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Remote Plasma Atomic Layer Deposition of Co_3O_4 Thin Films

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Cobalt oxide thin films have been deposited with remote plasma atomic layer deposition (ALD) within a wide temperature window (100–400°C), using CoCp_2 as a cobalt precursor and with remote O_2 plasma as the oxidant source. The growth rate was 0.05 nm/cycle and both the precursor dosing and plasma exposure exhibit saturation after 2 s, all independent of the substrate temperature. This novel combination resulted in the deposition of high density ($\sim 5.8 \text{ g/cm}^3$), stoichiometric Co_3O_4 showing a preferential (111) orientation for all temperatures. X-ray diffraction, spectroscopic ellipsometry, and Fourier transform infrared spectroscopy independently indicate an increasing crystallinity with increasing substrate temperature, whereas the surface roughness remains low ($\leq 1 \text{ nm}$). CO_2 and H_2O are detected by mass spectrometry measurements as reaction by-products during the remote O_2 plasma step, revealing a combustion-like reaction process.

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Cobalt oxides are well-known electrochromic materials that have attracted a lot of attention for applications in smart windows,¹ solar cells,² heterogeneous catalysts,³ and gas sensors.⁴ Mixed valence Co_3O_4 ($\text{Co}^{2+}\text{Co}_2^{3+}\text{O}_4^{2-}$) is the most stable phase in the Co–O system and adopts a spinel-type cubic structure, unlike the high temperature phase CoO , which crystallizes in a cubic rock salt structure.⁵ Previously Co_3O_4 has been deposited by radio frequency magnetron sputtering,⁶ sol-gel processing,^{7,8} electron beam evaporation,⁹ spray pyrolysis,¹⁰ pulsed laser deposition,¹¹ (metal organic) chemical vapor deposition (CVD),^{12–16} and atomic layer deposition (ALD).^{5,17,18} All these methods can produce high purity Co_3O_4 . However, ALD is chosen due to the surface chemistry controlled deposition process, which provides an excellent conformality and thickness control at the atomic scale, even in challenging high aspect ratio structures. The novel features of this work can predominantly be found in the wide temperature window (100–400°C) for the ALD growth, while maintaining good and consistent material properties. This aspect is particularly important for future combinations of the Co_3O_4 ALD processes with ALD processes of other materials, for example, for the synthesis of ternary compounds. An overlap in the temperature windows is very important to ensure good ALD growth for such materials.¹⁹ Most recently, thermal ALD was employed by Klepper et al. to prepare Co_3O_4 thin films by using $\text{Co}(\text{thd})_2$ ($\text{Hthd} = 2,2,6,6\text{-tetramethylheptan-3,5-dione}$) as a cobalt precursor in combination with O_3 .^{17,18} A list of cobalt precursors of interest for CVD/ALD processes reported in the literature is presented in Table I. The use of bis(η^5 -cyclopentadienyl) $\text{Co}(\text{II})$ (cobaltocene, CoCp_2) as a precursor has so far been limited to plasma-enhanced ALD of cobalt thin films, administering a NH_3 plasma.²⁰ Several benefits can be obtained by using a Cp-based precursor: a higher volatility and protection of the metallic center from nucleophilic attacks (due to the steric packing). Further, the use of metalorganic precursors is preferred over halogen-based precursors. Moreover, Cp-based precursors are generally preferred over β -diketonate precursors. One of the drawbacks of this precursor is that the Cp ligand is tightly bound to the metal center via a π interaction and can leave hydrogen and carbon contamination during CVD and thermal ALD processes. However, in this research an O_2 plasma was used, which has the power to combust the cyclopentadienyl ligand and can result in a fully oxidized material.²⁴ The obtained growth rate of Co_3O_4 in this work is 0.05 nm/cycle, which is a typical rate compared to other ALD oxides and also compared to processes employing Cp-based precursors.^{19,20} However, when comparing the growth rate to other ALD Co_3O_4 processes it is relatively high. The Co_3O_4 ALD process, combining CoCp_2 and O_2 plasma, was investigated with respect

to growth rate, substrate temperature dependence, and material properties.

Experimental

Film preparation.— The Co_3O_4 films were deposited using a home-built open-load ALD setup (“ALD-I”) as shown schematically in Fig. 1 and as described extensively by Langereis et al.²⁵ In this setup an inductively coupled plasma source is connected to a deposition chamber along with a pump unit through gate valves. The pump unit consists of a rotary and turbomolecular pump, which can reach a base pressure of $<10^{-5}$ mbar by overnight pumping. The CoCp_2 precursor (98%, Strem Chemicals) was heated to 80°C and bubbled with Ar at a pressure of 0.02 mbar. The substrate was heated to 100–400°C, whereas the reactor walls, Ar lines, and CoCp_2 precursor lines were maintained at a temperature of 105°C (100°C when depositing at 100°C) to prevent precursor condensation. Si(100) with native oxide and Si(100) with 400 nm thermally grown SiO_2 were used as substrates.

The remote plasma ALD cycle for Co_3O_4 consists of two half-cycles with a total cycle time of 20.5 s. The first half-cycle of the process is a 2 s CoCp_2 precursor dosing with Ar bubbling. The second half-cycle consists of an O_2 exposure at 0.01 mbar chamber pressure while applying a 100 W plasma power for 5 s to ensure complete combustion of the Cp ligands. During and after the precursor dosing and plasma exposure, the reaction chamber is being evacuated.

In situ film analysis.— The reaction by-products were identified by quadrupole mass spectrometry (QMS) using a QMS200 from Pfeiffer with an ionizing electron energy of 70 eV. The thickness and dielectric function of the films were monitored during the ALD process by in situ spectroscopic ellipsometry (SE) with a J.A. Woollam, Inc. M2000U (0.75–5.0 eV) ellipsometer.²⁶ The optical range was extended to 6.5 eV after the deposition process, using ex situ variable angle measurements with a J.A. Woollam, Inc. M2000D ellipsometer. The dielectric function of Co_3O_4 was parameterized using a combination of four oscillators (a Gauss, a Tauc–Lorentz and two Lorentz oscillators) as addressed further in this paper. This enabled in situ thickness measurements and determination of the optical properties of the deposited films.

Ex situ film analysis.— Rutherford backscattering spectrometry (RBS) using 2 MeV $^4\text{He}^+$ ions was used to determine the atomic composition and mass density of the cobalt oxide films. The microstructure was studied using x-ray diffraction (XRD) with a Philips X’Pert MPD diffractometer equipped with a Cu K_α source (1.54 Å radiation). Additionally, the film thickness and mass density were determined by x-ray reflectometry (XRR) measurements on a Bruker D8 Advance X-ray diffractometer to validate the SE

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Table I. Overview of ALD and CVD processes for the deposition of Co_3O_4 and Co metal reported in the literature.

Material	Cobalt precursor	Deposition technique	Reaction gas/plasma	Deposition temperature ($^{\circ}\text{C}$)	Growth rate	References
Co_3O_4	$\text{Co}(\text{thd})_2$	ALD	O_3	117–307	0.02 nm/cycle	17, 18
		(MO) CVD	O_2	350–540	8 nm/min	2
	$\text{Co}(\text{acac})_2$	(MO) CVD	O_2	350–600	5–28 nm/min	22
		ALD	O_2	475–600	0.1–0.2 nm/cycle	5
Co	CoCp_2	ALD	O_2 plasma	100–400	0.05 nm/cycle	This work
	$\text{Co}(\text{CO})_8$	ALD	H_2 plasma	75–110	0.12 nm/cycle	21
	$\text{CoCp}(\text{CO})_2$	CVD ^a	NH_3 plasma	300	0.15–0.45 nm/cycle	20
	CoCp_2	ALD	NH_3 plasma	300	0.048 nm/cycle	20
	$\text{Co}(\text{CpAMD})^b$	ALD	NH_3 plasma	100–250	0.05 nm/cycle	23

^aProcess is set up for ALD, but the growth is revealed to be not self-limiting.^bCyclopentadienyl isopropyl acetamidinato-cobalt.

measurements. The x-ray photoelectron spectroscopy (XPS) measurements are carried out with a Kratos AXIS Ultra spectrometer, equipped with a monochromatic Al K_{α} x-ray source and a delay-line detector. Infrared absorption spectra were measured by Fourier transform infrared spectroscopy (FTIR) using a Tensor 27 from Bruker Optics (mid-IR, 4 cm^{-1} resolution) within the infrared spectral range of $7000\text{--}350\text{ cm}^{-1}$. A Signatone four-point probe (FPP) in combination with a Keithley 2400 Sourcemeter was employed to measure the electrical resistivity at room temperature. The surface roughness of the films was determined by atomic force microscopy (AFM) using an NT-MDT Solver P47 SPM.

Results and Discussion

ALD growth.— Remote plasma ALD Co_3O_4 films were deposited using CoCp_2 and O_2 plasma, with various thicknesses (5–65 nm) within a wide temperature window (100–400 $^{\circ}\text{C}$). The growth per cycle values for this process are shown in Figs. 2 and 3 at various precursor dosing times (Fig. 2a), plasma exposure times (Fig. 2b) and substrate temperatures (Fig. 3). After 2 s saturation is observed for the CoCp_2 precursor dosing and this value therefore is chosen as the Co_3O_4 process setting. A saturation time of 2 s was also observed for the plasma exposure, however 5 s was chosen as the process setting to ensure saturation over the entire temperature window. In addition, a longer plasma exposure might also contribute to possible improvement of the material properties due to the intensified combustion of the Cp ligands and therefore less carbon contamination. The saturation times mentioned previously are in agreement with the results presented by Lee and Kim for the deposition of cobalt metal using CoCp_2 and NH_3 plasma.²⁰ Because of possible

precursor decomposition at higher substrate temperatures, the saturation with precursor dosing time was also specifically verified at 400 $^{\circ}\text{C}$ and presented no significant difference from the 300 $^{\circ}\text{C}$ data. The saturation curves in Figs. 2a and 2b are therefore assumed to be valid for the entire temperature range of 100–400 $^{\circ}\text{C}$. Also, no indication of a significant nucleation delay was observed at the start of the ALD process.

Reaction mechanism.— As shown in Figs. 2 and 3, the use of CoCp_2 as precursor in combination with O_2 plasma leads to a

Figure 1. (Color online) A schematic overview of the ALD-I setup. Also the in situ spectroscopic ellipsometer and quadrupole mass spectrometer are depicted.

Figure 2. (a) Growth rate as a function of precursor dosing time for remote plasma ALD of Co_3O_4 at 300 $^{\circ}\text{C}$, while the plasma exposure time is kept constant at 5 s. (b) Growth rate as a function of plasma exposure time for remote plasma ALD of Co_3O_4 at 300 $^{\circ}\text{C}$, while the plasma exposure time is kept constant at 2 s. The lines serve as guides to the eye.

growth per cycle of 0.05 nm/cycle (2.1 Co atoms/nm² per cycle as measured by RBS), almost independent of the substrate temperature (100–400°C).

Time-dependent mass scans shown in Fig. 4 revealed slightly elevated signal intensities during the precursor dosing step. However, these increased intensities cannot be separated from the pressure effect caused by the introduction of Ar carrier gas in the reactor. This same effect can be seen during the introduction of O₂ gas into the reactor when there is a strong pressure spike. However, when the plasma power is turned on, signals due to CO⁺ (mass 28) and CO₂⁺ (mass 44 and 28) can be observed, together with a decrease in O₂⁺ signal (mass 32), indicating combustion-like surface reactions of the oxygen radicals with the cyclopentadienyl ligands of the precursor. Although, part of the CO production can also be caused by the dissociation of CO₂ in the O₂ plasma where CO₂⁺ and CO⁺ are produced.²⁷ The small increase in signal intensity for H₂O (mass 18) is barely visible due to the high background signal, however H₂O is assumed to be present in the gas phase based on the standard combustion reaction of hydrocarbons. Using the QMS data, a two-step reaction mechanism is suggested in the following reactions, where the CoCp₂ molecule adsorbs on the surface in the first step and reacts with oxygen in the second step

If we assume that the adsorption takes place as described above, in combination with the saturation characteristics of ALD, a hexagonal packing structure, and an average growth of 2.1 Co atoms/nm² per cycle, then a surface coverage of 66% is calculated. After the start of the O₂ plasma exposure mass 39 and 66 (both belonging to the cracking pattern of HCp) show a slight increase in intensity, which suggests that some hydrocarbon reaction by-products are produced during this step.

Material composition and properties.—RBS data reveal that stoichiometric Co₃O₄ thin films were obtained for the whole temperature range investigated. No carbon contamination was measured by RBS. However, the typical detection limit for carbon is in between 10 and 20% for the RBS measurements carried out in this work. The mass density measured by XRR was between 6.1 and 6.4 ± 0.3 g/cm³ showing no clear trend with temperature. However, the mass density calculated from RBS data and SE film thickness was slightly lower at 5.8 ± 0.3 g/cm³. These values are in agreement with

Figure 3. Growth rate of Co₃O₄ on Si(100) as a function of the substrate temperature. (Inset) Thickness, as measured with in situ SE vs the number of ALD cycles.

Figure 4. Quadrupole mass spectrometry for one remote plasma ALD cycle of Co₃O₄, including 5 s CoCp₂ precursor dosing and 8 s O₂ plasma exposure. Numbers indicate the mass-to-charge ratios of the species measured in the QMS.

the Co₃O₄ bulk density of 6.1 g/cm³. X-ray diffraction pattern, presented in Fig. 5, showed cubic Co₃O₄ films with a strong preferential (111) direction for all substrate temperatures.

The root-mean-square roughness, as measured by AFM, was ≤ 1 nm for all film thicknesses and substrate temperatures investigated and represents smoother films than reported in the literature.^{14,17} Interestingly, this reveals that the surface roughness is not significantly influenced by conditions such as substrate temperature and film thickness. The electrical resistivity at room temperature was measured by FPP and found to vary between 0.5 and 5.3 Ω-cm for all deposited Co₃O₄ showing no clear trend with temperature or thickness. These results correspond well with values reported elsewhere.¹⁷

Temperature dependence.—As mentioned previously, the deposition rate is independent of the substrate temperature and the temperature window is relatively large compared to the processes reported in

Figure 5. (Color online) X-ray diffraction measurements ($\lambda = 1.54 \text{ \AA}$) revealing cubic Co₃O₄ with a preferential (111) orientation for all substrate temperatures. The powder diffraction pattern of cubic Co₃O₄ is given as a reference and the spectra have been offset vertically for clarity.

Table II. Material properties for ALD Co_3O_4 films deposited by ALD from CoCp_2 and O_2 plasma (typical errors are displayed in the first row).

Substrate temperature ($^{\circ}\text{C}$)	Growth rate (nm/cycle)	Density (g/cm^3)	Resistivity ($\Omega\text{ cm}$)	Roughness (nm)	Preferential orientation
100	0.053 ± 0.003	6.2 ± 0.3	0.55 ± 0.05	1 ± 0.05	(111)
200	0.050	6.3	2.2	<1	(111)
300	0.050	6.3^a	0.65	<1	(111)
400	0.051	6.4	5.3	1	(111)

^aMass density calculated from RBS data and SE film thickness is $5.8 \pm 0.3\text{ g}/\text{cm}^3$ for a substrate temperature of 300°C .

the literature (Tables I and II). A low deposition temperature of Co_3O_4 can be beneficial for several applications; e.g., as anodic coloration materials for electrochromic devices on flexible polymers.²⁸

A (100) preferential direction was found in previous work on Co_3O_4 by Klepper et al. for low substrate temperatures (114°C) and a (111) preferential direction for high temperatures (307°C) (17). The difference with our results, where a strong preferential (111) direction was found for all deposition temperatures, could be related to either the use of a different precursor or to the use of a remote O_2 plasma process instead of thermal ALD with O_3 . Interestingly, it is seen that the XRD peaks shift slightly to higher 2θ values with increasing deposition temperature, most notably for the (111) and (222) reflection. This suggests a decrease of the lattice parameter a for higher deposition temperatures and thus to a more closely packed crystal structure. The XRD results also revealed that the peaks are more intense at high deposition temperatures. Although the film deposited at 400°C is slightly thicker than the films deposited at lower temperatures (42 vs 32 nm), it is not expected that this can account for the relatively large increase in intensity. It can therefore be concluded that an increasing crystallinity of the Co_3O_4 films with temperature is observed.

Optical properties.— FTIR was used to investigate the increasing crystallinity further. The main absorption peaks of Co_3O_4 are located at 580 and 667 cm^{-1} in the powder spectrum¹⁷; however, as shown in Fig. 6, the thin films of Co_3O_4 show peaks with a slight redshift toward lower wave numbers. This is similar to what has been reported in literature,¹⁷ but it is not yet clear what these Co_3O_4 absorption wavelengths represent. According to Nkeng et al. these infrared peaks could be assigned to the vibrations of Co^{3+} in octahedral sites of the lattice.²⁹ Figure 6 also reveals more intense and sharper absorption peaks at higher substrate temperatures. These FTIR results corroborate the conclusion of a higher crystallinity with increasing temperature.

Figure 7 shows the dielectric function ϵ_2 of Co_3O_4 between 0.73 and 6.5 eV as obtained at the various deposition temperatures. The

Figure 6. (Color online) Fourier transform infrared spectra of Co_3O_4 films deposited between 100 and 400°C . The films are $\sim 30\text{ nm}$ thick, except for the film deposited at 400°C , which has a thickness of 42 nm .

Figure 7. (Color online) The imaginary part of the dielectric function (ϵ_2) of the Co_3O_4 films as determined by in situ spectroscopic ellipsometry. The films are $\sim 30\text{ nm}$ thick, except for the film deposited at 400°C which has a thickness of 42 nm .

dielectric functions have been extracted from the SE measurements using an optical model employing a Gauss, a Tauc–Lorentz, and two Lorentz oscillators, to account for the absorption bands, and expanded into the infrared region using the FTIR measurements. The dielectric function also reveals sharper and more intense peaks at higher deposition temperatures; a similar effect as observed in the infrared spectra. Three of the peaks present in the dielectric function were also found and assigned by Athey et al.³⁰ These are: (a) the 0.9 eV band, which was assigned to a charge transfer reaction between $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$, representing an internal oxidation–reduction process (modeled using a Gauss oscillator); (b) the 1.7 eV band, which was assigned to a reverse charge transfer reaction at higher energy $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ (modeled using a Tauc–Lorentz oscillator); and (c) the 2.9 eV band, which is caused by a ligand to metal charge transfer band $\text{O}^{2-} \rightarrow \text{Co}^{2+}$ (modeled using a Lorentz oscillator).³⁰ The final peak (d) has not been assigned in the literature, but this can be attributed to a charge transfer reaction at higher energy $\text{O}^{2-} \rightarrow \text{Co}^{3+}$ (modeled using a Lorentz oscillator).

Conclusions

A remote plasma ALD process for Co_3O_4 was developed using the combination of CoCp_2 as the cobalt precursor and O_2 plasma as the oxidant source. The temperature window for the Co_3O_4 process was found to range from 100 to 400°C with a virtually temperature-independent growth rate of $0.05\text{ nm}/\text{cycle}$. Cubic, stoichiometric Co_3O_4 was obtained with a resistivity between 0.5 and $5.3\text{ }\Omega\text{-cm}$ for all thicknesses and temperatures investigated. A strong preferential (111) orientation was found, independent of the substrate temperature. Moreover XRD, SE, and FTIR independently indicate an increasing crystallinity with increasing substrate temperature, whereas the surface roughness remains low. Mass spectrometry measurements reveal a combustion-like reaction process with CO_2 and H_2O as reaction by-products during the remote O_2 plasma step.

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