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2018-05-22

Väyrynen , K , Hatanpää , T , Mattinen , M , Heikkilä , M , Mizohata , K , Meinander , K , Räisänen , J , Ritala , M & Leskelä , M 2018 , ' 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 ' , Chemistry of Materials , vol. 30 , no. 10 , pp. 3499-3507 . <https://doi.org/10.1021/acs.chemmater.8b01271>

<http://hdl.handle.net/10138/256020>

<https://doi.org/10.1021/acs.chemmater.8b01271>

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reduction temperature was as high as 430°C , causing the formation of Co nanoparticles instead of a continuous film.

Most Co precursors are unreactive toward water; therefore, ozone has been the dominant oxygen source in CoO ALD.^{54,56,64} The use of ozone, however, usually leads to the formation of Co_2O_3 instead of CoO. The deposition of CoO instead of Co_2O_3 is challenging but would be beneficial if the aim was, for example, to make Co metals indirectly by oxide reduction. Because of the lower oxidation state of cobalt, CoO is more readily reduced to Co metal than Co_2O_3 . So far, only $\text{Co}(\text{P}^i\text{AMD})_2$ (P^iAMD = N,N-diisopropylacetamidinate) and $\text{Co}(\text{BTSA})_2$ (BTSA = bistrimethylsilylamide) have been shown to react with water to deposit CoO by ALD.^{2,65,66} Saturation has not been verified for $\text{Co}(\text{P}^i\text{AMD})_2$, and the use of $\text{Co}(\text{BTSA})_2$ leads to Si impurities in films. $\text{Co}(\text{P}^i\text{DAD})_2$ (P^iDAD = 1,4-diisopropyl-1,4-diaza-1,3-butadiene) has also been used with water but no self-limiting growth was shown, and the deposited films were Co_2O_3 instead of CoO.⁶⁷

Cobalt halides have a polymeric structure and low volatility. To evaporate them efficiently, high temperatures and vacuum are needed. On the other hand, many of the known adducts of cobalt halides, such as diamine adducts, are monomeric. The monomeric structure might manifest itself in better volatility, providing that the adduct compounds stay intact also at elevated temperatures. In the literature, there are, however, no mentions of volatility in connection of these compounds. Considering that Co is a transition metal with 9 electrons available for bonding, and it has medium electronegativity resulting in significant amount of covalency in its bonds, it seems possible that these adducts may well be volatile and exhibit sufficient thermal stability.

Herein, we present a promising new precursor $\text{CoCl}_2(\text{TMEDA})$, 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

Figure 1. Schematic structure of $\text{CoCl}_2(\text{TMEDA})$.

by establishing a new process for the deposition of CoO thin films. Pure, stoichiometric CoO films were deposited with a saturated growth rate of $0.4 \text{ \AA}/\text{cycle}$ at 275°C . The CoO films were readily reduced to Co metal at 250°C in 10% forming gas. Since $\text{CoCl}_2(\text{TMEDA})$ 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 precursor itself, the CoO process, and the postdeposition reduction of the CoO films.

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 CoCl_2 (99%, Aldrich) and N,N,N',N'-tetramethylethylenediamine (99%, Aldrich) were used as received. CoCl_2 was

deoxygenized and dried over $4 \text{ \AA}$ 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 ($40 \text{ mL}/\text{min}$) atmosphere at 1 atm, and under dynamic vacuum (0.1 mbar). The heating rate was $5^{\circ}\text{C}/\text{min}$, and the weight of the sample was 10 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 320°C .

Synthesis of $\text{CoCl}_2(\text{TMEDA})$. 6.00 g of CoCl_2 (46.211 mmol) was weighed into a 300 mL Schlenk bottle. 100 mL of THF was added. A stoichiometric amount of TMEDA (5.37 g, 46.211 mmol) was then added dropwise to a stirred suspension. The resulting blue solution was stirred for 1 h at room temperature. The solution was evaporated to dryness leaving a blue colored raw product that was transferred into a sublimator. The product was sublimed out at $320^{\circ}\text{C}/0.4 \text{ mbar}$. The yield of the blue product was 11.30 g (theoretical 11.37 g), that is, 99.4%. mp 167.79°C ; m/z (EI, 70 eV) 245 [M]⁺, 210 [M-Cl]⁺, 116 [L]⁺.

Film Deposition. All the films were deposited in a hot-wall cross-flow F-120 ALD reactor (ASM Microchemistry). Nitrogen (AGA, 99.999%; H₂, 3 ppm; O₂, 3 ppm) was employed as the carrier gas and for purging the reaction chamber. The carrier gas rate was 400 sccm. The reactor was operated under a pressure of 0.1 mbar. $\text{CoCl}_2(\text{TMEDA})$ 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 $\text{CoCl}_2(\text{TMEDA})$ 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 $\text{CoCl}_2(\text{TMEDA})$ pulse length was studied with 1.0 s pulse lengths for water. The oxide process was investigated within a temperature range of 225°C . The films were deposited on 5 cm $\times$ 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 thin films were verified with cross-sectional scanning electron microscopy (SEM) using a Hitachi S-4800 tool. Crystal structure of films was determined by grazing incidence X-ray diffraction (GI-XRD) using a Rigaku SmartLab X-ray diffractometer. The incident angle of the Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation was 1° . In situ XRD measurements were carried out on 1.5 $\times$ 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 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 KX-ray lines with the GMRFILM program assuming CoO and Co bulk density (6.4 and $8.9 \text{ g}/\text{cm}^3$) 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 (RMS) value.

Film composition was examined by time-of-flight elastic recoil detection analysis (ToF-ERDA) using a 40 keV 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 AEGIS spectrometer operated at a pass energy of 20 eV. The X-rays were emitted from a Mg source (1185 eV) at a photon energy of 1253.6 eV. Helms were not sputtered for the analysis. Binding

energies were calibrated using the C 1s peak of ambient hydrocarbon (284.8 eV). Peak fitting was done using the CasaXPS software package.

RESULTS

Properties of $\text{CoCl}_2(\text{TMEDA})$. $\text{CoCl}_2(\text{TMEDA})$ 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.

After the synthesis, $\text{CoCl}_2(\text{TMEDA})$ was purified by vacuum sublimation with a practically quantitative yield of 52.0% at 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 $\text{CoCl}_2(\text{TMEDA})$ showed the molecular ion and fragments, which further indicates that the compound stays intact in the vapor phase. $\text{CoCl}_2(\text{TMEDA})$ melts at 163–179 °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

Figure 2. TGA curve measured for $\text{CoCl}_2(\text{TMEDA})$ in N_2 (1 atm) and vacuum.

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 measurement (600 °C) was 33.7%. Though the theoretical CoCl_2 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 CoCl . 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 residue. Handling the residue in air after the TGA measurement has caused CoCl 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 180–220 °C. In the second step at 225–250 °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 $\text{CoCl}_2(\text{TMEDA})$ pulse length was studied at 275 °C. As shown in Figure 3, the growth rate was

Figure 3. Growth rate with respect to the (a) $\text{CoCl}_2(\text{TMEDA})$ 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: $\text{CoCl}_2(\text{TMEDA})$, purge, water, purge. The lines are drawn to guide the eye.

0.2 Å/cycle regardless of the Co precursor pulse length when 1.0 s water pulses were used. Figure 3 depicts the growth rate as a function of the water pulse duration at 275 °C. Pulse lengths as long as 4.5 s were required to reach saturation (0.4 Å/cycle). The gradual increase of the growth rate is an indication of a slow reaction between the Co precursor and water. Fast saturation with respect to the Co precursor was verified also with the longer water pulses of 4.5 s. All the films deposited under saturative conditions with 1.0 and 4.5 $\text{s}_2(\text{TMEDA})$ and water pulses, respectively, unless otherwise noted. As is typical for an ALD process, 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

Figure 4. Film thickness as a function of cycle count at 275

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

Figure 5. Film growth rate as a function of deposition temperature.

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 225 °C. The growth rate of 0.33 Å/cycle was measured. The decomposition was detected visually at the hot end of the Co(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 and temperatures were not considered necessary at this point.

Film Characterization Figure 6 shows the X-ray diffractograms of 50 nm lms deposited at 250, 275, and 300 °C. The lms deposited at 250 and 275 °C are mostly hexagonal CoO with reflections corresponding to the cubic phase of CoO at 42.4 and 61.2°. The reflection at 36.2° refers to both the (101) plane of the hexagonal phase and the (111) plane of cubic structure. No reflections corresponding to the Co phase were observed. The lm deposited at 300 °C is mostly cubic CoO but exhibits also weak reflections corresponding to the hexagonal phase at 34.6 and 42.4° and to the (111) plane of cubic Co metal. The appearance of the Co phase might derive from precursor decomposition or from partial reduction of the CoO lm by the amine or hydrocarbon moieties of the TMEDA.

Figure 6. Grazing incidence X-ray diffractograms of (a) 50 nm lms deposited at 250, 275, and 300 °C and (b) 20 nm lms deposited with 1.0 and 4.5 s water pulses at 275

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 Stewart et al.

over the first to isolate hexagonal CoO nanocrystals using bimetrically tuned thermal decomposition of Co(acac)₃ and ethylamine. The hexagonal structure of CoO is similar to the wurtzite-type structure of ZnO. The unit cell size $a = b = 3.25$ Å and $c = 5.20$ Å determined from the diffractogram of the CoO lm deposited at 275 °C was close to that of ZnO ($a = b = 3.25$ Å and $c = 5.21$ Å). The CoO lms deposited by Iivonen et al. and using Co(BTSA) and water at 100–150 °C were also partly hexagonal but due to the high impurity levels and low deposition temperatures, they were far less crystalline than the lms deposited here.

Figure 6 depicts the X-ray diffractograms of 20 nm lms deposited with 1.0 s Co(TMEDA) pulses and with different water pulse lengths at 275 °C. The 50 nm lms shown in Figure 6a were a mixture of the hexagonal and cubic phases of CoO, whereas the 20 nm lms were almost completely hexagonal CoO. Thus, it can be deduced that the crystallization begins with the formation of the hexagonal structure. When the lm 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 6). When comparing the two 20 nm lms, the lm deposited with longer water pulses is less crystalline than the lm deposited with 1.0 s water pulses. Also, the peak at 42.4° corresponding to the (200) plane of the cubic phase is more intense when the lm is deposited with longer water

pulses. The $\text{CoCl}_2(\text{TMEDA})$ pulse length had no significant effect on the crystal structure.

Figure 7 shows SEM images taken from 50 nm CoO films deposited at 250, 275, and 300 °C. All the films comprise two

Figure 7. Top view SEM images of 50 nm CoO films deposited on Si with native oxide at 250, 275, and 300 °C (scale bar 500 nm) and a tilted image of the film deposited at 275 °C (scale bar 300 nm).

kinds of grains: pyramid-like crystallites surrounded by a smoother layer consisting of smaller grains. It is not clear 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 pyramid-like grains covered the majority of the surface increases with increasing temperature. At 300 °C, when decomposition starts to take place, the pyramids are collapsed, revealing some small grains underneath. Additionally, there were areas with holes and cracks as well as higher grains. 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 . The morphology of the smoother layer is similar to the CoO deposited on TiN that in XRD showed reflections corresponding only to the cubic phase of CoO (see below Figure 12). Seo et al. were able to control the shape and size of the nanocrystals by changing the precursor concentration and temperature. Therefore, 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 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 than the film deposited with short water pulses. The differences in crystal structure were also translated into differences in 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 cubic CoO on TiN, and they also resemble the cubic CoO nanoparticles shown by Seo et al.

Figure 8. SEM images of 20 nm CoO films deposited with 1.0 s $\text{CoCl}_2(\text{TMEDA})$ pulses and with 1.0 or 4.5 s water pulses at 275 °C on native oxide terminated Si.

According to AFM, the 50 nm CoO films deposited at 250, 275, and 300 °C were all rough, with the R_a value being around 10 nm for each sample (Figure 9). The film deposited at 250 °C

Figure 9. AFM images from 50 nm CoO films deposited at different temperatures.

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 275 and 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 CoO films deposited at 250, 275, and 300 °C were analyzed by ToF-ERDA (Table 1).

Table 1. ToF-ERDA results (at.%) from 50 nm films deposited on native oxide terminated Si at 250, 275, and 300 °C

Element	250 °C	275 °C	300 °C
Co	46.8 ± 0.5	48.0 ± 0.5	54.7 ± 0.4
O	49.8 ± 0.7	47.7 ± 0.7	42.8 ± 0.4
C	0.7 ± 0.3	0.5 ± 0.2	0.4 ± 0.1
N	0.22 ± 0.04	0.53 ± 0.07	0.67 ± 0.05
Cl	0.16 ± 0.03	0.18 ± 0.04	0.22 ± 0.03
Si	1.15 ± 0.09	0.77 ± 0.07	0.45 ± 0.04
Co:O ratio	1.2 ± 0.09	2.4 ± 0.2	0.7 ± 0.06
Co:O ratio	0.9	1.0	1.3

CoO

lists the atomic percentages of the detected elements and the Co:O ratio of each sample. All films were of high purity with impurity levels below 1.2 at. % for each element. Even the Cl content was low at all temperatures. The Si signal results from the gradients in the elemental depth profile caused by surface 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 CoO thin films deposited at 250, 275, and 300 °C were determined by XPS. Figure 10 illustrates, Co is mostly at an

Figure 10. Co 2p and O 1s photoelectron spectra of 50 nm CoO thin films deposited at different temperatures.

oxidation state of +II regardless of the temperature. The amount of Co_3O_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_3O_4 was low at all temperatures. Both the Co(OH)_2 signal and the OH groups in the oxygen signal derived 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) levels scale with the deposition temperature similar to the hydrogen contents measured in the bulk by ToF-ERDA (Table 1).

Reduction of CoO to Co Metal. $\text{CoCl}_2(\text{TMEDA})$ was tested with many different reducing agents, such as tertiary butyl hydrazine, and borane dimethylamine, but with no success, which is why an indirect approach toward ALD of 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 to Co metal typically requires temperatures above 400 °C.^{53,79} 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.⁵² For instance, the extent of agglomeration was significantly lower in the Cd film reduced isothermally at 250 °C than in the film reduced by increasing the temperature

Figure 11. SEM images of nominal 50 nm CoO thin 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 diffraction patterns show the reduction processes as a function of temperature (left) and as a function of time at 250 °C (right).

°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 substrates; 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 film deposited on Si. The higher density is likely to facilitate reduction into a continuous metal film.

Figure 12 illustrates the morphology of 16, 34, and 50 nm CoO films obtained by reducing CoO on TiN. Even the 16 nm film formed a continuous network of Co, though it did not cover the substrate fully. The amount of voids and cracks along the grain boundaries was diminished to some extent when a thicker CoO film was reduced; however, full coverage of the

Figure 12. SEM images of a TiN substrate, CoO on TiN, and Co metal films of different thicknesses of Co on TiN.

substrate was not obtained even with a Co thickness of 50 nm. $\text{CoCl}_2(\text{TMEDA})$ 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.

The formation of fully continuous Co films with this recipe would probably require even lower reduction temperatures. According to ToF-ERDA, however, the 50 nm Co 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 reached. Nevertheless, at least the thicknesses of the CoO and the reduced Co increased quite linearly as a function of increasing cycle count used to deposit the oxides at 275°C (Figure 13). Because of the

Figure 13. Thicknesses of the CoO films and the corresponding reduced Co metal films as a function of the oxide process cycle count on TiN.

decreasing film density, the thicknesses of the reduced Co were 55–58% 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, $\text{CoCl}_2(\text{TMEDA})$, 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 thickness with increasing cycle count. There were a mixture of hexagonal and cubic CoO, with the ratio depending on deposition temperature, water pulse length, thickness, and substrate. Different from the ALD cobalt oxide processes using ozone as the oxygen source, in these no Co_3O_4 was observed. The 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. %. Appl. Phys. 99, 2, 1865 (1997).

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 $\text{CoCl}_2(\text{TMEDA})$; elemental depth profile of CoO deposited at 275°C (PDF)

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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.

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