# HIGH-INDEX NICKEL SURFACE FOR GRAPHENE SYNTHESIS

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**Abstract.** Although the CVD method is considered one of the most efficient techniques for the synthesis of graphene with electronic and mechanical properties and high chemical stability, one of the main problems in the synthesis of graphene by this method is the choice of an effective substrate. In this work, using the molecular dynamics (MD) method, the probability of graphene growth on high-index Ni(331) surfaces as compared to low-index Ni(111) surfaces was studied. We found that although Ni(111) surface is more stable than the Ni(331) surface, with respect to their surface energies, the surface energy of the graphene-covered Ni(331) surface is 0.5 J/m$^2$ lower than its Ni(111) counterpart. This strongly indicates that graphene can be grown on high-index Ni(331) surfaces better than on conventional Ni(111) surfaces. These results improve our experimental and theoretical knowledge about growing high-quality graphene for carbon-based nanodevices.

***Keywords:*** *nickel surfaces, chemical vapor deposition (CVD), graphene, molecular dynamics, surface energy.*

## Introduction

Graphene [1] is one of the famous carbon nanostructures with unique electronic [2] and mechanical properties [3], as well as high chemical stability [4]. In recent years, it has found application in many areas [5] such as electrochemistry [6], energy storage [7], solar engineering [8], and nanoelectronics [3]. Therefore, the demand for its synthesis is increasing, and in connection with this, extensive research work is being carried out [9].

In recent years, several methods for graphene synthesis, including mechanical exfoliation [10], decomposition of SiC [10], pulsed laser deposition (PLD) [11], and chemical vapor deposition (CVD) methods [12] are being used [11]. In addition to experimental [13], theoretical [14] and computational [15] studies have been also conducted on the production of graphene using the abovementioned synthesis methods. Although PLD and CVD are relatively more efficient among these methods, control of graphene formation (by selecting stabile substrates [15] with higher catalytic activity [16]) is more convenient with CVD than with PLD. In particular, the CVD method facilitates the control of a number of graphene layers using different metal surfaces due to the high solubility of carbon in them [15]. As a result of growing graphene on various metal surfaces (i.e., Au, Cu, Ni, Co, Fe, Pt, Pd, Ru, Rh, Ir, Cu-Ni) using the CVD method, it was found that the order of the catalytic activity of the surfaces is Ni ≈ Rh ≈Co ≈ Ru > Pd ≈ Pt ≈ Ir > Cu > Au [17]. With respect to this order, Ni(100), Ni(110), and Ni(111) surfaces have been particularly recognized as catalytically active surfaces for graphene growth among others [18]. Nevertheless, efficient control of graphene synthesis using metal catalyst surfaces still remains one of the main challenges of CVD-based growth. Therefore, in recent years, high-index nickel surfaces (e.g., Ni(210), Ni(331), Ni(411), Ni(630), Ni(722), Ni(730), Ni(755), Ni(830)) have also attracted attention due to the fact that they have demonstrated sufficient thermal and chemical stability in chemical reactions [16]. However, the properties of these surfaces as well as the mechanisms of graphene synthesis using these surfaces have not been fully understood. Therefore, in this research work, the surface energy of the new Ni(331) surface is estimated by the molecular dynamics MD method in comparison with the surface energy of the Ni(111) surface, which is used as a conventional surface for graphene CVD synthesis.

## Computational details

In this research work, simulation of the processes is performed using the LAMMPS package [19], which is based on the molecular dynamics (MD) method. The parameters of the ReaxFF potential are developed by Zou et al. [20] to describe interactions between atoms in the thermodynamic system. Single-crystals with selected Ni(111) and Ni(331) surfaces are generated using VESTA 3D software [21] (see Fig. 1a). The size of the nickel single-crystals with (111) and (331) surfaces is 25×25×22 and 24×32×31 Å$^3$, respectively. Periodic boundary conditions are applied for both x and y directions of the simulation box. Each layer of Ni crystal with (111) and (331) surfaces (along the z direction) consist of 120 and 60 atoms, as well as, the distance between each layer is 2.03 and 0.8 Å, respectively. In addition, in some cases, graphene patches ($C_{48}H_{18}$) are placed on the both Ni surfaces (Fig. 1b).

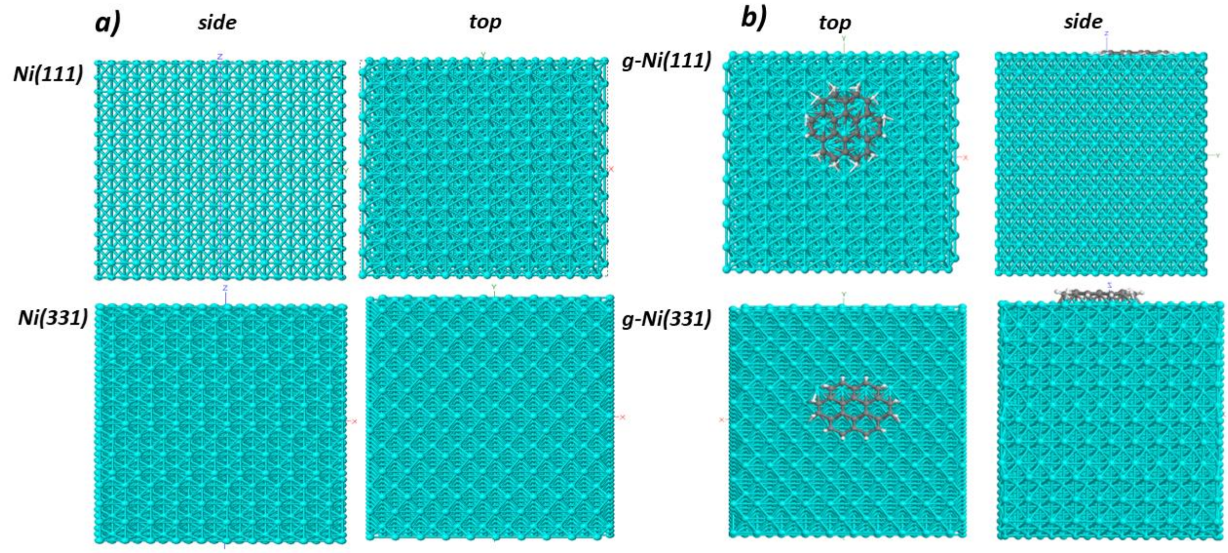

**Fig. 1. Top and side view of (a) a pure Ni(111) and (331) (left side) surfaces and (b) graphene-containing g-Ni(111) and (331) (in right side) surfaces. The number of layers of Ni crystals with (111) and (331) surfaces is 16 and 26, respectively, along the z axis.**

To calculate the surface energy, the potential energy of the selected model structure is minimized by steep-descent and conjugated gradient methods. Before the energy minimization, the structure is first heated up to 50 K (with a heating rate of 1 K/ps) in the NpT ensemble using a Nose–Hoover thermostat. Subsequently, the structure is cooled down to 0.001 K. During the heating and cooling processes, the pressure of the thermodynamic system is kept constant at about 0 atm). Finally, the surface energy of the structure is calculated as follows [22]:

$$\gamma = \frac{1}{2A}(E_{slab} - \frac{N_{slab}}{N_{bulk}} E_{bulk}) \quad (1)$$

where, $E_{slab}$ and $E_{bulk}$ are the potential energies of the pure nickel slab and nickel bulk, respectively, $N_{slab}$ and $N_{bulk}$ are the number of atoms of the pure nickel slab and nickel bulk, respectively, A is the area of the pure nickel surface. In addition, the surface energy for graphene ($C_{48}H_{18}$)-containing Ni crystal is calculated as follows [22]:

$$\gamma_g = \frac{1}{A}\left(E_{slab} - \frac{N_{slab}}{N_{bulk}} E_{bulk}\right) - \gamma \quad (2)$$

where, $E_{slab}$ and $E_{bulk}$ are the potential energies of the graphene-containing nickel slab and nickel bulk, respectively, $N_{slab}$ and $N_{bulk}$ are the number of atoms of the graphene-containing nickel slab and nickel bulk, respectively, A is the area of the graphene-containing nickel surface.

## Results and Discussion

The results showed that an increase in the thickness of the Ni crystal leads to decrease in the surface energy. In particular, Fig. 2 shows the dependence of the surface energy of Ni(331) and Ni(111) structures on their thicknesses, i.e., number of layers in z-direction.

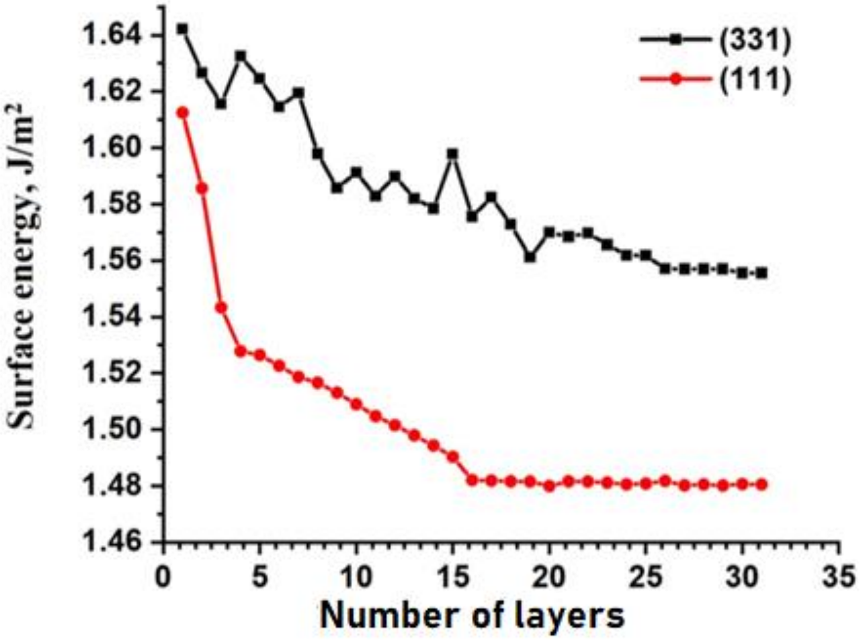

**Fig. 2. Surface energies of Ni(311) and Ni(111) crystals as a function of their thicknesses.**

It can be seen from the figure that while the surface energy for Ni(331) and Ni(111) structures consist of single layer is 1.64 J/m$^2$ and 1.61 J/m$^2$, respectively, these values gradually decrease when the number of layers increases. Subsequently, the surface energies reach values of 1.55 J/m$^2$ and 1.48 J/m$^2$ for Ni(331) and Ni(111) surfaces, respectively, and these values starting from 26 and 16 layers, respectively, remain unchanged with further increase in the number of layers. This phenomenon can be explained by the fact that the thermodynamic system has reached stability, which is calculated by the molar Gibbs free energy (ΔG) [23]. In particular, the free energy consists of the sum of the (positive) surface energy and the energy of the rest of the crystal (negative), that is, as the crystal thickens (the number of layers increases) its negative value (i.e., system stability) increases [23].

The obtained results are compared with those obtained by other calculation/simulation methods obtained for Ni(331) and Ni(111) surfaces (Fig. 3a). These data indicate that although there is a slight difference in results obtained on the basis of CEM-LMTO (2.36 and 2.08 J/m$^2$) [24], EAM (1.97 and 1.62 J/m$^2$) [25] and MEAM (2.34 and 2.04 J/m$^2$) potentials and our results, they are almost consistent with the results obtained on the basis of EAM-CG (1.60 and 1.36 J/m$^2$) [26], MC-EAM (1.91 and 1.65 J/m$^2$) [27] and EAM (1.75 and 1.49 J/m$^2$) [28] potentials. Namely, the calculated surface energy values for the Ni(111) and Ni(331) surfaces are found to differ by 0.80, 0.55 J/m2 and 0.20, 0.01 J/m$^2$, respectively, when compared with the results obtained based on MEAM and EAM potentials. In general, although the values obtained for both surfaces do not match those obtained by other methods, our results show that the surface energy of Ni(331) is greater than that of

Ni(111), as in the other results. Also, Fig. 3b shows that the energies of clean Ni(331) and Ni(111) surfaces are 1.55 and 1.48 J/m$^2$, respectively, while in the case of g-Ni(331) and g-Ni(111) these values are 0.95 and 1.38 J/m$^2$. These results show that when the graphene patch is placed on the Ni(331) surface, the surface energy is 0.5 J/m$^2$ lower than when the graphene patch is placed on the Ni(111) surface. This result indicates that graphene can be grown using a selected high-index (331) surface similar to a conventional (111) surface [29].

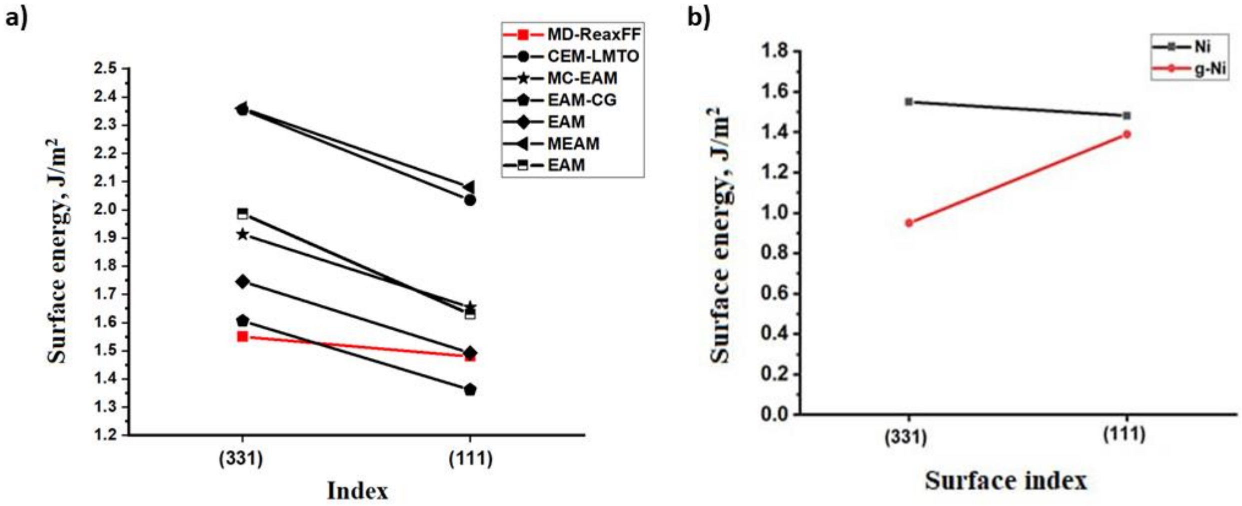

**Fig. 3. (a) Surface energies for Ni(331) and Ni(111) surfaces, obtained by different calculation/simulation methods; (b) surface energy of pure and graphene-containing Ni(331) and Ni(111) surfaces.**

## Conclusion

In this work, the surface energies of high-index Ni(331) and low-index Ni(111) surfaces were comparatively studied using MD method. The simulation/calculation results showed that the increase in the number of layers (or crystal thickness) leads to a decrease in surface energy and stability of the crystal surface. In particular, it was found that the energies of the Ni(331) and Ni(111) surfaces (1.55 J/m$^2$ and 1.48 J/m$^2$, respectively), which are in good agreement with the surface energies determined by other methods. The calculation results also showed that the surface energy of the Ni(331) surface with graphene is 0.5 J/m$^2$ lower than the surface energy of the graphene-coated Ni(111) surface. This means that graphene can be grown on a high-index Ni(331) surface better than on a conventional Ni(111) surface.

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