Atomic Layer Deposition of Nickel Using a Heteroleptic Ni Precursor with NH₃ and Selective Deposition on Defects of Graphene

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ABSTRACT: Atomic layer deposition (ALD) of Ni was demonstrated by introducing a novel oxygen-free heteroleptic Ni precursor, (η⁵-cyclohexenyl)(η⁵-cyclopentadienyl)nickel(II) [Ni(Chex)(Cp)]. For this process, non-oxygen-containing reactants (NH₃ and H₂ molecules) were used within a deposition temperature range of 320−340 °C. Typical ALD growth behavior was confirmed at 340 °C with a self-limiting growth rate of 1.1 Å/cycle. Furthermore, a postannealing process was carried out in a H₂ ambient environment to improve the quality of the as-deposited Ni film. As a result, a high-quality Ni film with a substantially low resistivity (44.9 μΩ·cm) was obtained, owing to the high purity and excellent crystallinity. Finally, this Ni ALD process was also performed on a graphene surface. Selective deposition of Ni on defects of graphene was confirmed by transmission electron microscopy and atomic force microscopy analyses with a low growth rate (∼0.27 Å/cycle). This unique method can be further used to fabricate two-dimensional functional materials for several potential applications.

1. INTRODUCTION

Ni and Ni-based compounds have attracted considerable attention toward several potential applications owing to their favorable electrical and catalytic properties. For example, they have been widely used as electrocatalysts in energy applications,¹ and NiSi has many advantages for reducing the dimensions of complementary metal−oxide−semiconductor (CMOS) devices.²,³ Among the various preparation techniques for Ni, atomic layer deposition (ALD) is a promising process in nanotechnology, owing to its outstanding conformality, uniformity, and pinhole-free thin-film deposition.⁴−⁶ The self-limited surface reaction, which is the basic principle of ALD, allows precise control of the film thickness and stoichiometry at the atomic level. Accordingly, ALD has been considered as a key process for fabricating nanoscale devices.⁷−⁹ However, Ni ALD technology has not yet matured despite the increasing demand for its potential applications. More specifically, as shown by the standard reduction potentials in Table S1 in the Supporting Information, the reduction of Ni is more difficult than that of noble metals such as Ru and Pt. This fact indicates that Ni bonds more strongly to electronegative elements such as oxygen. This high oxygen affinity is a limiting factor that has restricted the development of Ni ALD as NiO, is easily formed during or after the ALD process. Moreover, this behavior restricts the reactants of Ni ALD to oxygen-free molecules,⁷−¹⁸ whereas oxygen-containing reactants (e.g., O₂ and O₃) are widely used in ALD of noble metals.¹⁹ The development of Ni precursors is also challenging, and only a limited number of them have been developed so far.²⁰,²¹ Processes using bis(dimethylamino-2-methyl-2-butoxo)nickel [Ni-(dmamb)$_2$] showed the typical deposition behavior of the self-limited reaction and produced Ni films with low resistivities. However, a considerable amount of impurities such as C,⁷,²² N,⁷ and O⁹ remained in the films after the ALD process. The C impurities issue was also reported in the process using N$_2$-hydroxyhexafluoroisopropyl-N$^1$ Ni precursor [Ni(hfp)$_2$].²² Further processes using bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)nickel [Ni(iPrMeCOCNiBu)$_2$] or bis(2,4-pentanedionato)nickel [Ni(acac)$_2$] have also been reported, but the growth rates obtained for these cases (0.09 Å/cycle¹¹ and 0.07 Å/cycle²²) were significantly low. In addition, a large quantity of C impurities was evident in the films when Ni(acac)$_2$ was used as the Ni precursor.²² Recently, Ni(acac)$_2$ was modified to Ni(acac)$_2$(tmeda) (tmeda:
Table 1. Summary of Previous Ni ALD Processes

| Ni precursor          | reactant   | key process                  | deposition temperature (°C) | growth rate (Å/cycle) | resistivity (μΩcm) | impurity (ref. no.) |
|-----------------------|------------|------------------------------|-----------------------------|-----------------------|-------------------|-------------------|
| Ni(dmamb)$_2$         | H$_2$      | ALD                          | 220                         | 1.25                  | NR                | C 7               |
| Ni(dmamb)$_2$         | NH$_3$, H$_2$ | PEALD                       | 250                         | 2.0 (NH$_3$)          | 43 (NH$_3$)       | C, N 8            |
| Ni(dmamb)$_2$         | NH$_3$     | ALD                          | 300                         | 0.64                  | 25                | O 9               |
| Ni(ipr)$_2$           | H$_2$      | ALD                          | 220                         | 1.25                  | NR                | C 10              |
| Ni(AMD(iPr)$_2$)$_2$  | BH$_4$(NHMe)$_2$ | ALD                       | 180                         | 0.09                  | NR                | C 11              |
| Ni(Cp)$_2$            | H$_2$O (deposition)/H$_2$ (reduction) | PEALD(NiO) + reduction | 165                         | NR                    | 25–30             | C, O 12           |
| Ni(Cp)$_2$            | NH$_3$     | PEALD + annealing            | 280                         | 0.2                   | 71 (as-deposited) | C, N 15           |
| Ni(Cp)$_2$            | tBuNH$_2$  | hot-wire ALD                 | 250                         | 0.63                  | 27.9              | C 16              |
| Ni(acac)$_2$ (tmeda)  | N$_2$H$_4$ | ALD                          | 260                         | 2.1                   | 18.1              | C 18              |
| Ni(acac)$_2$          | CH$_3$OH   | ALD                          | 300                         | ~0.07                 | 27                | C 22              |

"NR means that the value was not reported in the reference.

Figure 1. Molecular structure of the Ni precursor Ni(Chex)(Cp).

tetramethyl ethylenediamine), and a Ni ALD process using Ni(acac)$_2$ (tmeda) showed enhanced reactivity of the precursor.\textsuperscript{18}

All of the Ni precursors mentioned above contain O, which has a certain possibility of forming an oxide phase with Ni or remaining as an impurity in the as-deposited films. In this regard, bis(N$_2$N'-disopropylacetamidinato)nickel [Ni(AMD-iPr)$_2$]\textsuperscript{12} and bis(cyclopentadienyl)nickel [Ni(Cp)$_2$]\textsuperscript{13–16} as O-free Ni precursors, have been studied for Ni deposition. The process using Ni(AMD(iPr)$_2$)$_2$ showed a low growth rate (0.04 Å/cycle), and any other information was not mentioned in the study.\textsuperscript{12} It has also been confirmed that the reactivity of Ni(Cp)$_2$ is too low to act as a precursor for thermal ALD. As a result, the Ni ALD process using Ni(Cp)$_2$ requires a highly chemically reactive reactant such as NH$_3$ radicals, which are produced by plasma\textsuperscript{14,15} or hot wire.\textsuperscript{16} Further, additional processes such as reduction of NiO\textsuperscript{13} and postannealing\textsuperscript{15} were also required to obtain a pure Ni film. A recent study reported a process involving bis(1,4-di-tet-butyl-1,3-diazadienyl)nickel [Ni(tBu$_2$DAD)$_2$]\textsuperscript{16} that produced high-quality Ni films at low process temperatures (180 °C), but the deposition of the film was only possible on noble metal substrates (Pt and Ru).\textsuperscript{17} In summary, the low reactivity of the precursor and impurities in the deposited films are the main issues to be solved in the Ni ALD processes. Table 1 provides some key information of the previous Ni ALD processes. Thus, new Ni precursors should be designed to have suitable reactivities without impurities in the deposited films. The precursor should also be compatible with thermal ALD to prevent sample damage, which might be caused by the use of plasma or additional processes during postdeposition of the films.

Herein, we report a new thermal ALD process for depositing Ni thin films using a novel heteroleptic Ni precursor, namely, (η$^5$-cyclohexenyl) (η$^5$-cyclopentadienyl)nickel(II) [Ni(Chex)-(Cp), C$_{11}$H$_{14}$Ni] (Figure 1). We expect the precursor reactivity to be enhanced by replacing one Cp ring in Ni(Cp)$_2$ with a cyclohexenyl ring. In general, the Cp ligand ensures thermal stability of a metal–organic precursor\textsuperscript{22,23} due to its coordination (i.e., η$^5$-cyclopentadienyl metal–organic compound). The strong C–metal bonds improve the thermal stability of the precursor but also cause a too low reactivity issue that leads to low growth rate and retained impurities. Therefore, the substitution of Cp ligands or combination with other chemical compounds can be a viable alternative for improving the reactivity of the precursor. In fact, this approach is already found in other metal ALDs. For example, improvement of the reactivity has been already confirmed in Ru ALD processes using precursors having other ligands such as six-membered rings (benzyl- or cyclohexadienyl-type ligands) or carbonyl ligands.\textsuperscript{24–26} Comparing Ru(Cp)$_2$ published research clearly shows a fast growth rate,\textsuperscript{26} low growth temperature,\textsuperscript{24,25} and enhanced volatility of the precursor.\textsuperscript{24–26} Accordingly, the Ni precursor is also expected to improve the reactivity by the substitution and combination of the Cp ligand from Ni(Cp)$_2$. Finally, we performed the Ni ALD process on graphene as an application of Ni ALD, which shows unique deposition behavior. The ideal basal plane of graphene is chemically stable because it contains no dangling bonds or functional groups. As a result, materials are deposited selectively on chemically active regions such as line defects.\textsuperscript{29} In recent years, graphene composites have been actively investigated for many applications.\textsuperscript{30,31} Graphene–metal composites with metals such as Ru\textsuperscript{32} and Pt\textsuperscript{33} acquired by selective deposition, have demonstrated that the electrical properties of graphene are improved. Hydrogen detector applications are also feasible. The Ni ALD process has not yet been applied to graphene, although it has been applied to other carbon materials.\textsuperscript{34,35} Thus, research on Ni ALD on graphene is needed. We applied our Ni ALD process to single-layer graphene grown by a chemical vapor deposition (CVD) process. The selective deposition was then systematically investigated and compared with typical growth processes.
2. RESULTS AND DISCUSSION

2.1. Ni Film Deposition Using Oxygen, Hydrogen, and Ammonia Molecules as Reactants. Prior to deposition of the Ni films by ALD, the thermal stability of the new metal–organic Ni precursor was verified. For this test, only the Ni precursor was provided with a N2 carrier gas into the chamber up to a temperature of 340 °C for 10 min, without introducing any counter-reactants such as O2, H2, and NH3 like the pyrolysis process of CVD. Here, the Ni precursor is not trapped in the chamber but continuously flows from the canister line to the chamber and exhaust line to the pump, which is the same situation with the ALD process, except that purging (N2 gas only) and reactant pulsing are not done. In the current study, the continuous provision of the precursor was done for 10 min, or 600 s, which corresponds to 60 ALD cycles considering the precursor pulsing time in one ALD cycle of the present study. In this case, no film growth was observed, which indicates that the new Ni precursor is thermally stable up to 340 °C, excluding the possibility of growth by thermal decomposition. Figure 2a shows the X-ray diffraction (XRD) patterns of ALD Ni films obtained using O2, H2, and NH3 reactants at a deposition temperature of 320 °C and (b) resistivity of deposited films. XPS analysis of the NH3-340 °C Ni film. Spectra of (c) C 1s, (d) N 1s, (e) O 1s, and (f) Ni 2p.

Figure 2. Reactant tests. (a) XRD analysis of ALD Ni films obtained using O2, H2, and NH3 reactants at a deposition temperature of 320 °C and (b) resistivity of deposited films. XPS analysis of the NH3-340 °C Ni film. Spectra of (c) C 1s, (d) N 1s, (e) O 1s, and (f) Ni 2p.

reactivity of the Ni precursor under thermal ALD conditions. Therefore, two different reducing agents were further tested. By contrast, an fcc Ni peak (indexed by PDF no.00-004-0850) is observed when NH3 or H2 is used as the reactant. Although the peaks (44.49° in H2-320 °C and 44.51° in NH3-320 °C) correspond exactly to the Ni(111) peak in the reference (44.51°, PDF no.00-004-0850), there is no experimental evidence from our data to completely rule out the interpretation of the broad peak reported by recent research,36−38 which implies the coexistence of Ni3C peaks in the Ni(111) peak. This result further confirms that an oxygen-free reactant is indispensable for obtaining Ni metal films by ALD. As a consequence, the remainder of the work related to this study was carried out only with O-free reactants, unless stated otherwise. Resistivity is another critical parameter of this Ni ALD process, so we have compared the resistivities of films deposited under the same condition using NH3 and H2 as reactants, as shown in Figure 2b. The resistivities of films deposited by the 320 °C processes were very high (H2-320 °C: 6.83 × 104 μΩcm, NH3-320 °C: 5.23 × 104 μΩcm) and showed different values depending on the reactants. It was observed that the resistivity of the Ni film was considerably lower when NH3 was used rather than H2, so the former has been chosen as a reactant for various studies on the Ni ALD process.8,14−16 In particular, it was confirmed that NH3 species play a key role in removing Cp from metal ions.4,14,50 Previous research on this phenomenon and the data at 320 °C compel us to consider NH3 as an optimum reactant. Therefore, the films were further deposited at another
2.2. Growth Behavior during the Ni ALD Process. To determine the self-limiting growth behavior during the Ni ALD process, we measured the growth rates of the films separately as a function of the precursor and reactant exposure with increasing pulsing time at a deposition temperature of 340 °C. It should also be noted here that, for all of the depositions carried out in the current work, a purging (of an ultrapure N2 gas) time of 10 s was fixed, which should provide enough room to remove the by-products as well as the residual chemicals (precursor and reactant), if any. Figure 3a shows the growth rate as a function of the precursor pulse time \( t_{\text{Ni}} \), while the reactant (NH3) pulsing time \( t_{\text{NH3}} \) was maintained constant at 5 s. It can be easily realized that the growth rate was increasing when \( t_{\text{Ni}} \) was continuously increased from 3 to 10 s. However, there was no further increment in the growth rate beyond 10 s (from 10 to 20 s) of pulsing for the Ni precursor, which clearly reveals a self-saturation of the film’s growth with increasing precursor exposure. By contrast, the growth rate remains constant with increasing \( t_{\text{NH3}} \) as shown in Figure 3b, which means that the growth rate was already saturated after \( t_{\text{NH3}} \) of 3 s. These results indicate that the self-limiting reaction is well validated with a growth rate of 1.1 Å/cycle during the Ni ALD process. Figure 3c shows the Ni film thickness as a function of the number of ALD cycles under a self-limiting growth condition. The linear dependence of the film thickness with ALD cycles further reflects a typical thin-film growth behavior of this Ni ALD process. The incubation step (i.e., the x-intercept of the fitted line) is only six cycles, which indicates that the growth of the Ni film is initiated without delay. The obtained growth rate (1.1 Å/cycle) from this thickness linearity study is also in good agreement with the saturated growth rates observed during the pulse tests.

2.3. Postannealing of Ni ALD Films. An annealing process was introduced to improve the quality of the as-deposited Ni films. This postannealing process was performed under a hydrogen flux (50 sccm) at ~0.3 Torr for 30 min. Figure 4a shows the resistivity as a function of the annealing temperature. The resistivity decreased rapidly with increasing annealing temperatures at 360–380 °C and reached less than 100 μΩcm at 380 °C. Finally, the lowest value (44.9 μΩcm) was obtained by annealing the film at 400 °C, which is comparable with that of previous Ni ALD processes. This drastic reduction in resistivity can be explained by two factors. First, the C impurity in the as-deposited film is completely removed by the annealing process. Figure 4b shows the XPS spectrum of C 1s in the Ni film after annealing at 380 °C. The C peak observed with significant intensities in the as-deposited films (Figure 2c) disappears, indicating that a pure Ni film is formed by the annealing process. Second, the annealing process enhances the crystallinity of the Ni film. Figure 4c shows the XRD data of the Ni films before and after the annealing process. In the XRD patterns, only Ni peaks (as discussed earlier in detail, Figure 2a) are observed, and the shapes of the peaks are sharper as the annealing temperatures increase. Therefore, the XRD analyses of the annealed films reveal that the crystallinity improves continuously with increasing annealing temperatures. The results of the quantitative analysis of the Ni peaks are further shown in Figure 4d. The grain size \( D \) as a function of the annealing temperature was calculated using Scherrer’s equation, as given by
Figure 4. Postannealing process. (a) Resistivity of the Ni film as a function of annealing temperature. (b) XPS analysis of the film after annealing at 380 °C. (c) XRD result of the films before and after annealing. (d) Calculated grain size as a function of annealing temperature based on the fcc Ni (111) peaks in (c). (e) Tilted cross-sectional SEM images of the films before and after annealing. The number of ALD cycles is 300, and t_{Ni} is the thickness of the film.

\[
D = \frac{k\lambda}{B \cos \theta}
\]

where \( k \), taken as 0.9 in this work, is a shape constant, \( \lambda \) (0.154187 nm) is the wavelength of the incident beam, \( B \) is the full width at half-maximum (FWHM) of the peak, and \( \theta \) is the Bragg angle. Although uncertainty in the shape constant and many assumptions of this equation make it difficult to define a value of grain size correctly,\(^{53} \) the trend obtained for the grain size is well matched with that of the resistivity. The scanning electron microscopy (SEM) images shown in Figure 4e further confirm that the grain size of Ni increases after annealing. This significant increase in the grain size and removal of the impurities now clearly explain the drastic decrease in the resistivity of the Ni ALD films after postannealing. Once the Ni ALD process is established with detailed investigations of the growth and properties of as-deposited and annealed films, we move to grow these Ni ALD films on single-layer graphene while keeping in mind several potential applications of such composites.

### 2.4. Selective Deposition of Ni on Defects of Graphene

The selective deposition was confirmed by electron microscopy. Figure 5a shows SEM images of the graphene substrate before and after the Ni ALD process. The lines on the surface of as-prepared graphene are wrinkles, which are mainly formed during the transfer process.\(^{42} \) The SEM image of graphene after 200 cycles of Ni ALD clearly shows that Ni is mostly deposited on the lines, which act as nucleation sites. Unlike an ideal graphene surface, defects such as holes and residues are present in the basal plane. These defects also act as deposition sites. Therefore, Ni islands are observed on the basal plane of graphene as the number of Ni ALD cycles increases to 500 and 800. Figure 5b shows the transmission electron microscopy (TEM) image of graphene after 500 cycles of Ni ALD. There are three lines visible on the graphene surface in Figure 5b, and Ni is selectively deposited on these lines. Figure 5c shows diffraction patterns (DPs) in various regions seen in Figure 5b. DPs corresponding to three graphene grains are observed over the entire region (two grains in the green circle and one grain in the yellow circle). The DPs in each region (named A, B, and C in Figure 5b) clearly show that the graphene grains in the three regions have different orientations. Accordingly, the lines in Figure 5b are defined as grain boundaries, and the selective deposition of Ni is confirmed to occur on both wrinkles and grain boundaries. Thus, the grain boundaries and several kinds of defects inside the basal planes promote further growth of Ni on graphene substrates.

Further, indexing of the diffraction data enabled us to define the components of the deposited material. Figure 5d shows the DP of the graphene surface, which reveals the presence of polycrystalline fcc Ni and fcc NiO on the surface. Figure 5e shows a high-resolution TEM image and fast Fourier transform (FFT) of selected areas (D and E). The islands in D and E are defined as pure fcc Ni and an fcc NiO–Ni mixture, respectively. The presence of NiO can be interpreted only as the result of exposure to a small number of oxygen molecules in the chamber or air after the ALD process because no oxygen components (in the Ni precursor, reactant, and purging gas) are involved in the current ALD process.

Atomic force microscopy (AFM) analyses more clearly show the tendency of selective deposition according to the number of Ni ALD cycles and provide quantitative information. Figure 6a shows the AFM images of graphene before and after the Ni ALD process, and these are in good agreement with our earlier SEM analyses of these films. The contrast of lines on the graphene surface becomes more apparent as the number of Ni ALD cycles increases, indicating that the heights of the lines increase. This result confirms that the line defects act as deposition sites, and the growth of Ni preferentially proceeds along these lines. The surface morphology is a key factor in determining the quality of the interface between graphene and other materials in device applications.\(^{43,44} \) The surface root mean square (RMS) roughness of the graphene substrate presented in Figure 6b shows that the flatness of graphene is maintained even after the formation of numerous Ni lines and islands. Although the RMS roughness increases with increasing Ni ALD cycles, the graphene maintains almost a flat structure as the roughness is restricted within 5 nm.

Typically, it is difficult to evaluate the conventional growth rate of ALD processes on pristine graphene because selective deposition inhibits the formation of a film. Inevitably, a general qualitative description of the deposition behavior is provided, with the conclusion that the deposition is suppressed by the selective deposition.\(^{32,33} \) However, the growth rate can be estimated by only observing morphological changes in the region where the material is deposited. Thus, a line profile analysis was performed on the Ni deposited lines. Figure 6c shows the average heights of the lines as a function of the number of Ni ALD cycles in the region shown in Figure 6a. The height is defined as the average of the height of each line, as measured in the line profile at several arbitrary points on the graphene surface. The details are shown in Figures S1 and S2 in the Supporting Information. The changes in the line height clearly show the two steps of Ni growth. There is no remarkable change in the height over the first 200 cycles,
whereas a Ni film was already formed on the SiO$_2$ substrate after 200 cycles of Ni ALD, as shown in Figure 3c. Therefore, the process up to 200 cycles is considered an incubation step in which Ni nuclei form on the line defects. This long incubation step indicates that nucleation by adsorption of the Ni precursor and the subsequent chemical reaction progress very slowly on the graphene defects. However, substantive Ni growth was achieved after 200 cycles of Ni ALD. In the growth step, the height increases almost linearly to 9.6 nm after 500 cycles and 18 nm after 800 cycles. The slope of the fitted line is 0.27 Å/cycle, which corresponds to the growth rate of Ni on graphene defects. The growth rate on graphene, which was estimated by excluding the incubation step, is smaller than that (1.1 Å/cycle) on SiO$_2$. Nevertheless, a few nanometers of Ni ALD on a graphene sheet could be well expected to alter (or enhance) the optoelectronic and catalytic properties when compared to pristine graphene. For example, our Ni ALD process enables the high optical transmittance ($T$) of graphene to be maintained when Ni is deposited on defects of graphene. Figure S3 in the Supporting Information shows the $T$ of graphene after Ni ALD. The $T$ of graphene is higher than that of the glass substrate and is maintained at above 90% up to 500 cycles.

Figure 5. Selective deposition on defects of graphene. (a) SEM images of graphene before and after Ni ALD. (b) TEM image of graphene after 500 cycles of Ni ALD. (c) Electron diffraction patterns of graphene for the regions shown in (b); $z$ is the zone axis. (d) Electron diffraction pattern of fcc Ni and fcc NiO on graphene. (e) High-resolution TEM images and FFT of islands (selected regions D and E) on the graphene.

3. CONCLUSIONS

A new thermal ALD process for depositing Ni thin films was developed using a novel heteroleptic Ni precursor, Ni(Chex)-(Cp)$_2$, and NH$_3$ as a reactant. Oxygen was excluded as a reactant, owing to the formation of NiO, whereas an oxygen-free Ni film was obtained when non-oxygen-based reactants (H$_2$ and NH$_3$) were used during the ALD process. However, the lowest resistivity achieved for the as-deposited film was obtained for the NH$_3$ reactant at a growth temperature of 340 °C. The self-limiting surface reaction was also confirmed by varying the exposure of both the precursor and reactant. As a result, the self-limited growth rate of 1.1 Å/cycle was obtained for Ni ALD on the SiO$_2$ substrate. An annealing process improved the quality of the as-deposited film by removing impurities and increasing the crystallinity of the film. Thus, low resistivity (44.9 $\mu\Omega$cm) was demonstrated by thermal ALD.
with a postannealing process. Graphene substrates exhibit distinctive deposition behavior, and Ni was selectively deposited on the chemically active sites of graphene such as wrinkles and grain boundaries. A relatively lower growth rate (0.27 Å/cycle) on defects of graphene indicates that the overall growth of Ni was slowed down. Consequently, the graphene maintained a flat structure after the ALD process, which may provide applicability as a two-dimensional functional material.

4. EXPERIMENTAL SECTION

4.1. Ni ALD and Annealing. The Ni precursor [Ni-(Chex)(Cp)] was developed as a prototype product of Tanaka Kikinzoku Kogyo K.K. (Japan). Ni thin films were deposited in a traveling wave-type ALD reactor (Lucida-D100, NCD Technology) using the precursor as a Ni source and various reactants (O2, H2, and NH3) within deposition temperatures of 320–340 °C. Ni(Chex)(Cp) is a liquid precursor (melting temperature: ~24 °C) and has a vapor pressure of ~1 Torr at 85 °C. The precursor was vaporized in a bubbler maintained at 50 °C and carried by a N2 gas with a flow rate of 50 sccm (standard cubic centimeters per minute). N2 gas (100 sccm) was also flowed during the purge steps between the precursor (reactant) pulse and reactant (precursor) pulse to remove the reaction by-products and residual precursor/reactant, if any. The purge time was fixed at 10 s, and the working pressure of the reactor chamber was maintained at ~1 Torr during all of the reactions. A SiO2 (100 nm)/Si substrate was used for Ni deposition. The postannealing process was performed in a rapid thermal annealing (RTA) chamber under a hydrogen atmosphere (with a flow rate of 50 sccm) and at ~0.3 Torr for 30 min.

4.2. Graphene Synthesis and Transfer Process. Single-layer graphene was synthesized on Cu through a CVD process. The first growth step was performed under a source gas flux (0.5 sccm CH4, 12 sccm H2, and 50 sccm Ar). In the second growth step, to synthesize fully covered graphene, the flow of CH4 was increased to 1 sccm. The process time for each step was 30 min, and the growth temperature was 1030 °C. Graphene transfer was achieved using a typical wet chemical transfer process35 whereby polymethylmethacrylate (PMMA) was first spin-coated onto the as-grown graphene. PMMA/graphene/Cu was then floated on a solution of 0.1 M ammonium persulfate overnight to etch the Cu. The remaining PMMA/graphene layers were then scooped onto a Si/SiO2 (285 nm) substrate. The residual PMMA was then removed by an annealing process (380 °C, in ambient air, 1 atm). Other details of the synthesis and transfer are the same as previously reported.32

4.3. Characterizations. XRD patterns were collected using an X’Pert MRD diffractometer (PANalytical) used for identification of materials and crystallinity. SEM analyses using an S-4800 system (Hitachi High Technologies) were performed to observe surface morphologies and measure the thicknesses of Ni films. The resistivities of the Ni films were measured using a four-point probe. Graphene was transferred onto a 20 nm-thick Si3N4 membrane using the transfer process described above, and then TEM analyses were conducted using a JEM-2100F system (JEOL). SEM images of graphene were acquired with a SUPRA 55VP field-emission scanning electron microscope (Carl Zeiss). AFM images were obtained using an S-4800 system (Hitachi High Technologies). TEM analyses were performed using an AXIS-HIS spectrometer (Kratos Inc.) with an X-ray source (Mg Kα, source energy: 1.254 keV, pass energy: 20 eV, step size: 0.1 eV) at a chamber base pressure of 5 × 10−10 bar. Spectra were recorded using a five-channel detector with a hemispherical analyzer (radius: 127 mm). An XPS software package (casa XPS, fitting method: a combination of Gaussian and Lorentzian GL(30)) was used to collect and quantify the data. Sputtering was performed using an argon sputter gun positioned at a 45° angle from the substrate normal. The Ni film was sputtered with Ar ions of 2 keV. During the XPS analysis of the Ni films, Ar-ion etching (300 s) was first performed to exclude surface contamination and to remove native metal oxides, which could be formed by exposure to air.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01003.

Standard reduction potentials of metals (Ni, Ru, and Pt), additional AFM data, and optical transmittance of

Figure 6. AFM analysis of the selective deposition of Ni on graphene. (a) AFM images of graphene before and after Ni ALD. (b) Surface RMS roughness of graphene and (c) average height of the lines as a function of the number of ALD cycles.
graphene as a function of the number of ALD cycles PDF)

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**Notes**
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