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Electronic Supplementary Information for:

High growth per cycle thermal atomic layer deposition of Ni films using an electron-rich precursor†

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Experimental section

All manipulations and reactions were carried out using standard Schlenk techniques or in a glovebox under nitrogen atmosphere. Toluene and hexane were freshly distilled from Na prior to use. $Ni(acac)_2$ (**1**) was purchased from J&K Chemical and used without further purification. $Ni(acac)_2(tmeda)$ (**2**), $Ni(acac)_2(py)_2$ (**3**), $Ni(acac)_2(pipz)$ (**4**), $Ni(acac)_2(dppe)$ (**5**), $Ni(acac)_2(pph_3)_2$, and $Ni(acac)_2$(γ-pico) was synthensized according to the literature.[1-4] Anhydrous hydrazine (N_2H_4) was purified from hydrazine hydrate. Nickel powder (99.9%) was purchased from J&K Chemical and annealed at 600 °C for 12 h in the forming gas (N_2/10%-H_2) prior to use.

The thermal properties of compounds were analyzed by an STA 449 F3 analyzer in argon at a heating rate of 10 °C min^{-1} from 30 to 600 °C. The thermal chemistry of selected compounds were studied by a Thermo Fisher Scientific Nicolet 6700 attenuated total internal reflectance fourier transform infrared spectroscopy (ATR-FTIR). The samples for measurement were prepared through sufficient vapor of compounds adsorb on nickel powder under different deposition temperature in a thermal ALD reactor. The sublimation temperatures of $Ni(acac)_2(tmeda)$, $Ni(acac)_2$, $Ni(acac)_2(py)_2$ and $Ni(acac)_2(dppe)$ were kept at 95°C, 150 °C, 130 °C and 150 °C, respectively.

The ALD of nickel films were deposited on SiO_2/Si(100) substrates and the substrates were ultrasonically cleaned in acetone, isopropanol and deionized water in sequence prior to ALD. The SiO_2 thickness was about 100 nm, which is a thickness sufficient to avoid the formation of silicides.[5]

A thermal ALD reactor (MNT f-150-212) was employed for depositing. The sublimation temperatures of $Ni(acac)_2(tmeda)$, $Ni(acac)_2(py)_2$ and N_2H_4 were maintained at 95°C, 130 °C and 40 °C, respectively. The working pressure was kept at 50-60 Pa under a flow of nitrogen (99.999%), and nitrogen was also used as both the carrier and purge gas. The substrate temperature was investigated at 220-300 °C for $Ni(acac)_2(tmeda)$ and 200-300 °C for $Ni(acac)_2(py)_2$. One ALD cycle include alternate pulses of precursor ($Ni(acac)_2(tmeda)$ or $Ni(acac)_2(py)_2$) (pulse time t_s) and reducing agent (N_2H_4) (pulse time t_r), separated by a purge time (t_p) which was fixed at 20 s. The modified ALD process, which was used to verify the "anchoring" mechanism, was described as follows: the initially thin Ni layer deposition ($Ni(acac)_2(tmeda)$ (10 s) – purge (20 s) – hydrazine (2 s) – purge (20 s), 30 ALD cycles), subsequently, the modified ALD mode (tmeda (2 s) – purge (20 s) – $Ni(acac)_2(tmeda)$ (10 s) – purge (20 s) – hydrazine (2 s) – purge (20s), 470 ALD cycles) was performed.

The surface morphology and thickness of the films were studied by a Bruker Multimode 8 atomic force microscopy (AFM), a Hitachi S-4800 scanning electron microscopy (SEM) and a Bruker D8 X-ray reflection (XRR). The growth per cycle (GPC) value of process was calculated by divide film thickness by the number of deposition cycles. The composition and the crystalline phase of films were analysed using a Thermo ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS) and a Bruker D8 X-ray diffraction (XRD). The resistivity of films was measured by four-point-probe measurements.

Thermal properties of electron-rich nickel compounds

Table S1. Thermal properties of several reported electron-rich nickel compounds.

Compound[a]	Volatilization temperature (^{o}C)	Reference
$Ni(acac)_2$(γ-pico)	201-295	---
$Ni(acac)_2$(pipz)	183-313	---
$Ni(acac)_2(py)_2$	199-303	---
$Ni(acac)_2$(teen)	95-322	6
$Ni(acac)_2$(*unsym*-dmen)	135-230	6
$Ni(acac)_2$(tmeda)	114-208	---
$Ni(acac)_2(pph_3)_2$	233-286	---
$Ni(acac)_2$(dppe)	238-341	---

[a] Abbreviations: acac, acetylacetonate; γ-pico, 4-methylpyridine; pipz, piperazine; py, pyridine; teen, N,N,N',N'-tetraethylethylenediamine; *unsym*-dmen, N,N-diethylenediamine; tmeda, N,N,N’,N’-tetramethylethylenediamine; pph_3, triphenylphosphine; dppe, 1,2-bisdiphenyl-phosphinoethane.

Cross sectional SEM image of Ni film grown by thermal ALD using $Ni(acac)_2(tmeda)$ and N_2H_4 under different deposition temperature

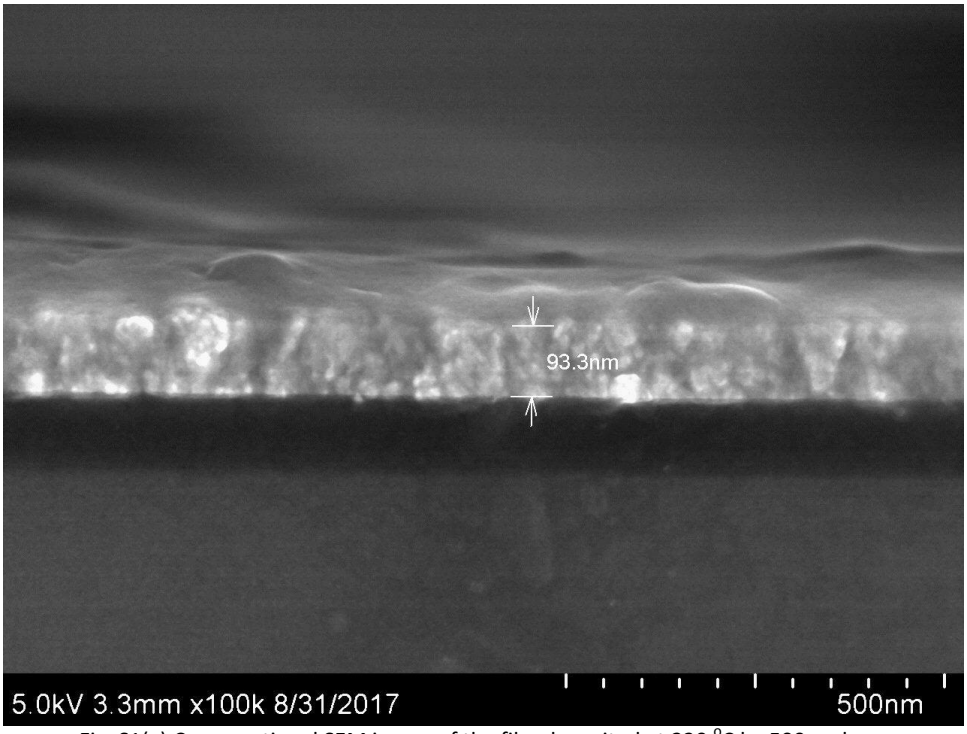

Fig. S1(a) Cross sectional SEM image of the film deposited at 220 ^{o}C by 500 cycles.

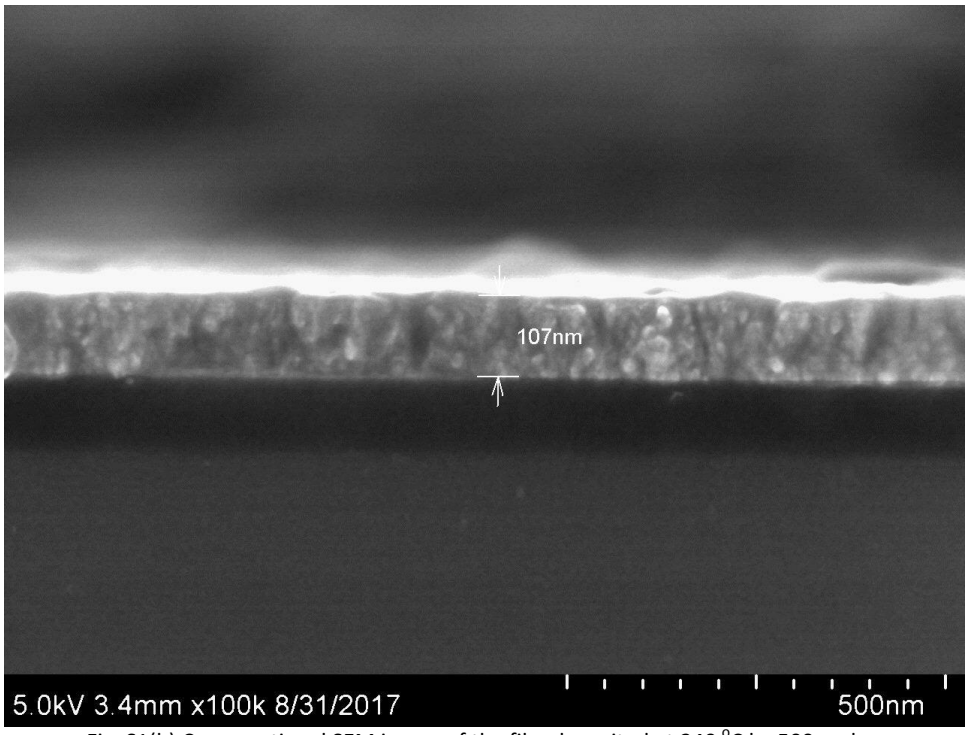

Fig. S1(b) Cross sectional SEM image of the film deposited at 240 ^{o}C by 500 cycles.

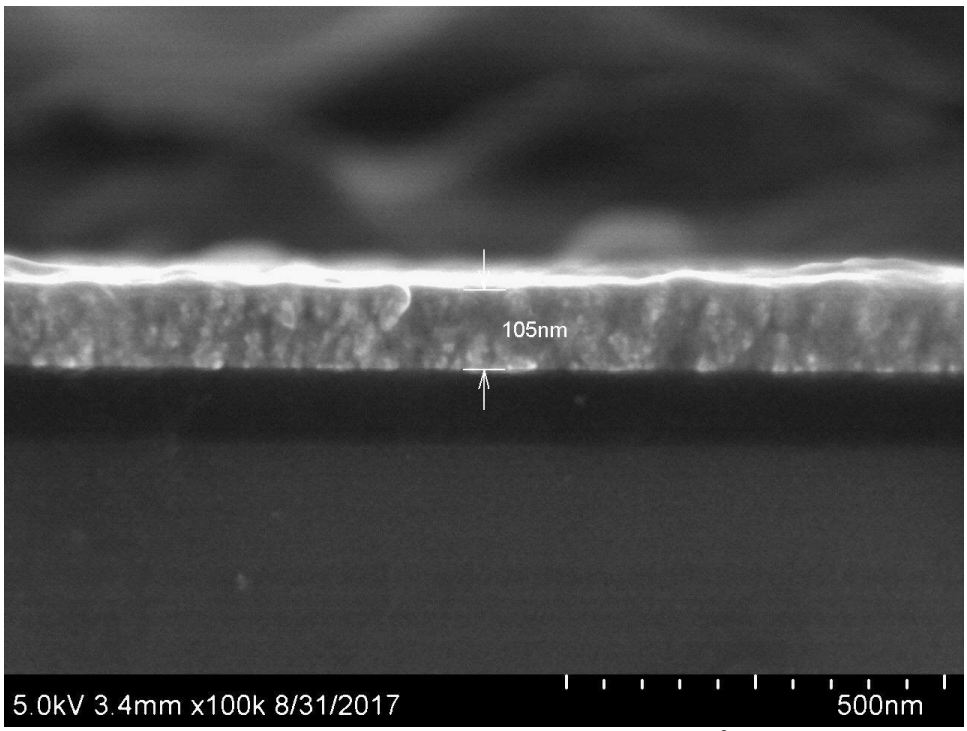

Fig. S1(c) Cross sectional SEM image of the film deposited at 260 ^{o}C by 500 cycles.

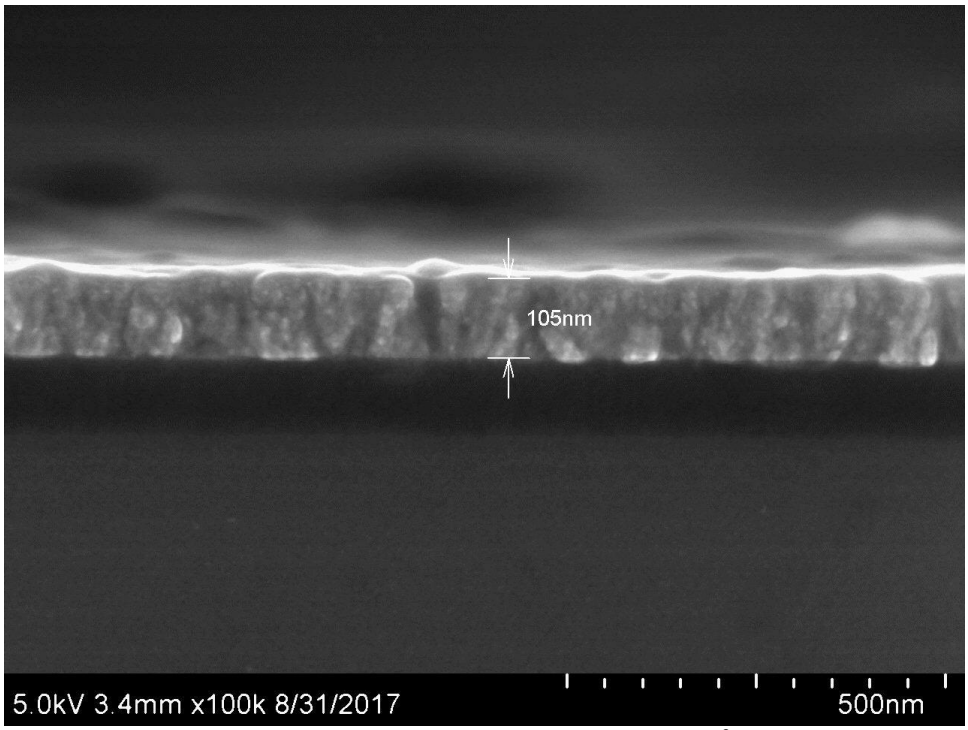

Fig. S1(d) Cross sectional SEM image of the film deposited at 280 ^{o}C by 500 cycles.

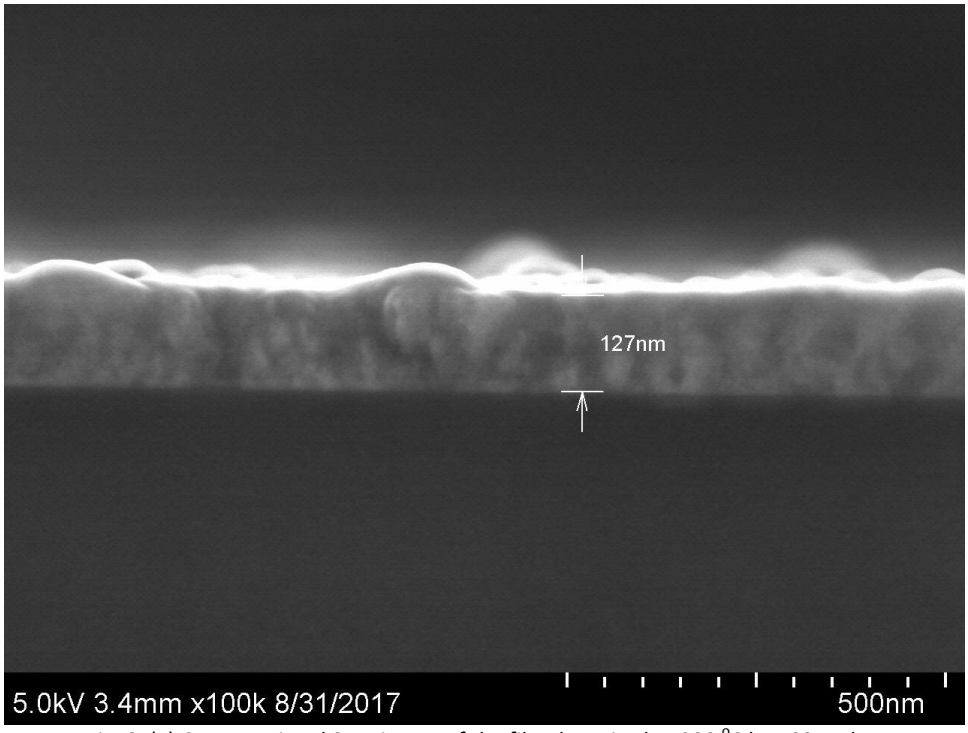

Fig. S1(e) Cross sectional SEM image of the film deposited at 300 ^{o}C by 500 cycles.

Resistivity of Ni film grown at different deposition temperatures

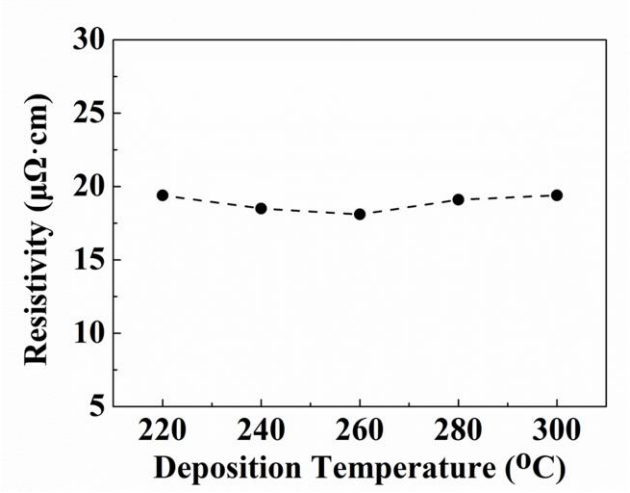

Fig. S2 Resistivity of Ni film as a function of deposition temperature at a fixed $Ni(acac)_2(tmeda)$ pulse time of 10 s and N_2H_4 pulse time of 2 s.

XPS of Ni film grown by thermal ALD using $Ni(acac)_2(tmeda)$ and N_2H_4

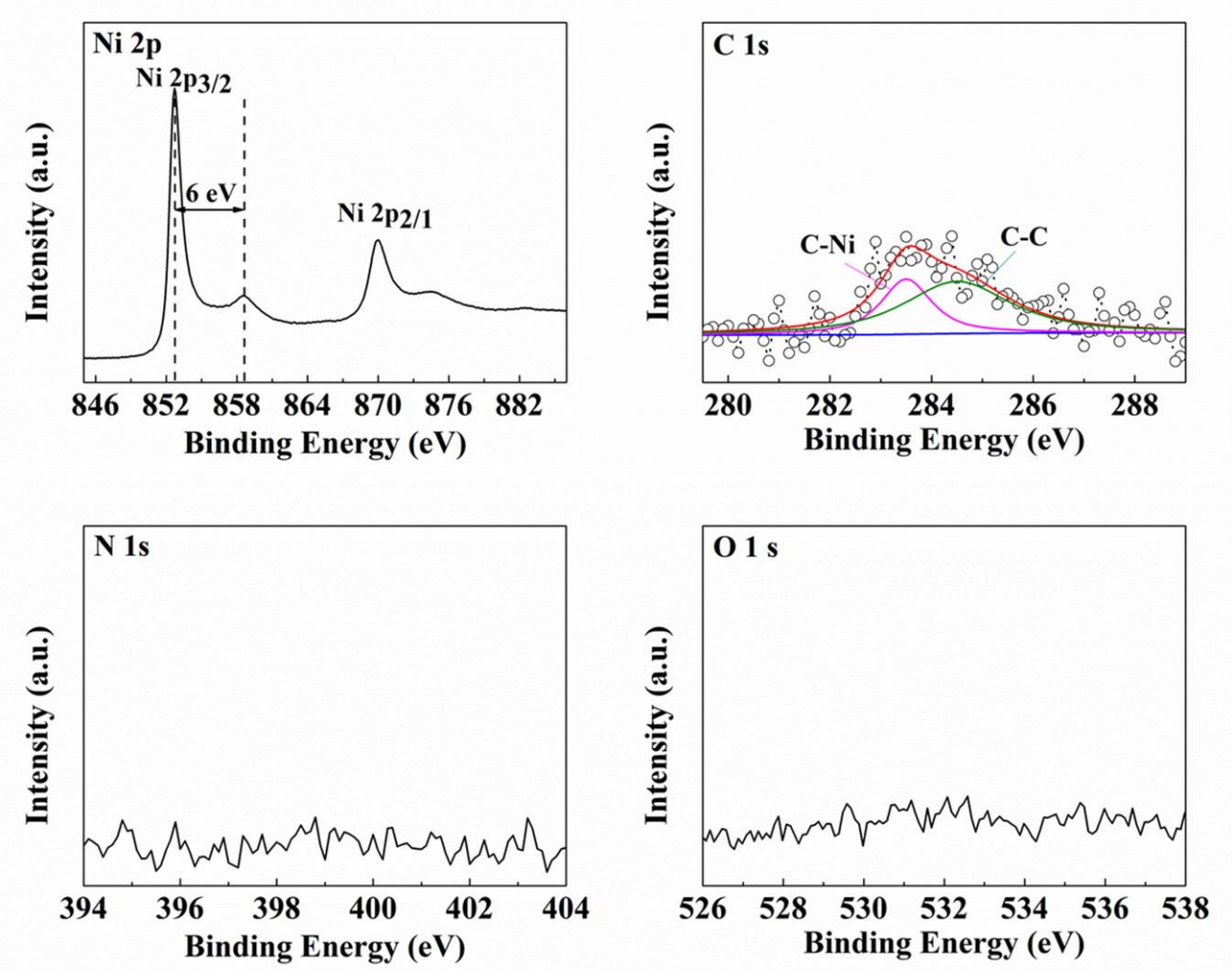

Fig. S3 Ni 2p, C 1s, N 1s and O 1s XPS spectra of Ni film grown at 260 °C.

The composition of 100 nm nickel film grown at 260 ^{o}C was studied by X-ray photoelectron spectroscopy (XPS). The deposited film is composed of Ni content (95.1%), few C content and a negligible amount of N and O after in situ Ar ion etching for 30 s. Ni $2p_{3/2}$ and Ni $2p_{2/1}$ peaks of metallic Ni are observed at 852.7 eV and 870.0 eV, and a satellite peak of Ni $2p_{3/2}$ is observed at 858.7 eV that is due to surface plasmon loss and interband transitions effect.[7,8] Moreover, the C 1s spectrum can be divided into two peaks by Gaussian–Lorentzian function, each of which can be attributed to C-Ni at 283.5 eV and C-C at 284.5 eV, respectively.[9] And the small carbon content of film is possibly introduced by incorporation of the produced byproducts into the film in the deposition process, and then forms bonding of Ni and C element.[10]

SEM and AFM images of Ni film grown by thermal ALD using $Ni(acac)_2(tmeda)$ and N_2H_4

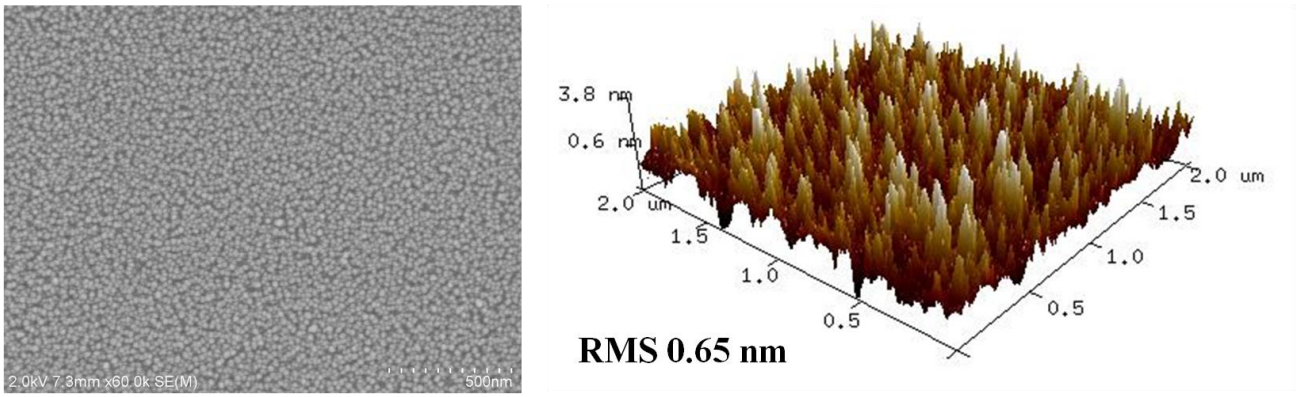

Fig. S4 SEM (left) and AFM (right) of Ni film grown at 260 °C.

As seen in Fig. S4, the film deposited at 260 °C is continuous and composed of grains, and the root-meansquare (RMS) roughness about 0.65 nm of film indicates a smooth surface.

Structure transition of electron-rich compounds

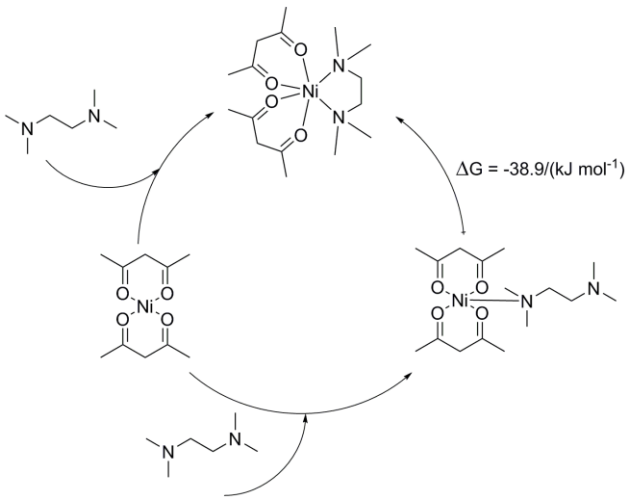

Fig. S5 Free energy for the transformation process from $Ni(acac)_2$ to $Ni(acac)_2$(TMEDA) at 298 K.

Taking $Ni(acac)_2$(TMEDA) as a sample, $Ni(acac)_2$ initially reacts with TMEDA and form a pentacoordinate intermediate, and then form a hesacoordinate compound ($Ni(acac)_2$(TMEDA)). It is found that the total ΔG for transition of $Ni(acac)_2$(TMEDA) from hesacoordinate to pentacoordinate at 298 K is 38.9 KJ mol^{-1}, which suggests that the transformation process is possible with some addition thermal energy. Therefore, in the temperature range of ALD, one of the N atom can break away from $Ni(acac)_2$(TMEDA) and form a pentacoordinate intermediate.[11]

ALD process of Ni film grown by thermal ALD using $Ni(acac)_2(py)_2$ and N_2H_4

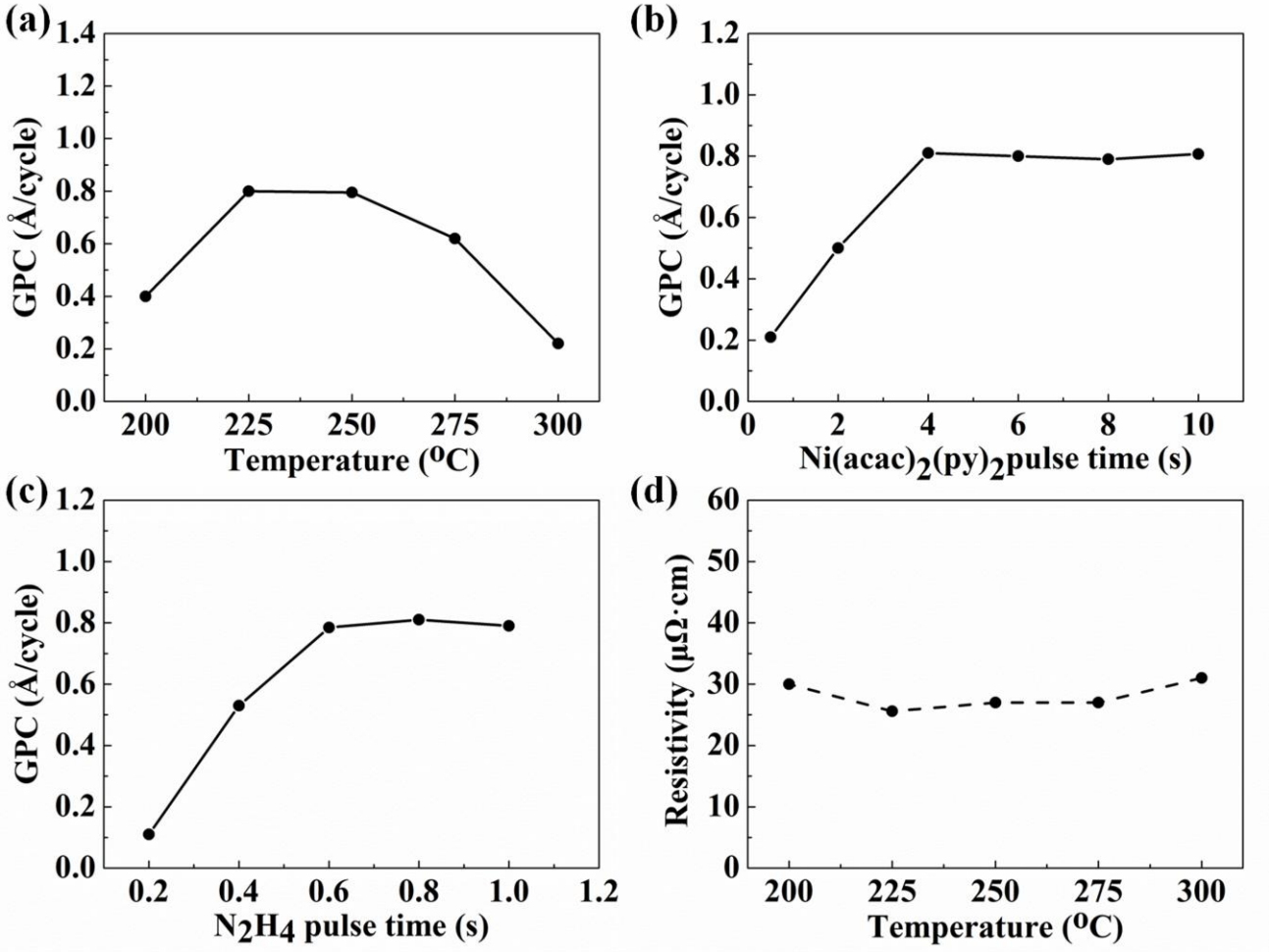

Fig. S6 (a) GPC of Ni film as a function of deposition temperature at a fixed $Ni(acac)_2(py)_2$ pulse time of 10 s and N_2H_4 pulse time of 2 s. (b) GPC of Ni film versus $Ni(acac)_2(py)_2$ pulse time at 250 °C with a fixed N_2H_4 pulse time of 2 s. (c) GPC of Ni film versus N_2H_4 pulse time at 250 °C with a fixed $Ni(acac)_2(py)_2$ pulse time of 10 s. (d) Resistivity of Ni film as a function of deposition temperature at a fixed $Ni(acac)_2(py)_2$ pulse time of 10 s and N_2H_4 pulse time of 2 s.

Fig. S6a shows plots of GPC value versus deposition temperature with $Ni(acac)_2(py)_2$ (10 s) and N_2H_4 (2 s). It is found that a stable value (0.79 Å/cycle) is achieved between 225 and 250 ^{o}C. Obviously, the temperature of 225-250 ^{o}C should be an ALD window in this process. The GPC value decreases at > 250 °C, mostly likely because of the desorption of precursor.[12,13] Fig. S6b shows plots of GPC value versus pulse time of $Ni(acac)_2(py)_2$ at 250 ^{o}C. The GPC value achieves a saturated value (0.79 Å/cycle) when the pulse time of $Ni(acac)_2(py)_2$ exceeds 4 s. Similar, a saturated value (0.80 Å/cycle) is achieved when the N_2H_4 pulse

time exceeds 0.6 s (Fig. S6c). Certainly, these experiment datas demonstrate that this process is a typical ALD process. Moreover, the resistivity of deposited films were measured about 25.7-31.1 μΩ·cm (Fig. S6d).

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