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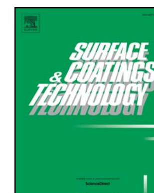

Phase-controlled growth of cobalt oxide thin films by atomic layer deposition

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ABSTRACT

Cobalt oxide (CoO_x) thin films were deposited on thermally grown SiO_2 substrates by atomic layer deposition (ALD) using bis(1,4-di-iso-propyl-1,4-diazabutadiene)cobalt ($C_{16}H_{32}N_4Co$) and oxygen (O_2) as reactants at deposition temperatures ranging from 125 to 300 °C. X-ray diffraction (XRD) and Raman spectroscopic analysis indicated that a mixed-phase oxide consisting of CoO and Co_3O_4 was deposited at temperatures ranging from 125 to 250 °C. However, single-phase Co_3O_4 was deposited above the deposition temperature of 275 °C. Further, analyses by Rutherford backscattering spectrometry, transmission electron microscopy, and selected area electron diffraction along with XRD and Raman spectroscopy revealed that the single-phase cobalt oxide film was stoichiometric crystalline (spinel structure) with negligible N and C impurities. The optical band gap of the single-phase Co_3O_4 film was 1.98 eV and increased with decreasing deposition temperature. It was also shown that the mixed-phase cobalt oxide thin films could be converted into single-phase spinel Co_3O_4 by annealing at 350 °C in O_2 ambient. It was further observed that the phase of the ALD-grown cobalt oxide thin film could be controlled by controlling the precursor or reactant pulsing condition. The study revealed that pure Co_3O_4 phase could be grown at a relatively low temperature (250 °C) by using water vapor as a reactant. Therefore, this work systemically demonstrated several pathways to grow single-phase Co_3O_4 by ALD using a novel metalorganic cobalt precursor.

1. Introduction

Transition metal oxides have drawn considerable attention of the scientific community due to their abundance, non-toxicity, and chemical stability, as well as low-cost production methods [1]. Among the transition metal oxides, cobalt oxide (CoO_x) has been extensively studied for its potential use in various applications such as solid-state gas sensors [2], heterogeneous catalysts [3–5], resistance random access memory devices [6], solar absorbers [7], catalysts for oxidation of different volatile organic compounds [8], intercalation compounds for energy storage, and protective coatings on the interconnects of solid oxide fuel cells [9]. Cobalt oxides exist in two different stable phases: one is Co_3O_4, which is a mixed valence compound, $Co^{II}Co_2^{III}O_4$, with a normal spinel structure, and the other is the thermodynamically stable CoO, which is stable in a rock-salt structure at temperatures above 900 °C. However, the $Co^{II}O$ phase is known to be kinetically stable at room temperature. Along with thermodynamic stability, several other advantages render spinel Co_3O_4 preferable over rock-salt CoO. For example, spinel Co_3O_4 is beneficial as an intercalation host material in Li-ion batteries because of its large unit cell (0.808 nm) compared with that of rock-salt CoO (0.427 nm) and greater number of interstitial sites. As a result, Co_3O_4 exhibits a higher reversible capacity of 1100 mAh/g in Li-ion batteries compared with the 640 mAh/g capacity of CoO [10]. The other advantages of Co_3O_4 over the CoO phase include its relatively high electrochromic efficiency ($\approx$25 cm^2/C), large surface area, high conductivity, and better electrochemically stability [11].

Many kinds of thin film deposition techniques such as sputtering [12,13], reactive electron-beam evaporation [14], pulsed laser deposition (PLD) [15], spray pyrolysis [7,16–18], and chemical vapor deposition (CVD) [9,11,19–23] have been used for obtaining single-phase Co_3O_4 thin films. All these studies reported that single-phase Co_3O_4 thin films were difficult to prepare and could be obtained only in limited conditions of oxygen partial pressure and deposition temperature. For example, a previous work on CVD cobalt oxide [11] showed that single-

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phase Co_3O_4 was generally formed at relatively high O_2 flow rates, a high chamber pressure of 10 mbar, and high deposition temperatures above 450 °C. Moreover, even though the fabrication of single-phase Co_3O_4 is possible using physical vapor deposition (PVD)-based methods or CVD, these methods have an inherent limitation against application to potential high-performance devices with complex, small-sized, and high-aspect ratio structures.

Atomic layer deposition (ALD), as a thin film deposition technique, has attracted great interest due to its self-limiting nature of growth and exceptional coating conformality on three-dimensional structures with high aspect ratios. The self-limiting nature of ALD further provides the scope for monolayer growth as well as precise control over the film thickness over a large area. Cobalt oxide films have been prepared by ALD using an inorganic precursor such as cobalt diiodide (CoI_2) and O_2 [24]. Even though the resulting phase was single-phase Co_3O_4, the growth temperature was high, ranging from 475 to 600 °C. The deposition temperature could be decreased reasonably down to 100–400 °C using metalorganic cobalt precursors such as Co(II)-2,2,6,6-tetramethyl-3,5-heptanedionate [$Co(thd)_2$] [25] or bis(cyclopentadienyl) cobalt ($CoCp_2$) [26]. The single-phase Co_3O_4 was formed with these two Co precursors and highly reactive oxidants compared with O_2 such as O_3 and O_2 plasma. However, the growth rates were significantly low at around 0.02–0.05 nm/cycle. Moreover, $Co(thd)_2$ and $CoCp_2$ are solid at room temperature; thus, high sublimation temperatures are required to obtain sufficient vapor pressures of the precursors. Further, cobalt oxide films were grown by ALD using carbonyl-based cobalt metalorganic precursors such as dicobalt hexacarbonyl *tert*-butylacetylene [$Co_2(CO_6)(HCC(CH_3)_3)$, CCTBA] [27] or cyclopentadienylcobalt dicarbonyl [$CpCo(CO)_2$] [28] with O_3 at 50–150 °C. Relatively high growths per cycle (approximately 0.08–0.1 nm/cycle) were obtained; however, when CCTBA was used, the mixed-phase CoO_x was deposited. Recently, a ALD-CoO_x process at a very low temperature of 50 °C using a new carbonyl-based precursor such as dicobalt octacarbonyl [$Co_2(CO)_8$] and O_3 was reported; the results showed the formation of mixed-phase films of CoO and Co_3O_4 [29]. The above results indicate that the presence of the carbonyl (CO) ligand in the metal precursors might be the cause of such a low-temperature ALD growth of the CoO_x film. However, it was difficult to grow single-phase Co_3O_4 at low deposition temperatures by using these carbonyl-based precursors. Moreover, thermal decompositions of precursors such as CCTBA, CpCo$(CO)_2$, or $Co_2(CO)_8$ do not allow cobalt oxide films to be deposited by an ideal ALD process at high temperatures, restricting the growth of pure spinel Co_3O_4. Table 1 summarizes the ALD-CoO_x processes previously reported.

In this paper, we report the development of a new ALD-CoO_x process using a novel Co metalorganic precursor and O_2 as the reactant, which is relatively milder than O_3 or O_2 plasma. Several process parameters such as deposition temperature, precursor and reactant pulsing times, and post-annealing were carefully considered, and finally, controlled growth of high-quality single-phase Co_3O_4 was achieved.

Table 1
Summary of results of the ALD-CoO_x processes.

Precursor	Reactant	ALD window (°C)	Growth rate (nm/cycle)	Phase	Refs.
CoI_2	O_2	475–600	0.20	Co_3O_4	[24]
$Co(thd)_2$	O_3	114–307	0.02	Co_3O_4	[25]
$CoCp_2$	O_3	137–331	0.041–0.045	CoO, Co_3O_4	[26]
$CoCp_2$	O_2 plasma	100–400	0.05	Co_3O_4	[26]
CCTBA	O_3	68–138	~0.083 (@68 °C) 0.11 (@80 °C)	CoO, Co_3O_4	[27]
$CpCo(CO)_2$	O_3	50–150	0.08–0.11	Co_3O_4	[28]
$Co_2(CO)_8$	O_3	N/A	0.57	CoO, Co_3O_4	[29]

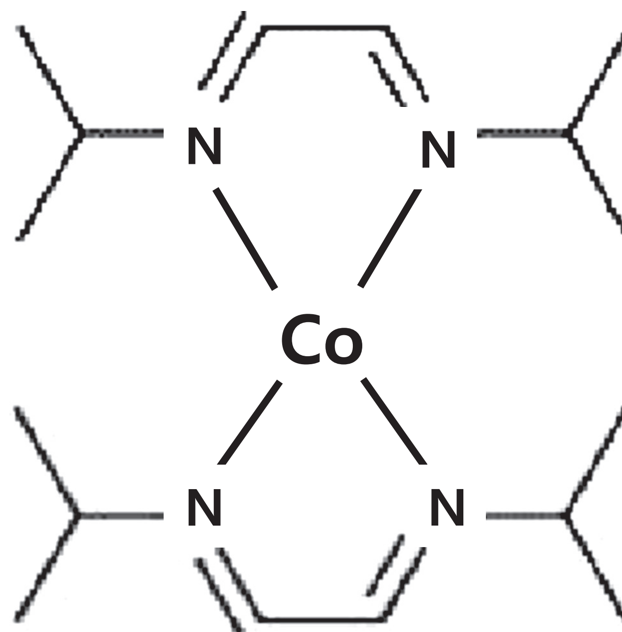

Fig. 1. Molecular structure of bis(1,4-di-iso-propyl-1,4-diazabutadiene)cobalt [$C_{16}H_{32}N_4Co$, $Co(dpdab)_2$] precursor.

2. Experiments

CoO_x films were deposited in a traveling-wave-type ALD reactor (Lucida-D100, NCD technology) using bis(1,4-di-iso-propyl-1,4-diazabutadiene)cobalt [$C_{16}H_{32}N_4Co$, $Co(dpdab)_2$] as the precursor and oxygen (O_2) or water vapor (H_2O) as the reactant (the typical reactant was O_2). The molecular structure of Co precursor is shown in Fig. 1. The Co precursor is liquid at room temperature and was heated to 95 °C during deposition, at which the vapor pressure was 0.25 Torr. The CoO_x films were deposited on p-type Si (100) wafers covered with a 100-nm-thick thermally grown SiO_2 layer and on glass substrates. The deposition temperature was varied from 125 to 300 °C, and the chamber pressure was fixed at approximately 0.5 Torr. The gas delivery line temperature was maintained at 105 °C to prevent condensation of the Co precursor during delivery. O_2 gas diluted with N_2 carrier gas was provided as a reactant into the chamber with a flow rate of 50 sccm. H_2O as a reactant was provided without a carrier gas. After each precursor and reactant pulsing step, a purging process was performed with 100 sccm of N_2. The basic pulsing conditions were set as follows: precursor pulsing for 10 s, reactant pulsing for 10 s, and purging for 10 s. These conditions were found to be sufficient to guarantee the self-limiting growth of the ALD-CoO_x films.

The properties of the CoO_x thin films were analyzed using various analytical techniques. The thicknesses of the CoO_x films were determined by X-ray reflectance (XRR, PANalytical X′-pert MRD with Cu-K_α radiation at 1.5 kW) and cross-sectional view scanning electron microscopy (XSEM, Hitachi S-4800, at 20 kV accelerating voltage and equipped with a field emission electron gun). For phase identification, grazing-incidence angle (incident angle, $\theta = 3°$) X-ray diffraction (GIAXRD) was performed. For precise phase identification, Raman spectroscopy was performed (HORIBA XploRA Plus with a 532-nm incident laser). Rutherford backscattering spectrometry (RBS) was performed to determine the film composition and possible incorporation of impurities in the film using He^{2+} with an incident energy of 2 MeV. Plan-view transmission electron microscopy (TEM, Tecnai F20, at 200 kV accelerating voltage and equipped with a field emission gun) was used to analyze the microstructures of the as-grown CoO_x films in

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