Growth chemistry of cobalt nitride by plasma enhanced atomic layer deposition

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Abstract

State-of-the-art atomic layer deposition (ALD) and photoemission characterisation are applied to grow and characterise cobalt nitride, a material that has applications in renewable energy and semiconductor technologies. The growth process is characterised using an in situ cycle-by-cycle methodology to identify the main factors which underpin optimal material growth. The role of co-reactant dosing and substrate temperature is analysed in detail to demonstrate the impact these parameters have on the overall composition of the film. The in situ approach, combined with high-energy synchrotron-based photoemission studies of the resulting films, enables understanding of the bulk chemical properties without need for physical removal of material by sputtering. The results provide an insight into optimising plasma assisted ALD processes for deposition of cobalt nitride, and strategies for minimizing carbon incorporation into the film from the precursor ligands.

Introduction

This work examines the growth of cobalt nitride via atomic layer deposition (ALD). Cobalt nitride is recognised as a material capable of catalysing the oxygen evolution reaction (OER) in water electrolysis for the generation of green hydrogen, showing impressive performance when compared to current benchmarks in the field [1-5]. Additionally, ultrathin cobalt nitride films have been suggested as a possible adhesion promoter for copper interconnects in the backend of complementary metal oxide semiconductors (CMOS) processes [6]. Cobalt nitride is also a promising candidate in the study of inexpensive and non-rare earth materials for magnetic applications [7]. These fields of application each require a high degree of control over material properties such as stoichiometry and thickness, and growth techniques such as ALD are particularly suitable, offering a pathway to control the films properties such that they can be tailored to individual applications.

ALD is a thin film deposition technique based on a variant of chemical vapor deposition where precursors and co-reactants are admitted to the reaction chamber and purged in sequence. Great strides have been made in the last 20 years in developing ALD processes for a wide range of metals, oxides, nitrides, and other materials. ALD processes are designed to be ’self-limiting’ whereby the precursor or co-reactant can only react with the finite number of surface sites available during each half-cycle. This feature of the technique allows for precise control over the film’s thickness and chemical state once the growth rate for the process has been established, with the deposition of pristine films which are conformal over a large area. ALD has been applied to fields as diverse as large-scale CMOS processing, energy technology, and biocompatible coatings.

ALD processes can broadly be split into two categories: thermal (T-ALD) and plasma enhanced (PE-ALD). In thermal ALD, the co-reactant is admitted to the chamber using a pulse, similar to the precursor. Typical co-reactants in T-ALD processes include H₂O and O₂ for oxides, N₂ and NH₃ for nitrides, and H₂ for metals. In PE-ALD processes the co-reactant pulse step is replaced with exposure of the surface to a plasma. The plasma drives self-limiting surface
reactions and is followed by a purging step as is the case in T-ALD processes. The advantage of PE-ALD is that it can allow for lower processing temperatures than T-ALD and can also allow for the use of less reactive precursors. PE-ALD can be useful in the growth of metal nitrides [8, 9]. Many transition metal nitrides are difficult to grow using T-ALD owing to instability due to the small electrochemical potential of the metal [10]. Furthermore PE-ALD can assist with improving the growth rate in ALD processes where precursor reactivity is low [11, 12].

Growing cobalt nitride through ALD processing is an interesting field of study. As illustrated by van Straaten et al [13] in earlier work, the electrochemical potential of cobalt nitride is close to 0 kJ mol$^{-1}$ suggesting the metal should be more stable than the nitride. Using cobaltocene (CoCp$_2$) as the cobalt precursor and NH$_3$ plasma as a co-reactant, their work showed that the formation of nitride or metal was dictated by the processing temperature, with chiefly Co$_3$N formed at temperatures below 260 °C and metal above 350 °C and a mixed phase material at intermediate temperatures. Argon sputtering of the films and subsequent x-ray photoelectron spectroscopy (XPS) showed bulk nitrogen concentrations of approximately 20% at low temperatures and little to no carbon incorporation. Reif et al [14] also studied cobalt thin film growth by PE-ALD, employing cyclopentadienylcobalt dicarbonyl [CpCo(CO)$_2$] as the cobalt precursor, investigating H$_2$, N$_2$, NH$_3$ and argon plasma doses. Their work shows that an optimised H$_2$/N$_2$ plasma yielded films with approximately 20% nitrogen and very little carbon incorporation from the precursor ligands, while the use of an NH$_3$ plasma yielded films with 30% nitrogen but also 30% carbon. This work however, does not discuss optimisation of the NH$_3$ plasma process to reduce carbon incorporation, and all experiments are performed at relatively low temperature (< 250 °C). From comparison of these two studies it appears that a CpCo(CO)$_2$—NH$_3$ combination results in films that are carbon rich while CoCp$_2$/NH$_3$ yields cleaner films.

In this work we examine the growth of cobalt nitride using CoCp$_2$ as the cobalt precursor and NH$_3$ plasma as the co-reactant, and explore strategies to minimise carbon incorporation into the resulting films. We present an in situ XPS study of the CoCp$_2$/NH$_3$ PE-ALD growth process at temperatures from 200 °C–400 °C. Films are grown in an Oxford Instruments FlexAl ALD reactor and transferred by a robotic handler to an XPS chamber to allow for a cycle-by-cycle analysis of the growth chemistry, and without atmospheric exposure. This in situ approach offers a clear understanding of the ALD process which is not complicated by the effects of contamination from atmospheric carbon and oxygen. Combining this analysis with synchrotron-based hard X-ray photoelectron spectroscopy (HAXPES) studies of the resulting films gives an understanding of the bulk properties without the need for physical removal of material by sputtering. We examine the impact of the temperature and plasma pulse duration on the film composition, with adaptations shown to have several effects on the stoichiometry of the resulting cobalt nitride film. We show that rather than displaying saturation, longer plasma pulses severely inhibit the growth rate at all temperatures. The optimum plasma pulse duration for maximum growth per cycle is shown to reduce with increasing temperature. Furthermore, our results are similar to those of Reif and colleagues whereby carbon concentrations of up to approximately 40% are observed [14]. The study shows that the only set of process parameters which allow for reduced carbon incorporation are a combination of high temperature and long plasma pulse time which are accompanied by an exceptionally low growth rate and yield cobalt rich films. The ability to form cobalt nitride films that have a homogenous chemical composition is shown, however these films contain high amounts of carbon–nitrogen bonding throughout the film.

**Experimental details**

ALD and XPS analysis was performed in a custom designed Oxford Instruments FlexAl ALD system (base pressure 5 × 10$^{-5}$ Pa) equipped with an inductively coupled plasma source. The FlexAl system is coupled in-vacuum by a fast-transfer robotic handler to a Scienta Omicron XPS (monochromatic Al Ka X-ray source, base pressure 6 × 10$^{-7}$ Pa) with a 128 channel Argus CU detector. Transfer time between chambers is approximately 1 min. This setup allowed for photoemission analysis to be performed on samples without the need for the sample to break vacuum. The XPS pass energy applied was 100 eV and 50 eV for survey and high resolution spectra, respectively.

All ALD films were grown on silicon samples of approximately 2 cm$^2$. Prior to entering the deposition chamber, the silicon was ultrasonicated in isopropyl alcohol for 15 min, before being blown dry with compressed N$_2$. Upon entering the ALD chamber, samples were heated to the desired process temperature for 20 min, before being exposed to a 5.3 Pa (40 mTorr), 300 W plasma process that consisted of 3 min of O$_2$ flowed at 100 sccm followed by 3 min of NH$_3$ flowed at 50 sccm [13]. By considering the intensities of the Si$^{2p}$ and Si$^{+2}/2^{+3}/3^{+4}/4^{+}$ in the Si $2p$ XPS spectra, the residual silicon oxide thickness after this cleaning process was estimated at 0.8 nm [15].

The ALD process began immediately after the cleaning step, using CoCp$_2$ (Bis(cyclopentadienyl)cobalt(II), purchased from Merck and heated to 80 °C) as the precursor and NH$_3$ as the PE-ALD co-reactant. An ALD cycle
consisted of a dose of CoCp₂, followed by a purge of Ar gas. The chamber was pumped for 6 s before a 4 Pa (30 mTorr), 100 W and 50 sccm NH₃ plasma step. The plasma was followed by a purge of Ar and 3 s of pumping before the next cycle began. Aside from temperature, the other variables investigated were the time duration of the CoCp₂ and NH₃ plasma steps, which is discussed in the results section. An example of a typical process is shown in the supporting information (table S1).

Ellipsometry measurements were performed using a Woollam XLS-100 and employing a Cauchy model. HAXPES measurements were performed at the National Institute of Standards and Technology beamline 7-ID-2, located at the National Synchrotron Light Source II, Brookhaven, New York (NSLS-II). To depth profile the samples, photon energies of 2, 4 and 6 keV were implemented, with a pass energy of 100 eV applied for the 2 keV and 200 eV for the 4 and 6 keV photon energies.

All XPS/HAXPES spectra analysis was performed using the software AAnalyzer [16]. All fitted spectra used a Shirley Sherwood type background and a Voigt type curve profile. Where possible, all spectra were shifted so that the Si 2p (bulk) peak for the relevant dataset was located at 99.4 eV [17], with care taken due to the overlap of the Si 2p and Co 3s binding energy positions.

Results

ALD process characterisation

Prior to ALD characterisation, an investigation into obtaining an optimal CoCp₂ dose time for the FlexAl system was performed. Saturation was determined by monitoring the ratio of the Co 2p₃/₂ XPS peak intensity to the Si 2s in situ. A saturation point is established through analysing the rate of Si 2s peak suppression as a function of Co deposition cycles. It was found that CoCp₂ saturation occurred between 0.5–3 s (figure S1, supporting information) for a 270 °C—chuck temperature that received a 10 s NH₃ plasma dose. All further investigations implemented a 3 s CoCp₂ dose time.

The same principle of monitoring the Co 2p₃/₂/Si 2s intensity was performed for the determination of the optimal NH₃ plasma dose time. The XPS intensity graphs of the ICo₂⁺/ISi₂⁺ versus plasma dose time at three different temperatures, normalised to the maximum signal for that temperature, is shown in figure 1. Unlike typical ALD processes, saturation in growth rate with increasing plasma exposure time was not observed.

As expected, we see an increasing growth rate initially where longer plasma exposure times allow for precursor ligand removal and activation of the surface for the next ALD cycle. However, as exposure time was further increased, it was observed that cobalt nitride growth was severely inhibited at high plasma dose times, thereby creating a window for NH₃ plasma dosing to achieve the highest growth rates. The drop off in growth rate was more severe at higher temperature. Following the acquisition of the saturation curves, XPS analysis of the growth of the cobalt nitride at different stages of the ALD process was performed in order to understand the growth chemistry. Films were processed at 200 °C, 300 °C, 350 °C and 400 °C, and XPS analysis was carried out immediately after 50, 100, 200, 500 and 1000 cycles in each case. To enable easy cross analysis, the four ALD processes used identical process parameters. As figure 1 shows, high plasma times resulted in very slow growth for high temperature processes, resulting in a NH₃ time of 5 s being chosen for all temperatures. Estimations of the growth rate for each ALD process were obtained through ellipsometry, with films analysed ex situ after 1000 cycles. Figure 2 shows the thickness and the calculated growth per cycle (GPC, in Å/cycle) for the four process temperatures. Despite decreasing the NH₃ plasma dose time to encourage reasonable growth at high temperatures, the GPC clearly scales inversely with temperature.

The XPS spectra of the Co 2p for the four ALD process temperatures are shown in figure 3. Both the 200 °C (a) and 300 °C (b) depositions have peak maxima located at approximately 781 eV at all stages of the process, which is associated with cobalt nitride. The Co 2p spectra for the 350 °C process (c) has a peak maximum at approximately 781 eV, attributed to cobalt nitride, and a lower binding energy component at 779 eV, which is associated with metallic cobalt [18, 19]. This result supports previous work which showed that a blend of cobalt nitride and Co⁰ is formed during ALD processes at 350 °C [13]. Our results show however that only Co⁰ is present for the first 200 cycles, with cobalt nitride forming at 500 + cycles. At 400 °C, the growth of Co⁰ is observed with no other Co oxidations state observable in the chosen cycle range. The position of the main Co 2p₃/₂ peak at approximately 778.5 eV, in addition to the asymmetry of the spectra, confirms the growth of metallic Co [20].

Clear N 1s signals (figure S2, supporting information) are observed for all processing temperatures, despite only Co⁰ being visible for the 400 °C process in figure 3(d). The maxima for each process are located at approximately 399 eV, however the broad and asymmetric peak profile, suggests that more than one chemical state of nitrogen is present in the film.

ALD grown films of cobalt nitride have typically exhibited a high concentration of carbon impurities [14, 21]. Our results show similar behaviour, with XPS spectra of the C 1s region revealing significant carbon
incorporation after 1000 cycles in the temperature range of 200 °C–350 °C. Figures 4(a)–(c) for the 200 °C, 300 °C and 350 °C ALD process respectively show that the carbon exists in two main states, a lower binding energy component associated to C–C type bonding, and a higher binding energy component which is attributed

\[ \text{Co}^{2+}_{p3/2} / \text{Si}^{2s} \]  

Intensity vs.  

NH\textsubscript{3} Dose Time, 150 cyc  

\[ \frac{I_{\text{Co}^{2+}_{p3/2}}}{I_{\text{Si}^{2s}}} \text{(Normalised)} \]  

NH\textsubscript{3} Dose (s)  

**Figure 1.** NH\textsubscript{3} plasma dose time saturation curves for 150 cycle processes at three temperatures. The Co dose time was 3s. The data was obtained by monitoring the ratio of the XPS intensity of the Co 2p\textsubscript{3/2} peak to the intensity of the Si 2s spectra. A time window for achieving optimal cobalt nitride growth was observed, which narrowed with increasing temperature. Si peaks from the substrate were always visible.

\[ \text{Ellipsometry measured thickness, 1000 cyc, 5s NH}_3 \]  

**Figure 2.** Ellipsometry thickness measurements of a 1000 cycle ALD recipe for 4 different process temperatures. The growth rate in Å/cyc is also shown.
Notably there is no evidence of carbidic carbon in the films. The ratio of C–C to C–N type bonding favours C–C in the early stage of the ALD process, however C–N becomes dominant with increasing cycles. Due to the in situ nature of the analysis we can confidently identify that the C–C component of the peak is associated with the carbon from the precursor that

to C–N bonds (all oxygen in the spectra is associated with the SiO₂ interlayer). Notably there is no evidence of carbidic carbon in the films. The ratio of C–C to C–N type bonding favours C–C in the early stage of the ALD process, however C–N becomes dominant with increasing cycles. Due to the in situ nature of the analysis we can confidently identify that the C–C component of the peak is associated with the carbon from the precursor that

**Figure 3.** XPS Co 2p spectra for the four ALD process temperatures at different stages of a 1000 cycle process, (a) 200 °C, (b) 300 °C, (c) 350 °C and (d) 400 °C. Coₙₓ is visible for the 200 °C and 300 °C process. The 350 °C process consists of Co⁰ only until approximately 500 cycles, where a Coₙₓ and Co⁰ blend is formed. The 400 °C yields Co⁰ only.

**Figure 4.** XPS C 1s spectra for the four ALD process temperatures at different stages of a 1000 cycle process, (a) 200 °C, (b) 300 °C, (c) 350 °C and (d) 400 °C. Two major components are visible in the spectra for the 200 °C, 300 °C and 350 °C processes, the low and high binding energy components are associated with C–C and C–N bonds respectively.
has not been effectively removed by the co-reactant plasma (and not adventitious carbon), with a gradual growth in C–N in the film being obtained through continued exposure to NH3 plasma. This correlates with the broad spectra of the N 1s as seen in figure S2, and is discussed in more detail with the HAXPES analysis.

The XPS chemical compositions of each ALD process for increasing cycle numbers are shown in figure 5. Carbon, nitrogen, and cobalt were the only signals considered, with the oxygen and silicon signals attributed to the substrate only. The compositions were calculated by applying the relevant atomic sensitivity factors [22] to the C 1s, N 1s and Co 2p3/2 spectra.

The carbon concentration in the film is seen to be relatively steady throughout the ALD process at all temperatures, with the sample processed at 200 °C (a) containing the highest amount of incorporation. This decreases with increasing temperature, with carbon incorporation at 1000 cycles being 47%, 42%, 31% and 21% for the 200 °C, 300 °C (b), 350 °C (c) and 400 °C (d) respectively. In contrast to this behaviour, cobalt in the film tends to increase with increasing temperature—at 1000 cycles, the concentration of cobalt is 11%, 16%, 24% and 17% for the 200 °C, 300 °C, 350 °C and 400 °C (d) respectively, although it should be noted that this coincides with dramatic decrease in growth rate as shown in figure 2. The cobalt concentration appears to act oppositely to the nitrogen concentration—there is a slight increase of nitrogen at the expense of cobalt with increasing ALD cycles at 200 °C and 300 °C, while decreasing amounts of nitrogen can be linked with increasing amounts of cobalt concentration at 350 °C and 400 °C.

Characterising optimised films

Further analysis is now focused on the characterisation of cobalt nitride films grown at 200 °C and 300 °C, as it was observed from figure 3 that higher temperatures yielded films with increasing amounts of CoO. Thick (10 + nm) cobalt nitride films were fabricated in order to assess the bulk and surface of the ALD films, with 1000 and 2000 cycles used for the 200 °C and 300 °C process, respectively. Based on the learnings from figure 1, the optimal parameters for both processes consisted of a 3 s and 10 s dose time for the CoCp2 and NH3 plasma, respectively.

XPS measurements were performed on the cobalt nitride samples immediately after the ALD process before being removed and exposed to atmosphere to allow for ellipsometry thickness measurements. These samples were then loaded back into the XPS vacuum chamber to reveal the effect of atmospheric exposure before being treated with a 2 h NH3 plasma (5.3 Pa/40 mTorr, 50 SCCM, 300 W) at the same temperature as the corresponding ALD process, to assess whether carbon removal to yield cleaner more stoichiometric cobalt nitride films using such a treatment is achievable.
The ellipsometry and XPS chemical compositions for each stage of the process is shown in Table 1. The XPS compositions were calculated from the survey scans (shown in Figure S3, supporting information) for each sample. Each column represents the film at different stages of the process: 200/500 °C ALD—post ALD, 200/500 °C + post atmosphere exposure (atm), 200/300 °C + NH3—post 2 h NH3 plasma.

The ellipsometry revealed a GPC of 0.18 Å/cyc and 0.07 Å/cyc for the 200 °C and 300 °C processes, respectively. Post ALD, the XPS compositions reveal films that are dominated by nitrogen and carbon, with negligible oxygen seen in the film. Pre-atmospheric exposure, the 200 °C and 300 °C compositions show consistent correlation with figure 5—a slightly higher carbon incorporation is observed for the lower temperature process. The oxygen contribution increases slightly after atmospheric exposure, but remains extremely minor to the overall makeup of the film. The carbon concentration also increases, due to the adsorption of adventitious carbon, which results in the attenuation of the cobalt and nitrogen signals. After prolonged NH3 plasma exposure, carbon removal is noted but in a limited capacity. These results are corroborated by the high resolution XPS spectra of the C 1s, N 1s, O 1s, and Co 2p spectra for the 200 °C and 300 °C processes, shown in Figures S4 and S5 respectively from the Supporting Information. It is noted that the peak shape of the N 1s and Co 2p spectra remain consistent throughout each stage of the process, showing that the Co–N and C–N aspects of the film are constant regardless of exposure to atmosphere and additional NH3 plasma. This is not the case for the C–C associated components of the C 1s, which increase after atmospheric exposure before decreasing after the additional NH3 plasma treatment.

Both the 200 °C and 300 °C samples were analysed ex situ with HAXPES. The Co 2p and N 1s spectra for the different processing temperatures are shown in Figure 6. Photon energies of 2 keV, 4 keV and 6 keV were used, with higher values providing more information about the cobalt nitride bulk chemical composition. Varying the photon energy allows for an unobtrusive method of obtaining depth profile information of the films.

Additionally, using a different photon energy from Al Kα simplified the fitting process of the Co 2p spectra, shown in Figures 6(a), (b), due to the removal of the overlap between the Co 2p and the Co LMM Auger line [23].

The curve fit for the Co 2p was applied with caution, due to the presence of strong satellite features. These satellite peaks, associated with multiplet splitting or shakeup features, are usually attributed with cobalt oxides [24, 25], with strong satellites indicating the presence of Co2+ [26]. The Co 2p spectra profiles remained unchanged following the atmospheric exposure (figures S4 and S5), and therefore these satellites are attributed to the Co–N bonding that is occurring in the film.

For the 200 °C process in Figure 6(a) the Co 2p profile was fitted with 5 peaks. The non-satellite components had a Lorentzian and Gaussian width of 0.1 and 2.5 eV respectively. Two satellite peaks were fitted in the spectra, located at approximately 786 and 788 eV. The peak positions, and the Gaussian value of 5.8 eV (correlated to be 2.4 times larger than the non-satellite peaks) were chosen after fitting and comparison to previous work by Biesinger et al [20]. A minor peak at 784.0 eV was associated with nitrogen-rich cobalt nitride (Co2Nx, where x < 1) such as Co2N3. A peak at 782.6 eV was associated with CoN. The most predominant and lowest binding energy peak was associated with the most cobalt-rich component (Co2Nx, where x ≈ 1). The position of this peak (highlighted in the figure) was found to increase slightly with decreasing photon energy, being located at 780.6, 780.7, and 781.0 eV for hv = 6, 4 and 2 keV, respectively. The same peak parameters and positions were applied to the 300 °C process in Figure 6(b), with the notable exception of the Co2Nx peak. The position of this component also increased with decreasing photon energy, however it occurred at a slightly lower binding energy of 780.4, 780.5 and 780.6 eV for hv = 6, 4 and 2 keV, respectively.

It can therefore be concluded that both ALD processing temperatures produce cobalt nitride films dominated by a cobalt rich component, Co2Nx. The higher binding energy position of this peak in the 200 °C compared to the 300 °C process suggests that lower temperature processes contain more nitrogen in this component as verified in Figures 6(a), (b) showing a small 4 eV shift to higher binding energy. Furthermore, from Figure 7 the C–N bond peak is seen to be more prominent in the 300 °C film compared to that seen in the 200 °C. These findings are consistent with previous reports however, conclusions are speculative based on data obtained and as such remain open to interpretation [13]. For both temperatures, the binding energy of this peak gradually

\[
\begin{array}{cccccc}
\text{Thickness (nm)} & 200 \text{ °C ALD} & 200 \text{ °C + atm} & 200 \text{ °C + NH3} & 300 \text{ °C ALD} & 300 \text{ °C + atm} & 300 \text{ °C + NH3} \\
\text{Co %} & 12 & 10 & 15 & 17 & 14 & 19 \\
\text{N %} & 44 & 37 & 46 & 45 & 39 & 45 \\
\text{C %} & 43 & 47 & 37 & 37 & 42 & 34 \\
\text{O %} & 1 & 6 & 2 & 0 & 5 & 2 \\
\end{array}
\]

Table 1. Ellipsometry and XPS chemical compositions for a 200 °C and 300 °C ALD process (1000 and 2000 cycles respectively). Multiple samples were measured via ellipsometry to obtain a standard deviation.
shifts to higher binding energy with decreasing photon energy, suggesting that both films are slightly more nitrogen rich closer to the surface. Additionally, it is observed that the 300 °C process contains significantly more nitrogen-rich cobalt nitride, Co$_{2}$N$_{ω}$.

The N 1s peaks for the 200 °C and 300 °C processes are shown in figures 6(c) and (d), respectively. The spectra were fitted with a Lorentzian width fixed at 0.28 eV [26], and a Gaussian value of 0.86 eV. The low binding energy components at 397.5, 398.0 and 398.6 eV are associated with Co$_{2}$N$_{ω}$, CoN and Co$_{x}$Ny, respectively. The 300 °C process results in a significantly broader peak profile containing larger amounts of Co$_{2}$N$_{ω}$ and CoN, consistent with the Co 2p fit. For the 200 °C process, the Co$_{x}$Ny related peak at 386.6 eV is significantly higher than the other cobalt containing peaks, which is expected as the Co$_{x}$Ny is more nitrogen rich than the 300 °C process.

Three additional peaks are associated with the N 1s fit, occurring at higher binding energies, are associated with nitrogen—carbon bonding. The component at 399.1 eV lies within the agreed ‘pyridinic nitrogen’ range [27], while the peaks at 399.8 eV is associated with pyrrolic nitrogen [28]. The high binding energy peak at 400.9 eV may represent protonated or graphitic nitrogen, however it is a minor peak in the fit [27–29]. For both ALD processes, the peak shape remains consistent regardless of photon energy used, suggesting a film that is chemically homogenous within the analysis depth of HAXPES measurements, aside from the slight increase in nitrogen towards the surface of the film noted in the slight shifting as described in the Co 2p spectra in figures 6(a), (b).

Figure 6 shows the HAXPES C 1s spectra for the 200 °C (a) and 300 °C (b) processes. While assignment of the different components in the C 1s is complex, it is clear that two main components are present at approximately 285 and 287 eV. Due to the exposure to atmosphere, the lower binding energy region can be attributed to adsorbed hydrocarbons [30, 31], as well as precursor that has not been effectively removed by the co-reactant plasma, while the higher binding energy region is attributed to the various forms of C–N bonding observed in the N 1s spectra [27, 29]. Unlike the Co 2p and N 1s spectra, which display broadly consistent peak profiles at a
range of photon energies, the peak profile of the C 1s changes significantly. As the C 1s is the only spectrum to show change with photon energy, it is hypothesized that the only variation in the film is with the C–C/ hydrocarbons contained within the film, which are found at greater concentration towards the surface of the film due to exposure to atmosphere. This correlates well with the data presented in table 1, which showed increases in carbon upon exposure to atmosphere for both samples. Additionally, by comparing the intensity of the C–C and C–N associated regions, the 200 °C ALD process yields films with a slightly higher C–C contribution, correlating with the data presented in table 1, which shows the 200 °C process contains more carbon in the entire film.

The Co 2p and N 1s spectra in figure 6 show good correlation with the X-ray diffraction results in the work by Van Straaten et al [13], whom demonstrated that CoCP2-NH3 ALD processes at 260 °C and 230 °C yield Co2N while a 300 °C process yields Co3N. However, by depth profiling the films via Ar ion sputtering, the authors noted that minimal carbon is visible in the film, contradicting the results presented here in figure 7. We hypothesize that this difference arises from the destructive aspect of the argon sputtering depth profiling. Argon ion sputtering is known to reduce cobalt oxides [32, 33], and the resulting Co 2p XPS spectra presented after sputtering does not represent cobalt nitride. The depth profiling technique applied in the current work is non-destructive, and may indicate that the argon ion sputtering resulted in the preferential removal of carbon from...
the film. We conclude that, like CpCo(CO)$_2$—NH$_3$ ALD processes, CoCP$_2$-NH$_3$ ALD processes are impacted by large amounts of carbon impurities that post treatments have limited effects in resolving.

**Conclusions**

To achieve cobalt nitride growth, an ALD window for NH$_3$ plasma dose time was observed, with plasma doses above a certain time duration severely inhibiting growth. This window decreased with increasing process temperature. Optimal growth rates for a range of temperatures were determined, and it was found that the growth rate decreased rapidly with increasing temperature. The *in situ* XPS measurements revealed that films processed at 300 °C and under yielded cobalt nitride films, while a process temperature of 350 °C resulted in a cobalt nitride and metallic cobalt blend. A 400 °C process resulted in the acquisition of metallic cobalt only, albeit at a low growth rate with large amounts of nitrogen still contained in the film. The cobalt nitride films contained high levels of carbon, associated with precursor not removed from the plasma dosing and also carbon nitrogen bonding. A lower ALD temperature results in higher amounts of leftover precursor in the film. This was an unexpected result, as previous reports concerning argon ion sputtering of CoCP$_2$-NH$_3$ ALD processes had suggested minimal amounts of carbon were incorporated into the film. Upon exposure to atmosphere, increases in the C 1s XPS signal was attributed to adventitious carbon. The rest of the film Co–N and N–C bonding was unchanged.

HAXPES allowed for a depth profiling technique that was non-destructive, with no concern over the reduction of the cobalt in the film or the preferential removal of carbon and nitrogen species. The large satellite features in the Co 2p spectra were attributed to Co-N due to the lack of oxygen in the film. This work shows that a 300 °C ALD process contains larger amounts of different cobalt nitride chemical states in the film when compared to a 200 °C process. Both films had a main component associated to cobalt nitride that was cobalt rich (Co$_x$N$_y$ x > y). From the binding energy positions, it was observed that this Co$_x$N$_y$ signal for the 300 °C film has a higher cobalt concentration than the 200 °C film. The HAXPES measurements also reveal that the Co–N and C–N aspects of the film are consistent with depth, with the only change in the films associated to adventitious carbon at the top of the film due to atmosphere exposure. This work highlights the current challenges in the growth of cobalt nitride films using a state-of-the-art *in situ* characterisation approach, and provides insight into the effect of changing fundamental ALD parameters for the novel CoCP$_2$-NH$_3$ ALD process.

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**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

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**References**

[1] Chen P, Xu K, Tong Y, Li X, Tao S, Fang Z, Chu W, Wu X and Wu C 2016 Cobalt nitrides as a class of metallic electrocatalysts for the oxygen evolution reaction Inorg. Chem. Front. 3 236–42
[2] Liu C, Bai G, Tong X, Wang Y, Lv B, Yang N and Guo X Y 2019 Mesoporous and ultrathin arrays of cobalt nitride nanosheets for electrocatalytic oxygen evolution Electrochem. Commun. 98 87–91
[3] Zhang X, Yang Z, Lu Z and Wang W 2018 Bifunctional CoNx embedded graphene electrocatalysts for OER and ORR: a theoretical evaluation Carbon N. Y. 130 112–9
[4] Zhang Y, Ouyang R, Xu J, Jia G, Chen S, Raway R S and Fan H J 2016 Rapid synthesis of cobalt nitride nanowires: highly efficient and low-cost catalysts for oxygen evolution Angew. Chemie Int. Ed. 55 8670–4
[5] Chen Z, Ha Y, Liu Y, Wang H, Yang H, Xu H, Li Y and Wu R 2018 In situ formation of cobalt nitrides/graphitic carbon composites as efficient bifunctional electrocatalysts for overall water splitting ACS Appl. Mater. Interfaces 10 7134–44
[6] Bhandari H B, Yang J, Kim H, Lin Y, Gordon R G, Wang Q M, Lehn J-S M, Li H and Shenai D 2012 Chemical vapor deposition of cobalt nitride and its application as an adhesion-enhancing layer for advanced copper interconnects ECS J. Solid State Sci. Technol. 1 N79–84
[7] Balasubramanian B et al 2018 Magnetism of new metastable cobalt-nitride compounds Nanoscale 10 13011–21
[8] Fang Z, Williams P A, Oledra R, Jeon H and Potter B J 2012 Gadolinium nitride films deposited using a PEALD based process J. Cryst. Growth 338 111–7
[9] Elers K E, Winkler J and Marcus S 2004 TiCN4 as a precursor in the TiN deposition by ALD and PEALD Proc. - Electrochem. Soc. 1361–8
[10] Bernal Ramos K, Saly M J and Chabal Y J 2013 Precursor design and reaction mechanisms for the atomic layer deposition of metal films Coord. Chem. Rev. 257 3271–81
[11] Proffit H B, Potts S E, van de Sanden M C M and Kessels W M M 2011 Plasma-assisted atomic layer deposition: basics, opportunities, and challenges J. Vac. Sci. Technol. A Vacuum, Surfaces, Films. 29 050501
[12] Park J, Lee H B R, Kim D, Yoon J, Lansalot C, Gatanine J, Chevre H and Kim H 2013 Plasma-enhanced atomic layer deposition of Co using CoMeCp2 precursor J. Energy Chem. 22 403–7
[13] Van Straaten G, Deckers R, Vos M F J, Kessels W M M and Creatore M 2020 Plasma-enhanced atomic layer deposition of cobalt and cobalt nitride: what controls the incorporation of nitrogen? J. Phys. Chem. C 124 22046–54
[14] Reif J, Knaut M, Killge S, Winkler F, Albert M and Bartha J W 2020 In vacuo studies on plasma-enhanced atomic layer deposition of cobalt thin films J. Vac. Sci. Technol. A 38 012405
[15] Jensen D S, Kanyal S S, Madaan N, Vail M A, Dadson A E, Engelhard M H and Linford M R 2013 Silicon (100)/SiO2 by XPS Surf. Sci. Spectra 20 36–42
[16] Herrera-Gomez A, Bravo-Sanchez M, Coballas-Sanchez O and Vazquez-Lepe M O 2014 Practical methods for background subtraction in photoemission spectra Surf. Interface Anal. 46 897–905
[17] Herrera-Gomez A, Sun Y, Aguirre-Tostado F-S, Hwang C, Mani-Gonzalez P-G, Flint E, Espinosa-Magaña F and Wallace R M 2010 Structure of ultra-thin diamond-like carbon films grown with filtered cathodic arc on Si(001) Surf. Anal. 26 267–72
[18] Zhong X, Jiang Y, Chen X, Wang L, Zhuang G, Li X and Wang J G 2016 Integrating cobalt phosphide and cobalt nitride-embedded nitrogen-rich nanocarbons: high-performance bifunctional electrocatalysts for oxygen reduction and evolution J. Mater. Chem. A 4 10575–84
[19] Wu W, Zhang Q, Wang X, Han C, Shao X, Wang Y, Liu J, Li Z, Lu X and Wu M 2017 Enhancing selective photooxidation through CoN4-doped carbon materials as single-tit oxygen photosensitzers ACS Catal. 7 7267–73
[20] Biesinger M C, Payne B P, Grosvenor A P, Lau L W M, Gerson A R and Smart R S C 2011 Resolving surface chemical states in XPS films grown with precursor by plasma etching Electron. Solid-State Lett. G323
[21] cruz-Ramos C D, Davis L E, Zeller M V, Taylor J A, Raymond R H and Gale L H 1981 Empirical atomic sensitivity factors for quantitative analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni Appl. Surf. Sci. 257 2717–30
[22] Lee H B R and Kim H 2006 High-quality cobalt thin films by plasma-enhanced atomic layer deposition Electrochim. Solid-State Lett. 9 G523
[23] Wagner C D, Davis L E, Zeller M V, Taylor J A, Raymond R H and Gale L H 1981 Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis Surf. Interface Anal. 3 211–25
[24] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 Handbook of X-Ray Photoelectron Spectroscopy ed J Chastain (Eden Prairie: Perkin-Elmer Corporation)
[25] McIntyre N S and Cook M G 1975 X-ray photoelectron studies on some oxides and hydroxides of cobalt, nickel, and copper Anal. Chem. 47 2208–13
[26] Groovenor A P, Wilk S D, Cavell R G and Mar A 2005 Examination of the bonding in binary transition-metal monophosphides MP (M = Cr, Mn, Fe, Co) by x-ray photoelectron spectroscopy Inorganic Chemistry 44 8988–98
[27] Johansson I and Johansson H I P 1996 Core level study of NbC(100) and NbN(100) J. Electron Spectros. Relat. Phenomena 80 237–40
[28] Art'yushkova K 2020 Misconceptions in interpretation of nitrogen chemistry from x-ray photoelectron spectra J. Vac. Sci. Technol. A 38 031002
[29] Fei H et al 2015 Atomic cobalt on nitrogen-doped graphene for hydrogen generation Nature Communications 6 8668
[30] Hellgren N, Haasch R T, Schmidt S, Hultman L and Petrov I 2016 Interpretation of x-ray photoelectron spectra of carbon-nitride thin films: new insights from in situ XPS Carbon N. Y. 108 242–52
[31] Gelius U, Heden P F, Hedman J, Lindberg B J, Manne R, Nordberg R, Nordling C and Siegbahn K 1970 Molecular spectroscopy by means of ESCA: III carbon compounds Phys. Scr. 2 70–80
[32] Miller D J, Biesinger M C and McIntyre N S 2002 Interactions of CO2 and CO at fractional atmosphere pressures with iron and iron oxides: one possible mechanism for surface contamination? Surf. Interface Anal. 33 299–305
[33] Grezynski G and Hultman L 2021 Towards reliable x-ray photoelectron spectroscopy: sputter–damage effects in transition metal borides, carbides, nitrides, and oxides Appl. Surf. Sci. 542 148599
[34] Patrinou G et al 2020 Versatile by design: hollow Co3O4 architectures for superior lithium storage prepared by alternative green pechini method Appl. Surf. Sci. 510 145431