbon precipitation on metal nanostructures and diamond surfaces

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Abstract

The interaction between diamond and a nickel (Ni) layer plays a crucial role in understanding the formation of graphene and its energy dynamics on metal-diamond substrates. In this study, we investigate the optimal positions of graphene relative to a catalyst layer on diamond by analyzing total energies obtained from self-consistent field (SCF) calculations using Quantum ESPRESSO. The structures of graphene, diamond (100), and the catalyst layers were constructed and simulated both individually and in combination. Energy comparisons between the combined structures and the sum of their individual components were conducted to identify favorable graphene positions. Our simulations show that graphene is stable both beneath and above the Ni layer, with energy differences of –0.04 Ry and –0.33 Ry, respectively, relative to the sum of the individual energies, indicating that graphene formation is more favorable above the Ni layer. Furthermore, an energy barrier analysis reveals that carbon atoms on the diamond surface can diffuse through the catalyst layer. These findings provide insights into graphene formation and carbon diffusion in the case of Ni as a catalyst, offering a foundation for further experimental and computational studies.

1. Introduction

Graphene, composed of a single layer of sp^2-hybridized carbon atoms arranged in a hexagonal lattice, has received considerable attention due to its outstanding electronic, thermal, and mechanical properties [1]. The combination of graphene with diamond substrates has been proposed to enable advanced applications in electronic devices, offering benefits such as enhanced thermal management, electronic performance, and bandgap engineering [2]. As a wide-bandgap semiconductor with exceptional thermal conductivity, high electron mobility, and high dielectric strength, diamond is an ideal substrate for graphene integration [3]. Among the various approaches for graphene formation, direct growth on diamond substrates is particularly attractive, as it eliminates the need for complex transfer process, defects and contamination [4]. Rapid thermal annealing (RTA) has been shown to be an effective technique for achieving graphene growth at relatively low temperatures compared to other methods [5]. For instance, nickel-catalyzed processes have successfully produced high-quality graphene layers on single-crystalline diamond substrates, demonstrating their potential for scalable fabrication [6]. Furthermore, studies suggest that graphene can be grown directly out of diamond through surface reconstruction and doping under controlled conditions [7]. Previous studies have explored methods using metal catalysts such as nickel (Ni), copper (Cu), and iron (Fe) to facilitate graphene formation on diamond surfaces [8]. This study focuses on theoretical and computational analysis of graphene formation on diamond (100) surfaces in the presence of a nickel catalyst. SCF calculations were performed to investigate the total energy variations for different configurations of graphene relative to the nickel and diamond layers. The configurations examined include graphene positioned above, beneath, and embedded within the nickel layer. By analyzing energy differences between these configurations, this work identifies the most energetically favorable positions for graphene formation [9]. Additionally, the study explores the diffusion of carbon atoms from the diamond surface through the nickel layer. Energy barrier analysis reveals the existence of an energy minimum when carbon atoms reach specific positions above the nickel layer, suggesting possible stabilization points for graphene formation [10]. These results enhance our understanding of graphene growth mechanisms on diamond and underscore the importance of catalyst-assisted processes in forming graphene-diamond heterostructures, while supporting the refinement of synthesis techniques for advanced applications. This theoretical framework guides future graphene-on-diamond fabrication techniques and aids in optimizing catalyst design for improved material performance.

2. Computational methods

Following convergence tests and relaxation calculations, a kinetic energy cutoff of 40 Ry and a $4 \times 4 \times 1$ k-point mesh were selected as the most appropriate settings based on our computational resources. In this work, a mixed pseudopotential scheme with the same exchange–correlation functional was adopted, employing PAW pseudopotentials for C, Cu, and Fe, and ultrasoft pseudopotentials for Ni and Co. To determine the most appropriate positions of graphene within the structure, we assume that the most favorable configuration corresponds to the lowest total energy. First, we separately prepare and perform SCF calculations to determine the total energy of graphene, diamond

(100), and the Ni layer. Next, we combine these structures and compute the total energy of the combined system. We varied graphene and catalyst layer positions until SCF calculations converged, then selected the optimal model. Graphene is positioned in three configurations: above, embedded within, and beneath the Ni layer, as shown in Figure 1. In Figure 1(a), the unit cell is expanded to a 3 × 3 × 1 supercell, similar to Figure 1(b-d). In Figure 1(b), the model was constructed with a distance of 2.09 Å between the Ni layer and the graphene, and a distance of 3.73 Å between the diamond surface and the graphene. In Figure 1(c), where graphene is embedded within the Ni layer, the distance between graphene and the diamond surface is 3.73 Å. In Figure 1(d), the distance between graphene and the Ni layer is 2.03 Å, while the distance between the Ni layer and the diamond surface is 1.70 Å. The following images illustrate the results as described below.

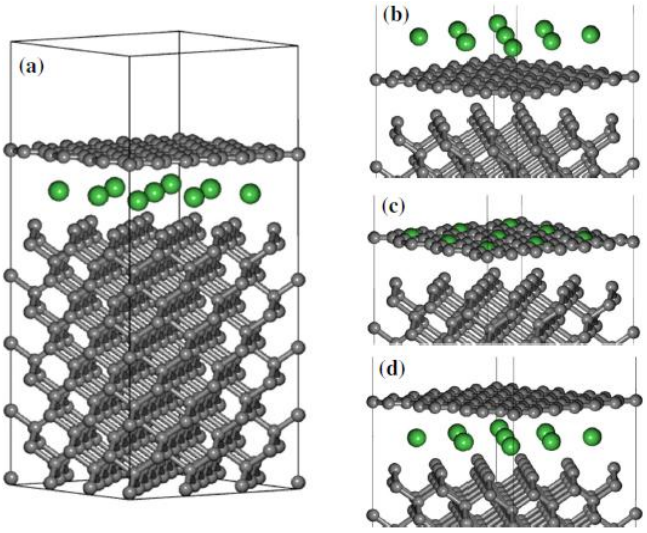

Figure 1. (a) Illustration of the combined structure. Gray spheres represent carbon atoms, and green spheres represent Ni atoms, (b) Graphene positioned beneath the Ni layer, (c) Ni layer embedded within graphene, and (d) Graphene positioned above the Ni layer.

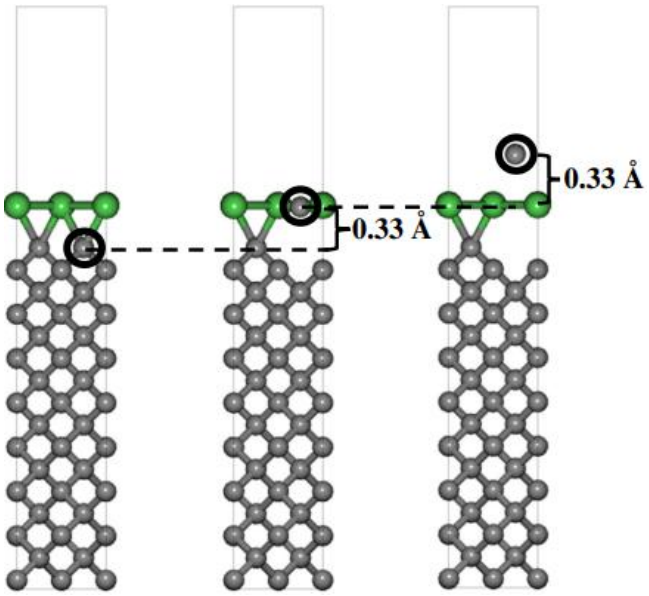

Figure 2. Side view illustrating the positional variation of the carbon atom on the diamond surface.

Subsequently, we replace the Ni layer with Cu, Fe, and Co, keeping all other parameters the same, and perform SCF calculations to evaluate the total energies of all configurations. To further investigate whether graphene can form above a catalyst layer, we conduct a more thorough analysis. This hypothesis can be tested by varying the position of a carbon atom at the diamond surface. Firstly, we construct the structures of diamond (100) and a catalyst layer and then perform a relaxation simulation. Secondly, we gradually move a carbon atom from the diamond surface to a position above the catalyst layer, as illustrated in Figure 2. The total energies of each configuration are collected and plotted to show the relationship between total energy and the position of the migrating carbon atom, allowing us to observe its behavior. The setup is shown below.

In Figure 2, a side view of the 1 × 1 × 1 unit cell is shown. We vary the position of the carbon atom along the z-axis, covering a total of 20 positions. We gradually increased the vertical position of the carbon atom at the diamond surface in steps of 0.33 Å, which was an appropriate choice given our computational resources. After setting all positions, we perform SCF calculations to determine the total energy of each configuration. The total energies corresponding to each position are calculated and will be presented in the following section.

3. Results and discussion

After performing SCF calculations on each individual material and the combined structure, we obtained their respective total energies. We define the sum of the total energies of the individual structures as E_{total} and the total energy of the combined structure as E_{sim}. Specifically, E_{total} represents the sum of the total energies of graphene, diamond, and the catalyst layer, while E_{sim} is calculated from the combined structure containing graphene, diamond, and the catalyst layer within the same unit cell. A structure with lower total energy is naturally more favorable and stable. The results are summarized in Table 1.

From Table 1, we observe that graphene can form at certain positions. For Ni, Cu, and Fe, the $E_{sim} - E_{total}$ values in Figure 1(b) and Figure 1(d) are negative, indicating that graphene is energetically allowed to form both above and beneath these catalysts. In contrast, for Co, the E_{sim}-E_{total} value is negative only in Figure 1(d), indicating that graphene is more likely to form on the Co layer rather than beneath it in the configuration consisting of Co, graphene, and diamond. Moreover, all $E_{sim} - E_{total}$ values in Figure 1(c) are positive, suggesting that graphene is unlikely to be embedded within the catalyst layer. However, to further confirm whether graphene can form above these catalyst layers, we examine the following figures.

In Figure 3(a-d) we observe both an energy barrier and an energy well as a single carbon atom is displaced from the diamond surface through the metal catalyst layers (Ni, Cu, Fe, and Co). The energy wells correspond to local minimum in the total energy, indicating favorable positions where the carbon atom can stably reside. The minimum total energies at the positions of the energy wells for Ni, Cu, Fe, and Co are –1275.20 Ry, –1014.80 Ry, –1246.90 Ry, and –1185.60 Ry, respectively. These results indicate that for each catalyst, there exists a specific position above the diamond where the carbon atom achieves a stable configuration. The presence of an energy barrier followed by a well implies that the carbon atom can overcome

the initial resistance and migrate into the catalyst layer. This supports the hypothesis that carbon atoms originating from the diamond substrate can migrate through the catalyst layer and potentially contribute to the formation of graphene on the catalyst surface. Moreover, the energy barriers for each catalyst indicate that the difficulty of carbon migration varies among the catalysts. In particular, Figure 3(b) exhibits the highest barrier energy (18.19 eV), indicating that carbon migration is most difficult when Cu is used as the catalyst.

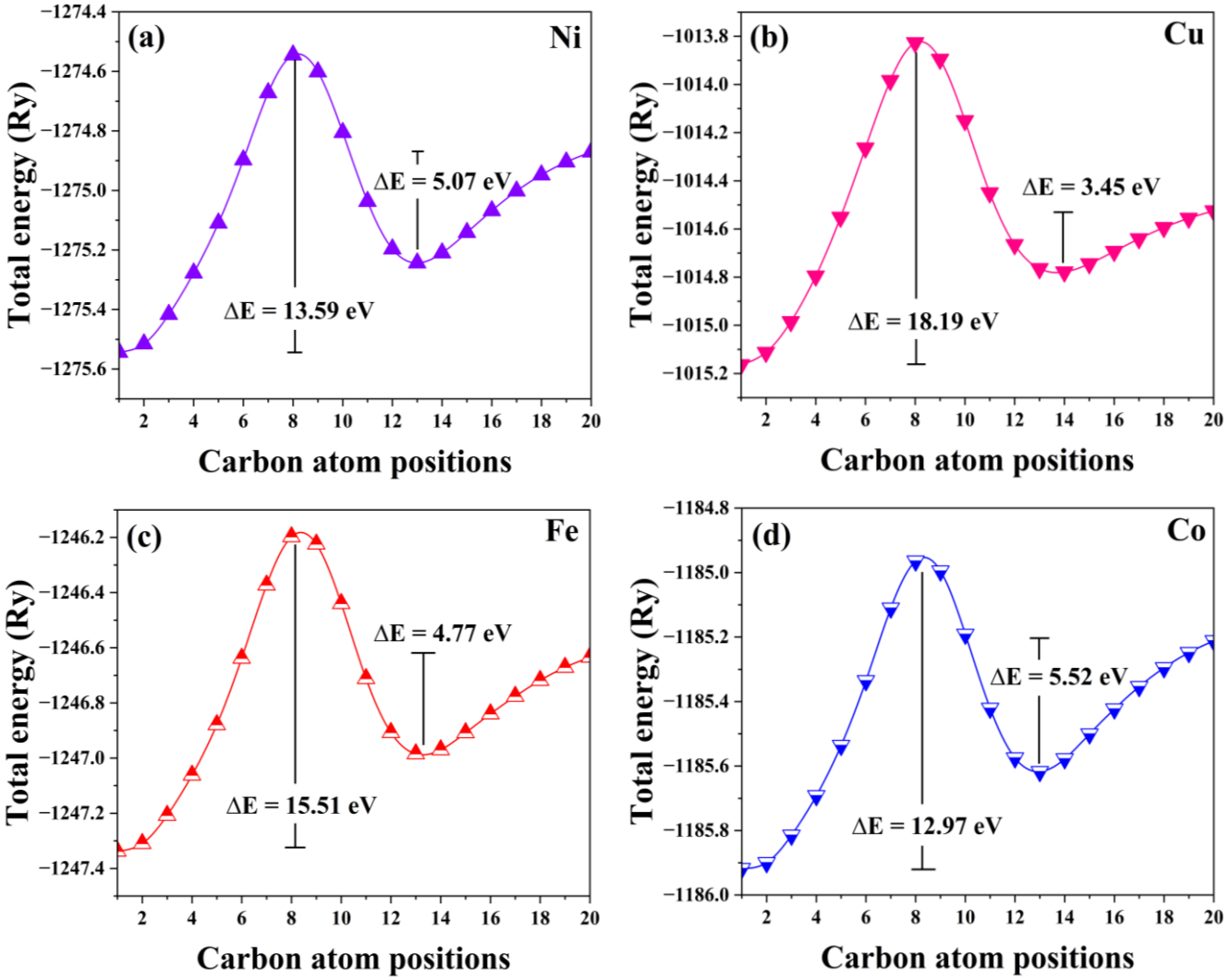

Figure 3. Relationship between the total energy and the position of a carbon atom as it moves through the Ni (a), Cu (b), Fe (c), and Co (d) layers, showing the corresponding migration barriers and local energy well depths.

Table 1. Total energies and the energy difference between E_{sim} and E_{total}.

Catalyst	Figure	E_{total} [Ry]	E_{sim} [Ry]	$E_{sim} - E_{total}$ [Ry]
Ni	1b	–1075.58	–1075.62	–0.04
	1c	–1075.58	–1065.52	10.06
	1d	–1075.58	–1075.91	–0.33
Cu	1b	–945.47	–945.48	–0.01
	1c	–945.47	–934.74	10.73
	1d	–945.47	–945.71	–0.24
Fe	1b	–1061.53	–1061.54	–0.01
	1c	–1061.53	–1050.90	10.63
	1d	–1061.53	–1061.80	–0.27
Co	1b	–1030.76	–1030.75	0.01
	1c	–1030.76	–1020.86	9.90
	1d	–1030.75	–1031.06	–0.31

* 1b: graphene located beneath the catalyst layer, 1c: graphene embedded within the catalyst layer, 1d: graphene located above the catalyst layer

The results for Ni as a catalyst, as presented in Table 1 show that graphene can form both above and below the Ni layer, facilitated by the diffusion of carbon atoms from the diamond substrate through the Ni layer. The experimental process has confirmed that graphene forms at both positions during annealing at high temperatures (above 1073 K) using Ni as the catalyst [6,8]. Although our simulations suggest that graphene formation could be energetically favorable both above and beneath the Cu layer, an experimental study [11] that used high-temperature vacuum annealing at 1223 K for 90 min at the Cu/diamond interface reported that carbon from the diamond was transformed into graphene through the catalytic effect of Cu. This indicates that the catalytic effect of Cu plays a key role in converting the diamond surface into graphene. Moreover, the experiment does not discuss how carbon atoms might migrate through the Cu layer to form graphene on its surface. For Fe, although simulations indicate that graphene could theoretically form both above and beneath the Fe layer, experimental work [12], where the graphitization process on diamond (111) was monitored in real time during heating to approximately 675°C (≈ 948 K), shows that graphene forms only on the Fe surface rather than at the Fe–diamond interface. This behavior can be explained by carbon segregating toward the Fe surface during annealing, where catalytic sp^3-to-sp^2 conversion and lattice registry favor graphene precipitation at the Fe surface. For Co, to date, there is no specific experimental report documenting graphene growth on diamond using Co as a catalyst. However, our simulation results suggest that graphene may be able to form above the Co layer. These findings provide insight and motivation for future experimental investigation, potentially validating our theoretical predictions. In addition, previous studies on graphene-reinforced metal matrix systems have emphasized that the dispersion state and interfacial bonding between graphene and metallic phases critically influence the stability and overall performance of graphene-containing structures [13]. Similarly, graphene-based metal matrix composite coatings have been shown to exhibit enhanced surface stability and improved barrier properties when graphene is homogeneously distributed within the metal matrix, underscoring the importance of controlled graphene–metal interactions in determining structural integrity and functional performance [14]. In this context, our simulation results further support the view that the energetic favorability of graphene formation on catalyst layers is closely related to the interaction between carbon species and metallic surfaces. Therefore, understanding carbon diffusion pathways and interfacial energetics at the atomic scale is essential for designing optimized catalyst-assisted graphene-on-diamond systems for future electronic and protective surface applications.

4. Conclusions

By analyzing the total energies associated with different graphene positions, we find that graphene formation is energetically allowed both above and beneath all catalyst layers, except in the case of Co, where graphene appears to be more stable above the Co layer. This suggests that graphene is unstable when forming beneath the Co layer. To test the hypothesis that graphene can form above the catalyst layers, we investigated the energy landscape of a single carbon atom displaced from the diamond surface through each catalyst. The results reveal that the carbon atom can, in principle, migrate through all catalyst layers and become trapped at specific positions above them. This behavior is supported by the presence of energy wells shown in Figure 3, which indicate the existence of stable sites for carbon atoms above the catalyst surfaces. These findings suggest that graphene formation above catalyst layers is energetically feasible and may occur under suitable conditions. These simulation results provide insightful information that may inform future experimental investigations.

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