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Graphene growth and stability at nickel surfaces

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Abstract. The formation of single-layer graphene by exposure of a Ni(111) surface to ethylene at low pressure has been investigated. Two different growth regimes were found. At temperatures between 480 and 650 °C, graphene grows on a pure Ni(111) surface in the absence of a carbide. Below 480 °C, graphene growth competes with the formation of a surface Ni$_2$C carbide. This Ni$_2$C phase suppresses the nucleation of graphene. Destabilization of the surface carbide by the addition of Cu to the surface layer facilitates the nucleation and growth of graphene at temperatures below 480 °C. In addition to the growth of graphene on Ni substrates, the interaction between graphene and Ni was also studied. This was done both experimentally by Ni deposition on Ni-supported graphene and by density functional theory calculation of the work of adhesion between graphene and Ni. For graphene sandwiched between two Ni-layers, the work of adhesion between graphene and the Ni substrate was found to be four times as large as that for the Ni-supported graphene without a top layer. This stronger interaction may cause the destruction of graphene that is shown experimentally to occur at ~200 °C when Ni is deposited on top of Ni-supported graphene. The destruction of graphene allows the Ni deposits to merge with the substrate Ni. After the completion of this process, the graphene sheet is re-formed on top of the Ni substrate, leaving no Ni at the surface.

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Catalytic decomposition of hydrocarbons on hot metal surfaces is a promising method for growth of large-area graphene [1]–[3]. The possibility of chemically dissolving the metal substrate once the growth of graphene is completed enables the production of free-standing graphene wafers that can be subsequently transferred to any other substrate for further investigation or device fabrication. It has been shown that many transition metal substrates catalyze graphene formation [3]. However, it is expected that the growth mechanisms are substrate specific. In this regard, two important differentiating characteristics of a metallic substrate are carbon solubility [4] and a tendency for carbide formation. Typical examples of materials with low carbon solubility are copper [1], platinum [5] and iridium [6]. A material having some carbon solubility but no well-defined carbide phase is Ru [7]. A prototypical carbide-forming material is iron. Although iron has not been used for large-area graphene growth, it is widely used as a catalyst for carbon nanotube growth. However, the role of the iron carbide appearing during the growth of carbon nanotubes remains controversial [8, 9].

Another typical catalyst for nanotube growth, and a material that has been used for graphene formation, is nickel [10]. The bulk phase of an ordered nickel-carbide is metastable and does not form easily. However, the carbon atoms easily dissolve in Ni, which exhibits high carbon solubility [11, 12]. An important distinguishing characteristic of Ni compared to other transition metals is that it forms an ordered surface carbide. This surface carbide is a single atomic-layer-thick Ni\textsubscript{2}C phase, and its formation competes with graphene growth. The surface carbide phase has been studied extensively by surface science techniques [13]–[15]. It was found that it forms an ordered $\sqrt{39} R16.1^\circ \times \sqrt{39} R16.1^\circ$ surface structure on Ni(111). This large unit cell is due to the incommensurate structure of an almost-square base unit of the Ni\textsubscript{2}C surface carbide with respect to the hexagonal Ni(111) substrate. We demonstrate in this study that the formation of this ordered surface carbide substantially influences graphene formation and thus makes Ni a special case compared to other graphene-forming transition metals.

The fairly high carbon solubility of Ni causes carbon to dissolve into the bulk at elevated temperatures and to precipitate to the surface when the sample is cooled. Therefore, it is commonly assumed that graphene is formed upon cooling because carbon is expelled from...
the bulk as its solubility decreases with temperature. Such a situation is common in the case of chemical vapor deposition (CVD) growth of graphene because at the high pressures and temperatures employed in CVD reactors, the Ni substrate is likely to be saturated with carbon. Precipitation of carbon is difficult to control, and this is the reason for multilayer graphene growth on Ni in CVD reactors [2]. The segregation and precipitation processes taking place in carbon-saturated Ni crystals have already been thoroughly studied by Blakely and co-workers more than 30 years ago [11, 16, 17]. They found that upon cooling a carbon-saturated crystal, a single layer of graphene segregates to the surface first, because it is a phase equilibrium structure. Further cooling causes carbon precipitation and the formation of multilayer graphitic carbon.

In the experiments reported here, the situation is different from that in CVD reactors. The Ni(111) single crystal is not saturated with carbon. Instead, the carbon is introduced by decomposition of hydrocarbons on the Ni(111) surface at pressures ($10^{-5}$ torr) and temperatures that are low compared to common CVD conditions. It is accepted in the surface science community that under such conditions only monolayer graphene is grown and multilayer carbon precipitation is not observed. This is because the bulk Ni acts as a reservoir to ‘soak up’ an excess of carbon, allowing the formation of the thermodynamic equilibrium structure of a single layer of graphene at the surface. The findings presented in this paper agree well with the conclusion of Blakely et al that monolayer graphene is a thermodynamically favored phase, while multilayer graphene only forms if an excess of carbon is expelled or precipitated from the metal.

The growth of graphene on Ni(111) under ultra-high vacuum (UHV) conditions has been studied earlier [18]–[24]. Exposing a clean Ni(111) surface to hydrocarbons yields either a surface carbide or graphene. Furthermore, it has been shown that the surface-carbide phase forms upon thermal decomposition of hydrocarbons at low temperatures, while graphene generally forms at higher temperatures between 500 and 700 °C. Recent time-dependent x-ray photoemission (XPS) studies showed that graphene grows on a clean Ni(111) surface, i.e. in the absence of a carbide [25]. Here, we re-examine these growth scenarios with a special focus on the interplay between carbide and graphene growth on a Ni(111) surface. We find that graphene is a thermodynamically favored surface termination of Ni below 650 °C. At higher temperatures, carbon is dissolved into the bulk forming a clean Ni(111) surface. At temperatures below 480 °C, surface carbide formation dominates over graphene growth. However, if the carbide is destabilized, graphene may grow below 480 °C as well.

2. Experimental and computational methods

2.1. Experimental methods

In this study, a Ni(111) single crystal was used, and the preparation and characterization of the sample was performed under UHV conditions. Before each experiment, the Ni crystal was cleaned by cycles of 0.5 keV Ar$^+$ ion sputtering followed by annealing at 800°C. Then, the sample was annealed in $10^{-6}$ torr O$_2$ for 10 min at 500 °C to burn off any remaining surface carbon, and flashed at 800°C in UHV. The cleanliness of the surface was checked by Auger electron spectroscopy (AES) or scanning tunneling microscopy (STM). Carbide or graphene was grown on the clean Ni(111) surface by exposure of the sample to $10^{-5}$ torr ethylene for 4 min at the temperature cited in the text. In additional experiments, Ni and Cu were deposited
Figure 1. Auger electron spectra of monolayer carbide and monolayer graphene on a Ni(111) surface. (a, b) The C-KVV Auger peak for carbide and graphene, respectively. (c) The carbon peak intensity in relation to the Ni-LMM peaks for carbide and graphene.

on the sample containing graphene and/or carbide. Ni deposition was performed by sublimation of a high-purity 2 mm diameter Ni rod in a water-cooled mini e-beam evaporator. For Cu deposition, a high-purity Cu wire was wrapped around a tungsten filament that was heated by an electrical current.

Most of the experiments were performed in a UHV chamber equipped with a quadrupole mass spectrometer, low-energy electron diffraction optics and a double pass cylindrical mirror analyzer for AES. In this chamber, the Ni single crystal was mounted between Ta wires that were used to heat the sample with a direct current. The sample temperature was measured accurately by a thermocouple spot-welded directly to the side of the Ni crystal. Some experiments were performed also in a commercial Omicron STM system. In the STM chamber, the sample was mounted on a Ta sample plate, which was heated indirectly with a pyrolytic boron nitride (PBN) heater. All the STM measurements were made at room temperature with a tungsten tip.

In this paper, AES was used as the main method to distinguish between carbide and graphene. This is possible because the C-KVV AES line has very characteristic and distinct shapes for both sp² hybridized carbon and carbidic carbon [26]–[30]. Figure 1 shows this C-KVV line for the surface carbide and a graphene monolayer. In addition to the distinct line shapes for the different carbon species, their intensity also reflects the difference in carbon concentrations in carbide and graphene monolayers. This is clearly visible from the carbon-to-nickel peak ratios in the spectra. For graphene, there are two carbon atoms per Ni atom, i.e. a graphene layer has the equivalent of 2 monolayers (ML) of carbon, where 1 ML corresponds to the number of Ni atoms in the Ni(111) plane. In contrast, the surface carbide phase contains only ∼ 0.5 ML of carbon.
2.2. Computational methods

First-principles density functional theory (DFT) studies of Ni/graphene interfaces were performed in order to provide additional insights into the nature of Ni–graphene bonding and other factors influencing growth mechanisms observed in experiments. The DFT calculations were performed using DMol code, which employs the numerical atomic-centered Linear Combination of Atomic Orbitals (LCAO) basis set with explicit treatment of both core and valence electrons, which allows us to avoid the use of pseudopotentials. It was found that generalized gradient approximation (GGA) does not provide an adequate description of Ni–graphene bonding, its weakness being reflected in large Ni–graphene separation in disagreement with experimental observations [20]. In contrast to GGA, local density approximation (LDA) describes the geometry of Ni/graphene interface in good agreement with experiment [20]. Therefore, the LDA functional was employed in the present study.

The basis sets and the k-point sampling of the Brillouin zone were optimized to provide an accurate and converged description of bulk metals and graphene. Because of the ferromagnetic nature of Ni, all the calculations were spin-polarized. It was found that the LDA bulk lattice constant of fcc Ni is 3.446 Å, which is within 2% of the experimental value 3.524 Å. The calculated magnetic moment of Ni atoms in fcc Ni is 0.56 \(\mu_B\), compared to the experimental value 0.6 \(\mu_B\). The C–C bond length in graphene as predicted by LDA is 1.415 Å, which is within 0.3% of the experimental C–C distance 1.42 Å.

The LDA lattice constant of graphene is 2.444 Å, while the LDA lattice constant of (111) surface unit cell of Ni is 2.436 Å. Therefore, the interface between Ni(111) and graphene was built by accommodating a 0.3% lattice mismatch between Ni and graphene by contracting graphene’s unit cell to match the underlying Ni(111) substrate. The latter consists of five Ni layers; the bottom two were fixed during geometry optimizations. To avoid artificial interactions between periodic images while using periodic boundary conditions, a sufficiently large vacuum layer of 90 Å was added to the multilayered interfacial structures.

3. Results

3.1. Graphene growth by carbon segregation on Ni(111)

Two slightly different approaches to sample preparation have been used. In the first approach, the sample was exposed to 10\(^{-5}\) torr ethylene at different temperatures, which resulted in graphene growth at temperatures higher than 500°C and the formation of a surface carbide below 500°C. In the second approach, a surface carbide was grown by exposing the clean Ni(111) crystal to 10\(^{-5}\) torr ethylene for 4 min at a fixed temperature of 400°C. Subsequently, the sample was annealed at different temperatures in UHV as the changes in the C-KVV peak in the AES spectra were monitored as a function of time.

Figure 2 shows the time sequence of the Auger spectra while annealing at 480 °C in UHV, for a sample initially exhibiting a surface carbide phase. Upon annealing, the carbide Auger signal almost immediately disappeared, forming a clean Ni(111) surface. After some time delay, a carbon signal reappears. However, the re-emerging carbon signal is from sp\(^2\) carbon. This carbon signal increases slowly with time and eventually saturates as a complete monolayer of graphene is formed. Figure 2(b) shows the intensity evolution of this carbon signal as a function of time. The absence of a carbide signal during growth indicates that graphene grows on clean Ni(111) in agreement with a recent XPS study [25].

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Figure 2. Time evolution of the carbon peak after annealing a carbide-covered surface to 480°C. (a) The C-KVV peak for the carbide at different times after raising the temperature to 480°C. In (b), the change in peak intensity is plotted versus time. After raising the temperature, the carbide C-KVV peak disappears almost immediately and graphene is formed. After a time period of ∼400 min, the entire surface is covered by monolayer graphene.

Keeping the sample in vacuum at 400°C after carbide formation results in one of two scenarios that are difficult to control; either the carbide remains stable for hours or graphene nucleates and then grows slowly with time. The time evolution of the AES signal for the second scenario is shown in figure 3. This AES signal is a superpositioning of carbide and graphene signals. To identify the percentage of carbide converted into graphene, a pure graphene AES spectrum is mixed with a pure carbide AES spectrum. The weights of the two spectra are varied to closely match the experimental data. This deconvolution of the carbon peak into graphene and carbide signals indicates that the graphene content increases at the expense of carbide. This means that the graphene phase grows by consuming the surface carbide. The fact that certain carbide samples remain stable for a long time (exceeding the time of the experiment, i.e. longer than 2 h) may indicate that either there is not enough carbon in the sample to form graphene or the carbide layer suppresses graphene formation. The latter would also explain why samples exposed to hydrocarbons at 400°C for longer periods do not transform into graphene.

To test whether the presence of carbide results in a barrier for graphene’s nucleation, an experiment has been designed to deliberately destabilize the surface carbide. The carbon–nickel bond is fairly strong, which facilitates carbide formation. Adding another element that does not form strong bonds with carbon but interacts strongly with Ni atoms of the carbide should destabilize the surface carbide. A good candidate is copper, because it interacts weakly with carbon (see DFT results below). In addition, it is known that Cu interacts strongly with Ni in the bulk, forming an isomorphous Cu–Ni alloy with the complete liquid and solid solubility of its constituents. However, due to the lower surface energy of copper compared to nickel, Cu stays on the surface at moderate temperatures [31]. Therefore, in order to explore the potential
of Cu to destabilize the carbide phase, sub-monolayer amounts (0.25 ML) of copper were deposited onto a surface Ni$_2$C. The stability of the nickel carbide was tested prior to copper deposition and it was found to be stable at least for 90 min at 400 °C. After copper deposition at room temperature, the surface carbide phase was still present. However, annealing at 400 °C immediately caused disappearance of the carbon signal, indicating the destabilization of the carbide by Cu and diffusion of the carbon into the bulk. After some time delay, carbon re-emerged at the surface in the form of graphene, while the C-AES signal grew with time. The time sequence of the carbon AES signal is shown in figure 4. The graphene growth in the presence of copper is very similar to the growth on pure Ni at temperatures above 480 °C in the sense that, in both cases, pure graphene phase is grown without any coexisting carbide phase. Furthermore, the experiment with copper deposition demonstrates that the system had sufficient carbon content dissolved in the bulk to support graphene growth. The fact that the sample containing a surface carbide was not converted into graphene, but such conversion took place as soon as the carbide was destabilized by copper, reveals the role of the carbide layer as an inhibitor of the nucleation of graphene.
Figure 4. Destabilization of surface carbide by alloying with Cu. The C-KVV Auger peak (a) and the full Auger spectrum (b) for: (i) surface carbide (blue), (ii) after deposition of $\sim 0.3$ ML Cu at room temperature (black), (iii) annealing at $400^\circ$C for 3 min (red) and after 152 min (green). It is apparent that after annealing at $400^\circ$C the carbide peak disappears and graphene is slowly formed.

3.2. Growth and stability of Ni clusters on graphene/Ni(111)

To further investigate Ni–graphene interactions, we vapor-deposited Ni on top of a graphene sheet supported on a Ni(111) substrate. This resulted in Ni-cluster formation on top of the graphene and the formation of local Ni–graphene–Ni sandwich structures.

3.2.1. Ni growth on Ni(111)-supported graphene. Auger electron intensities for the Ni-LMM and C-KVV peaks as a function of Ni deposition are shown in figure 5(a). The carbon signal displays continuous attenuation with increasing Ni deposition. However, the attenuation is nonlinear, indicating that the deposited Ni does not grow in a layer-by-layer fashion, but instead forms clusters at the surface. The cluster growth can be directly observed in STM measurements shown in figure 5(b). Ni deposits form 3D clusters with well-defined (111) facets. Using an approach developed by Hansen et al [32], the work of adhesion of the clusters to graphene can be determined from the measurements of the width of the top facet and the height of the clusters via the following relationship:

$$W_{\text{adh}} = 2\gamma_{111} - \frac{H}{W} \left( -\frac{3}{\sqrt{2}} + \sqrt{3}\gamma_{110} + \sqrt{3}\gamma_{100} \right).$$  \hspace{1cm} (1)

Here $H$ and $W$ are the height and width of the clusters, and $\gamma_{111}$, $\gamma_{110}$ and $\gamma_{100}$ are the surface free energies of the (111), (110) and (100) facets of the nickel crystal. The values for the surface energies are taken from [33]. The height and width of the top facet are two quantities easily determined from the STM images. The work of adhesion is plotted as a function of cluster width in figure 5(c). It is apparent that small clusters exhibit a smaller work of adhesion as...
Figure 5. Ni deposition on Ni(111)-supported graphene. (a) Auger peak intensity of C-KVV and Ni-LMM as a function of deposition time. The slow gradual change in slope of the C-KVV intensity indicates cluster growth. (b) STM images of Ni deposits on graphene at room temperature. 3D Ni-clusters with well-defined (111) facets are formed. The height/width ratio of these clusters is plotted against the cluster width in (c). This ratio corresponds to the work of adhesion. An increase in the work of adhesion with cluster width is observed, and it seems to saturate at \( \sim 3.5 \text{ J m}^{-2} \). C-KVV Auger peaks are shown in (d). The pristine graphene peak is shown in red, but after deposition of Ni at room temperature the graphene peak is attenuated (blue). Annealing at 300 °C for 15 min results in a (partial) transformation of graphene into carbide (green). Prolonged annealing at 300 °C (30 min) re-forms the graphene peak (magenta).

compared to large clusters. Similar behavior has been reported for metal clusters supported on metal oxides [34, 35]. In the limit for large clusters, we find a significant work of adhesion of 3.5 J m\(^{-2}\), which is consistent with the DFT results presented below (see section 3.3).

3.2.2. Temperature stability of Ni clusters on Ni(111)-supported graphene. Annealing of the deposited Ni clusters causes the transformation of the surface structure. Figure 5(d) shows the change in the Auger signal for \( \sim 2 \text{ ML} \) Ni deposited on graphene/Ni(111) after annealing at different temperatures. An inspection of C-KVV peak shape indicates the formation of carbide upon annealing. The spectrum in figure 5(d) after the annealing of the sample at 300 °C for
The numbering scheme for multilayer interfaces used in interface calculations: the first interface is at the top, followed by the second, and so on.

Figure 6. The numbering scheme for multilayer interfaces used in interface calculations: the first interface is at the top, followed by the second, and so on.

15 min shows a composition of 55% carbide and 45% graphene, which clearly demonstrates the formation of carbide during annealing. After prolonged annealing, or annealing to higher temperatures, the carbide contribution to the carbon signal diminishes and a pure graphene signal is again observed.

3.3. Density functional theory calculations of Ni/graphene interfaces

A major goal of the DFT calculations was to quantify the strength of interaction between different components in systems consisting of Ni(111) substrate, graphene, carbide and Ni, Cu adlayers and graphite. This involved the calculation of the work of adhesion between parts A and B of the combined system AB, which is defined as the energy per unit area required to separate the system into parts A and B: 

\[ W_{AB} = E_A + E_B - E_{AB}, \]

where \( E_A \), \( E_B \) and \( E_{AB} \) are the total energies of parts A and B and the combined system AB. The work of adhesion \( W_{AB} \) can also be correlated with the distance \( d_{AB} \) between layers A and B. In general, the stronger the bonding between A and B, the higher the work of adhesion \( W_{AB} \) and the shorter the interface distance \( d_{AB} \). In this paper, various possible interface structures were compared. The system with the highest work of adhesion was chosen as the most stable structure. In the case of the multilayer interface, we calculated several works of adhesion, \( W_1, W_2, \ldots \) and distances \( d_1, d_2, \ldots \), corresponding to each subsequent interface 1, 2, \ldots, the ordering being chosen from the top to the bottom (see figure 6).

We investigated three possible Ni(111)/graphene interfaces, which are termed as ‘fcc’, ‘hcp’ and ‘hollow’ based on in-plane arrangement of the carbon atoms with respect to the underlying close-packed sequence of planes \( a, b, c, a, \ldots \) of the Ni substrate (see figure 7). The atomic structures of all three interfaces were relaxed under the constraint of two fixed bottom layers of the substrate. Then, the work of adhesion and the interplanar Ni–graphene distances were calculated; they are reported in table 1. We found that the ‘fcc’ interface is the most stable as it has the highest work of adhesion. However, the ‘hcp’ interface is higher in energy by only 0.042 J m\(^{-2}\); therefore such an interface geometry might also appear during growth, which indeed was observed in experiments [36]. The Ni–graphene distance 2.17 Å is close to the value reported in experiments [20]. The ‘fcc’ interface was used in all subsequent calculations of the composite interfaces that include adlayers of Ni and Cu.

Once the ‘fcc’ structure of Ni (substrate)/graphene interface was chosen as the lowest energy structure, single adlayers of Ni and Cu were added on top of graphene. Again, three
Table 1. Work of adhesion and interface distance between graphene and Ni substrate. The geometry of ‘fcc’, ‘hcp’ and ‘hollow’ interfaces is shown in figure 7.

| Interface | \( W \) (J m\(^{-2}\)) | \( d \) (Å) |
|-----------|-----------------|---------|
| fcc       | 0.81            | 2.16    |
| hcp       | 0.77            | 2.17    |
| Hollow    | 0.31            | 3.26    |

Figure 7. Atomic structure of (a) ‘fcc’, (b) ‘hcp’ and (c) ‘hollow’ Ni(s)/graphene interfaces. Gray-colored atoms belong to the Ni(111) substrate (only three layers are shown, with decreasing diameter from the surface), and the green atoms are carbon within the graphene sheet. The ‘fcc’ interface (a) was found to be the most stable interface structure.

Possible stacking geometries of the metal adlayer with respect to graphene were considered (see figure 8), and in both the cases of Ni and Cu, the preferred adsorption geometry was found to be ‘top’ (see figure 8(a)), which involves the adsorption of the metal adlayer atom on top of the carbon atom that is situated in the threefold fcc-hollow site of the Ni(111) substrate. Although there is a substantial energy difference between all three interface structures in the case of the Ni adlayer, the energy differences between ‘top’, ‘top-corner’ and ‘hollow’ structures are small for Cu, which is a consequence of a very weak interaction of Cu with the graphene. The latter conclusion is also quantified using the calculated work of adhesion and interface separation distances reported in table 2. There, the work of adhesion \( W_1 \) in the first two rows describes the strength of binding between the metal adlayer and graphene. It is clearly seen that the Cu–graphene work of adhesion, 0.51 J m\(^{-2}\), is almost seven times weaker than that between Ni adlayer and graphene, which we calculate as 3.47 J m\(^{-2}\). The interface distance \( d_1 \) between the Cu adlayer and graphene is also larger by 0.7 Å compared to that for Ni–graphene.

Surprisingly, the work of adhesion of graphene to the Ni substrate increased as a result of adsorption of the metal adlayer for both Ni and Cu. The effect is especially pronounced in the
Table 2. Work of adhesion and corresponding interface distances for Ni(s)/graphene/{Ni,Cu} multilayer systems (first two rows) and for {Ni,Cu} adlayers intercalated between the substrate and graphene (the third and fourth rows). Data are reported only for the most stable interfaces with ‘top’ arrangement of the Ni/Cu adlayer with respect to graphene (see figure 8). The interfaces are numbered according to the scheme shown in figure 6 (from the top to the bottom). In addition to work of separation and interface distances, the corrugation of graphene, $\Delta d_C$, defined as the height difference of graphene’s carbon atoms, is also shown. The interface graphene/metal distances are determined with respect to the averaged height of the C atoms to account for the case of observed graphene buckling.

| Interface                  | $W_1$ (J m$^{-2}$) | $d_1$ (Å) | $W_2$ (J m$^{-2}$) | $d_2$ (Å) | $\Delta d_C$ (Å) |
|----------------------------|--------------------|-----------|--------------------|-----------|------------------|
| Ni(s)/graphene/Ni          | 3.47               | 2.15      | 3.65               | 2.16      | 0.30             |
| Ni(s)/graphene/Cu          | 0.51               | 2.91      | 1.40               | 2.13      | 0.05             |
| Ni(s)/Ni/graphene          | 0.81               | 2.16      | 5.36               | 2.01      | 0.032            |
| Ni(s)/Cu/graphene          | 0.34               | 3.12      | 3.77               | 2.04      | 0.002            |

Figure 8. Interface geometries for Ni(s)/graphene/{Cu,Ni} adlayer interfaces: (a) ‘top corner’, (b) ‘hole’ and (c) ‘top’ interfaces. The coloring scheme is the same as in figure 7. The atoms in an additional top layer of either Ni or Cu are in colored magenta. The top interface structure possesses the highest work of adhesion; therefore, it is considered to be the most stable. All the results reported in table 2 are for the ‘top’ interface (b).

case of the Ni adlayer: the work of adhesion increased from 0.81 J m$^{-2}$ (single graphene sheet) to 3.65 J m$^{-2}$ (Ni on top of graphene, see the value of $W_2$ in table 2), but the interface distance between the Ni substrate and graphene did not change at all (compare $d$ in table 1 with $d_2$ in table 2). Such an increase of interfacial bonding between the substrate and graphene was also
observed in the case of Cu (from 0.81 J m\(^{-2}\) (single graphene sheet) to 1.40 J m\(^{-2}\) (Cu on top of graphene)), but the effect was smaller. The increase in the substrate–graphene work of adhesion might be due to an increase in the bonding strength between graphene and the Ni substrate caused by an additional increase of the electronic density in the interfacial region. This effect requires further investigation. Interestingly, the presence of the Ni adlayer caused a substantial corrugation of the graphene sheet. An example of such a corrugation \(\Delta d_c\) is reported in table 2 as the difference in height of two C atoms of graphene: \(\Delta d_c = 0.30\ \text{Å}\). In the case of the Cu adlayer, the corrugation is vanishingly small.

We also considered the intercalation of Ni and Cu adlayers between the Ni substrate and graphene. The work of adhesion and interfacial distances between the adlayer on top of the Ni substrate and graphene are reported as values \(W_1\) and \(d_1\) in the third (Ni) and fourth (Cu) rows of table 2. For the Ni adlayer, it is not surprising that the work of adhesion is identical to the values obtained in the case of the Ni/graphene interface (see table 1). We have not considered the interactions between the Cu substrate and graphene in this paper, but we expect that they will be close to the values \(W_1 = 0.34\ \text{J m}^{-2}\) and \(d_1 = 3.12\ \text{Å}\) obtained for a Cu adlayer on top of the Ni substrate (see the fourth row in table 2). It is clearly seen that the strength of Cu–graphene bonding is weakly affected if the Cu adlayer is on top of graphene, or underneath: \(W_1 = 0.51\ \text{J m}^{-2}\) as compared to \(W_1 = 0.34\ \text{J m}^{-2}\), which is another manifestation of the weak graphene–Cu bonding. As we have already discussed above, this is not the case for the Ni adlayer: the strength of Ni–graphene bonding in the case of the Ni adlayer on top of graphene is several times higher than that for Ni-supported graphene without the adlayer.

In the experiments, Ni clusters formed on top of graphene are several layers thick. Therefore, in order to compare the DFT and experimental work of adhesion, we also calculated the work of adhesion as a function of the thickness of the top Ni layer on top of Ni-supported graphene. The work of adhesion decreases slightly as the thickness changes from monolayer to three-layer Ni, from 3.5 to 3.0 J m\(^{-2}\). Despite this decrease, the DFT work of adhesion is in good agreement with the experimental value of \(\sim 3.5\ \text{J m}^{-2}\). Based on experimental observation, it has been suggested that there is a large barrier for carbon attachment to the edge of a graphene island. In order to investigate further the atomic scale mechanism of the appearance of such a barrier, we performed DFT calculations of a graphene island on Ni(111). It was found that the edge carbon atoms that have unsaturated dangling bonds form strong bonds with the Ni atoms in the first surface layer of the substrate (see figure 9). Therefore, the attachment of a single carbon atom to the graphene edge requires the breaking of these bonds, which is expected to produce a large activation barrier for such
Figure 10. (a) Top view and (b) side view of Ni(s)/carbide interface. (c) Top view and (d) side view of the Ni(s)/carbide/Cu interface. In addition to carbide atoms, orange atoms represent the Cu adlayer. A change in the symmetry of the Ni surface sublattice of carbide from rectangular in (a, b) to hexagonal in (c, d) is clearly seen. Also an increase in interaction strength of carbide’s carbon atoms with the Ni substrate can be discerned by comparing side views (b) and (d).

A chemical reaction. The effect of a strong interaction between edge carbon atoms and the Ni substrate on the growth kinetics will be quantitatively investigated in future work.

Finally, we performed a DFT investigation of bonding within Ni/Ni$_2$C interfaces, and looked specifically into the destabilizing effect of Cu. As it was mentioned above, the surface Ni$_2$C carbide phase on the Ni(111) substrate is subjected to a complex $\sqrt{39}$ $R$ 16.1° × $\sqrt{39}$ $R$ 16.1° reconstruction. Its crystal structure consists of 45 elementary surface unit cells of Ni(111) and 20 elementary unit cells of Ni$_2$C. In order to make the problem tractable, we built a model of the Ni/carbide interface by slightly modifying the angle between surface cell vectors of carbide, from 92.2° to 90°, which allowed us to build the model of the interface with smaller dimensions of the surface carbide unit cell, 4.96 Å × 4.32 Å, containing only two Ni$_2$C structural units (see figures 10(a) and (b)). This simplification slightly distorts the bond angles within Ni$_2$C with minimal changes in the Ni–C bond lengths. The relaxed structure of the Ni/carbide interface is shown in figures 10(a) and (b). The prominent feature of interfacial bonding is the formation of strong Ni–C bonds with the Ni substrate, which results in the carbide surface structure such that the carbon atoms are slightly below (by 0.3 Å) the Ni atoms. This is consistent with STM imaging of the surface carbide where the carbon atoms are invisible and represented by dark spots on the STM images [13]. When a monolayer of Cu is added on top of the surface carbide, drastic changes in the atomic structure of the interface are observed (see figures 10(c) and (d)). Firstly, the almost square symmetry of the carbide surface structure is transformed into a hexagonal symmetry (see figures 10(a) and (c)). Secondly, the carbon atoms
move further down towards interstitial sites of the Ni(111) substrate (see figure 10(d)). At the same time the formation of strong Cu–Ni bonds reduces the strength of C–Ni interactions within the carbide layer. These observations clearly indicate the destabilization of surface carbide upon adsorption of the Cu adlayer, which is consistent with experimental observations.

4. Discussion

The existence of two carbon-containing thermodynamic equilibrium phases on Ni, carbide and graphene makes Ni unique compared to other transition metals. These two phases differ in their carbon content and phase stability temperature. The surface Ni$_2$C phase has a carbon concentration of 0.5 ML compared to 2 ML for graphene. Furthermore, the surface carbide has a lower phase stability temperature and dissolves into the bulk at $\sim 460$ °C, whereas monolayer graphene is stable up to $\sim 650$ °C on Ni(111) before carbon dissolves into the bulk. The higher thermal stability of graphene suggests that it has a lower formation energy compared to the carbide surface phase. Also, once graphene is formed, it is stable and never converts into a carbide below 650 °C.

If graphene is favored, why does the surface carbide form at all? For a low carbon concentration, the surface carbide is the thermodynamic equilibrium phase. To form the lower-energy graphene phase, more carbon needs to be added to the surface layer. Furthermore, it appears that the carbide forms very rapidly while the graphene growth is rather slow, indicating a large kinetic barrier for graphene growth. Therefore, exposing the surface to carbon at the temperature at which the carbide is stable results in the carbide phase forming first. This carbide phase is a line phase, i.e. it has a fixed carbon concentration within the carbon–Ni surface phase diagram. As a consequence, it is difficult to add carbon to this phase because for an ordered line phase, small changes from its ideal composition increase its free energy, which makes any compositional variations highly unfavorable. For the atomic-thick carbide phase, avoiding a change in composition is easy because the Ni bulk can ‘soak up’ any excess carbon. Consequently, since an increased carbon density is a prerequisite for nucleating the carbon-denser graphene, the presence of the carbide phase at the surface suppresses graphene formation. Evidence for the suppression of graphene nucleation in the presence of a surface carbide comes from several experimental observations: (i) graphene is not formed if the sample is exposed to ethylene at 400 °C and only a surface carbide is formed; (ii) some of the surface carbides once formed are stable in vacuum at 400 °C for hours; and (iii) if the surface carbide is destabilized by sub-monolayer copper deposition, graphene can nucleate and grow, indicating that there has been enough carbon in the sample to form graphene, but the carbide had prevented its formation.

The fact that we sometimes observe the conversion of a carbide into graphene at 400 °C is not inconsistent with the scenario of carbide suppressing graphene nucleation. This is because local inhomogeneities exist within a macroscopic sample, which may act as nucleation sites for graphene. Therefore, it appears that the carbide only suppresses nucleation of graphene but does not prevent its growth once nucleated. The growth of nucleated graphene in the presence of a carbide is supported by the observation of carbide conversion into graphene as shown, for example, in figure 3.

At above 460 °C, i.e. at a temperature where the carbide is dissolved, graphene can nucleate on the bare Ni surface, similar to graphene growth on many of the other transition metal surfaces. If the carbide is destabilized, either by heating the sample above the carbide phase stability temperature or chemically by copper addition, the carbon atoms from the carbide phase first
dissolve into the bulk and then later reappear to form graphene. The fast disappearance of carbide carbon and the slow graphene growth indicates that carbon diffusion is much faster than the graphene growth process. Information about the graphene growth rate can also be obtained from the AES peak intensity, which is a direct measure of the portion of the surface covered with graphene. The variation of the peak intensity as a function of time, shown in figure 2, indicates that the growth rate is strongly nonlinear. This is in agreement with the assertion that the graphene growth rate is not limited by carbon diffusion to the surface because for a diffusion-limited growth, one would expect the growth rate to be linear with time. Instead, the carbon attachment to the growing graphene appears to be the rate-limiting process. Large barriers for carbon attachment have also been reported for graphene growing on other transition metal surfaces [37, 38]. In these reports, the attachment barrier for carbon atoms to the edges of the graphene sheet was associated with the strong bonding of carbon adatoms to the transition metal substrate, compared to the relatively weak interaction of the graphene sheet with the substrate. This may also contribute to the growth barrier for graphene on Ni(111). In addition, our DFT calculations indicate that the edge carbon atoms of the graphene form strong bonds with the Ni substrate. Therefore, in order to add the carbon atoms to the edge, the strong carbon–nickel bonds have to be broken, which also contributes to the kinetic growth barrier. Such a barrier for carbon attachment suggests that the growth rate increases as the total number of edge atoms in the graphene island increases. This means that as the graphene islands grow and their circumference increases, the carbon attachment rate increases resulting in an accelerated growth. This is observed in the AES peak intensity plots shown in figure 2(b) for less than 150 min, i.e. during the initial growth stages. For longer growth times, i.e. at higher graphene coverage, when the graphene grains coalesce, the growth rate decreases again, and eventually growth stops as the monolayer is completed. It appears that the growth rate for graphene as measured in AES differs for different sample preparation conditions. Therefore, it is tempting to use these data to extract information on growth barriers. Unfortunately, this is not possible because key information on the nucleation density is not available in these AES data.

In order to quantify the interaction between graphene and Ni, we deposited Ni on top of graphene and analyzed the shape of the Ni clusters. These measurements allowed us to extract information on the bonding strength between Ni and graphene quantified as the work of adhesion. The experimental value of $\sim 3.5 \text{ J m}^{-2}$ was well reproduced by DFT calculations for a graphene layer sandwiched between two Ni layers. However, the calculations also revealed that the interaction between graphene and the Ni substrate is much stronger if Ni is present on either side of the graphene, compared to the case when graphene interacts with the Ni substrate only. The increased Ni–C interaction for the Ni–graphene–Ni sandwich resulted in a weakening of in-plane C–C bonds, which is reflected in the substantial buckling of graphene observed in the DFT calculations. This strengthening of the Ni–C interaction is an indication of the increased reactivity of Ni deposited on graphene/Ni(111), as compared to the fairly unreactive state of the weakly interacting graphene/Ni(111) system. This conclusion is substantiated by our experimental observation that the graphene is destroyed, and that constituting carbon atoms form a carbide layer if the system with Ni deposit is annealed above 200 °C.

Experimentally, we observed that annealing the Ni deposits to temperatures above 200 °C resulted in partial conversion of the graphene into carbide, followed by re-formation of graphene after annealing either at higher temperatures or at the same temperature but over long annealing periods. From a thermodynamics standpoint, Ni clusters on top of graphene are not energetically favorable, because the pure Ni surface has a high surface energy compared to Ni covered
by graphene. Therefore, the lowering of the free energy of the system by the transfer of Ni atoms from the clusters on top of graphene to the Ni substrate provides a driving force for this process. Similar thermodynamic arguments hold for other metals deposited on Ni-supported graphene, and the intercalation of different elements, such as Cu, Au and Ag deposited on Ni-supported graphene has been observed in several experiments [19], [22, 23]. Our measurements show carbide formation as an intermediate state for the Ni-intercalation process. This implies that Ni deposits can merge with the substrate via diffusion through a carbide layer. For Ni deposits, our DFT calculations support the destabilization of graphene. For other elements, namely Cu, the DFT results do not indicate the same destabilization of graphene and therefore the intercalation process for Cu may be different from that of Ni. Consequently, there may not exist a universal mechanism of metal intercalation on Ni-supported graphene. Therefore, the intercalation of metals other than Ni might proceed through a different mechanism that requires further experimental and theoretical investigations.

5. Summary and conclusions

This paper presents the results of a comprehensive investigation of graphene growth on Ni(111) substrates and the stability of Ni/graphene interfaces. We showed that a single graphene layer is the thermodynamically preferred carbon-containing surface phase on Ni(111). However, at low carbon concentration, a monolayer-thick surface carbide phase may also form on Ni(111). This carbide phase forms rapidly upon hydrocarbon decomposition on the Ni(111) surface and covers the entire surface before the nucleation of slowly growing graphene. Once the carbide has formed, it suppresses graphene nucleation. We demonstrated that the carbide surface phase can be chemically destabilized by alloying the surface with a non-carbide-forming metal such as Cu. This carbide destabilization results in the nucleation of graphene and its growth at the surface by carbon segregation from the bulk. Alternatively, the carbide phase can be thermally destabilized by annealing the Ni sample above 460°C, which also causes the unhindered nucleation of graphene. These studies of the nucleation and growth of graphene on transition metal surfaces contribute towards an understanding of the growth process, which is urgently sought for the development of effective approaches to growth of large-area, high-quality graphene samples [39] and for tuning its properties by controlled defect formation [36].

In addition to the growth studies, we also investigated the nickel/graphene interfaces. Surprisingly, the interaction between graphene and nickel was found to be strongly amplified when additional Ni is deposited on top of Ni-supported graphene: DFT calculations showed that for graphene sandwiched between two Ni layers, the work of graphene–substrate adhesion is more than 4 times as large as that for graphene on a Ni substrate. Such an increase in Ni–graphene interaction may be responsible for the experimentally observed destruction of graphene upon deposition of Ni clusters followed by annealing at 200°C. The increased reactivity between Ni and graphene by the formation of sandwich structures may be constructively utilized for patterning graphene sheets by the controlled deposition of Ni [40]. DFT calculations of Cu on top of graphene show a substantially weaker graphene–metal interaction, which is why Cu deposits on Ni-supported graphene are expected to be less reactive than Ni.
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