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Electronic Supplementary Information (ESI)

Direct-Liquid-Evaporation Chemical Vapor Deposition of Smooth, Highly Conformal Cobalt and Cobalt Nitride Thin Films

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Figure S1. Electron Diffraction (ED) image of DLE-CVD Co deposited with 50 sccm NH_3 and 150 sccm H_2 on a silicon nitride membrane.

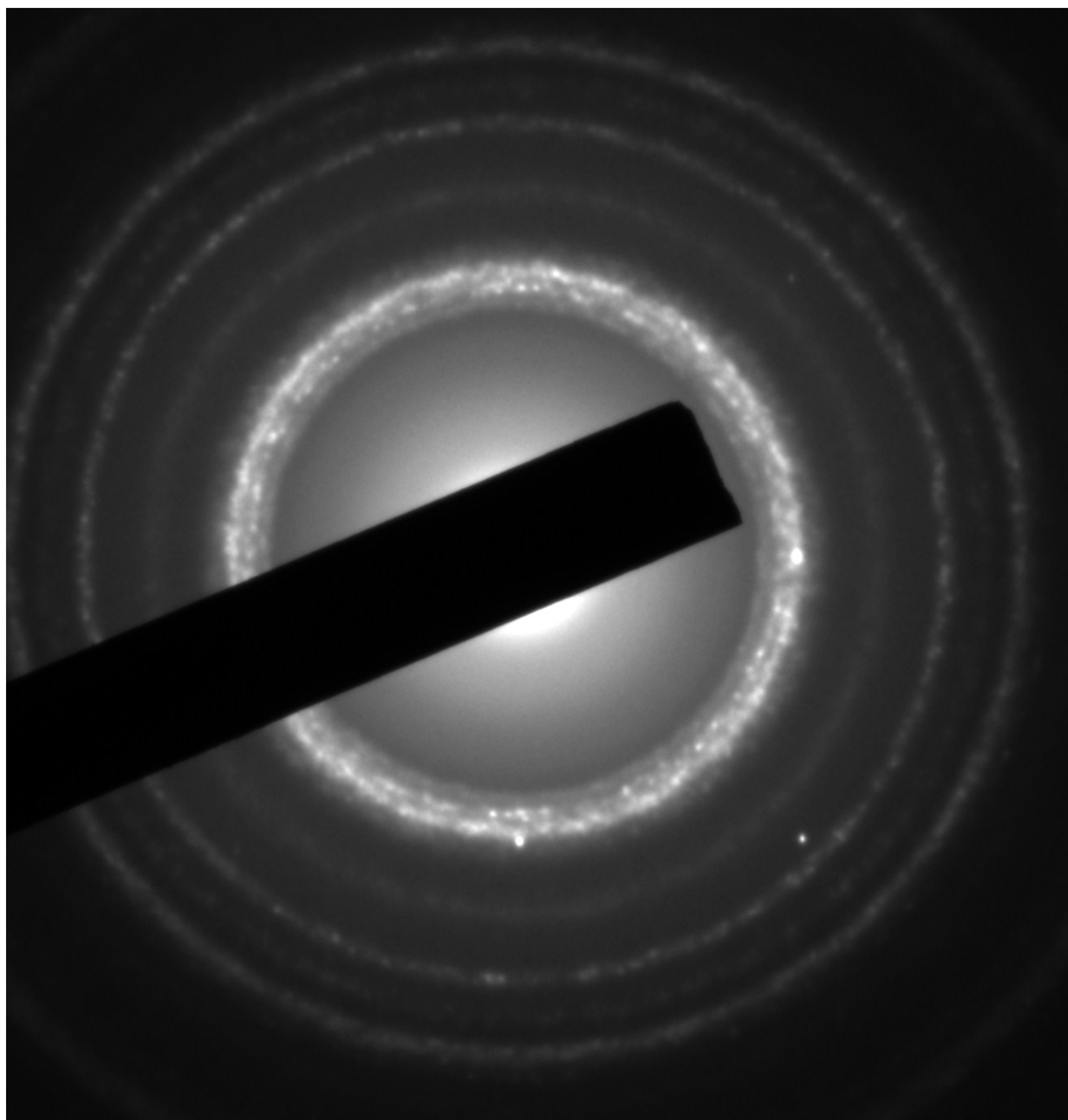

Table S1. ED results for a DLE-CVD Co film deposited on a TEM grid formed by a SiN_x membrane (50 nm thick) suspended across a hole in a silicon substrate. The film was deposited using a mixture of 20 sccm NH_3 and 180 sccm H_2 gases as co-reactants. The rings belong to the cubic Co phase, and the discrete spots came from the Si substrate, which was used for internal calibration.

	fcc β-Co				
No.	hkl	d (Å)[a]	Int[a]	measured d (Å)	error (%)
1	111	2.05	100	2.04	-0.5
2	200	1.77	40	1.78	0.6
3	220	1.25	25	1.26	0.8
4	311	1.07	30	1.08	0.9

[a] The indices of planes (hkl), interplanar spacings (d), and intensities (Int) shown in this table represent the reference crystal structures of fcc β-Co (PDF Card No.15-0806).

Table S2. ED results for DLE-CVD CoN_x film using a mixture of 50 sccm NH_3 and 150 sccm H_2 as co-reactants. The rings belong to a mixture of cubic and hexagonal Co phase, with major diffraction peaks corresponding to cubic Co phase.

	fcc β-Co			hcp α-Co				
No.	hkl	d (Å)[a]	Int[a]	hkl	d (Å)[a]	Int[a]	measured d (Å)	error (%)[b]
1				100	2.17	27	2.15	-0.9
2	111	2.05	100	2	2.03	28	2.05	0.0
3				101	1.92	100	1.91	-0.5
4	200	1.77	40				1.77	0.0
5	220	1.25	25				1.26	0.8
6	311	1.07	30				1.07	0.0
7	222	1.02	12				1.02	0.0

[a] For Tables S2 through S4, the indices of planes (hkl), interplanar spacings (d), and intensities (Int) represent the reference crystal structures of fcc β-Co (PDF Card No.15-0806), hcp α-Co (PDF Card No. 71-4239).

[b] For Tables S2 through S4, error means the difference between measured value and the closest reference value, expressed as a percentage.

Table S3. ED Results for a DLE-CVD Co film made using a mixture of 100 sccm NH_3 and 100 sccm H_2 as co-reactants. The rings belong to a mixture of cubic and hexagonal Co phase, with major diffraction peaks corresponding to cubic Co phase.

	fcc β-Co			hcp α-Co				
No.	hkl	d (Å)[a]	Int[a]	hkl	d (Å)[a]	Int[a]	Measured d (Å)	error (%)[b]
1				100	2.17	27	2.18	0.5
2	111	2.05	100	002	2.03	28	2.06	0.5
3				101	1.92	100	1.92	0
4	200	1.77	40				1.79	1.1
5				102	1.48	11	1.49	0.7
6	220	1.25	25				1.26	0.8
7	311	1.07	30				1.07	0

Table S4. ED results for a DLE-CVD Co film made using a mixture of 150 sccm NH_3 and 50 sccm H_2 as co-reactants. The rings belong to a mixture of cubic and hexagonal Co phase, with major diffraction peaks corresponding to cubic Co phase.

	fcc β-Co			hcp α-Co				
No.	hkl	d (Å)[a]	Int[a]	hkl	d (Å)	Int	Measured d (Å)	error [b](%)
1				100	2.17	27	2.18	0.5
2	111	2.05	100	2	2.03	28	2.05	0.0
3				101	1.92	100	1.91	-0.5
4	200	1.77	40				1.79	1.1
5				102	1.48	11	1.49	0.4
6	220	1.25	25	110	1.25	10	1.26	0.8
7				103	1.15	10	1.15	0.0
8	311	1.07	30				1.07	0.0

Table S5. ED results for a DLE-CVD Co_3N film made using 200 sccm NH_3 as the only co-reactant.

No.	hcp Co_3N hkl	d (Å)[a]	Int[a]	measured d (Å)	Error (%)
1	100	2.31	20	2.32	0.4
2	002	2.17	50	2.19	0.9
3	101	2.04	100	2.06	1.0
4	102	1.59	50	1.59	0
5	110	1.33	50	1.35	1.5
6	103	1.23	70	1.23	0
7	112	1.14	50	1.14	0

The rings belong to the hexagonal Co_3N phase, and the discrete spots came from Si substrate, which was used for internal calibration.

[a] The indices of planes (hkl), interplanar spacings (d), and intensities (Int) shown in this table represent the reference crystal structures of hcp Co_3N (PDF Card No. 06-0691)

Figure S2. Arrhenius plot showing the natural logarithm of the DLE-CVD Co deposition rate at temperatures from 200 to 240°C versus the reciprocal of the temperature. The cobalt precursor solution (12 wt% of Co(^{i}Pr-MeAMD)$_2$ in tetradecane) was delivered at a flow rate of 5g/hr along with 100 sccm N_2 carrier gas, and then vaporized at 180°C before entering the reactor. The deposition was performed on thermal oxide substrates using 100 sccm NH_3 and 100 sccm H_2, at 10 Torr total pressure.

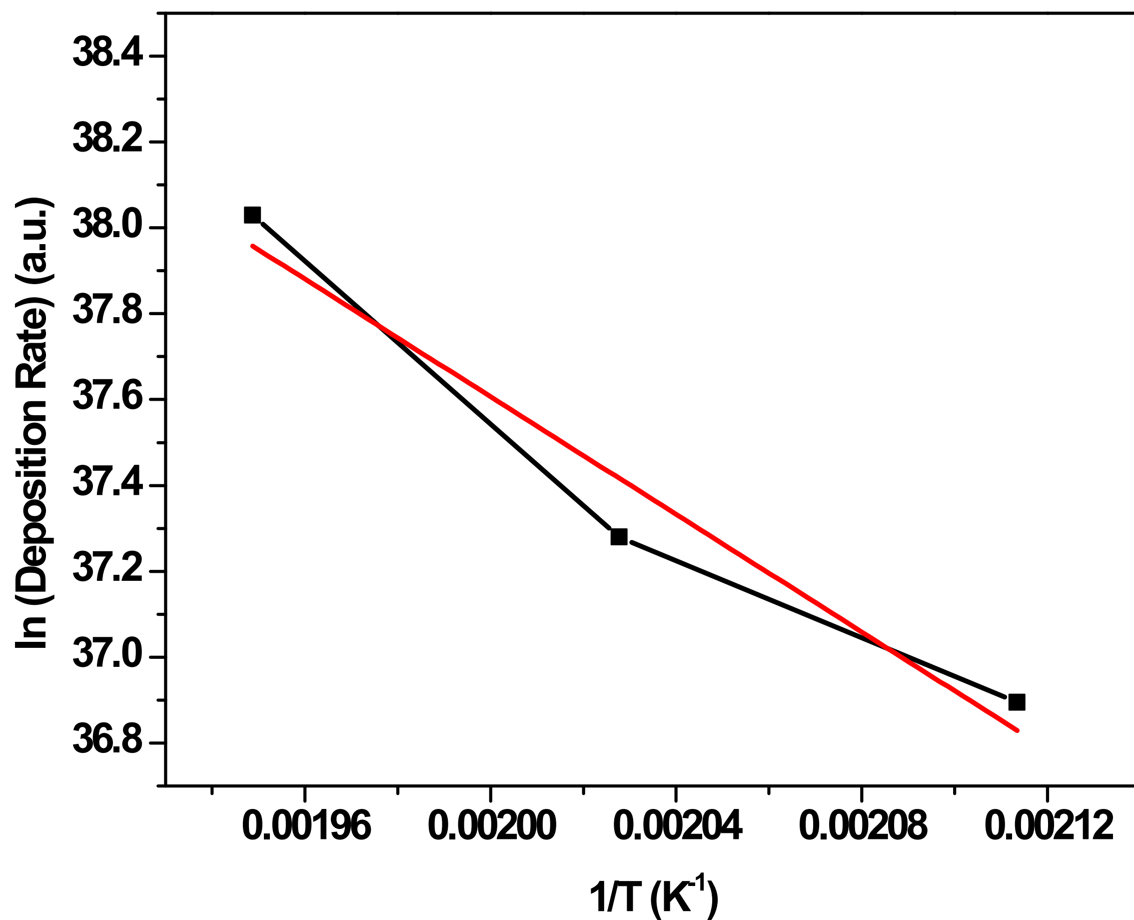

Figure S3. (a) The deposition rate (measured by XRF counts per minute) and (b) the sheet resistance of DLE-CVD Co films as a function of the cobalt precursor solution delivery rate. The cobalt precursor solution (12 wt% of Co(^{i}Pr-MeAMD)$_2$ in tetradecane) was delivered at flow rates between 5 and 20 g/hr along with 100 sccm N_2 carrier gas, and vaporized at 180°C before entering the reactor. The deposition was performed on thermal oxide substrates at 200°C using 100 sccm NH_3 and 100 sccm H_2, at 10 Torr.

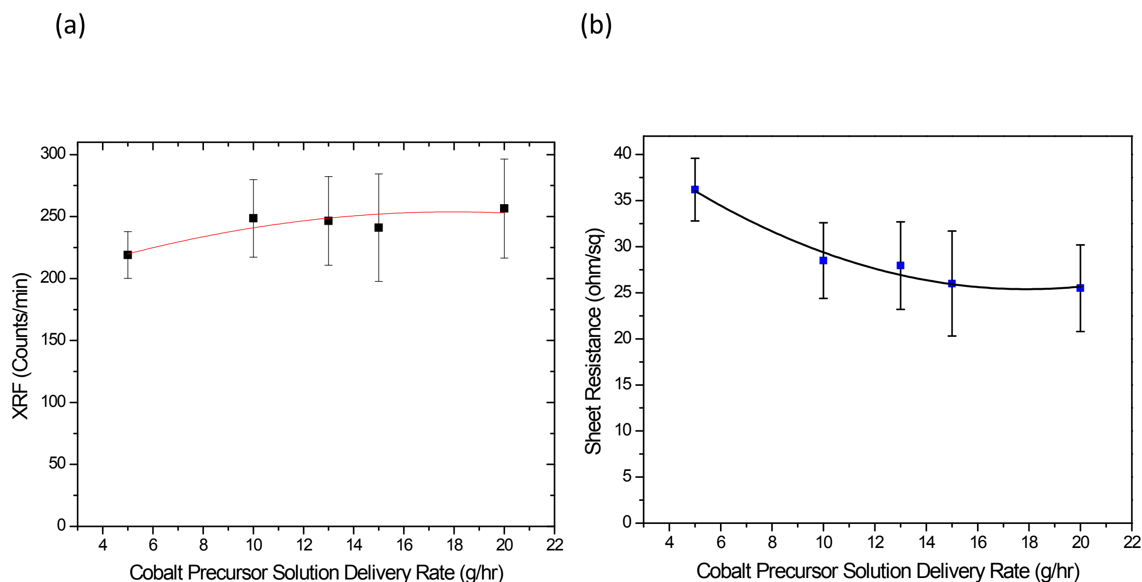

Figure S4. (a) XRR experimental curve and (b) fitted simulation line of a DLE-CVD Co film deposited on thermal oxide; the thickness is calculated to be 23 nm.

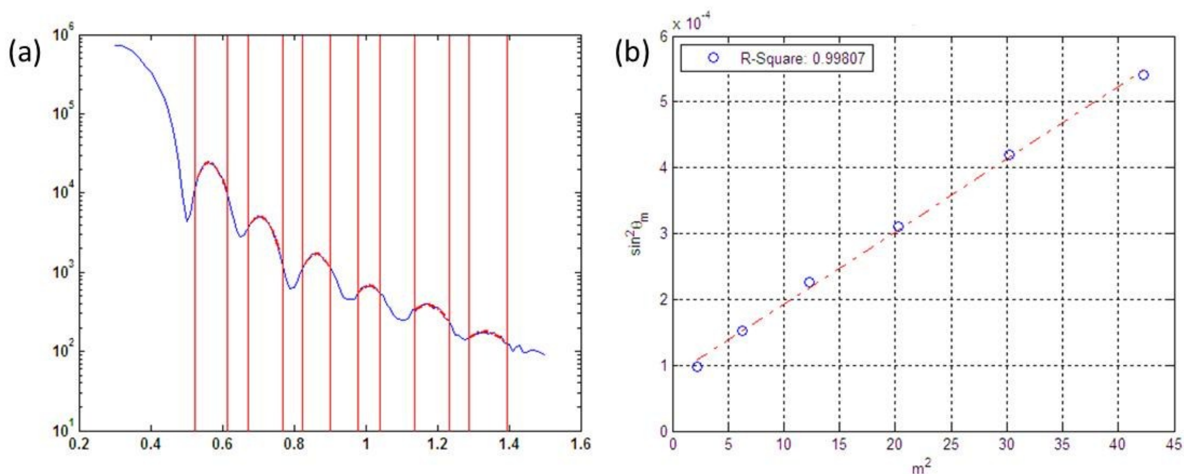

Figure S5. Schematic diagram of the DLE-CVD system

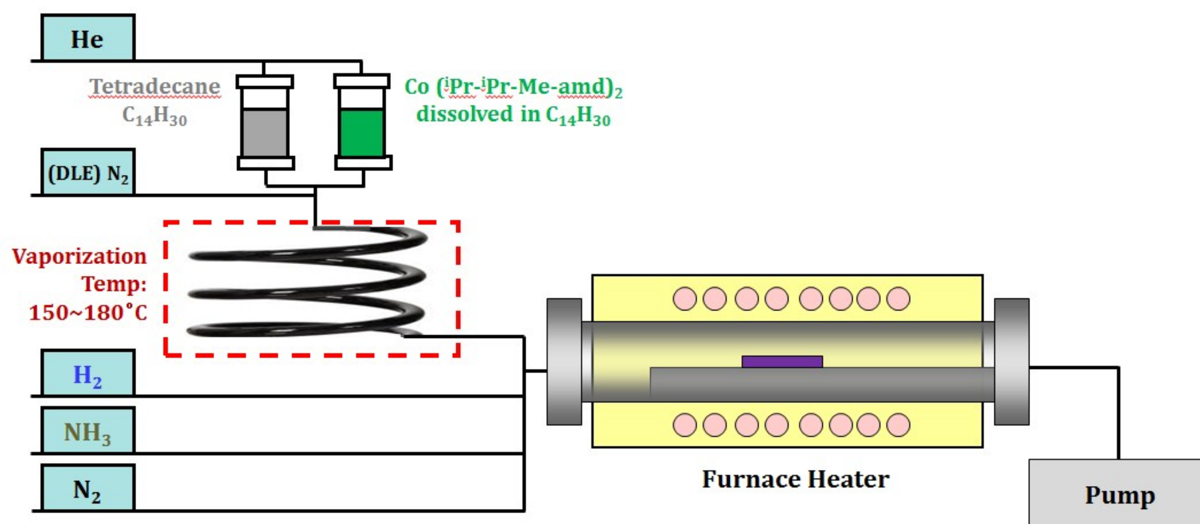

Figure S6. The deposition rate (cobalt film growth rate) as a function of the cobalt precursor partial pressure. The cobalt precursor solution (12 wt% of $Co(^{i}Pr\text{-}MeAMD)_2$ in tetradecane) was delivered at flow rates between 5 and 20 g/hr along with 100 sccm N_2 carrier gas, and vaporized at 180°C before entering the reactor. The deposition was performed on thermal oxide substrates at 200°C using 100 sccm NH_3 and 100 sccm H_2, at 10 Torr.