Diamine Adduct of Cobalt(II) Chloride as a Precursor for Atomic Layer Deposition of Stoichiometric Cobalt(II) Oxide and Reduction Thereof to Cobalt Metal Thin Films

Katja Väyrynen,*†‡ Timo Hatanpää,‡ Miika Mattinen,‡ Mikko Heikkilä,‡ Kenichiro Mizohata,‡ Kristoffer Meinander,‡ Jyrki Raisänen,‡ Mikko Ritala,‡ and Markku Leskelä‡

Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014 Helsinki, Finland
Department of Physics, University of Helsinki, P.O. Box 43, FI-00014 Helsinki, Finland

Supporting Information

ABSTRACT: In this paper, we introduce a new Co precursor for the atomic layer deposition (ALD) of Co metal and other Co containing materials. CoCl₂(TMEDA) (TMEDA = N,N,N',N'-tetramethylethylenediamine) is a diamine adduct of cobalt(II) chloride that is inexpensive and easy to synthesize, making it an industrially viable precursor. Furthermore, CoCl₂(TMEDA) shows good volatility at reasonably low temperatures and is thermally stable up to a temperature of ~300 °C. We also present a full ALD study for the deposition of CoO thin films using CoCl₂(TMEDA) and water as precursors. The process was investigated within a temperature range of 225–300 °C. Saturation of the film growth with respect to both precursor pulse lengths was verified. According to X-ray diffraction, the films were a mixture of hexagonal and cubic CoO. No reflections corresponding to Co₃O₄ were detected. The hexagonal phase is characteristic to nanomaterials only and is not seen in bulk CoO. The crystal structure of the films could be tuned by temperature, water pulse lengths, and type of substrate material. The films deposited at 275 °C exhibited 1:1 Co:O stoichiometry and very high purity. The CoO films could be reduced to Co metal at an exceptionally low temperature of 250 ºC in 10% forming gas. Continuity of the reduced Co films was improved when the CoO film was deposited on TiN instead of native oxide terminated Si. The Co content of a 50 nm reduced metal film was as high as 95 at. %, with negligible amounts of oxygen and hydrogen.

INTRODUCTION

Cobalt metal serves as an important material for liners and caps needed to suppress electromigration in copper interconnects.1–4 As feature sizes in microelectronics get smaller, Co may at some point replace Cu as the dominant conductor material altogether.5 In fact, Intel has already replaced Cu with Co at the bottom layers of their 10 nm technology interconnect stack.6 Additionally, Co thin films are needed as precursors for the deposition of CoSi₂, a useful contact material, and for the development of magnetic memories.7–9 The oxides of cobalt, on the other hand, have applications in emerging energy technologies, such as Li-ion batteries and electrochemical water oxidation, as well as catalysis and gas sensing.10–18

For the majority of future applications, it is essential to have high-quality thin films deposited uniformly over large areas and complex 3D structures. The only method that can match these requirements is atomic layer deposition (ALD).19–21 The development of ALD processes for Co and its oxides has, however, been hindered by the lack of suitable precursors. The deposition of Co metal usually requires temperatures above 300 °C or plasma-enhancement.22–24 The only low-temperature ALD processes for Co have been realized using bis[(1,4-di-tert-butyl-1,4-diaza-1,3-butadiene) cobalt(II) [Co(tBuDAD)₂] with formic acid, tert-butylamine, or diethylamine as the reducing agent.47–49 Even then, a catalytic metal substrate was needed to initiate nucleation. A metal substrate (Ru) was necessary also when Co was deposited with a Co(II) α-imino alkoxide complex and BH₃(NHMe)₂, and the film growth stopped after the substrate surface was covered.50 Low-temperature ALD has also been claimed from (Bu-Allyl)Co(CO)₃ and dimethylhydrazine, though no ALD characteristics were shown.51 An alternative way to obtain Co metal films by ALD is to reduce ALD grown CoO films. The indirect approach may be useful especially in cases where a catalytic metallic substrate or plasma-enhancement is unsuitable. The deposition of thin yet continuous metal films requires low process temperatures and proper wetting layers to suppress agglomeration.52 Alburquenque et al. have deposited Co metal films indirectly via reduction of CoOₓ deposited with CoCp₂ and ozone; however, the
by establishing a new process for the deposition of CoO thin films. Pure, stoichiometric CoO films were deposited with a saturated growth rate of 0.4 Å/cycle at 275 °C. The CoO films were readily reduced to Co metal at 250 °C in 10% forming gas. Since CoCl2(TMEDA) shows high enough reactivity toward water, it may also be suitable for the direct ALD of Co metal, provided that it is combined with a strong enough reducing agent. The focus of this paper will, however, be on the deposition of CoO and exhibit sufficient thermal stability.

Herein, we present a promising new precursor, CoCl2(TMEDA), for the ALD of Co containing materials. The schematic structure of the compound is illustrated in Figure 1. The suitability of the precursor for ALD was verified by deposition on a variety of substrates and materials.

**Experimental Section**

**Precursor Synthesis and Characterization.** Synthesis and manipulation of all compounds were done under rigorous exclusion of air and moisture using standard Schlenk and glovebox techniques. Anhydrous CoCl2 (99%, Aldrich) and N,N,N′,N′-tetramethyl ethylenediamine (99%, Aldrich) were used as received. CH2Cl2 was deoxygenized and dried over 4 Å molecular sieves. Thermogravimetric analyses (TGA) were carried out on a Netzsch STA 449F3 Jupiter simultaneous thermal analyzer (STA). The measurements were done using a flowing nitrogen (40 mL/min) atmosphere at 1 atm, and under dynamic vacuum (~0.1 mbar). The heating rate was 10 °C/min, and the weight of the sample was 10 ± 1 mg. Melting point was taken from the differential scanning calorimetry (DSC) data measured by the STA. Mass spectrum was recorded with a JEOL JMS-700 operating in an electron impact mode (70 eV) using a direct insertion probe and a sublimation temperature range of 25–300 °C.

**Synthesis of CoCl2(TMEDA).** 6.00 g of CoCl2 (46.211 mmol) was weighed into a 300 mL Schlenk bottle. 100 mL of CH2Cl2 was added. A stoichiometric amount of TMEDA (5.37 g, 46.211 mmol) was then added dropwise to a stirred suspension. The product was sublimed out at 150–200 °C/0.1 mbar. The yield of the blue product was 11.30 g (theoretical 11.37 g), that is, 99.4%, mp 167–179 °C; m/z (EI, 70 eV) 245 [M]+, 210 [M − Cl]+, 116 [Cl]+.

**Film Deposition.** All the films were deposited in a hot-wall cross-flow F-120 ALD reactor (ASM Microchemistry). Nitrogen (AGA, 99.9999%; H2O ≤ 3 ppm; O2 ≤ 3 ppm) was employed as the carrier gas and for purging the reaction chamber. The carrier gas flow rate was 400 sccm. The reactor was operated under a pressure of ~10 mbar. CoCl2(TMEDA) was sublimed from an open glass boat held inside the reactor at 170 °C. Deionized water was used as the oxygen source. The pulse lengths, controlled by inert gas and mechanical valving, were varied from 0.5 to 2.0 s for CoCl2(TMEDA) and from 0.5 to 5.5 s for water. The purge times following the Co precursor and water pulses were typically 1.0 and 3.0 s, respectively. Saturation of the growth rate with respect to the CoCl2(TMEDA) pulse length was studied with 1.0 s purges for water. The oxide process was investigated within a temperature range of 225–300 °C. The films were deposited on 5 cm × 5 cm Si(100) with native oxide and soda lime glass substrates. The reduction behavior of CoO was studied on native oxide terminated Si and TiN substrates.

**Film Characterization.** Film thicknesses were measured on native oxide terminated Si(100) substrates using a Film Sense FS-1 Multi-Wavelength ellipsometer. Thicknesses of the thickest films were verified with cross-sectional scanning electron microscopy (SEM) using a Hitachi S-4800 tool. Crystal structure of the films was determined by powder X-ray diffraction (XRD) using a Rigaku SmartLab X-ray diffractometer. The incident angle of the Cu Kα line (λ = 1.54 Å) was 1°. In situ XRD measurements were carried out on 1.5 cm × 1.5 cm samples in 10% forming gas using an Anton-Paar HTK1200N oven connected to a PANalytical X’Pert Pro MPD X-ray diffractometer. The forming gas pressure was close to atmospheric pressure. Thicknesses of the CoO films on TiN and of the reduced Co films were determined by energy-dispersive X-ray spectrometry (EDS) using an Oxford INCA 350 connected to the SEM. The electron energy was 20 keV. The thicknesses were calculated from Co Kα X-ray lines with the GMRFILM program assuming CoO and Co bulk density (6.4 and 8.9 g/cm3) and composition.

Film morphology was assessed by SEM and atomic force microscopy (AFM). The AFM images were recorded using a Veeco Multimode V instrument. Tapping mode images were captured in air using silicon probes with a nominal tip radius of 10 nm and a nominal spring constant of 40 N/m (NTESP from Bruker). The images were flattened to remove artifacts caused by sample tilt and scanner bow. Roughness was calculated as a root-mean-square value (Rq).

Film composition was examined by time-of-flight elastic recoil detection analysis (ToF-ERDA) using a 40 MeV 79Br7+ ion beam. The incident angle of the beam with respect to the sample surface was 16°, and the angle between the surface and the detector was 24°. X-ray photoelectron spectra (XPS) were acquired using an Omicron ARUGS spectrometer operated at a pass energy of 20 eV. The X-rays were emitted from a Mg source (Kα line) at a photon energy of 1253.6 eV. The films were not sputtered for the analysis. Binding
energies were calibrated using the C 1s peak of ambient hydrocarbons (284.8 eV). Peak fitting was done using the CasaXPS software package.

**RESULTS**

**Properties of CoCl₂(TMEDA).** CoCl₂(TMEDA) is a strictly monomeric compound where the cobalt atom has a tetrahedral coordination sphere. The structure of the compound shown in Figure 1 is known from the literature.⁷¹

After the synthesis, CoCl₂(TMEDA) was purified by vacuum sublimation with a practically quantitative yield at 150−200 °C/0.4 mbar. Thus, the compound is thermally stable at the evaporation temperature used in the ALD experiments (170 °C). The mass spectrum of CoCl₂(TMEDA) showed the molecular ion and fragments, which further indicates that the compound stays intact in the vapor phase. CoCl₂(TMEDA) melts at 167−179 °C that is close to its ALD source temperature. Lower melting compounds may form if amines with less symmetry or more degrees of freedom were used as the adduct forming ligands.

To evaluate the thermal properties of the compound further, TGA was conducted (Figure 2). The sample starts to lose weight around 200 °C. The rate of weight loss constantly increases up to 340 °C at which temperature there is a turning point where a second step starts. Residue at the end of the measurement (600 °C) was 33.7%. Though the theoretical CoCl₂ content of the compound is 52.8%, it is obvious that part of the compound evaporates and part of it decomposes. The decomposition most likely involves dissociation of the TMEDA and formation of CoCl₂. The theoretical Co content of the compound is 24.0%. EDS revealed that the residue contained 23.5 at. % Co, 32.6 at. % Cl, and 42.8 at. % O. Neither carbon nor nitrogen was observed. This result corroborates the dissociation of TMEDA and formation of the CoCl₂ residue. Handling the residue in air after the TGA measurement has caused CoCl₂ to partially oxidize. DSC (Figure S1 in the Supporting Information) revealed endothermic changes around 108 and 178 °C. The first change is most likely due to some structural transition in the solid. The second one is due to melting. Around 310 °C, that is, during the weight loss step, an exothermic transition starts. The exothermic change peaking at 342 °C is followed by an endothermic change probably due to evaporation of the decomposition products.

TGA measurement under dynamic vacuum was also conducted (Figure 2). In this measurement, 81.7% of the weight is lost in the first step at 120−220 °C. In the second step at 220−250 °C, 10.7% is lost. At the end of the measurement, a residue of only 2.5% is left. Based on this result, it appears that as a bulk material the compound decomposes slightly already at around 200 °C. In the ALD experiments, however, no signs of decomposition were observed below 300 °C.

**Oxide Process. Film Deposition.** Saturation of the growth rate with respect to the CoCl₂(TMEDA) pulse length was studied at 275 °C. As shown in Figure 3a, the growth rate was ~0.2 Å/cycle regardless of the Co precursor pulse length when 1.0 s water pulses were used. Figure 3b depicts the number of cycles and the pulsing sequence in seconds in the following order: CoCl₂(TMEDA), purge, water, purge. The lines are drawn to guide the eye.

Figure 2. TGA curve measured for CoCl₂(TMEDA) in N₂ (1 atm) and vacuum.

Figure 3. Growth rate with respect to the (a) CoCl₂(TMEDA) and (b) water pulse length at 275 °C. The labels depict the number of cycles and the pulsing sequence in seconds in the following order: CoCl₂(TMEDA), purge, water, purge. The lines are drawn to guide the eye.

As is typical for an ALD process, film thickness increased linearly when the number of cycles was increased (Figure 4). The CoO process was examined between temperatures of 225 and 300 °C. The growth rates at different temperatures...
were studied under conditions that were saturative with respect to both precursor pulse lengths at 275 °C. As illustrated in Figure 5, the growth rate was highly dependent on the substrate temperature. The growth rate increased almost linearly from 0.06 to 0.38 Å/cycle when the temperature was increased from 225 to 275 °C. Precursor decomposition started to take place at 300 °C and, consequently, a lower growth rate of 0.33 Å/cycle was measured. The decomposition was detected visually as color at the hot end of the CoCl₂(TMEDA) source tube. The strong temperature dependence of the process is probably related to the slow reaction between the Co precursor and water. It is possible that the differences in the growth rates would even out if longer pulses were applied at the lower temperatures; however, saturation studies at different temperatures were not considered necessary at this point.

Film Characterization. Figure 6a shows the X-ray diffractograms of ~50 nm films deposited at 250, 275, and 300 °C. The films deposited at 250 and 275 °C are mostly hexagonal CoO with reflections corresponding to the cubic phase of CoO at 42.4 and 61.5°2θ. The reflection at 36.5°2θ refers to both the (101) plane of the hexagonal phase and the (111) plane of the cubic structure. No reflections corresponding to the Co₃O₄ phase were observed. The film deposited at 300 °C is mostly cubic CoO but exhibits also weak reflections corresponding to the hexagonal phase at 34.6 and 47.6°2θ and to the (111) plane of cubic Co metal. The appearance of the Co reflection might derive from precursor decomposition or from partial reduction of the CoO film by the amine or hydrocarbon moieties of the TMEDA.

The hexagonal phase of CoO is typical to nanomaterials only and is not observed in bulk CoO. The hexagonal structure of CoO was first discovered by Redman and Steward. They were the first to isolate hexagonal CoO nanocrystals using kinetically tuned thermal decomposition of Co(acac)₃ in oleylamine. The hexagonal structure of CoO is similar to the wurtzite-type structure of ZnO. The unit cell size (a = 3.25 Å and c = 5.20 Å) determined from the diffractogram of the CoO film deposited at 275 °C was close to that of ZnO (a = 3.25 Å and c = 5.21 Å). The CoO films deposited by Livonen et al. using Co(BTSA)₂ and water at 100–150 °C were also partly hexagonal but due to the high impurity levels and low deposition temperatures, the films were far less crystalline than the films deposited here.

Figure 6b depicts the X-ray diffractograms of ~20 nm films deposited with 1.0 s CoCl₂(TMEDA) pulses and with different water pulse lengths at 275 °C. The films showed a mixture of the hexagonal and cubic phases of CoO, whereas the ~20 nm films were almost completely hexagonal CoO. Thus, it can be deduced that the crystallization begins with the formation of the hexagonal structure. When the film grows thicker, that is, when the contribution of bulk material increases, the cubic phase appears.

The water pulse length seems to affect the crystal structure as well (Figure 6b). When comparing the two ~20 nm films, the film deposited with longer water pulses is less crystalline than the film deposited with 1.0 s water pulses. Also, the reflection at 42.4° corresponding to the (200) plane of the cubic phase is more intense when the film is deposited with longer water pulses.
pulses. The CoCl₂(TMEDA) pulse length had no significant effect on the crystal structure.

Figure 7 shows SEM images taken from ~50 nm films deposited at 250, 275, and 300 °C. All the films comprise two kinds of grains: pyramid-like crystallites surrounded by a smoother layer consisting of smaller grains. It is difficult to say whether the pyramids start to form already on the substrate or only after a certain film thickness is reached. Based on the tilted image of the film deposited at 275 °C, it would anyhow seem that the pyramids emerge from the smoother layer instead of forming on top of the layer. The amount of the pyramids increases with increasing temperature. At 300 °C, that is, when decomposition starts to take place, the pyramids are collapsed. According to Seo et al., the hexagonal phase appears in two shapes: rods and pyramids. The pyramids observed here resemble those shown by Seo et al. The smoother layer of the films deposited at 275 and 300 °C, on the other hand, resembles the appearance of cubic CoO films. The morphology of the smoother layer is similar to the CoO films deposited on TiN that in XRD showed reflections corresponding only to the cubic phase of CoO (see below in Figure 12). Seo et al. were able to control the shape and size of the nanocrystals by changing the precursor concentration and temperature. Thus, the temperature-dependent morphology changes observed here are in agreement with the literature. The different morphologies also correlate with the variations in phase composition seen in Figure 6.

As discussed earlier, the crystal structure of the CoO films was affected not only by the deposition temperature but also by the duration of the water pulse. The film deposited with long water pulses contained less hexagonal and more cubic CoO than the film deposited with short water pulses. The differences in crystal structure were also translated into differences in the film morphologies. Figure 8 shows SEM images of ~20 nm CoO films deposited at 275 °C on Si with native oxide with 1.0 and 4.5 s water pulses. The film deposited with 1.0 s water pulses was denser and exhibited more of the pyramid-shaped grains attributed to the hexagonal phase than the film deposited with 4.5 s pulses. The smaller, spherical grains that form the film deposited with 4.5 s water pulses are similar to the ones that form the cubic CoO film on TiN, and they also resemble the cubic CoO nanoparticles shown by Seo et al. Seven

According to AFM, the ~50 nm films deposited at 250, 275, and 300 °C were all rough, with the Ra value being around 10 nm for each sample (Figure 9). The film deposited at 250 °C consisted of smaller grains and a few scattered, larger pyramid-like grains. The film deposited at 275 °C had more of these pyramid-like grains but the rest of the film was smoother. Because of the partial precursor decomposition at 300 °C, the morphology of the film was less controlled. Quite smooth pyramid-like grains covered the majority of the surface revealing some small grains underneath. Additionally, there were areas with holes and cracks as well as higher grains.

The elemental compositions of ~50 nm films deposited at 250, 275, and 300 °C were analyzed by ToF-ERDA. Table 1 lists the atomic percentages of the detected elements and the Co:O ratio of each sample. All the films were of high purity with impurity levels below 1.2 at. % for each element. Even the CI content was low at all temperatures. The Si signal results from the gradients in the elemental depth profiles caused by film roughness and can thus be discarded from the analysis. The film deposited at 275 °C exhibited the highest purity, and the Co:O ratio corresponded to stoichiometric CoO. At 300 °C, the Co level was higher because of the precursor decomposition. Figure S2 in the Supporting Information shows the depth profile of the film deposited at 275 °C.
The chemical states of cobalt and oxygen on the surface of ∼50 nm films deposited at 250, 275, and 300 °C were determined by XPS. As Figure 10 illustrates, Co is mostly at an oxidation state of +II regardless of the temperature. The amount of Co$_2$O$_4$ is negligible. The main peaks of the Co 2p spectrum are at binding energies of 780 and 795 eV. The shakeup satellites for Co$^{2+}$ are visible at 785 and 800 eV. At 250 °C, the signals are shifted to lower energies possibly because of the hexagonal crystal structure of the film. The amount of the hexagonal phase is lower in the films deposited at 275 and 300 °C. The Biesinger models used for fitting are based on bulk CoO that most likely has a cubic crystal structure. The amount of Co$_3$O$_4$ was low at all temperatures. Both the Co(OH)$_2$ signal and the OH groups in the oxygen signal derive from water that is left from the process or adsorbed on the surface from ambient air as no sputtering was done before the measurement. The differences in the apparent Co(OH)$_2$ levels scale with the deposition temperature similar to the hydrogen contents measured in the film bulk by ToF-ERDA (Table 1).

Reduction of CoO to Co Metal. CoCl$_2$(TMEDA) was tested with many different reducing agents, such as H$_2$, tertiary butyl hydrazine, and borane dimethylamine, but with no success, which is why an indirect approach toward ALD of Co metal was chosen instead. Reduction propensity of the deposited CoO thin films was studied with high temperature XRD. The measurements were carried out in 10% forming gas. The reduction of a ∼50 nm CoO film on Si with native oxide started at an exceptionally low temperature of 250 °C (Figure 11). The reduction of CoO$_x$ to Co metal typically requires temperatures above 400 °C. An isothermal measurement at 250 °C showed rapid reduction; the ∼50 nm CoO film was completely reduced to Co metal in 45 min (Figure 11).

In the case of metals, low deposition and processing temperatures are needed to minimize agglomeration of the films. For instance, the extent of agglomeration was significantly lower in the Co film reduced isothermally at 250 °C than in the film reduced by increasing the temperature stepwise from 25 to 650 °C (Figure 11).

In addition to the reduction temperature, the underlying substrate has an essential role in suppressing agglomeration. Figure 12 shows SEM images of a bare TiN substrate, a 68 nm CoO film on TiN, and Co metal films of different thicknesses on TiN obtained by reduction at 250 °C. CoO has a different morphology on TiN and on the native oxide terminated Si substrate (Figure 7). This difference originates from the different crystal structures of the two films; the film deposited on TiN is cubic CoO, whereas the film on Si was a mixture of both cubic and hexagonal phases. The film on TiN is also much denser than the pyramid-like films deposited on Si. The higher density is likely to facilitate reduction into a continuous metal film.

![Figure 10. Co 2p and O 1s photoelectron spectra of ∼50 nm CoO films deposited at different temperatures.](image1)

![Figure 11. SEM images of nominally ∼20 nm Co films on native oxide terminated Si prepared by increasing the reduction temperature stepwise from 25 to 650 °C (left) and keeping the temperature constant (right). The X-ray diffractograms show the reduction processes as a function of temperature (left) and as a function of time at 250 °C (right).](image2)

![Figure 12. SEM images of a TiN substrate, CoO on TiN, and different thicknesses of Co on TiN.](image3)
substrate was not obtained even with a Co thickness of 50 nm. The formation of fully continuous Co films with this recipe would probably require even lower reduction temperatures or thicker CoO films. Resistivity of the Co films could not be measured because of the conductive TiN substrate. According to ToF-ERDA, however, the 50 nm Co film exhibited high purity; the Co content exceeded 95 at. %, with the rest being oxygen and hydrogen. With a longer reduction time, the amount of oxygen would probably be even lower.

The CoO films were deposited on the TiN substrates under conditions that were saturative on Si with native oxide, but saturation on TiN was not verified. Nevertheless, at least the thicknesses of the CoO and the reduced Co films increased quite linearly as a function of increasing cycle count used to deposit the oxide films at 275 °C (Figure 13). Because of the decreasing film density, the thicknesses of the reduced Co films were 50–58% of the original CoO films (16, 34, and 50 nm versus 27, 68, and 89 nm). The growth rate of CoO was slightly higher on TiN (0.47 Å/cycle) than on Si with native oxide (∼0.4 Å/cycle).

**CONCLUSIONS**

In this paper, we have introduced a new Co precursor, CoCl2(TMEDA), with good thermal properties and demonstrated its suitability for ALD by developing a process for CoO thin films. The process exhibited typical ALD characteristics, such as saturated growth rate and a linear increase of film thickness with increasing cycle count. The films were a mixture of hexagonal and cubic CoO, with the ratio depending on deposition temperature, water pulse length, film thickness, and substrate. Different from the ALD cobalt oxide processes using other precursors, the CoO films were, in general, of high purity and exhibited 1:1 Co:O stoichiometry when deposited at 275 °C. In addition to a working CoO ALD process, we have also presented a fairly robust, substrate independent way of making pure Co metal films by postdeposition reduction. The CoO films could be reduced to Co metal at a low temperature of 250 °C in 10% forming gas. A continuous network of Co was formed at a critical thickness of 16 nm. The extent of voids was diminished as thicker CoO films were reduced. The Co content of a reduced 50 nm Co metal film was as high as 95 at. %.

CoCl2(TMEDA) is merely one example of an adduct of cobalt(II) halides suitable for ALD conditions. By changing the ligands, a precursor with even better thermal properties and higher reactivity may be developed. Furthermore, the same approach can be applied also to other transition metals, for example nickel, leaving many potential breakthroughs to be discovered.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b01271.

STA data of CoCl2(TMEDA); elemental depth profile of CoO deposited at 275 °C (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*K. Väyrynen. E-mail: katja.vayrynen@helsinki.fi; Phone: +358-407157402.

**ORCID**

Katja Väyrynen: 0000-0002-8886-6997
Timo Hatanpää: 0000-0003-3745-8296
Miika Mattinen: 0000-0003-4837-1823

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Funding from ASM Microchemistry Oy and Finnish Centre of Excellence in Atomic Layer Deposition is gratefully acknowledged. Dr. Marianna Kemell is thanked for helping with tilted SEM imaging.

**REFERENCES**


