Deposition of metal clusters on single-layer graphene/Ru(0001): Factors that govern cluster growth

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1. Introduction

Graphene, also known as one layer graphite, has attracted extensive attention of scientists since its free-standing version was obtained in 2004 [1–3]. Graphene is a fascinating material with a two-dimensional (2D) structure, which has extremely high hardness, high crystallographic quality, high thermal and chemical stability, and special electronic properties. These properties will undoubtedly lead to its wide applications as new materials and electronic devices in the near future [2,3]. The crystallographic quality as well as thermal and chemical stability make graphene an attractive supporting material for metal clusters in model catalyst and catalytic reaction studies, where in principle effects caused by the supporting material can be largely eliminated.

Several studies have been reported regarding the growth of metal clusters on graphene supported on transition metals [4–6]. N'Diaye et al. have focused on studying metals on a moiré-patterned graphene/Ir (111) surface and have found that at the lowest coverages, Ir forms uniformly monodispersed clusters when deposited on graphene. The metal clusters so formed grow exclusively in hcp hollow regions and maintain the 2D structure [4]. At higher coverages these clusters transform to 3D structures yet remain largely monodispersed. Feibelman performed density functional theory (DFT) calculations to elucidate the patterning and growth of these clusters [7,8] and showed there to be sp² → sp³ rehybridization of C beneath clusters comprised of more than two Ir atoms. This rehybridization contributes to Ir–C bond formation as well as graphene layer chemisorption onto the Ir(111) substrate. Furthermore, other metals, namely Pt, W, Re, Fe and Au on graphene/Ir(111) have been studied by N'Diaye et al. who reported that Pt, W, and Re form epitaxial cluster superlattices while Fe and Au do not. Based on these results, they concluded that the metals which grow epitaxial cluster superlattices have three characteristics: (i) a large cohesive strength to form strong bonds; (ii) a large extension of a localized valence orbital to efficiently interact with graphene and thus to initiate rehybridization of carbon atoms; and (iii) a certain match with the graphene unit cell [9].

In more recent investigations, Pt cluster deposition was studied on graphene/Ru(0001) surfaces [5,6]. Although some similar properties are observed, such as high dispersion of metal clusters and no preferential step edge decoration, there are mainly three differences between graphene/Ru(0001) and graphene/Ir(111). For Pt clusters grown on graphene/Ru(0001), (i) the smallest 2D clusters prefer fcc hollow regions instead of hcp sites; (ii) clusters are less uniform and epitaxial cluster superlattices cannot be fabricated at room temperature; and (iii) conversion from 2D to 3D of clusters occurs at much lower coverages. Owing to these differences, it is instructive to carry out studies of other metals deposited on graphene/Ru(0001). Here we present results of Pd, Pt, Rh, Co and Au deposition on graphene/Ru (0001) obtained with STM, aiming to elucidate the key factors that govern metal growth on graphene/Ru(0001).
2. Experimental

Experiments were carried out in a UHV analysis chamber (base pressure $\sim 1 \times 10^{-10}$ Torr) equipped with a double-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), low energy electron diffraction (LEED) optics, and STM (Omicron). The Ru(0001) substrate was cleaned using a standard approach that includes cycles of Ar ion sputtering, annealing in $4.0 \times 10^{-8}$ Torr of O$_2$ at $\sim 1100$ K, and flashing in vacuum to $\sim 2000$ K. Sample cleanliness was confirmed with AES, LEED, and STM. Single-layer graphene was formed by first dissociating methane (at 700 K) or ethylene (at 300 K) on the clean Ru(0001) and then annealing to $\sim 1400$ K. This process can be repeated several times to generate graphene that fully covers the Ru substrate. Metal deposition was achieved by evaporating the target metal from a heated source. Deposition (in monolayers, ML) was quantified using Auger break points of the ratios of the most intensive Auger transitions of the target metals and single crystal metal Mo (112). Deposition, unless otherwise specified, was performed at a substrate temperature of room temperature. All images were scanned in constant–current mode with an electrochemically etched tungsten tip. The bias voltages are reported with reference to the sample.

3. Results

3.1. Graphene preparation

A graphene layer was prepared by first dissociating CH$_4$ or C$_2$H$_4$ on clean Ru(0001) followed by annealing the sample in vacuo to $\sim 1400$ K. Due to the chemical inertness of CH$_4$, a higher dissociation temperature (700 K) and relatively large exposures are generally required compared with C$_2$H$_4$ [10]. Graphene formation is generally easy to control due to the self-limitation of the process, however, occasionally large carbon particles form due to the defects of the substrate.

Fig. 1(a) and (b) displays typical STM topographic images of the graphene moiré template. As indicated by the marked moiré unit cell, three different sites, i.e., bright, medium dark and dark sites, are observed. A typical LEED pattern is shown as an inset where the satellite points surrounding the (1×1) spots of the Ru(0001) substrate demonstrates the formation of a graphene overlayer [10,11]. An atomic model of the surface structure is displayed in Fig. 1(c) using one graphene layer of (12×12) unit cells over two Ru layers of (11×11) unit cells. Three different sites, i.e. atop, fcc and hcp sites are found within such a unit cell. The bright, medium dark and dark regions displayed in Fig. 1(b) are assigned to

![Fig. 1.](image-url)
3.2. Metal growth at room temperature

Five catalytically important metals, namely Rh, Pt, Pd, Co and Au were used in this study. As shown in Fig. 2, templated growth of Rh clusters is observed at a coverage of 0.05 ML where the majority of the clusters are found to occupy the fcc sites of the moiré structure. A closer examination of the image reveals that even at such a low coverage, the cluster growth has deviated substantially from monodispersity. The dashed circles mark the selected clusters and the numbers indicate the approximate layers of the clusters. This is verified by the height profiles of each cluster, in which clusters 1, 2, 3, 4 are shown to be of heights 0.3, 0.6, 0.9 and 1.2 nm, respectively. Clearly clusters from one to four layers coexist and most of the clusters grow in the 3D mode. Fig. 3 depicts STM images acquired at various Rh coverages from 0.05 to 0.8 ML, and the size histograms are shown in Fig. 4 based on randomly chosen 100 nm × 100 nm STM images at every coverage, indicating that Rh on graphene/Ru(0001) grows with a narrow size distribution in a self-limiting manner. Fig. 5 is a plot of the density (upper panel) and average dimension (middle and bottom panels) of the Rh clusters as a function of coverage. It is obvious that at later stages of cluster growth, cluster size and height increase steadily whereas cluster density only increases slightly. Identical experiments were also conducted with Pt. The behavior of Pt is very similar to Rh where highly dispersed Pt clusters with a diameter of ~2 nm prefer fcc sites at low coverages (~0.1 ML) and clusters (diameter ~5 nm) with rather narrow size distribution are observed at coverages less than ~1 ML (data not shown). Note that this is fully consistent with recent studies by other groups on this system [5,6].

Fig. 6(a) and (b) are STM images of 0.1 and 0.4 ML Pd deposited on graphene/Ru(0001), respectively. Although Pd also prefers fcc sites at extremely low coverages (data not shown), large clusters develop at the very early stages of growth. For example, average cluster diameters of ~8 and ~14 nm are found at Pd coverages of 0.1 and 0.4 ML, respectively. Compared with Rh or Pt clusters at the same coverages, Pd clusters are substantially larger in size with a much lower number density. Fig. 6(c) and (d) displays images of 0.2 and 0.4 ML of Co on graphene/Ru(0001). Clearly Co also forms 3D clusters at the very early stages of growth; however, average cluster sizes of ~10 and ~12 nm are observed at coverages of 0.2 and 0.4 ML, respectively.

Fig. 6(e) and (f) are STM images of 0.2 and 0.6 ML Au on graphene/Ru(0001). At the onset of deposition, similar to the metals studied above, small 2D Au cluster seeds are observed to reside at fcc sites (data not shown); however, with an increase in coverage, Au forms a monolayer film following the graphene moiré pattern. This is confirmed by height profiles of these 2D islands, in which the islands are shown to be of height approximately 0.4 nm and the distance between the neighboring bright spots are exactly the same as the graphene moiré pattern.

3.3. Thermal stability

Unlike Pd, Co or Au, the metals Ir, Rh, and Pt can be nucleated at certain sites on graphene yielding clusters that are highly dispersed and with a narrow size distribution, thus allowing them to be potential candidates for nanocatalysts. In our studies, the thermal stability of Rh was carefully examined by STM. The thermal evolution of the 0.8 ML Rh clusters deposited on graphene is shown in Fig. 7. Prior to imaging, the sample was first annealed to the target temperature and maintained for 10 min before cooling to room temperature. No detectable change is obvious at an annealing temperature of 900 K or lower. Sintering initiates at ~900 K as indicated by the decreased cluster density and larger dimensions, and becomes more pronounced at 1100 K. It should be noted that these annealing temperatures are not high enough for Rh to desorb from the surface. To further test the stability of Rh under reaction conditions, the effect of cluster annealing in an atmosphere of CO was also studied. STM results (data not shown) indicate those Rh clusters maintain their original morphology even after annealing to 700 K in 1 Torr CO for 10 min.

4. Discussion

4.1. Growth mechanism of metal clusters (Pt, Rh, Pd and Co)

The surface free energy of graphene is reported to be 46.7 mJ/m² [14], which is substantially smaller than those of the deposited metal particles, e.g. 2.05 J/m² for Pd [15]. This suggests that all deposited metals should form 3D clusters at temperatures where metal atoms have sufficient mobility (for example at room temperature), were there not strong interaction between the metal atoms and the graphene substrate. Indeed N’Diaye et al. have observed significant 3D clustering of Ir graphene/Ir(111) at relatively high metal coverage; however, up to an Ir coverage of ~0.2 ML, monodispersed 2D clusters are stable at room temperature with the clusters located at hollow sites of the moiré unit cell [5]. This extra stabilization has been suggested to be due to sp² → sp³ rehybridization of C in the graphene layer beneath the overlayer metal and metal–carbon (M–C) bond formation [8,9]. Following this mechanism, we can attribute the difference among the metals on graphene/Ru(0001) to the different strengths of the M–C bond, which, in turn, determine the diffusion coefficients. The stronger the M–C bond, the smaller the diffusion coefficient for the metal on graphene at a given flux. In other words, a smaller coefficient means a larger nucleation rate, thus facilitating better dispersion of the 2D clusters (seeds) at the initial growth stage.

Table 1 displays metal–carbon (M–C) bond dissociation energies that are relevant to the current study. As expected, the metals with higher M–C bond dissociation energies, i.e. Ir, Pt, and Rh, form highly dispersed clusters while Pd and Co, with weaker M–C bonds form...
large 3D clusters with low number densities. Note the degree of dispersion also follows the order of M–C bond strength.

With increasing coverage, the cluster growth becomes a competitive process between adsorption on graphene and nucleation on the initial 2D cluster seeds. The cohesive energy is the key parameter in estimating the strength of the metallic bonds. It is expected that metals with higher cohesive energies will favor nucleation on the 2D seeds to form 3D clusters. However, the cohesive energy is difficult to

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**Fig. 3.** STM images (50 nm × 50 nm, Vb = 1.0 V, It = 0.1 nA) of (a) 0.05 ML, (b) 0.1 ML, (c) 0.2 ML, (d) 0.4 ML, (e) 0.6 ML and (f) 0.8 ML Rh deposited on graphene/Ru(0001) at room temperature.

**Fig. 4.** Histograms of the number of particles as a function of their diameter based on randomly chosen 100 × 100 nm STM images at each coverage: (a) 0.05 ML, (b) 0.1 ML, (c) 0.2 ML, (d) 0.4 ML, (e) 0.6 ML and (f) 0.8 ML Rh.
determine since it depends on the size, shape, and structure of the nanoclusters. For nanoclusters that are not embedded in the substrate, the cohesive energy decreases with decreasing cluster size if the nanoclusters maintain a specific shape and structure, as has been shown experimentally [18] and interpreted by various models [19,20]. Therefore one cannot simply compare the cohesive energies of bulk crystals with the M–C bond strength in predicting the growth mode at high metal coverages.

Nevertheless, the STM images observed in our study can be explained by the competitive process mentioned above. In the case of Rh, for example, at the onset of deposition, the strong interaction between Rh and rehybridized carbon leads to a small diffusion coefficient of Rh in the fcc areas, thus allowing for the high dispersion of 2D Rh seeds located at fcc sites. At an Rh coverage of 0.05 ML, the coexistence of both 2D and 3D clusters indicates that the Rh–C bond strength and cohesive energy are essentially equal. As the coverage increases, the increasing cohesive energy (absolute value) surpasses the Rh–C dissociation energy, resulting in the conversion of most of the Rh clusters to 3D and some unoccupied fcc sites. This also accounts for the fact that the cluster density essentially saturates whereas the cluster size and height increase steadily with deposition at high coverages (See Fig. 5). This explanation is further supported by the fact that the cohesive energy of Rh in a bulk crystal has been estimated to be $-742$ kJ/mol [21]. Fig. 8(a) shows the cohesive energy of Rh nanocrystal as a function of nanocrystal size under ideal conditions based on the surface–area-difference (SAD) model [20], where the cohesive energy is computed using

\[ E_{\text{coh}} = E_b \left(1 - \frac{3\alpha d_{\text{bulk}}}{D}\right) \]

where $E_b$ is the cohesive energy (absolute value) of the bulk crystal; $p$ is the parameter used in determining the coherence between the nanocrystals and the matrix; $\alpha$ is related to the shape of nanocrystals; $d_{\text{bulk}}$ is the interplanar distance of (hkl); and $D$ is the size of the nanocrystal. From STM images, most Rh nanoclusters are found to be spherical. As such, a shape factor of $\alpha = 1$ for spherical nanoparticles has been chosen in our calculation. It is also well known that nanoparticles tend to adopt low index surface planes to lower the total surface energy. Therefore, we assume Rh nanoparticles are surrounded by (100) crystal planes. The results of Fig. 8(a) were obtained assuming that spherical Rh nanoparticles ($\alpha = 1$) with (100) crystal planes on the surface grow on graphene with a non-coherent interface ($p = 1$). From Fig. 8(a), the SAD model predicts that the conversion from 2D to 3D should occur at a cluster size of 3.6 nm, where the cohesive energy of the Rh nanocrystal is equal to the Rh–C dissociation energy of 580 kJ/mol. In fact, even if a shape factor of $\alpha = 1.245$ (the mean value for regular polyhedral nanoparticles) is chosen [20], the plot deviates only slightly from the original line and identical trend could be obtained. In this case, crossover point will be 4.5 nm. If we consider some level of coherence interaction between Rh clusters and graphene, $p$ will be slightly lower than 1, and the crossover point will get closer to our experimental observations (2.5 nm). The same analysis also applies to Pt as shown in Fig. 8(b), which predicts that the conversion of Pt should occur at 3.5 nm. This result also agrees well with our experimental findings. The trend in Fig. 8 indicates that, for Rh and Pt, a critical point exists where the cohesive energy (absolute value) of the clusters with a certain size and shape is equal to the dissociation energy of the M–C bond. 2D seeds form before the critical point and conversion to 3D occurs after this critical point. To sum up, for Ir, Pt and Rh, the strong interaction between metals and rehybridized carbon plays a more important role at the initial growth stage, thus allowing for the formation of more finely dispersed small clusters. On the other hand, the Pd–C and Co–C bonds are too weak to compete with the cohesive energies, resulting in the formation of large 3D clusters at a very early growth stage.

4.2. Effect of substrate metals

Based on our experimental findings and recent studies by N’Diaye et al, we note that the behavior of the same metal, such as Pt, is not exactly the same on different substrates, i.e. graphene/Ru(0001) and graphene/Ir(111), as pointed out in the Introduction. We attribute this difference to the different interactions between graphene and the substrate metals. Based on DFT calculations, the distance between graphene and the Ir(111) surface has been predicted to be 0.34 nm [7], which is close to the distance between graphene planes in graphite (0.334 nm), indicative of the weak electronic interaction between graphene and the Ir substrate. Whereas the distance between the graphene and the Ru(0001) surface has been estimated to be 0.145 nm, a result of the strong electronic interaction [22]. It is expected that graphene with a strong electronic interaction with the substrate should have less interaction with a deposited metal, which explains the facts that metal clusters on graphene/Ru(0001) are less ordered and that the conversion from 2D to 3D of clusters on graphene/Ru(0001) occurs at much lower coverages. The above explanation still cannot answer the question as to why the deposited metal clusters prefer different locations, i.e. hcp sites on graphene/Ir (111) and fcc sites on graphene/Ru(0001). The difference between fcc...
Fig. 6. STM images (50 nm × 50 nm, V_b = 1.0 V, I_t = 0.1 nA) of (a) 0.1 ML Pd, (b) 0.4 ML Pd, (c) 0.2 ML Co, (d) 0.4 ML Co, (e) 0.2 ML Au and (f) 0.6 ML Au deposited on graphene/Ru (0001) at room temperature.

Fig. 7. STM images (200 nm × 200 nm, V_b = 1.0 V, I_t = 0.1 nA) of 0.8 ML Rh on graphene/Ru(0001) annealed to (a) 600 K, (b) 700 K, (c) 800 K, (d) 900 K, (e) 1000 K and (f) 1100 K. All images are acquired after the sample has been cooled to room temperature after a 10 min anneal.
sites and hcp sites only lies in the fact that either a threefold coordinated fcc hollow site or a threefold coordinated hcp hollow site is centered in the carbon ring (See Fig. 1(c)). Owing to this slight difference, DFT calculation should be very informative in addressing this question.

### 4.3. Growth mechanism of an Au film

Following the growth mechanism mentioned above, Au clusters should also form large 3D clusters on graphene due to the weak interaction between Au and carbon. As expected, the formation of Au 3D large clusters was observed by N’Diaye et al. on graphene/Ir(111) surface [9]. However, this is not the case for Au grown on graphene/Ru(0001), where formation of a single-layer gold film has been observed by STM (see Fig. 6(e), (f)). The formation of a Au film can be attributed to three factors: (i) the effect of the Ru substrate on Au cannot be neglected due to the fact that the distance between graphene and Ru (0001) is small, only 0.145 nm, as discussed above; (ii) metals with low cohesive energy, such as Au tend to wet a metal surface with a larger cohesive energy; (iii) the size of Au is too large to match the graphene lattice. N’Diaye et al estimated that metal with a nearest-neighbor distance of 0.27 nm can perfectly fit the graphene lattice (0.245 nm) based on their experimental results and the assumption that small clusters have a smaller lattice parameter compared with bulk metals at the onset of cluster growth [9]. The nearest-neighbor distance for Au is 0.288 nm, making it difficult to fit the graphene lattice. Considering the fact that lattice parameter of Ru(0001) is 0.265 nm as well as the strong effect of the Ru substrate, it is entirely possible for Au atoms on the layer graphene to fit the underlying Ru support. This explains why the exact moiré pattern is still observed on the film. Also the height of the 2D islands, shown to be ~0.4 nm, can be interpreted as due to the higher electron density caused by the compact arrangement of Au atoms.

### 4.4. Thermal stability of metal clusters

The high thermal stability of Rh clusters can also be rationalized in terms of strong Rh–C bond formation due to sp$^2$ → sp$^3$ rehybridization of carbon atoms beneath the metal atoms. It is proposed that the sintering mode for Rh on graphene is Ostwald ripening instead of migration of the whole particle for two reasons: (i) Rh clusters are fixed at fcc sites due to the formation of strong Rh–C bonds, making it difficult for a cluster to move; and (ii) from the STM images (see Fig. 7), some smaller clusters appear at 900 K, which are not observed at lower temperatures, indicating some Rh atoms dissociate from small particles, diffuse to, and then coalesce with larger particles. For more conclusive evidence, in situ STM studies are required and are underway. Also, it is expected that Ir and Rh should have similar thermal stabilities due to their strong M–C bonds.

### 5. Conclusions

Our experimental findings show that Pt and Rh form finely dispersed small clusters on graphene/Ru(0001) whereas Pd and Co form large clusters at similar coverages. These results, coupled with previous finding that Ir forms the best finely dispersed clusters [5], suggest that both M–C bond strength and metal cohesive energies play significant roles. The final structures of various clusters then are a competitive effect between these two factors. At coverages lower than the critical point, where the M–C bond dissociation energy is higher than the cohesive energy, 2D cluster seeds form. At coverages higher than the critical point, the effect of cohesive energy exceeds the interaction between metals and graphene, leading to the formation of 3D clusters. With this understanding of cluster growth of these metals on graphene, it is possible to predict the morphology of other transition metals that have not been explored. The M–C bond dissociation energy is the most important factor that affects the morphology of clusters at the initial stages of growth. This suggests that higher M–C dissociation energies should lead to more finely dispersed clusters. On the other hand, the fact that Au forms a single-layer film on graphene indicates that other factors such as the effect of the substrate metal and the lattice match should also be considered. Finally, the thermal stability of metal clusters supported on graphene is quite impressive. This is very important for studies in heterogeneous catalysis since many metal catalyzed reactions require high reaction temperatures. Our results show that metals with strong M–C interaction tend to have high thermal stabilities and are resistant to sintering even under harsh reaction conditions, which makes them potential candidates as realistic heterogeneous catalysts.

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**Table 1**

Metal–carbon bond dissociation energies [16,17].

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<tr>
<th>Metal</th>
<th>D(M–C), kJ/mol</th>
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<tr>
<td>Ir</td>
<td>631</td>
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<tr>
<td>Pt</td>
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<td>Rh</td>
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<td>Pd</td>
<td>436</td>
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<td>Co</td>
<td>347</td>
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Acknowledgments

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References