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Cobalt oxide thin film low pressure metal-organic chemical vapor deposition

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ABSTRACT

Cobalt oxide thin films were deposited by metal-organic chemical vapor deposition at low pressure using dicarbonyl cyclopentadienyl cobalt ($CoCp(CO)_2$) and oxygen as reactant gas. Depending on substrate temperature and oxygen partial pressure, thin films consist of metallic cobalt, cobalt (II) oxide (CoO) or cobalt (II,III) oxide (Co_3O_4). The films show excellent conformality on three dimensional surface structures. Films were characterized using photoelectron spectroscopy (XPS), Raman spectroscopy and scanning electron spectroscopy. XPS analysis was performed in-situ after the deposition process, allowing insights into the decomposition process of the precursor.
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1. Introduction

Cobalt oxide thin films are of interest with respect to numerous applications, such as optical sensors, magnetic detectors, catalytic membranes, solar selective absorbers and optical gas sensors [1–5]. Recently, cobalt oxide has also attracted attention as anode material for lithium-ion batteries [6–8].

For the deposition of cobalt oxide thin films, different deposition techniques have been used, e.g. sputtering [9,10], molecular beam epitaxy [11], spray pyrolysis [12–14] or metal-organic chemical vapor deposition (MOCVD) [15]. Nevertheless, process development is ongoing as applications demand low cost, high deposition rate and excellent conformality. In this regard, MOCVD is an especially promising process.

The MOCVD process depends strongly on the type of precursor used. Often precursors require reactant gas to yield the desired process and layer properties, e.g. high deposition rate and deposits with low carbon content. For MOCVD of cobalt oxides, mainly $Co(acac)_2$ [16] and $CoCp_2$ have been used as precursors. The precursors $Co_2(CO)_8$ and $CoCp(CO)_2$ were utilized preferentially for metallic deposits, due to the low oxidation state of cobalt. Because of its high vapor pressure, especially $CoCp(CO)_2$ [17,18] is interesting also for cobalt oxide-compounds.

In this paper, we present the deposition of cobalt oxide at low pressure using $CoCp(CO)_2$ as precursor. Oxygen is used as a reactant gas to decompose the precursor and oxidize the cobalt. We investigate the composition and morphology of the deposited film as functions of oxygen partial pressure as well as substrate temperature and demonstrate the conformality of the films. For analysis, photoelectron spectroscopy (XPS), Raman spectroscopy and scanning electron microscopy are employed. XPS analysis is performed in-situ, allowing an unaltered view of the surface of the films directly after deposition.

2. Experimental

The deposition of cobalt oxide thin films was performed in a cold wall steel reactor (base pressure 10^{-5} Pa) at 0.1–1 Pa total pressure. The reactor features a manipulator with integrated halogen heater which can be heated up to 650 °C. Silicon wafer (area 1×1 cm^2) was used as substrate material. As cobalt precursor dicarbonyl cyclopentadienyl cobalt ($CoCp(CO)_2$, Sigma-Aldrich Co., Germany) was used, which is a liquid at room temperature with a vapor pressure of 67 Pa [18]. The precursor was evaporated at room temperature from a stainless steel vessel into the reactor. A scheme of the reactor and its peripheral components is shown in Fig. 1.

The reactor is pumped with a turbomolecular pump and a rotary pump. The pressure is controlled with a butterfly valve in downstream configuration. Argon and oxygen is used as carrier and reactive gas and controlled by mass flow controllers. After deposition, i.e. after the subsequent shut-off of precursor delivery and substrate heater, the samples were cooled down with otherwise unchanged gas flows.

The deposition chamber is connected to an integrated UHV-system (DAISY-MAT, Darmstadt Integrated System of Materials Science) with

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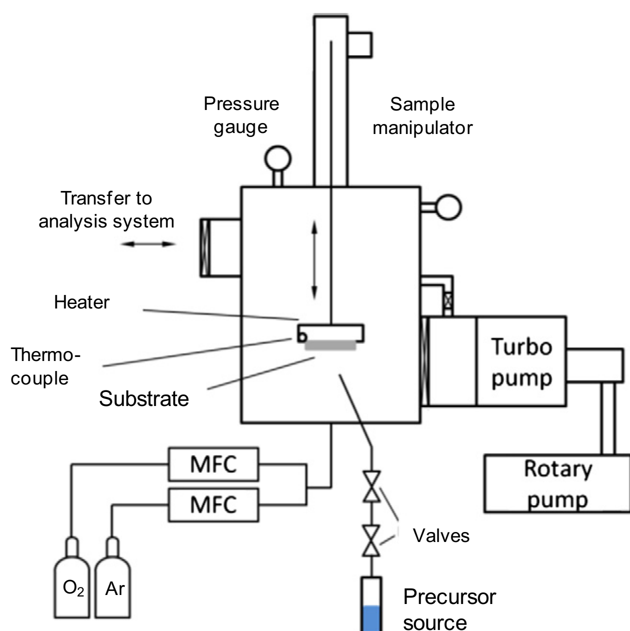

Fig. 1. Schematic drawing of the MOCVD reactor. The construction is based on UHV technique with a base pressure of 10^{-5} Pa. The precursor is attached in a stainless steel bottle which can be easily dismounted and re-filled in a glove box.

a base pressure of 1×10^{-7} Pa. This enables to perform X-ray photoelectron spectroscopy (XPS) (Physical Electronics, Inc., USA) measurements without surface contamination or modification throughout contact to atmosphere. The survey spectra were taken with a pass energy of 187.87 eV and a step width of 0.80 eV with monochromated Al K radiation (1486.6 eV excitation energy). For the high resolution detail spectra the pass energy is set to 5.85 eV with an energy step of 0.05 eV.

Further structural characterization of the samples has been performed by Raman measurements (HORIBA Jobin Yvon LabRAM HR; HORIBA Jobin Yvon GmbH, Bensheim, Germany) and morphology investigation by scanning electron microscopy (SEM) (Pilips XL 30 FEG). Structural analysis by X-ray diffractometry was not performed due to insufficient signal intensity of the very thin films.

3. Results and discussion

3.1. Overview

Fig. 2 shows XP survey spectra, obtained after deposition at different substrate temperatures using an oxygen flow rate of 2 sccm and a total pressure of 2 Pa for 20 min deposition time. The spectrum taken at a temperature of 200 °C shows strong Si2s and Si2p emission lines (respectively 150.4 eV and 99.2 eV [19]) and O1s for oxygen, which represent the native oxygen layer on the silicon substrate. The signal for cobalt is very small in intensity and only visible in the detailed XP spectrum, consequently the thickness of the deposit is low (below 3 nm). Deposition at higher temperatures (500 and 600 °C) yields spectra of cobalt oxide. For all temperatures carbon is detected, decreasing with temperature in the range 400–600 °C. Principally, this carbon may be present on the surface or in the near surface region, in the latter case reflecting the carbon content in the bulk of the film. In our case surface carbon species can be identified with remnants (or intermediates) from the deposition process, which remain adsorbed until surface analysis. An exception is the carbon detected at a temperature of 200 °C, which is attributed mainly to carbon contamination originating from the preparation of the silicon substrate and its exposure to ambient air. However, such carbon contamination is only relevant for the initial stages of deposition, i.e. for very thin films, and will not be present on the surface of thicker films. Sputter-depth profiling of the films

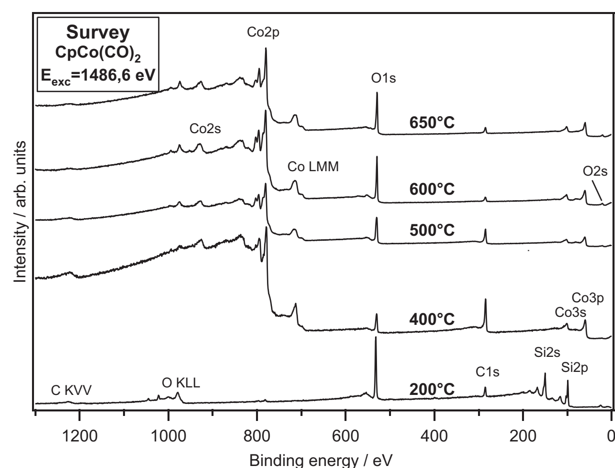

Fig. 2. XP survey spectra of deposited films at different substrate temperatures.

(ex-situ, not shown) indicate that the carbon content in the bulk is almost zero, indicating that contribution of carbon in the near surface region is minor for the presented XPS spectra.

3.2. Kinetics of deposition process

Table 1 presents the thickness of the deposited films and the deposition rates. The film thickness of the deposition at 200 °C is an estimated value from the XPS measurements, using Beer's law to calculate the thickness of the cobalt oxide layer from attenuation of the substrate signal by the film. Notably the use of Beer's law introduces some error as surface morphology, i.e. growth mode, is not considered. The respective Arrhenius plot is shown in Fig. 3. Starting from a temperature of 200 °C, the deposition rate increases exponentially with the temperature until it reaches a maximum of 9.4 nm/min at 500 °C and decreases again at higher temperatures. We thus observe a kinetically controlled regime (i.e. thermally activated regime) with an activation energy of ca. 12.0 kJ/mol. We identify the thermally activated process with a surface reaction. Reasons for the decreasing growth rate at higher temperatures may be gas phase reactions or re-evaporation processes, which is further elaborated in the discussion section.

3.3. Dependence of film properties on temperature

After the deposition process, the films were analyzed with XPS without exposure to atmosphere. In this way changes in oxygen stoichiometry due to further oxidation of cobalt as well as further carbon contamination are avoided. From core level and valence band spectra the oxidation state of the cobalt can be specified, and structural information can be extracted.

Fig. 4 shows the XP core level spectra of films deposited at different temperatures. The Co2p core level shows multiple peaks due to the spin orbital splitting and final state features (shake-up satellites) of the $3d^6$ and $3d^7\underline{L}$ lines electronic structure for Co^{3+} and Co^{2+} in different cobalt oxide modification [20–22]. The position and intensity of the satellite indicates the valence state of the cobalt. At 400 °C the main

Table 1
Film thickness and deposition rate for temperatures between 200 and 650 °C, based on SEM cross sections (except for 200 °C, see text).

Deposition temperature [°C]	Film thickness [nm]	Deposition rate a [nm/min]
200	≈2	0.1
400	50	2.5
500	190	9.4
600	140	7.0
650	100	5.0

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