

Effects of substrate defects on the carbon cluster formation in graphene growth on Ni(111) surface



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ABSTRACT

The growth of graphene by chemical vapor deposition on transition metal has shown promise in this regard. The main hurdle for further improvement is the lack of complete understanding of the atomistic processes involved in the early growth stages, which is conceivable because there are too many factors affecting the growth process. Using first-principles calculations, we investigate the effect of substrate defects on the graphene nucleation on the Ni(111) surface. Our calculations reveal that the defects on substrates can induce the carbon aggregation, and the corresponding structures are completely different from that on the perfect Ni surface. We also compare the critical cluster sizes for the transition from one-dimensional carbon chains to two-dimensional graphene flakes in the growth sequence. Our investigations on the effects of substrate defects would be extremely useful for the future experimental synthesis of high-quality graphene.

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1. Introduction

Graphene has been attracting much attention owing to its special and unique physical properties, which make it one of the most fascinating materials for applications in nanoelectronics [1,2], electrochemistry [3], and gas sensing [4]. Therefore, during the recent years, much work has been devoted to the development of various synthesis methods for the growth of graphene. Among them, the catalyzed chemical vapor deposition (CVD) is considered to be quite promising and has been widely adopted [5–10]. The graphene growth in a CVD experiment can be divided into three relatively independent steps: (1) C monomers or dimers are formed by the dissociation of the hydrocarbon molecules (e.g., CH₄, C₂H₂) on transition metal (TM) surface; (2) the nucleation will occur under a special concentration of C monomers or dimers, in which small C clusters with various sizes will be generated by the C monomers (or dimers) aggregations and these carbon clusters are not stable until their sizes exceed a critical size; (3) once the carbon cluster sizes are larger than critical nucleation sizes, graphene islands will coalesce continuously on the catalyst surface to form large size graphene [11]. Though the CVD is one of the most used approaches in synthesizing graphene, it still represents a challenging way to achieve large, high-quality single crystals.

In order to get a perfect graphene, the control of the nucleation and growth during the synthesis process is obviously important [12]. To arrive at this purpose it is necessary to find out the factors that affect the graphene nucleation. The investigations of the graphene nucleation by experiments are relatively difficult due to small scale and short time. Therefore many experimental researches of the graphene growth mainly focused on the continuous growth in the third step. Computer simulations based on density functional theory can fill in the gaps to some extent and provide insight to some details of the nucleation [13–15]. As for the factors that affect the graphene nucleation, lots of related investigations have been reported: (a) the influence of interaction strength between C cluster and metal substrates, for example, for different substrates the graphene growth behavior will be different due to the interaction strength differences [16–18]; (b) the influence of the adsorbed nonhydrocarbon molecules on metal substrates, for example, it has been discovered that oxygen (O) on the Cu surface can substantially decrease the graphene nucleation density by passivating Cu surface active sites [12]; (c) the influence of the growth temperature, for example, the recent report gave the graphene growth kinetics from temperature perspective on Cu by ambient pressure CVD at different growth temperatures [19]; (d) the effects of alloying substrate [20,21], for example, it has been found that the alloy catalyst can lead to a drastic increase in the quality of graphene films even at low CVD temperatures; (e) the effects of lattice mismatch between graphene and substrate metals [22,23].

From a theoretical point of view, besides the above-mentioned central factors, the effect of substrate defects on graphene growth

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should also be taken into account. Recently, some authors have pointed out that the step sites on the metal substrate play an important role for graphene nucleation [22,24]. Some relevant work has been reported [24], but only the formation of carbon dimer (C_2) was discussed at the step sites. In our present work, we will consider all possible stable configurations of C_n clusters ($n = 8, 9, 10, 11, 12$) on a defective surface. Therefore, extensive adsorption configurations need to be calculated. To reduce the computational time-consuming, only the small vacancy defects are taken into account in our model though the step defects could be more dominant on metal surface. As far as the carbon cluster formation is concerned, the key performances of defective substrates and the roles of defects can be reflected to some extent by the simple defect model. In addition, some researchers have pointed out, considering the high temperature of graphene CVD growth (1300 K), active metal atoms may be excited to interact strongly with carbon species, where an extra metal atom is drawn from metal bulk [25]. Therefore, surface vacancies could also play an interesting role in growth process. Importantly, in experiments it has been found that the roughness of substrate surface has effects on the quality of the synthesized graphene samples [18,26]. So it is significant to study the influences of the surface roughness on graphene growth, including the mounds [27], steps [24] and defects of the metal surfaces, which will be studied in the future. However, to our knowledge, there are little reports of theoretical researches on this aspect. In this work, using the first-principles calculations we take the Ni(111) surface as an example and perform a mechanistic study on the effects of substrate defects on the carbon cluster formation in the CVD process. The following three aspects will be discussed in detail: (a) the influences of substrate defects on the stable configurations of carbon clusters; (b) the influences of substrate defects on the adsorption strength of graphene islands; (c) the competition and transition between the one-dimensional carbon chain and the two-dimensional graphene flake on the defective substrate as the surface coverages of carbon atoms increase.

2. Model and methods

Spin-polarized density functional theory (DFT) calculations are performed by the Vienna Ab-Initio Simulation Package (VASP) [28]. The exchange and correlation interaction among electrons are described at the level of the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof (PBE) formula [29]. The electron–ion interactions are treated using the projector augmented wave (PAW) method [30,31]. The Kohn–Sham orbitals are expanded using plane waves with a well-converged cutoff energy of 400 eV. The Monkhorst–Pack k-point mesh of $1 \times 2 \times 1$ is used for the Brillouin zone (BZ) sampling. Structural optimization of all systems is performed until the atomic forces drop below 0.02 eV/Å.

In this study, we take Ni as the metal substrate, which is one of the most used catalysts for graphene CVD synthesis because Ni(111) surface matches the graphene lattice very well [32]. A slab model of four atom layers is used to simulate the Ni(111) surface with the two bottom layers fixed. A vacuum layer of 12 Å along the z direction is placed between the slabs to avoid periodic interactions. The models of C_n clusters include carbon chains, carbon rings and graphene flake, therefore Ni(111) slab unit cell are expanded to make sure the distance between two neighboring C clusters large enough. A (4×8) supercell of Ni(111) including 128 Ni atoms is adopted. In all the calculations, the formation energy of a given carbon cluster supported on Ni surface is defined as

$$E_f = E_{C_n/Ni(111)} - n \cdot \varepsilon_{\text{adsorbed single C}} - E_{Ni(111)} \quad (1)$$

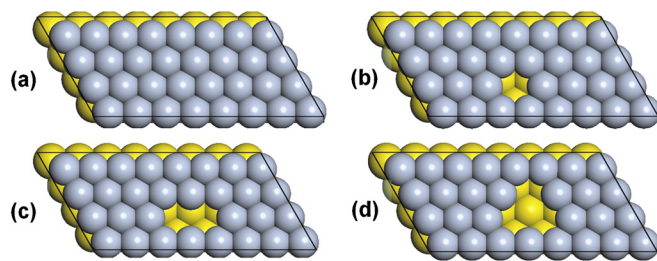


Fig. 1. (Color online.) The (4×8) Ni(111) surfaces with different defect sizes: (a) perfect surface, (b) single atom vacancy, (c) divacancy, (d) point defect of trivacancy. Where the subsurface are displayed by yellow to highlight the defects.

Table 1

The average formation energies of each vacancy (E_{vac}) for different vacancy distributions.

Defect size (N)	Single vacancy	Two vacancies		Three vacancies		
		Separated	Divacancy	V_{3S}	V_{3L}	V_{3P}
$\langle E_{\text{vac}} \rangle$ (eV)	6.0	6.0	5.8	6.0	5.7	5.6

where $E_{C_n/Ni(111)}$ is the energy of the hybrid system, $\varepsilon_{\text{adsorbed single C}}$ is the energy per C atom adsorbed on Ni(111) surface, and $E_{Ni(111)}$ is the energy of the Ni substrate. In addition, the adsorption strength of the carbon cluster on surface is depicted by the adsorption energy defined by the formula

$$E_{\text{ad}} = E_{C_n/Ni(111)} - E_{\text{free } C_n} - E_{Ni(111)} \quad (2)$$

where E_{C_n} is the energy of the free C_n cluster, and other terms are same as the aforementioned definitions.

3. Results and discussion

To study the effects of substrate defects on the formation of carbon clusters, the Ni(111) surfaces with defects are optimized. The surface defects of Ni(111) have been researched in some experimental work [33]. In this work small scale defects with single, double and triple Ni-atom vacancies are considered, respectively, and shown in Fig. 1. And for the surface with triple Ni-atom vacancies, different vacancy distributions are tested.

There exist three different surface models for the system of triple Ni vacancies: the separated distribution of three Ni-atom vacancies, marked by V_{3S} , three adjacent Ni vacancies in an orientation, marked by V_{3L} , and the triangle point defect with three close-packed Ni vacancies, marked by V_{3P} . The average formation energies of each vacancy (E_{vac}) are calculated for different vacancy distributions and listed in Table 1, where E_{vac} is defined by

$$E_{\text{vac}} = (E_{Ni(111) \text{ with } N \text{ vacancies}} + N \cdot \varepsilon_{\text{free Ni}} - E_{Ni(111)})/N \quad (3)$$

The results suggest that the single atom vacancies trend to aggregations and form a relative large point defect. The similar phenomena are observed generally for other metals [34]. In the present work single atom defect, divacancy defect and trivacancy point defect are taken into account.

At first, for the very small C_n clusters with $n = 1-7$, there are not enough C atoms to form a sp² island containing at least two connected polygonal rings in this size range. The possible structures are only open or closed C chains. In this work, we focus on the formation of graphene island, and therefore only C_n ($n \geq 8$) clusters are studied. Based on the reported low-lying isomers of carbon cluster [11], various configurations of carbon clusters (C_n , $8 \leq n \leq 12$) on the perfect and the defective Ni(111) surfaces are relaxed respectively. It is found that, for C_n ($n \geq 8$) on the perfect Ni(111) substrate, there exist two sorts of stable configurations, namely, the carbon chain (including the close and the open) and

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