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Citation for published version (APA):

DOI:
10.1149/1.3552616

Document status and date:
Published: 01/01/2011

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Remote Plasma Atomic Layer Deposition of Co₃O₄ 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 CoCp₂ as a cobalt precursor and with remote O₂ 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 (~5.8 g/cm³), stoichiometric Co₃O₄ 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 (<1 nm). CO₂ and H₂O are detected by mass spectrometry measurements as reaction by-products during the remote O₂ plasma step, revealing a combustion-like reaction process.

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Manuscript submitted July 28, 2010; revised manuscript received December 14, 2010. Published March 2, 2011.

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measurements. The x-ray photoelectron spectroscopy (XPS) measurements are carried out with a Kratos AXIS Ultra spectrometer, equipped with a monochromatic Al Kα 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 7000–350 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 Co₃O₄ films were deposited using CoCp₂ and O₂ plasma, with various thicknesses (5–65 nm) within a wide temperature window (100–400 °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 CoCp₂ precursor dosing and this value therefore is chosen as the Co₃O₄ 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 CoCp₂ and NH₃ plasma.²⁰ Because of possible precursor decomposition at higher substrate temperatures, the saturation with precursor dosing time was also specifically verified at 400 °C and presented no significant difference from the 300 °C data. The saturation curves in Figs. 2a and 2b are therefore assumed to be valid for the entire temperature range of 100–400 °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 CoCp₂ as precursor in combination with O₂ plasma leads to a

Table I. Overview of ALD and CVD processes for the deposition of Co₃O₄ and Co metal reported in the literature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cobalt precursor</th>
<th>Deposition technique</th>
<th>Reaction gas/plasma</th>
<th>Deposition temperature (°C)</th>
<th>Growth rate</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₃O₄</td>
<td>Co(thd)₂</td>
<td>ALD</td>
<td>O₂</td>
<td>117–307</td>
<td>0.02 nm/cycle</td>
<td>17, 18</td>
</tr>
<tr>
<td></td>
<td>(MO) CVD</td>
<td></td>
<td></td>
<td>350–540</td>
<td>8 nm/min</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Co(acac)₂</td>
<td>(MO) CVD</td>
<td>O₂</td>
<td>350–600</td>
<td>5–28 nm/min</td>
<td>22</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>Co₂</td>
<td>ALD</td>
<td>O₂</td>
<td>475–600</td>
<td>0.1–0.2 nm/cycle</td>
<td>5</td>
</tr>
<tr>
<td>CoCp₂</td>
<td>ALD</td>
<td>O₂ plasma</td>
<td>100–400</td>
<td>0.05 nm/cycle</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>Co(CO)₈</td>
<td>ALD</td>
<td>H₂ plasma</td>
<td>75–110</td>
<td>0.12 nm/cycle</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>CoCp(CO)₂</td>
<td>CVD</td>
<td>NH₃ plasma</td>
<td>300</td>
<td>0.15–0.45 nm/cycle</td>
<td>20</td>
</tr>
<tr>
<td>CoCp₂</td>
<td>ALD</td>
<td>NH₃ plasma</td>
<td>300</td>
<td>0.048 nm/cycle</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>Co(CpAMD)</td>
<td>ALD</td>
<td>NH₃ plasma</td>
<td>100–250</td>
<td>0.05 nm/cycle</td>
<td>23</td>
</tr>
</tbody>
</table>

²Process is set up for ALD, but the growth is revealed to be not self-limiting.  
²Cyclopentadienyl isopropyl acetamidinato-cobalt.

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

\[
\text{CoCp}_2(\text{s}) \rightarrow \text{CoCp}_2(\text{ads})
\]

\[
3\text{CoCp}_2(\text{s}) + 79 \text{O}_2(\text{g}) \rightarrow \text{Co}_3\text{O}_4(\text{s}) + 30\text{CO}_2(\text{g}) + 15\text{H}_2\text{O}(\text{g})
\]

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. 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 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. 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.

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

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**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.

**Figure 5.** (Color online) X-ray diffraction measurements (λ = 1.54 Å) 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 Co₃O₄ films deposited by ALD from CoCp₂ and O₂ plasma (typical errors are displayed in the first row).

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Growth rate (nm/cycle)</th>
<th>Density (g/cm³)</th>
<th>Resistivity (Ω cm)</th>
<th>Roughness (nm)</th>
<th>Preferential orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.053 ± 0.003</td>
<td>6.2 ± 0.3</td>
<td>0.55 ± 0.05</td>
<td>1 ± 0.05</td>
<td>(111)</td>
</tr>
<tr>
<td>200</td>
<td>0.050</td>
<td>6.3</td>
<td>2.2</td>
<td>&lt;1</td>
<td>(111)</td>
</tr>
<tr>
<td>300</td>
<td>0.050</td>
<td>6.3ᵖ</td>
<td>0.65</td>
<td>&lt;1</td>
<td>(111)</td>
</tr>
<tr>
<td>400</td>
<td>0.051</td>
<td>6.4</td>
<td>5.3</td>
<td>1</td>
<td>(111)</td>
</tr>
</tbody>
</table>

*pMass density calculated from RBS data and SE film thickness is 5.8 ± 0.3 g/cm³ for a substrate temperature of 300°C.

The dielectric functions have been extracted from the SE measurements using an optical model employing a Gauss, a Tau–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. These are: (a) the 0.9 eV band, which was assigned to a charge transfer reaction between Co²⁺ → Co³⁺, 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 Co³⁺ → Co²⁺ (modeled using a Tau–Lorentz oscillator); and (c) the 2.9 eV band, which is caused by a ligand to metal charge transfer band O²⁻ → Co²⁺ (modeled using a Lorentz oscillator). The final peak (d) has not been assigned in the literature, but this can be attributed to a charge transfer reaction at higher energy O²⁻ → Co³⁺ (modeled using a Lorentz oscillator).

Figure 7. (Color online) The imaginary part of the dielectric function (ε₂) of the Co₃O₄ films as determined by in situ spectroscopic ellipsometry. The films are ~30 nm thick, except for the film deposited at 400°C which has a thickness of 42 nm.

Conclusions

A remote plasma ALD process for Co₃O₄ was developed using the combination of CoCp₂ as the cobalt precursor and O₂ plasma as the oxidant source. The temperature window for the Co₃O₄ process was found to range from 100 to 400°C with a virtually temperature-independent growth rate of 0.05 nm/cycle. Cubic, stoichiometric Co₃O₄ was obtained with a resistivity between 0.5 and 5.3 Ω 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 CO₂ and H₂O as reaction by-products during the remote O₂ plasma step.
Acknowledgments

This research was carried out under the Project No. MC3.06278 in the framework of the Research Program of the Materials innovation institute M2i (www.m2i.nl).

Eindhoven University of Technology assisted in meeting the publication costs of this article.

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