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Atomic Layer Deposition of Cobalt Using H₂-, N₂-, and NH₃-Based Plasmas: On the Role of the Co-reactant

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Supporting Information

ABSTRACT: This work investigates the role of the co-reactant for the atomic layer deposition of cobalt (Co) films using cobaltocene (CoCp₂) as the precursor. Three different processes were compared: an AB process using NH₃ plasma, an AB process using H₂/N₂ plasma, and an ABC process using subsequent N₂ and H₂ plasmas. A connection was made between the plasma composition and film properties, thereby gaining an understanding of the role of the various plasma species. For NH₃ plasma, H₂ and N₂ were identified as the main species apart from the expected NH₃, whereas for the H₂/N₂ plasma, NH₃ was detected. Moreover, HCP was observed as a reaction product in the precursor and co-reactant subcycles. Both AB processes showed self-limiting half-reactions and yielded similar material properties, that is, high-purity and low-resistivity. For the AB process with H₂/N₂, the resistivity and impurity content depended on the H₂/N₂ mixing ratio, which was linked to the production of NH₃ molecules and related radicals. The ABC process resulted in high-resistivity and low-purity films, attributed to the lack of NH₄⁺ species during the co-reactant exposures. The obtained insights are summarized in a reaction scheme where CoCp₂ chemisorbs in the precursor subcycle and NH₃ species eliminate the remaining Cp in the consecutive subcycle.

1. INTRODUCTION

Atomic layer deposition (ALD) is a thin-film deposition technique, which relies on the cyclical alternation of precursor and co-reactant doses. The self-limiting nature of the surface reactions during ALD generally allows for good uniformity on large-area substrates and excellent conformality on three-dimensional structures. Although the precursor that is used for an ALD process generally receives considerable attention, the choice of the co-reactant is equally important because it can greatly affect the properties of the deposited material as well as the technological and industrial feasibility of the process. For the ALD of metals, a wide range of co-reactants have been explored, with gases or plasmas of O₂, H₂, N₂, or H₂/N₂ mixtures as source gases) have previously been used as co-reactants for the ALD of a wide range of metals and metal nitrides. See Table S1 in the Supporting Information for an overview of selected metals and metal nitrides, which have been deposited using a NH₃ plasma or a mixed H₂/N₂ plasma as the co-reactant. For instance, Kim et al. found that for the ALD of Ir using ((ethylcyclopentadienyl)-(1,5-cyclooctadiene))iridium, NH₃ plasma yielded a lower surface roughness in comparison to when using O₂ gas as the co-reactant. Furthermore, Ten Eyck et al. employed a H₂/N₂ plasma for the ALD of Pt on a polymer substrate and claimed that a H₂/N₂ plasma leads to the formation of reactive NH₂ groups on the polymer, needed for chemisorption of the palladium(II) hexafluoroacetylacetonate precursor. Moreover, the use of NH₃ plasmas instead of H₂ plasmas for the ALD of Ru, Ag, and Ni resulted in higher growth per cycle (GPC) and lower resistivity values.

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material properties has not been made so far. The connection between the plasma composition and the obtained comparison between the two different co-reactants. Specifically, the studies of Lee et al. and Yoon et al. reported the growth of high-quality Co films using NH3 plasma and H2/N2 plasma, respectively.26,27 A direct comparison between the two different processes as well as a connection between the plasma composition and the obtained material properties has not been made so far.

In this work, a detailed study of the use of H2, N2, and NH3-based plasmas as co-reactants for the ALD of Co using CoCp2 as the precursor is presented. As illustrated in Figure 1, three ALD processes with different co-reactants were investigated: an AB-type process with NH3 plasma (referred to as “AB-NH3 process”, Figure 1a), an AB process with a mixed H2/N2 plasma (“AB-H2/N2 process”, Figure 1b), and an ABC process with subsequent N2 and H2 plasmas (“ABC-N2 H2 process”, Figure 1c). As will be shown, the separation of the H2 and N2 plasmas in an ABC-type cycle provides an insight into the role of NH3 species that are present in both the NH3 plasma and the H2/N2 plasma (but not in the N2 or H2 plasmas).

This work is structured as follows. First, the experimental conditions related to the film deposition, the plasma studies, and the film analysis are discussed. In Section 3.1, the specimens present in the NH3 and H2/N2 plasmas are identified and the

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### Table 1. ALD Processes Reported in the Literature for the Deposition of Co, Listing Deposition Temperature T, GPC, and Resistivity ρ

<table>
<thead>
<tr>
<th>precursor</th>
<th>co-reactant</th>
<th>T (°C)</th>
<th>GPC (Å)</th>
<th>ρ (μΩ cm)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCp2</td>
<td>NH3 plasma</td>
<td>300</td>
<td>0.48</td>
<td>10</td>
<td>37</td>
</tr>
<tr>
<td>CoCp2</td>
<td>H2/N2 plasma</td>
<td>150–450</td>
<td>0.26–0.65</td>
<td>18</td>
<td>26</td>
</tr>
<tr>
<td>CoCp2</td>
<td>NH3, tert-butylamine</td>
<td>100–300</td>
<td>0.37–0.97</td>
<td>14</td>
<td>38</td>
</tr>
<tr>
<td>Co(MeCp)2</td>
<td>NH3 plasma</td>
<td>100–350</td>
<td>0.4–1.9</td>
<td>31</td>
<td>39</td>
</tr>
<tr>
<td>Co(CpAM)2</td>
<td>NH3 plasma</td>
<td>200–250</td>
<td>0.5</td>
<td>140</td>
<td>40</td>
</tr>
<tr>
<td>Co2(CO)8</td>
<td>H2 plasma</td>
<td>75–110</td>
<td>1.2</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>CpCo(CO)2</td>
<td>H2 plasma</td>
<td>125–175</td>
<td>1.1</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Co(AMD)2</td>
<td>H2</td>
<td>340</td>
<td>0.50</td>
<td>285</td>
<td>43</td>
</tr>
<tr>
<td>Co(AMD)2</td>
<td>NH3</td>
<td>350</td>
<td>0.26</td>
<td>50</td>
<td>44</td>
</tr>
<tr>
<td>‘Bu-allyl(CO)3</td>
<td>dimethylhydrazine</td>
<td>140</td>
<td>0.5</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>CCTBA</td>
<td>H2</td>
<td>125–200</td>
<td>0.8</td>
<td>90</td>
<td>46</td>
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<tr>
<td>Co(DBDB)</td>
<td>formic acid</td>
<td>170–180</td>
<td>0.95</td>
<td>13</td>
<td>4, 47</td>
</tr>
<tr>
<td>Co(DBDB)</td>
<td>tert-butylamine</td>
<td>170–200</td>
<td>0.98</td>
<td>15</td>
<td>4, 48</td>
</tr>
</tbody>
</table>

*Hot-wire ALD. †Cyclopentadienyl isopropyl acetamidinato-cobalt. ‡Bis(N,N′-diisopropylacetamidinato)cobalt(II). ††Dicobalt hexacarbonyl tert-butylacetylene. †‡Bis(1,4-difort-butyl-1,3-diazabutadienyl)cobalt(II). †§Measured on the Ru substrate.
role of the $H_2/N_2$ ratio on the plasma composition is investigated. This is followed in Section 3.2 by a study on the reaction products released during the plasma exposures of the three different ALD processes. In Section 3.3, the obtained material properties are compared. In addition, the effect of the $H_2/N_2$ ratio and $NH_3$ concentration in the plasma on the material properties are addressed. Next, the role of $NH_3$ species and a possible reaction mechanism are discussed in Sections 4.1 and 4.2, respectively. Finally, the main conclusions of this work are summarized.

2. EXPERIMENTAL SECTION

2.1. ALD Reactor and Conditions. Co films were deposited in a home-built ALD reactor, as described in the previous work.39 In short, the reactor is equipped with a remote inductively coupled plasma source and a turbo pump reaching a base pressure of $\sim 10^{-6}$ Torr. During all experiments, the temperature of the substrate table was set to 300 °C, whereas the walls were heated to 100 °C. Prior to all experiments, the reactor wall was covered by Co by running at least 200 cycles of the AB-NH$_3$ process. The CoCp$_2$ precursor (98%, Sigma-Aldrich) was contained in a stainless steel bubbler. The bubbler and the dosing line were heated to 80 °C, respectively, as was previously found to be appropriate for the deposition of CoO in the same reactor.30

The ALD recipe consisted of precursor dosing for 6 s in the first subcycle, using Ar as a carrier gas, which resulted in a chamber pressure of approximately 15 mTorr. Subsequently, the reactor was purged with Ar for 3 s and pumped down for 6 s. All plasma exposures were performed at a power of 100 W for 11 s and were followed by a purge and a pump step of 1 and 11 s, respectively. The NH$_3$, N$_2$, and H$_2$ plasmas were started after flowing the source gas into the reactor for 3 s. For the AB-H$_2$/N$_2$ process, the N$_2$ flow was started 2 s before the H$_2$ flow, and subsequently after 5 s, the H$_2$/N$_2$ plasma was ignited. This was done to stabilize the gas flows and minimize overpressures. The precursor dosing and plasma exposure times were based on saturation studies as shown in the Supporting Information (Figure S1).

The pressure used for the NH$_3$ plasma was 1.5 mTorr. For the standard H$_2$/N$_2$ plasma, the N$_2$ and H$_2$ pressures were separately set to 1.5 and 15 mTorr, respectively. Because of the addition of N$_2$ to the H$_2$ gas, the pumping speed increases (as compared to only H$_2$), leading to a lower total pressure of approximately 13 mTorr for the H$_2$/N$_2$ mixture. Moreover, the actual H$_2$/(H$_2$ + N$_2$) mixing ratio is approximately $\sim 0.77$ (for the H$_2$ and N$_2$ pressures of 1.5 and 15 mTorr, respectively) because of the shorter residence time of H$_2$ as compared to that of N$_2$ (see also Section 3.1). The results for different H$_2$/(H$_2$ + N$_2$) ratios in Sections 3.3 and 4.1 were obtained by varying the partial pressures of H$_2$ and N$_2$ while keeping the total pressure of the mixture constant at 13 mTorr. For the ABC-N$_2$-H$_2$ process, a pressure of 7.5 mTorr was used for both the N$_2$ and H$_2$ plasmas, and both plasma exposures were 11 s long.

To determine the effect of the $H_2/(H_2 + N_2)$ ratio on the NH$_3$ production in Section 3.1, a constant pressure of 75 mTorr was used for the gas mixture. This pressure was higher than the “standard” 13 mTorr to allow for more accurate variation of the gas flows and to enable mixing ratios higher than 80 vol %. For a pressure of 13 mTorr, it is not possible to keep the pressure constant for mixing ratios higher than $\sim 80$ vol % because of the low gas flows used and because of changes in pumping speed upon mixing gas flows.

2.2. Plasma Studies. Quadrupole mass spectrometry (QMS) measurements were performed using Pfeiffer Vacuum Prisma QME-200 (mass-to-charge ratio $m/z = 1$–200), attached to the side of the ALD chamber. Measurements were done with the substrate table, and reactor walls were kept at the standard temperatures of 300 and 100 °C, respectively. Note that a considerable part of the QMS signal can originate from the reactions at the reactor walls because the surface area of the wall is significantly larger than the surface area of the substrate table. It was confirmed that growth also occurs at a deposition temperature of 100 °C, albeit at a lower GPC ($\sim 0.13$ Å as compared to $\sim 0.29$ Å) and with a higher impurity content. Because the aim is to compare the three ALD processes with one another, the temperature difference between the wall and the table is considered to be of minor influence.

For determination of the main species in the NH$_3$ and H$_2$/N$_2$ plasmas, mass scans (i.e., ion current as a function of $m/z$) for masses 1–30 were used. These mass scans were collected after stabilization of the gas flows and plasma. The $H_2/(H_2 + N_2)$ mixing ratios were determined using the QMS ion currents at $m/z$ ratios 2 and 14 (corresponding to H$_2^+$ and N$_2^+$, respectively) from such mass scans. For a complete description of this method, see the Supporting Information.

The procedure for time-resolved QMS measurements was similar to the method as previously described by Knoops et al.31 In short, for $m/z \leq 40$, four $m/z$ ratios were measured simultaneously, of which one was always $m/z = 40$. This value corresponds to Ar$^+$ and is used as reference. For $m/z > 40$, besides $m/z = 40$, only one other $m/z$ ratio was followed per measurement, in order to keep the signal-to-noise ratio optimal while maintaining a reasonable time resolution. Three different cycles were studied using the QMS measurements: a “normal” (AB- or ABC-type) ALD cycle, a cycle without CoCp$_2$ dosing (but with Ar carrier gas dosing), and a cycle without igniting the plasma(s) (see Figure S2). This was done to discern reaction products from the species present because of the precursor dosing, source gas exposure, or plasma ignition. For each type of recipe, 10 cycles were performed, and only the signals over the last nine were averaged, assuming the first cycle can deviate because of the recipes performed previously.

To further minimize the influence of previous cycles, every set of cycles was preceded by a cleaning step consisting of an O$_2$ plasma for 90 s, followed by a NH$_3$ plasma for 120 s. Moreover, the purging and gas stabilization times were extended as compared to the standard ALD cycle, in order to separate the effects of pressure overshoots from the reaction products. See the Supporting Information (Figure S2) for a more detailed description and an example of the raw data that is collected using this procedure.

Optical emission spectroscopy (OES) was performed using a USB4000 spectrometer from OceanOptics, with a wavelength range of 180–1100 nm, mounted horizontally to the side of the plasma source.

2.3. Film Analysis. For characterization of the deposited material, Co films were grown on Si(100) coupons with 450 nm thermal SiO$_2$. Prior to deposition, the samples were cleaned in situ with an O$_2$ plasma for 2 min. It was found that unloading the samples after the deposition at a table temperature of 300 °C led to significant oxidation of the Co film. Therefore, the substrate table was cooled down from 300
to 100 °C after each deposition to minimize the oxidation. Although the effect of the table temperature was not investigated in detail in this study, the GPC and film purity were found to decrease when the sample temperatures were lowered, which will be addressed in a follow-up publication. The depositions for generating the saturation curves (Supporting Information, Figure S1) were performed on an ALD-grown Co seed layer to avoid nucleation effects. This Co seed layer was deposited by performing 400 cycles of the standard recipe using NH3 plasma on a thermal SiO2 wafer, resulting in a film thickness of approximately 12 nm. Coupons of this seed layer were loaded into the reactor with the table temperature set to 100 °C. After heating the substrate table in vacuum to the standard deposition temperature of 300 °C, the coupons were treated with a NH3 plasma for 3 min to reduce the surface oxidation. The ALD growth was monitored in situ by spectroscopic ellipsometry (SE) using a J.A. Woollam, Inc. M2000U ellipsometer. The dielectric function of the deposited films was parameterized using a B-spline model. The Co film microstructure was studied using transmission electron microscopy (TEM) using JEOL ARM 200F, operated at 200 kV. For the TEM analysis, a lamella was prepared using a focused ion beam (FIB) in a FEI Nova600i NanoLab. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific XA1066 spectrometer, using monochromatic Al Kα X-rays with an energy of 1486.6 eV. For XPS depth profiling, sputtering was carried out using Ar+ ions with an energy of 500 eV. In addition, four-point probe (FPP) resistivity measurements were done using a Keithley 2400 Sourcemeter and Signatron probe.

3. RESULTS

3.1. Species in NH3 and H2/N2 Plasmas. The similarities and differences between the NH3 plasma and H2/N2 plasma were identified by collecting mass spectra in the range m/z = 1–30. As can be seen in Figure 2, both plasmas mainly contain H2 (m/z = 2), N2 (m/z = 14 and 28), and NH3 (m/z = 15–17). However, the ratio between these species differs for the two plasmas, with the relative amount of NH3 being larger for the NH3 plasma. The mass-to-charge ratios 15 and 16 could correspond to NH2 (x < 3) species formed in the plasma as well as NH species formed by the dissociation of NH3 in the QMS analyzer. However, NH2 (x < 3) radicals present in the plasma are likely recombined before being detected in the QMS, indicating that the signals for m/z = 15–17 can mainly be attributed to NH3. Although NH2 (x < 3) species cannot directly be detected using the QMS, it can be assumed that they are present in the plasma as a consequence of dissociation of NH3. See also the Supporting Information (Table S2) for the assignment of species to corresponding mass-to-charge ratios.

By comparing the QMS spectrum for the source gas with the spectrum for the corresponding plasma, it becomes visible which species are formed upon plasma ignition (see Figure S4). When a NH3 plasma is ignited, the signals for m/z ratios 15, 16, and 17 decrease, whereas the signals at m/z = 7, 14, and 28 increase. These observations indicate that part of the NH3 is dissociated, leading to the formation of both N2 and H2. Similarly, in a H2/N2 plasma, N2 and H2 are dissociated upon plasma ignition, followed by the formation of NH3 (see Figure S4b). NH3 production using a H2/N2 plasma occurs mostly at the reactor walls because a three-body reaction in the gas phase is unlikely for the pressures used in this work.55,56

The two plasmas were further compared using OES measurements (see Figure S5). The emission spectra for the NH3 and H2/N2 plasmas were found to be very similar. Moreover, the emission peak at ~336 nm corresponds to the A^III → Σ transition of NH and was identified in the spectra for both plasmas (Figure S5b), corroborating the presence of NHx+3 species.

To study the composition of the H2/N2 plasma as a function of the mixing ratio between the H2 and N2 gases, QMS spectra were collected for different H2/(H2 + N2) ratios. The amount of NH3 species produced in the plasma was found to depend on the mixing ratio. Figure 3 shows the QMS ion currents at m/z ratios 16 and 17 as a function of the H2/(H2 + N2) ratio.

Figure 3. QMS ion current at m/z ratios 16 and 17 for H2/N2 plasmas as a function of H2 fraction in the H2/N2 mixture. The H2/(H2 + N2) mixing ratios on the horizontal axis were determined using the ion currents at m/z ratios 2 and 14, corresponding to H2+ and N2+ (see the Supporting Information), before igniting the plasma. The total chamber pressure was kept constant at 75 mTorr.

Figure 2. QMS spectra for a NH3 plasma and a H2/N2 plasma. The main plasma species (H2, N2, and NH3) are indicated in the figure. The NH3 pressure was 1.5 mTorr, whereas the H2/N2 pressure was 13 mTorr.

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80% H2 in the H2/N2 mixture, in agreement with the previous work.\textsuperscript{51,60} Interestingly, the optimum is found close to the ratio between N and H atoms in the NH3 molecule (0.75).\textsuperscript{60,61} Because the plasma composition depends strongly on the mixing ratio, selecting the H2/(H2 + N2) ratio is highly important when using a H2/N2 plasma for ALD, as will also be discussed later. On the basis of the optimum found in Figure 3, a H2/(H2 + N2) mixing ratio of ∼0.77 was employed for further QMS studies and depositions using the AB-H2/N2 process, unless specified otherwise.

3.2. Reaction Products during Plasma Subcycle. A further insight into the use of NH3 and H2/N2 plasmas was obtained by studying the reaction products formed during the ALD cycles using time-resolved QMS measurements. First, QMS signals were collected for m/z ratios 28 (N2+) and 66 (HCp+) during the precursor subcycle of the AB-NH3 process. The signals for m/z = 28 are released as a product during the precursor half-reaction (Figure S6). On the basis of these results, it can be concluded that HCp (C5H6, m/z = 66) is released as a product during the precursor half-reaction. Second, QMS signals were recorded during the co-reactant subcycles of the AB-NH3 process (Figure 4a), the AB-H2/N2 process (Figure 4b), and the ABC-N2-H2 process (Figure 4c). Measurements were done for a normal ALD cycle and for a reference cycle without CoCp2 dosing, using plasma exposures of 11 s (see Figure S3). Differences between the signals for the two cycles indicate the formation of species as a consequence of the ALD reactions.

Figure 4a shows the results collected during the plasma subcycle of the AB-NH3 process. The signals for m/z ratios 28 and 66 are very similar for the ALD cycle and the corresponding reference cycle and are related to the main plasma species, namely, NH3 and N2. The increase in ion current for m/z = 28 and a decrease for m/z = 17 after plasma ignition correspond to the formation of N2 (m/z = 28), which is a consequence of the dissociation of NH3 (m/z = 17). The current for m/z = 17 demonstrates a transient behavior, as NH3 is a "sticky" molecule and the NH3 flow does not stabilize within the time of the exposure.\textsuperscript{62} Meanwhile, the initial rise in ion currents (at ∼0 s) for m/z ratios 27, 39, and 66 upon plasma ignition for the (normal) ALD cycle can be attributed to the release of reaction products (see Table S2). This rise is not observed for the reference cycle without CoCp2 dosing. The increase for m/z = 66, assigned to HCp+ (C5H6+), upon plasma ignition indicates the elimination of the Cp ring from the surface. A similar increase in ion current was observed for m/z = 65 (C5H5+, data not shown). The detection of HCp+ reveals that some of the Cp ligands are still present on the surface after the CoCp2 subcycle. The mass-to-charge ratio 27 corresponds to C3H5+ or HCN+ and m/z = 39 to C2H4+ or C2HN+. The presence of, for example, HCN and C2HN might be caused by the reaction of C3H5 and NH3 species in the plasma. The detection of C2H3+ and C3H4+ might be explained by dissociative ionization of HCp in the QMS (see the cracking pattern in Figure S7) and/or by the formation of C2H3 and C2H4 in the plasma because of dissociation of HCp. Such production channels can unfortunately not be distinguished using the current experimental setup.

The QMS results for the AB-H2/N2 process are shown in Figure 4b. The ion currents for m/z ratios 17 and 28 behave very similar for the ALD cycle and the reference cycle and indicate the formation of NH3 (m/z = 17) and consumption of N2 (m/z = 28) in the H2/N2 plasma. These findings are in line with the QMS measurements discussed in Section 3.1 (and as shown in Figure S4). Note that the signal for m/z = 17 continues to increase during the plasma exposure because of the "sticky" nature of NH3 and/or ongoing stabilization of the NH3 production.\textsuperscript{62} However, the current for m/z = 17 starts to
drop after the plasma exposure, accompanied by a small increase in the signal for N₂, indicating that no more N₂ is being consumed. The ion currents for m/z ratios 27, 39, and 66 for the ALD cycle increase when the plasma is started (at t ≈ 0 s), similar to the data shown in Figure 4a. This increase can be explained by the release of reaction products, as was discussed for the AB-NH₃ process.

To examine the role of the NH₃ species in the plasma in the reaction mechanism, the H₂/N₂ plasma was replaced by separated N₂ and H₂ plasma steps in an ABC-type cycle (see Figure 1). The results for the ABC-N₂-H₂ process in Figure 4c show that no NH₃ was present during the N₂ exposure, as can be expected. Moreover, upon ignition of the N₂ plasma (at t ≈ 0 s), a minimal amount of HCP⁺ (m/z = 66) is detected (revealed by the small difference with the reference cycle), which is much smaller than for the AB-NH₃ and AB-H₂/N₂ processes. Upon ignition of the subsequent H₂ plasma, a rise in ion currents for both m/z = 17 and 28 (at t ≈ 32 s, observed for the ALD cycle and also for the reference cycle) indicates that NH₃ and N₂ are released. However, the amounts are almost negligible and are limited by the amount of nitrogen-containing species adsorbed to the substrate and reactor wall after the N₂ plasma exposure. The H₂ plasma mostly leads to the detection of C₂H₂⁺/HCN⁺ (m/z = 27) and C₂H₄⁺/C₂HN⁺ (m/z = 39) species and no significant amount of HCP⁺. The limited amount of HCP⁺ detected during both plasma exposures indicates that the Cp ring is not eliminated as a whole but rather dissociated because of the interaction with the plasmas.

Comparison of the results for the three different ALD processes provides an insight into the similarities and differences in reaction mechanisms. Except for the differences in plasma species (m/z = 17 and 28), the results in Figure 4a,b show very similar reaction products for the AB-NH₃ and AB-H₂/N₂ processes. These analogies between the two AB processes suggest a similar reaction pathway, where Cp ligands are eliminated from the surface during both the precursor and plasma subcycles. QMS measurements for the ABC-N₂-H₂ process show significant differences in terms of plasma species and reaction products (see Figure 4c), as compared to the AB processes, suggesting a different reaction pathway.

3.3. Film Properties. Before characterization of the material properties, the ALD behavior of the two AB processes was studied by determining the GPC as a function of the CoCP₂ dosing and the plasma exposure times. As can be seen in Figure S1, both the precursor and co-reactant subcycles demonstrated a self-limiting behavior for the NH₃ plasma as well as for the H₂/N₂ plasma processes. Moreover, the saturation curves for the two processes look very similar, in line with the finding that the two AB processes show similarities in terms of plasma composition and reaction pathways as discussed in Sections 3.1 and 3.2. The GPC saturates to a maximum value of 0.29 ± 0.02 Å, which is slightly lower than that reported by Kim and co-workers (0.48 Å).²⁶,²⁷

The material properties for the three different ALD processes were investigated for the films deposited using 1000 cycles. A film deposited using the AB-NH₃ process was investigated using TEM after preparation of a lamella using a FIB. The cross-sectional images in Figure 5 reveal that the film is polycrystalline and the crystal grains can clearly be observed. The film forms a closed layer of approximately 29 nm thick and has a low roughness. SE modeling yielded a film thickness of ∼32 nm. The difference between the thicknesses derived from SE and TEM is thought to be due to the film roughness, which is not included in the SE modeling.

The material properties obtained using the different processes are shown in Table 2. As can be seen, for both the AB-NH₃ and the AB-H₂/N₂ processes, the film thickness (determined using SE) is ∼25 nm after 1000 cycles, corresponding to an average GPC of approximately 0.25 Å. It is noted that the sample prepared for the TEM analysis was different from the sample listed in Table 2 and the film thickness was slightly higher. The ABC-N₂-H₂ process resulted in an average GPC as high as 0.44 Å. The films deposited using the AB-NH₃ and AB-H₂/N₂ processes both demonstrate a low resistivity (41–42 μΩ cm, as compared to a Co bulk resistivity of 6.24 μΩ cm) and have a similarly low impurity content.⁶³ The resistivity values obtained for the AB processes are slightly higher than the best reported value for Co ALD and lie within the range of values obtained for processes using NH₃ or H₂/N₂ plasma as the co-reactant (10–140 μΩ cm, see Table 1). This is in contrast to the film deposited using the ABC-N₂-H₂ process, which has a high resistivity (>1000 μΩ cm), likely caused by considerable amounts of impurities found in the film (O, N, and C add up to 25 at. %).

XPS measurements showed that the surface of the Co films is slightly oxidized (Figure S8). After Ar⁺ sputtering, the O contents of the films deposited using both AB processes (NH₃ and H₂/N₂) are however found to be close to 0 at. %, and metallic Co 2p peaks were detected at around 780.2 eV.⁶⁴ Apart from minimal amounts of O, C, and N, no other impurities were detected in the Co films grown using the AB-NH₃ and AB-H₂/N₂ processes. For the film deposited using the ABC-N₂-H₂ process, significant amounts of O, C, and N were detected in the bulk of the film (see the XPS results in Figures S8 and S9). It was found that exchanging the H₂ and N₂ plasma exposures, corresponding to an ABC-type cycle first with the H₂ plasma followed by the N₂ plasma, led to a comparable impurity content of approximately 25 at. % (see Table S3).

The significant higher GPC and resistivity for the ABC-N₂-H₂ process can be explained by the impurity incorporation, leading to a lower film density and/or a higher surface roughness. The difference between the two AB processes on one hand and the ABC-N₂-H₂ process on the other hand can most likely be attributed to the absence of NH₃ species in the
4. DISCUSSION

4.1. Role of NH3 Species. The results addressed in Section 3 can provide an insight into the role of different plasma species during the Co film growth. Specifically, the data in Table 3 show that the impurity content decreases with the H2 fraction in the H2/N2 plasma. Meanwhile, the ion current at $m/z = 17$, indicating NH3 in the plasma, increased when varying the H2/(H2 + N2) ratio up to ~0.77 (see Figure S10). This finding is in line with the dependence of the NH3 content on the mixing ratio as was discussed in Section 3.1. In Figure 6, the Co concentration of the films is plotted as a function of the ion current for $m/z = 17$. Interestingly, this graph shows a linear trend, suggesting that a higher amount of NH3 species in the plasma leads to a higher film purity. Note that with a higher NH3 concentration in the plasma, also the amount of NH$_{x<3}$ radical species increases, as a consequence of NH3 dissociation. The increase in Co purity is mostly due to the decrease in O content, suggesting that NH3 species facilitate the removal of O from the material or lead to a film which is less prone to post-deposition oxidation. Additional research is required to distinguish between these two possible explanations.

Overall, the findings show that careful consideration is needed when a H2/N2 plasma is employed as the co-reactant for ALD. Moreover, the dependence on the NH3 concentration explains why H2 plasmas or N2 plasmas are not suitable as co-reactants, mainly because of the lack of NH3 species. In addition, the fact that NH3 gas cannot be used as the co-reactant in a thermal ALD process substantiates the hypothesis that NH3 species are necessary. The results thus suggest that NH$_{x<3}$ species play a crucial role in the Co growth or post-deposition oxidation of the Co film structure (e.g., crystallinity, density, or porosity) might affect the film resistivity, and further research would be required to obtain a more detailed understanding. The O incorporation is likely due to the dissociation of background species (such as H2O) in the plasma during film growth or post-deposition oxidation of the films.65,66 Interestingly, the C and N contents of the films are relatively constant and do not show a clear trend as a function of H2/(H2 + N2) ratio. The relation between the H2/(H2 + N2) ratio and the material properties will be further discussed in Section 4.1.

Table 2. Material Properties of Co Films for the Three Different ALD Processes As Determined from SE, FPP, and XPS$^a$

<table>
<thead>
<tr>
<th>ALD process</th>
<th>d (nm)</th>
<th>$\rho$ ((\mu\Omega\cdot\text{cm}))</th>
<th>[O] (at. %)</th>
<th>[N] (at. %)</th>
<th>[C] (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB-NH3</td>
<td>25</td>
<td>41</td>
<td>0.5 ± 0.3</td>
<td>2.3 ± 0.5</td>
<td>0.6 ± 0.6</td>
</tr>
<tr>
<td>AB-H2/N2</td>
<td>25</td>
<td>42</td>
<td>1.0 ± 0.4</td>
<td>2.8 ± 0.5</td>
<td>0.7 ± 0.7</td>
</tr>
<tr>
<td>ABC-N2-H2</td>
<td>44</td>
<td>$1 \times 10^3$</td>
<td>10.0 ± 0.5</td>
<td>8.4 ± 0.5</td>
<td>7 ± 1</td>
</tr>
</tbody>
</table>

“1000 ALD cycles were performed. The impurity contents were determined using XPS after sputtering with Ar+ for 6 min. Absolute errors in the impurity content are indicated in the top row.

Table 3. Material Properties of Co Films for Different H2/N2 Mixing Ratios$^a$

<table>
<thead>
<tr>
<th>H2/(H2 + N2)</th>
<th>d (nm)</th>
<th>$\rho$ ((\mu\Omega\cdot\text{cm}))</th>
<th>[O] (at. %)</th>
<th>[N] (at. %)</th>
<th>[C] (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>17.9</td>
<td>$&gt;10^5$</td>
<td>7.0 ± 0.2</td>
<td>9.5 ± 0.5</td>
<td>4.0 ± 0.9</td>
</tr>
<tr>
<td>0.23</td>
<td>19.9</td>
<td>$&gt;10^5$</td>
<td>6.2</td>
<td>9.5</td>
<td>3.8</td>
</tr>
<tr>
<td>0.35</td>
<td>20.3</td>
<td>$3.6 \times 10^5$</td>
<td>5.6</td>
<td>9.3</td>
<td>3.8</td>
</tr>
<tr>
<td>0.42</td>
<td>20.3</td>
<td>$2.5 \times 10^5$</td>
<td>4.2</td>
<td>9.6</td>
<td>3.5</td>
</tr>
<tr>
<td>0.52</td>
<td>19.6</td>
<td>$1.5 \times 10^5$</td>
<td>4.4</td>
<td>8.8</td>
<td>3.8</td>
</tr>
<tr>
<td>0.77</td>
<td>17.5</td>
<td>78</td>
<td>0.2</td>
<td>8.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

“800 ALD cycles were performed. The total pressure was kept constant at 13 mTorr. The impurity contents were determined using XPS after sputtering with Ar+ for 3 min. Typical errors in the impurity content are indicated in the top row.

Figure 6. Co content from XPS as a function of QMS ion current at $m/z = 17$. The QMS ion current is a measure for the NH3 production in the H2/N2 plasma and was varied by changing the H2/N2 mixing ratio of the source gas. The pressure of the H2/N2 gas mixture was kept constant at 13 mTorr. The Co content was determined using XPS on films obtained by performing 800 ALD using the various H2/N2 mixing ratios. XPS was carried out after sputtering with Ar+ ions for 3 min. The resistivity values of the Co films are indicated in the figure, in which the dashed line represents a linear fit through the data. It is noted that the decrease of the film resistivity as a function of NH3 concentration might be related to the changes in the film structure, aside from the increased film purity.
growth. This is further elaborated on in Section 4.1, where a reaction mechanism is proposed.

Interestingly, the dependence of the film resistivity on the H₂/N₂ ratio is in agreement with the work of Yoon et al. and Hong et al. for the deposition of Co and Ru, respectively. Both studies observed high-resistivity values for high N₂ fractions and suggested that NH₃ species in the plasma play an important role in the growth. In addition, the work of Ten Eyck et al., the H₂/N₂ ratio was optimized in order to maximize the NH₃ generation in the plasma. Finally, ALD processes for Ru, Ni, and Ag have been reported to improve when NH₃ plasmas are used instead of H₂ plasmas (in terms of a higher GPC and lower resistivity), which also suggests an important role of NH₃ species present in the NH₃ plasmas.

### 4.2. Reaction Mechanism

The QMS studies addressed in Section 3.2 can help to unravel the reaction mechanisms for the ALD growth of Co. Before reviewing the main QMS results, it is relevant to obtain an understanding of the surface groups present on Co after plasma exposure (i.e., prior to precursor dosing). Although the interaction of a NH₃, H₂, or N₂ plasma with a Co surface has not been studied in detail, the surface science literature on Co provides some insights. For instance, Kizilayka et al. investigated the stability of NH₃ groups on Co after NH₃ exposure and found that NH₃ adsorption on Co is followed by decomposition, resulting in NH₃ groups remaining on the surface.

In addition, Wang et al. studied the nitridation of transition-metal surfaces and calculated that Co is not prone to nitridation, although a N-covered surface is stable after formation. On the basis of these reports, it can be expected that NH₃ groups are present on the Co film after NH₃ or H₂/N₂ plasma exposure. H adsorbed on the Co surface seems less likely because H is reported to desorb (as H₂) from Co between the temperatures of approximately 300 and 400 K, which is lower than the sample temperature during ALD (300 °C = 573 K table temperature).

Notably, the role of N-containing surface species has previously been addressed for the ALD of Pt and Ag using N₂ or NH₃ plasmas. Specifically, N-containing species were proposed to adsorb during the N₂ or NH₃ plasma exposures and to react with the precursor during the subsequent precursor dose. In short, the QMS studies in Section 3.2 revealed the following. During the precursor and co-reactant subcycles, HCp (C₅H₅) is released for both the AB-NH₃ and AB-H₂/N₂ processes. In addition, fragments of the Cp ring (e.g., C₅H₄ and C₅H₄N⁺) were detected during the plasma exposure. Furthermore, variation of the H₂/N₂ ratio showed that the NH₃ species (NH₃<sub>y</sub>≡<sub>3</sub>) play an important role in the growth mechanism. These observations suggest that during the precursor subcycle, the CoCp₅ molecules chemisorb to the surface and that part of the Cp rings react with H atoms present at the surface, followed by the release of HCp.

It is illustrated in step “A” in Figure 7. Considering that chemisorbed H is not stable on a Co surface, it is speculated that NH₃ surface groups present after the plasma exposure provide the source of H (NH₃ with the subscript y is used to indicate the distinction from the NH₃ species in the plasma). Additional research such as surface Fourier-transform infrared spectroscopy (FTIR) is required to identify the surface groups to which the precursor binds. Possibly the precursor chemisorbs directly to unoccupied Co surface sites or to the NH₃ species after the release of HCp.

In the co-reactant subcycle, the Cp ligands remaining after precursor dosing are eliminated by the NH₃ radical species from the plasma (NH₃<sub>y</sub>≡<sub>3</sub>). This reaction leads to the formation of HCp and Cₓₜ, Hₓ, and N-containing fragments, as illustrated in step “B” in Figure 7. The release of HCp was also observed during the NH₃ plasma exposure in the work of Oh et al. Moreover, Shimizu et al. and Yuan et al. used NH₃ as the co-reactant gas for Co and Ni hot-wire ALD using CoCp₅ and NiCp₅ as precursors, respectively, and claimed that the NH₃ gas-phase species formed on the hot wire are needed for the dissociation of the metal–Cp bond.

In the reaction mechanism shown in Figure 7, the NH₃<sub>y</sub>≡<sub>3</sub> species generated in the plasma thus fulfill this role. Furthermore, the NH₃<sub>y</sub>≡<sub>3</sub> species as well as NH₃ lead to the formation of NH₃ surface groups, which react with the precursor molecules in the next cycle. Although NH₃ can dissociate after adsorption on a clean Co surface, it is believed that the NH₃<sub>y</sub>≡<sub>3</sub> species are essential for complete ligand removal.

Note that a small amount of N (~2−3 at. %) is present in the Co films deposited using the AB-NH₃ and AB-H₂/N₂ processes and that this content is slightly higher (~4.5 at. %) in the (sub)surface region (see Figure S9). This corroborates the expectation based on the surface science literature that N-containing species (e.g., NH₃) are present and that they are more stable on the surface than in the bulk. However, a remaining question is how the surface NH₃ species leave the film, such that they are not incorporated in the film. Because the films contain only a small amount of N, it is speculated that most of the N diffuses out of the surface region and desorbs in the form of either NH₃ or N₂.

Interestingly, an analogy appears to exist between the proposed reaction mechanism and the ALD growth of noble metals using O₂ as the co-reactant. During noble metal ALD, chemisorbed O plays a crucial role in the reaction mechanism, while the stability of noble metal oxides is limited. This is similar to the ALD of Co, where NH₃ species appear needed for chemisorption of the precursor and removal of the Cp ligands but are not built into the film.

### 5. CONCLUSIONS

The use of H₂, N₂, and NH₃-based plasmas as co-reactants for the ALD of Co using CoCp₅ was investigated. A direct
comparison was made between ALD processes with a NH\textsubscript{3} plasma and a combined H\textsubscript{2}/N\textsubscript{2} plasma as the co-reactant. It was shown that the NH\textsubscript{3} and H\textsubscript{2}/N\textsubscript{2} plasmas contain comparable plasma species, including NH\textsubscript{several} although the relative concentrations are different. Moreover, the reaction products detected during the plasma subcycle are very similar, suggesting analogous reaction pathways. Variation of the mixing ratio of H\textsubscript{2} and N\textsubscript{2} in the H\textsubscript{2}/N\textsubscript{2} plasma showed that the lowest resistivity is achieved for the ratios with the highest NH\textsubscript{several} concentration. In addition, the films deposited using plasmas with a lower NH\textsubscript{several} concentration contained significant amounts of O impurities. Deposition using an ABC-type cycle with consecutive N\textsubscript{2} and H\textsubscript{2} plasma steps resulted in a Co film with significant amounts of impurities and a high resistivity. These insights indicate that the NH\textsubscript{several} present in both the NH\textsubscript{3} and H\textsubscript{2}/N\textsubscript{2} plasmas are necessary for eliminating the precursor ligands and for obtaining high-purity films, which explains why H\textsubscript{2} plasmas or N\textsubscript{2} plasmas are not suitable as co-reactants. Furthermore, on the basis of the QMS results and surface science literature, a reaction mechanism was proposed where NH\textsubscript{several} play an essential role, leading to the release of H\textsubscript{2}C\textsubscript{p} in both subcycles.

Overall, the work shows that the plasma composition can strongly affect the obtained material properties and that the co-reactant of a metal ALD process should be carefully selected. Specifically, when using a H\textsubscript{2}/N\textsubscript{2} plasma for Co ALD, selecting the H\textsubscript{2}/(H\textsubscript{2} + N\textsubscript{2}) ratio is crucial. Other literature reports further illustrate the importance of choosing a suitable co-reactant and demonstrate that NH\textsubscript{3} or H\textsubscript{2}/N\textsubscript{2} plasmas can be preferred over other co-reactants. This suggests that the findings of this work can be generalized and can also apply to other metal ALD processes.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b06342.

Additional OES and QMS data on the plasma composition, detailed description of the QMS procedures, assignment of species to corresponding m/z ratios, QMS data collected during the precursor subcycle, saturation curves, and XPS data showing the elemental film composition and ion currents for m/z = 16 and 17 as a function of H\textsubscript{2}/(H\textsubscript{2} + N\textsubscript{2}) for 13 and 75 mTorr, respectively (PDF)

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Notes
The authors declare no competing financial interest.

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