Atomistic modeling of the directed-assembly of bimetallic Pt-Ru nanoclusters on Ru(0001)-supported monolayer graphene

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Abstract
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Disciplines
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Atomistic modeling of the directed-assembly of bimetallic Pt-Ru nanoclusters on Ru(0001)-supported monolayer graphene

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The formation of Pt-Ru nanoclusters (NCs) by sequential deposition of Pt and Ru on a periodically rumpled graphene sheet supported on Ru(0001) is analyzed by atomistic-level modeling and kinetic Monte Carlo simulations. The “coarse-scale” periodic variation of the adsorption energy of metal adatoms across the graphene sheet directs the assembly of NCs to a periodic array of thermodynamically preferred locations. The modeling describes not only just the NC densities and size distributions, but also the composition distribution for mixed NCs. A strong dependence of these quantities on the deposition order is primarily related to different effective mobilities of Pt and Ru on the supported graphene. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4798348]

I. INTRODUCTION

Bimetallic nanoclusters (NCs) can exhibit enhanced functionality compared to single-component NCs for applications such as catalysis.1–3 Specifically, bimetallic Pt-Ru nanoclusters and nanoparticles are of interest due to their high activity for the oxidation of methanol and other small organic molecules, e.g., in polymer electrolyte fuel cells.4,5 However, in these real catalysts, it is hard to assess the origin of the catalytic activity, thus prompting analysis of model catalyst systems of the type considered here. Our focus is on the formation of bimetallic NCs by deposition on well-characterized surfaces at lower temperatures (T). This choice of formation pathway has the appealing feature that one can access a large phase space of far-from-equilibrium structures6–8 potentially allowing greater tuning of properties. In part motivated by these possibilities, a few studies have explored core-ring structures of two-dimensional (2D) epitaxial bimetallic NCs,9–11 systems for which predictive atomistic-level modeling of NC structure formation is becoming viable.11 A greater number of studies have examined the formation of 3D bimetallic NCs by deposition on a variety of substrates including Al2O3,12–14 TiO2,15,16 Ni3Al(111),17 and NaCl,18 sometimes finding core-shell structures. In all these cases, there is little control over the NC location which is determined by either stochastic homogeneous nucleation or by heterogeneous nucleation at generally randomly located defects or traps.

However, one strategy for control of the NC spatial location (which in turn impacts the NC size distribution), and also for stabilization of smaller NC sizes, is directed-assembly of NCs by metal deposition on templated substrates. In a number of recent studies, the template has been provided by a periodically rumpled monolayer of graphene (MLG) supported on a metal surface. Typically, a single type of metal is deposited to create single-component NCs.19–26 However, limited studies of sequential deposition of two metals have also been performed. N’Diaye et al.20 deposited first a high cohesive energy metal on MLG/Ir(111) which forms a perfect periodic array of NCs. This periodic array seeded the formation of perfect arrays of mixed NCs by subsequent deposition of a low cohesive energy metal (which in the absence of the seeds would form imperfect arrays or 2D layers). Engstfeld et al.27 explored the role of the deposition order on the NC structure for mixed Pt-Ru NCs on MLG/Ru(0001). There has been little atomistic-level modeling of the formation of 3D NCs, particularly for directed-assembly. Our goal is to develop and apply such modeling for the Pt-Ru on MLG/Ru(0001) system, focusing on the kinetics and spatial aspects of NC formation and the bimetallic NC size, height, and composition distributions. Our modeling is not designed to capture the details of NC structure.

In Sec. II, we provide some brief background on the experimental setup, on the structure of supported monolayers of graphene on Ru(0001), and on experimental results for deposition of Pt and Ru on MLG/Ru(0001). Section III provides a review of density functional theory (DFT) results for the energetics of these adsorption systems, and a description of our atomistic-level modeling of NC formation. In Sec. IV, we present “benchmark” modeling of single-component deposition of just Pt and of just Ru on MLG/Ru(0001). Then, detailed modeling of sequential deposition of Pt then Ru (Ru@Pt) is presented in Sec. V. The corresponding analysis of sequential deposition of Ru then Pt (Pt@Ru) is presented in Sec. VI. Conclusions are provided in Sec. VII.

II. BACKGROUND: EXPERIMENT FOR NC FORMATION ON MLG/Ru(0001)

A. Experimental setup

A detailed description of the experimental setup and procedure for sample preparation have been provided in previous publications.26,27 for pure Ru as well as bimetallic PtRu cluster growth on MLG supported on Ru(0001). In brief, the experiments were performed in an ultrahigh vacuum chamber with a base pressure of 1 × 10−10 mbar. The Ru(0001) surface was
sputtered with \( \text{Ar}^+ \) ions and cleaned with cycles of heating to 1600 K. Remaining carbon impurities were removed by cycles of oxygen adsorption and subsequent heating to 1500 K. The supported graphene layer was prepared by decomposition of ethylene at 1000 K. Subsequently, the metals were deposited using an electron beam evaporator. The arrays of metal NCs which self-assemble on the supported MLG surfaces were investigated at room temperature with a home-built pocket-size scanning tunneling microscopy (STM), using tunneling currents of 40 pA–100 pA and voltages of 1 V–2 V. For analysis of NC distributions for each choice of deposition condition, several STM images were recorded and evaluated using in-house software for statistical analysis of, e.g., the lateral and height distribution of the NCs. A more detailed description of the analysis of NC height distributions is provided in Appendix A.

B. Structure of MLG on Ru(0001) and directed-assembly of metal NCs

A MLG supported on Ru(0001) exhibits a periodically rumpled moiré structure due to lattice mismatch (with a moiré cell area of \( \sim 7.7 \text{ nm}^2 \)). This MLG is often described by a \( (12 \times 12)\text{C}/(11 \times 11)\text{Ru} \) structure model. It is useful to define the fcc, hcp, and atop regions of the moiré cell for which the center of the C-rings in the graphene layer is above the fcc, hcp, and atop sites of the underlying Ru(0001) substrate, respectively. As a result of this moiré structure, the adsorption and diffusion properties of deposited metals are correspondingly modulated which can result in directed-assembly. Most often, preferential nucleation and growth of metal NCs occurs in the so-called fcc region of the moiré cell.\(^{19-26} \) See Fig. 1. This scenario applies in this study, and is believed to reflect preferred adatom binding or adsorption in those regions.

In systems where there is negligible transport of adatoms between moiré cells during deposition, a NC is quickly formed in the fcc region of every cell.\(^ {19} \) However, active transport between cells allows for fractional population, FF, of moiré cells even for significant coverages, \( \theta \), of deposited materials. Here, FF is termed the “filling factor” and is given as a fraction or percentage of moiré cells populated by NCs. Also, a coverage of \( \theta = 1 \) monolayer (ML) is defined to correspond to one adatom for every Ru(0001) surface atom. Analysis of the FF can provide insight into surface transport and also into the NC formation process.\(^ {26} \) In Fig. 2, the behavior of FF versus \( \theta \) is compared for deposition of Pt and Ru on MLG/Ru(0001) just above room temperature. We make three key observations: (i) the FF values are well below the maximum implying facile transport between moiré cells and across the surface for tens of nm; (ii) the FF for Pt is significantly below that for Ru for roughly the same amount of deposited material, corresponding to a higher effective mobility as clarified in Sec. IV A; (iii) one finds an approximate proportionality FF \( \propto \theta^3 \), so that FF \( \propto \theta^{1/3} \). Typically, for nucleation and growth of NCs on flat surfaces, one does not have such simple scaling of the NC density. However, below we discuss why simple scaling is enhanced for directed-assembly, and explain why observed behavior is the signature of irreversible nucleation and growth of NCs.\(^ {7,30} \)

FIG. 1. Schematics showing various regions within the MLG/Ru(0001) moiré cell: (a) superimposed on an STM image of MLG. Reprinted with permission from A. L. V. de Parga, F. Calleja, B. Borca, M. C. G. Passeggi, Jr., J. J. Hinarejos, F. Guinea, and R. Miranda, Phys. Rev. Lett. 100, 056807 (2008). Copyright 2008 American Physical Society; (b) Indicating the coordinate system used to describe the adsorption energy below.

III. BACKGROUND: THEORY, MODELING FOR NC FORMATION ON MLG/Ru(0001)

A. DFT analysis of energetics

Next, we briefly discuss available DFT results for the interaction of Pt and Ru adatoms with freestanding MLG and with supported MLG/Ru(0001). The adsorption energy of a Pt (Ru) adatom on freestanding MLG has the value \( \sim -1.6 \text{ eV} \) (\( -2.0 \text{ eV} \)) and the diffusion barrier has the value \( \sim -0.17 \text{ eV} \) (0.62 eV).\(^ {26,31} \) Thus, the interaction of Pt with graphene is somewhat weaker than that of Ru. There also exist DFT results for the adsorption energy (\( E_{\text{ads}} \)) in preferred fcc region for these metals on supported MLG/Ru(0001): \( \sim -2.8 \text{ eV} \) for Pt versus \( -2.6 \text{ eV} \) for Ru.\(^ {32} \) No DFT results are available for diffusion barriers on MLG/Ru(0001). Our conclusions based on these results are that: (i) the strong interaction of Ru with freestanding MLG is not so greatly modified by underlying Ru(0001), so that the diffusion barrier on MLG/Ru(0001) may not be so different from that on freestanding MLG; (ii) the weaker interaction of Pt with freestanding MLG is greatly modified by underlying Ru(0001), so it is reasonable to expect that the diffusion barrier for Pt on MLG/Ru(0001) could be significantly modified (increased) from that on freestanding MLG. Finally, we remark that the large bulk cohesive energies for Pt and Ru suggest strong adatom-adatom attractions, consistent with the irreversible NC nucleation and growth mentioned above. [Our DFT value for the cohesive energy for Pt (Ru) is \( -5.577 \text{ eV} \) (\( -6.804 \text{ eV} \)) versus the experimental value \( -5.84 \text{ eV} \) (\( -6.74 \text{ eV} \)).]
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B. Potential energy surface for adsorption of metals on MLG/Ru(0001)

Atomistic modeling requires specification of the potential energy surface describing the lateral variation of the adsorption energy, \( E_{\text{ads}} \), for an isolated adatom. One has well-defined local adsorption sites in each carbon ring with separation \( a \sim 0.25 \text{ nm} \). Consequently, this potential energy surface includes a short-range highly oscillatory variation on a length scale of the moiré cell \( L_M = 2.98 \text{ nm} \). A schematic of the behavior of this surface is shown in Fig. 3, where it should be noted that adsorption is strongest at the center of the fcc region. Adsorption in the center of the hcp region, the fcc-boundary, and the atop regions are weaker by \( \Delta \approx \delta + \delta^* \), respectively. The explicit form used for the potential energy surface consistent with this behavior is provided in Ref. 26. Motivated by DFT analysis of Sutter et al. for Ru/MLG/Ru(0001), we will set \( \Delta = \delta \) and \( \delta^* = 0 \) for both Ru and Pt, thereby imposing a uniform adsorption energy over the entire hcp half of the moiré cell which is weaker than that in the fcc region. The local activation barrier, \( E_a(i \rightarrow f) \), for biased diffusion (i.e., hopping) from an initial site \( i \) to a neighboring final site \( f \) is chosen as \( E_a(i \rightarrow f) \approx E_{\text{ads}} + [E_{\text{ads}}(f) - E_{\text{ads}}(i)]/2 \), where \( E_{\text{ads}} \) is an upward shift of the transitional state energy (red dashed curve) from the adsorption site energy (green dashed curve), see Fig. 3. Hop rates, \( r \), are selected to have the Arrhenius form \( r(i \rightarrow f) = v \exp(-E_a(i \rightarrow f)/k_B T) \) where the common prefactor \( v = 10^{13}/\text{s} \) and \( k_B \) is the Boltzmann constant. This form is consistent with detailed-balance.

C. Atomistic lattice-gas modeling

Our atomistic lattice-gas model includes: (i) random deposition at adsorption sites on the substrate; (ii) biased hopping between adjacent adsorption sites with activation barriers, \( E_a(i \rightarrow f) \), and Arrhenius hop rates, \( r \), controlled by the modulated potential energy surface as specified above; and (iii) irreversible nucleation and growth of NCs. The model is readily adapted to treat deposition of a single type of atom or sequential (or simultaneous) deposition. In addition, a “point island” model is utilized which tracks only NC size and composition, but not structure. Specifically, in this model, each NC occupies a single adsorption site, but carries size labels to indicate the number of atoms of various types within the NCs. These point models have proved particularly efficient and effective in elucidating the behavior in various deposition systems of NC densities (corresponding here to filling fraction, FF), and NC size distributions. Here, we utilize kinetic Monte Carlo (KMC) simulation to assess model predictions for these quantities, and also for the composition distribution of mixed islands. In this work, the simulation cell size is always taken to be 100 \times 100 moiré cells with periodic boundary conditions. In certain cases, we have compared results for multiple simulations in order to check that we have sufficiently accurate statistics for quantities of interest.

Point island model behavior is not impacted by lateral growth and coalescence of NCs. As a result, such models produce clear and simple scaling of NC density or FF with coverage of the form \( \theta^{3/4} \) where \( \theta \) denotes the critical size (in atoms) above which NCs are stable. Point island models should be well-suited to modeling of directed-assembly where island coalescence is also inhibited (a least initially) due to the imposed separation of NCs. Consequently,
the simple scaling of the type mentioned above should be manifested, and experimental observations thus correspond to $i = 1$, i.e., irreversible NC formation.

For irreversible NC formation of uniform substrates, the FF scales like the inverse third power of the surface diffusivity. Thus, even for the systems of interest here with a templated substrate, lower values of the FF should correspond to a longer range or higher effective mobility. This effective mobility is some nontrivial combination of our model parameters, $E_{0}$ and $\Delta$, but it must clearly increase with both decreasing $E_{0}$ and decreasing $\Delta$. Figure 4 illustrates this fundamental dependence on model parameters.

IV. BENCHMARK MODELING: Pt ON MLG/Ru(0001) VERSUS Ru ON MLG/Ru(0001)

A. FF analysis

We select model parameters to match experimental values reported in Table I for $E_{0} = 20.7\%$ (30.5\%) for deposition on MLG/Ru(0001) of 0.05 ML of Pt (Ru) at $T = 307$ K (305 K) with a flux $F = 0.034$ ML/min (0.042 ML/min). (These experiments correspond to the first stage of the sequential deposition studies described in Secs. V and VI.) We can match the behavior for Pt by choosing the model parameters ($E_{0}$, $\Delta$) as (0.55, 0.43) or (0.58, 0.36) or (0.61, 0.29) or . . . with values in eV. This is illustrated in Fig. 5. We select ($E_{0}$, $\Delta$) as (0.55, 0.46) or (0.58, 0.38) or (0.61, 0.31) or . . . with values in eV. Thus, we cannot determine a unique choice of parameters to match the experiment without extra information, such as that provided by our DFT estimate of $E_{0}$ for Ru. However, it is clear that the effective mobility of Pt exceeds that of Ru (corresponding to a lower FF for deposition with similar $T$ and $F$). In subsequent modeling, we will select ($E_{0}$ = 0.55 eV, $\Delta = \delta = 0.43$ eV) for Pt, and ($E_{0}$ = 0.58 eV, $\Delta = \delta = 0.38$ eV) for Ru.

B. NC size and height distribution

The average NC size is determined from $s_{av} \approx 121\theta/FF$ (with $s_{av}$ in atoms, $\theta$ in ML, and FF as a fraction), given a negligible fraction of isolated diffusing adatoms. Thus, in the deposition studies described above, Pt NCs are on average roughly 50% larger than the Ru NCs due to the smaller FF for Pt. Our KMC simulations also determine the NC size distributions, which have the classic mono- or unimodal form expected for irreversible island formation by homogeneous nucleation on ideal (non-templated) surfaces. Thus, the periodic modulation of the PES on a length scale $L_{M}$ does not much affect the size distribution for the current experimental conditions.

The NC height distribution was also determined from the experimental data, as described in Appendix A. Results are reported in Table I, which gives the filling fraction, FF(h), for NCs with specific heights $h = 1, 2, 3, \ldots$ (in unit of atomic layers), so that $FF = \sum_{h \geq 1} FF(h)$. To

<table>
<thead>
<tr>
<th>Metal</th>
<th>$F$ (ML/min)</th>
<th>$T$ (K)</th>
<th>$\theta$ (ML)</th>
<th>FF (%)</th>
<th>FF(1) (%)</th>
<th>FF(2) (%)</th>
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<tr>
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<td>300</td>
<td>0.110</td>
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<td>300</td>
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<td>3.91</td>
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<td>10.48</td>
<td>4.65</td>
<td>1.78</td>
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elucidate the observed behavior, we suppose that there exist fairly well-defined threshold sizes (measured in number of atoms), \( S_{h \rightarrow h+1} \), at which the NC makes a transition from \( h \) to \( h+1 \) in height. Thus, a NC with \( S_{h \rightarrow h+1} \) atoms is the smallest NC of height \( h+1 \). We adjust the \( S_{h \rightarrow h+1} \), subject to reasonable physical constraints, to fit experimental observations. We expect that NCs have a hcp arrangement of atoms in each layer with 3-fold hollow adsorption sites. Note that for fcc stacking, the minimum possible thresholds for a stable NC which requires a nearest-neighbor pair of adatoms (a triangle of adatoms) in the top layer are \( S_{h \rightarrow h+1} = 7, 16, 30, 50, 77, \ldots \) for \( h = 1, 2, 3, \ldots \). For hcp stacking, \( S_{1 \rightarrow 2} \) is unchanged, and other \( S_{h \rightarrow h+1} \) are slightly higher: \( S_{h \rightarrow h+1} = 7, 17, 33, \ldots \) for \( h = 1, 2, 3, \ldots \) if a stable NC requires a nearest-neighbor pair (a triangle) in the top layer. To fit the experimental data, we can set \( S_{h \rightarrow h+1} = 9, 38, 70, \ldots \) for \( h = 1, 2, 3, \ldots \) for Pt, and \( S_{h \rightarrow h+1} = 7, 25, 60, \ldots \) for Ru (cf. Ref. 26). Our comparison with experimental results for FF(\( h \)) will be presented in Secs. V and VI. From these thresholds, the transition to \( h = 3 \) and higher layer clusters requires a larger than minimum possible number of atoms (corresponding to larger, wider clusters than the minimal pyramid). Still, the transition to 3D island growth is still more facile than for Ir on MLG/Ir(111).35

V. SEQUENTIAL DEPOSITION: Pt THEN Ru (Ru@Pt) ON MLG/Ru(0001)

A. FF analysis

Pt has a higher effective mobility than Ru, and thus a lower FF for deposition under similar conditions. Thus, one expects that for sequential deposition of 0.06 ML Ru following that of 0.05 ML Pt, the NC density should significantly increase in the second stage of deposition due to nucleation of new smaller pure Ru NCs. This feature is also clear in the chemically resolved size and height distributions presented in Sec. V B. These second stage pure Ru NCs should form at locations which according to nucleation theory7,30 tend to be further separated from existing Pt NCs. Indeed, experimental results in Figs. 6(a) and 6(b) and Table I reveal that the FF doubles from 20.7% to 41.7%. Thus, roughly half the final NCs are pure Ru NCs and half are mixed Ru@Pt NCs formed by aggregation of Ru with the Pt NCs formed in the first stage. Since extended Pt(111) surfaces are susceptible to Ru intermixing above 370 K, it is plausible that these mixed Ru@Pt NCs do not have a perfect “Pt core + Ru shell” structure.27 Our model with energetic parameters unchanged from Sec. III is quite successful in recovering observed behavior. This is clear from comparing Figs. 6(a) and 6(b) with Figs. 6(c) and 6(d) and from comparing Table I with Table II.

B. NC size, composition, and height distributions

Since our modeling allows complete chemical resolution of mixed NCs formed during deposition, it can provide additional insight relative to experimental observations which lack such resolution. Figure 7(a) shows various size distributions for NCs predicted by the model where the NC size is given by the total number of atoms: the size distributions for Pt NCs formed during the first Pt deposition (cf. Sec. IV A) which has the classic shape for irreversible island formation;7 separate size distributions for the mixed NCs and the pure Ru NCs formed in the second stage of deposition. Since many small pure Ru NCs are formed in the second stage and the existing Pt NCs grow significantly by addition of Ru, the final overall size distribution is bimodal.

In Fig. 7(b), we show the joint probability distribution for mixed NCs, i.e., NC population as a function of the number of constituent Pt and Ru atoms. The reduced distribution of Ru atoms in these mixed NCs is obtained by summing the joint distribution over the number of Pt atoms (for various

<table>
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<th>Metal</th>
<th>( F ) (ML/min)</th>
<th>( T ) (K)</th>
<th>( \vartheta ) (ML)</th>
<th>FF (%)</th>
</tr>
</thead>
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</tr>
<tr>
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<td>300</td>
<td>0.112</td>
<td>36.31</td>
</tr>
</tbody>
</table>

FIG. 6. (a) and (b) STM images of NC distributions for Pt deposition followed by Ru deposition (Ru@Pt) under conditions described in the text. Image size: \( 35 \times 35 \) nm\(^2\). (c) and (d) KMC simulation of NC distributions for Pt deposition followed by Ru deposition (Ru@Pt) under conditions described in the text. Image size: \( 89 \times 53 \) nm\(^2\). Pure Pt (Ru) NCs are green (red), and mixed NCs have a green core and red ring.
fixed numbers of Ru atoms). This reduced distribution is fairly sharply peaked about the average, see Fig. 7(c). This might be expected since this distribution of the number of Ru atoms should reflect the “capture zone” area distribution for the Pt NCs. Such area distributions are expected to have a generalized Gamma form, which is narrow compared to classic size distributions for irreversible island formation. One complication is that the capture zones for Pt and mixed NCs are modified by the nucleation of new Ru NCs.

The experimental NC height distribution is reasonably recovered from the above NC size distribution by choosing for mixed Ru@Pt NCs the height cutoffs $S_{h→h+1} = 7$ or 9, 34, 46, 74, ... for $h = 1, 2, 3, 4, ...$. Actually, since there are no mixed NCs for $h = 1$, the results are insensitive to $S_{1→2}$. Here, we have consistently chosen the same cutoffs as in Sec. III for pure Ru NCs, see Fig. 8. Note that the mixed NC cutoffs are smaller than those for pure Pt NCs, i.e., it is easier to form taller mixed NCs. This may indicate a stronger thermodynamic preference for Ru to climb to higher layers relative to Pt, perhaps due to the higher cohesive energy of Ru. Potentially, the feature that $S_{3→4}$ is not far above $S_{2→3}$ is due to the possibility to form small bilayer Ru NCs on top of the large number of previously formed bilayer Pt NCs.

Significantly, this proposal for the facile formation of bilayer Ru islands on the top (111)-facetted surface of Pt NCs is entirely consistent with previous experimental observations for Ru deposition on Pt(111): bilayer Ru islands were found to form readily during deposition at room temperature of Ru on extended Pt(111) single-crystal surfaces, and on Pt(111) monolayers supported on Ru(0001).

VI. SEQUENTIAL DEPOSITION: Ru THEN Pt (Pt@Ru) ON MLG/Ru(0001)

A. FF analysis

Deposition of Ru produces a high FF compared to Pt, so one expects that sequential deposition of 0.05 ML Ru and then 0.06 ML Pt should not significantly increase the NC density above that from the Ru deposition. Such an increase would require nucleation of a significant number of new pure Pt NCs. Indeed, experimental results in Figs. 9(a) and 9(b) and Table I reveal that the FF increases only slightly from 30.5% to 35.0%. Thus, most of the final NCs are mixed Pt@Ru NCs formed by aggregation of Pt with the smaller Ru NCs formed in the first stage. This feature is also clear in the chemically-resolved size and height distributions presented in Sec. VI B. Since extended Ru(0001) surfaces are resistant to Pt intermixing, these NCs likely have a perfect “Ru core + Pt shell” structure. Our model with energetic parameters unchanged from Sec. III is quite successful in recovering the observed behavior. Compare Figs. 9(c) and 9(d) with Figs. 9(a) and 9(b), and compare Table I with Table II.

B. NC size, composition, and height distributions

Figure 10(a) shows model predictions for various size distributions for NCs: size distributions for “small” Ru NCs formed during the first deposition (cf. Sec. V B); size distributions separately for the mixed NCs and the small number of pure Pt NCs formed in the second stage of deposition. Since few small pure Pt NCs are formed in the second stage, the final overall distribution is now mono- or unimodal being dominated by the mixed NCs. Figure 10(b) shows the joint probability distribution for mixed NCs which is similar to that in Fig. 7(b). The reduced distribution of Pt atoms in these mixed NCs is obtained by summing the joint distribution over the number of Ru atoms. This reduced distribution
FIG. 9. (a) and (b) STM images of NC distributions Ru deposition followed by Pt deposition (Pt@Ru) under conditions described in the text. Image size: 35 × 35 nm². (c) and (d) KMC simulation of NC distributions Ru deposition followed by Pt deposition (Pt@Ru) under conditions described in the text. Image size: 89 × 53 nm². Pure Ru (Pt) NCs are red (green), and mixed NCs have a red core and green ring.

FIG. 10. Pt@Ru deposition process. (a) Size distributions for Ru NCs after Ru deposition; and both pure Pt and mixed NCs after Pt deposition. Inset: schematic of NC formation. (b) Joint probability distribution for mixed NCs with various numbers of Pt and Ru atoms. Red (blue) denotes higher (lower) population as indicated in the scale. (c) Distribution of Pt atoms just in mixed NCs.

is fairly sharply peaked about the average, see Fig. 10(c), and should almost exactly correspond to the “capture zone” area distribution for the Ru NCs formed in the first stage of deposition.7, 36 Again, this area distribution should have a generalized Gamma form.37

The experimental height distribution is reasonably recovered from the above size distributions by choosing for mixed Pt@Ru NCs the height cutoffs \( S_{h \rightarrow h+1} = 7 \) or 9, 20, 42, 56, 77, … for \( h = 1, 2, 3, 4, 5, \ldots \) (where again no mixed NCs for \( h = 1 \) implies insensitivity to \( S_{1 \rightarrow 2} \)). Here, we have consistently chosen the same cutoffs as in Sec. III for pure Pt NCs. This is illustrated in Fig. 11, which shows that essentially all NCs with \( h = 1 \) and 2 are pure Pt, and essentially all mixed NCs have \( h \geq 3 \). Note that the mixed NC cutoffs are smaller than those for pure Pt or pure Ru NCs or for mixed “Pt core + Ru shell” NCs. Presumably, this reflects a stronger driving force for 3D cluster growth than for pure Pt or Ru NCs (or for mixed quasi “Ru core + Pt shell” NCs). This, in turn, reflects the large cohesive energy for Pt and a large adsorption energy for Pt on hcp Ru surfaces, see Appendix B.

VII. CONCLUSIONS

Our atomistic-level modeling of directed-assembly of bimetallic Pt-Ru NCs by sequential deposition on MLG/Ru(0001) is effective at describing not only just the NC densities (or filling fractions), and the size and height distributions, but also the composition distribution for mixed NCs. The latter quantities cannot be readily obtained from experiment. Our analysis also provides a quantitative assessment of the different effective mobilities of Pt and Ru on MLG/Ru(0001), and also the ease for formation of various 3D NCs.

ACKNOWLEDGMENTS

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APPENDIX A: EXPERIMENTAL ANALYSIS OF NC HEIGHT DISTRIBUTIONS

Discrete atomic-layer NC height distributions were determined from the experimental STM data using the following procedure. First we planarize the STM images and collect (quasi-continuous) height-distribution data over a single terrace which does not include any step edges. The typical image size is $150 \times 150 \text{ nm}^2$. The height distribution usually shows a multi-peak structure indicating preferences for specific discrete atomic layer heights. To obtain better statistics (particularly for lower coverages, and thus lower numbers of NCs), we combine data from a few images after suitably aligning the peaks. Next, the quasi-continuous height, $h$, is transformed into units of atomic layers, where each layer corresponds to the step height for fcc Ru on Ru(0001) of 2.14 nm. For convenience, we use this single value of the step height when analyzing height distributions for pure Ru NCs, for mixed Ru-Pt NCs, and for pure Pt NCs. (Note that the step height for fcc Pt on Pt(111) is 2.26 nm, close to the above value.) Integer values of $h$ are then suitably assigned to the peaks in the distribution. An example of a quasi-continuous height distribution for pure Ru NCs with a Ru coverage of 0.12 ML and a FF of 47%, which is obtained from this procedure, is shown in Fig. 12. Finally, we sum up the population of the quasi-continuous height distribution for all heights $h$ in a range of $n \pm 0.5$, with integer $n$ corresponding to a specific atomic layer height. (These ranges are shown in Fig. 12 delineated with dashed green vertical lines). The resulting discrete height distribution in atomic layers is shown in the insert.

The appearance in the STM data of a quasi-continuous height distribution (versus sharp discrete peaks) is not surprising. This feature was found for size-selected Pd clusters deposited on MLG/Ru(0001). It is even found for “mounded” morphologies for rough multilayer growth in simple homoepitaxial metal systems. Origins of the quasi-continuous distribution include: (i) slow response of the laterally scanning tip to the local morphology; (ii) convolution of a broad tip profile with the local height distribution; (iii) differing local density of states for clusters with the same height but different shapes, etc. One caveat is that there is no simple unique way to reliably extract a discrete height distribution from the observed continuous distribution.

APPENDIX B: THERMODYNAMICS FOR PURE AND MIXED 3D NC GROWTH

For the growth of pure single-component metal NCs, 3D growth is favored if the pure metal surface energy exceeds the adhesion energy for slabs of that metal on MLG/Ru(0001). We cannot readily calculate this adhesion energy, so instead we explore two simpler approximate assessments or analyses. First, although the surface energy of the metal should be compared to the above adhesion energy, one might also note that it is significantly higher than the low surface energy of graphene. This inequality is consistent with 3D growth. Second, we compare the adsorption energy of an isolated metal adatom on the relevant metal surfaces (see Table III) with the adsorption energy of that metal on MLG/Ru(0001): $-5.61 \text{ eV for Pt/Pt(111)}$ versus $-2.8 \text{ eV}$ for Pt/MLG/Ru(0001), $-5.49 \text{ eV for Ru/Ru(0001)}$ versus $-2.6 \text{ eV}$ for Ru/MLG/Ru(0001). The much greater magnitude of the metal-on-metal energies is also consistent with 3D growth.

Of particular interest and relevance here is the corresponding analysis for mixed NCs. Here, one also needs to calculate the adsorption energy of isolated Pt on Ru(0001) and of isolated Ru on Pt(111), see Table III. One finds $-4.14 \text{ eV for Ru/Pt(111)}$ versus $-2.6 \text{ eV for Ru/MLG/Ru(0001)}$ indicating a strong driving force for 3D quasi “Pt core + Ru shell” NCs. One finds $-5.61 \text{ eV for Pt/Ru(0001)}$ versus $-2.8 \text{ eV for Pt/MLG/Ru(0001)}$ indicating an even stronger driving force for 3D “Ru core + Pt shell” NCs, which are the tallest of all the observed 3D NCs. As an aside, the experimental surface lattice constant for Pt(111) is 0.277 nm (cf. our DFT

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{\text{ads}}($fcc$)$</th>
<th>$E_{\text{ads}}($hcp$)$</th>
<th>$E_{\text{ads}}($hcp$) - E_{\text{ads}}($fcc$)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Pt(111)</td>
<td>$-4.437$</td>
<td>$-4.264$</td>
<td>$0.173$</td>
</tr>
<tr>
<td>Ru/Pt(111)</td>
<td>$-4.138$</td>
<td>$-4.023$</td>
<td>$0.115$</td>
</tr>
<tr>
<td>Ru/Ru(0001)</td>
<td>$-5.030$</td>
<td>$-5.486$</td>
<td>$-0.457$</td>
</tr>
<tr>
<td>Pt/Ru(0001)</td>
<td>$-5.339$</td>
<td>$-5.609$</td>
<td>$-0.270$</td>
</tr>
</tbody>
</table>

TABLE III. DFT values of adsorption energies $E_{\text{ads}}($fcc$)$ and $E_{\text{ads}}($hcp$)$ (in eV) at fcc and hcp sites and their differences for an isolated Pt or Ru adatom on Pt(111) or Ru(0001) surface. Parameters for the DFT analysis using the VASP code: $2 \times 2$ supercell, 10 ML substrate, $19 \times 19 \text{ k}$-mesh, updated PAW-PBE potentials. For more computational details about DFT calculations of adsorption energy, see our previous work.
value of 0.2807 nm), and for Ru(0001) it is 0.271 nm (cf. our
DFT value of 0.2714 nm), so there should be little strain due
to metal lattice mismatch in these 3D mixed NCs.

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