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ABSTRACT

Layered cobalt oxides based on the hexagonal CoO_2 layer, e.g., Na_xCoO_2 and $[\text{CoCa}_3\text{O}_3]_{0.62}\text{CoO}_2$ (or “ $\text{Ca}_3\text{Co}_4\text{O}_9$ ”), are promising thermoelectric materials. Here, the authors investigate the atomic layer deposition (ALD) of these materials in a thin-film form; this is not trivial, in particular, for the former compound, as both Na and Co are little challenged as components of ALD thin films. The authors employ diketone precursors for all the metal constituents and ozone as the source of oxygen. In both cases, a postdeposition heat-treatment in O_2 is applied to get crystalline coatings; the processes are found amazingly robust in terms of metal precursor pulsing ratios. A striking difference between the two processes is the resultant morphology: while the $\text{Ca}_3\text{Co}_4\text{O}_9$ films grow highly homogeneous and smooth, the Na_xCoO_2 coatings exhibit a rather unique reproducible 10–20 μm scale channel-like island structure for all x values investigated. Finally, the authors characterized their ALD $\text{Ca}_3\text{Co}_4\text{O}_9$ films for their chemical, structural, and physical property details not previously reported.

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I. INTRODUCTION

Layered cobalt oxides A_xCoO_2 (A = alkali metal) based on the hexagonal CoO_2 layer are important functional materials for advanced energy applications. The most evident example is the Li-ion-battery cathode material Li_xCoO_2 showing facile deintercalation and intercalation of Li^+ ions.¹ Another important example is Na_xCoO_2 , which is a prominent thermoelectric (TE) material owing to its unusual combination of high electrical conductivity with high Seebeck coefficient.^{2,3} In this respect, Li_xCoO_2 behaves differently as it changes with increasing x from a semiconductor of high resistivity and high Seebeck coefficient to a metal-like conductor with low resistivity and low Seebeck coefficient.⁴

The interesting electrical properties of A_xCoO_2 materials derive from the fact that the d -band of the transition-metal oxide layer becomes filled with holes to compensate the charge when the alkali-cation content is below the stoichiometric value of $x = 1$. Charge carriers in a narrow d -band often experience strong correlation effects, which means that they can no longer be described by conventional single-particle approximations. For example, Khaliullin and Chaloupka⁵ discussed the electronic correlation effects in Na_xCoO_2 highlighting the importance of the degeneracy of Co^{3+} d electrons.

Excellent thermoelectric properties were also reported for the $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$ or “ $\text{Ca}_3\text{Co}_4\text{O}_9$ ” compound,^{6–9} which similarly to A_xCoO_2 contains conductive hexagonal CoO_2 sheets but separated by rock-salt-structured Ca_2CoO_3 layer-blocks instead of alkali-metal monolayers. For strontium, the related TE compound has the stoichiometry of $[\text{Sr}_2\text{O}_2]_{0.5}\text{CoO}_2$.¹⁰

Fabrication of nanostructures is a popular strategy to enhance the performance of TE materials.^{11–13} Another goal has been to grow these materials in high-quality thin-film form for application, e.g., in microelectronics.^{14–18} Among the thin-film deposition techniques, atomic layer deposition (ALD)¹⁹ would be most advantageous as it ideally offers the possibility to achieve both goals, i.e., to coat nanostructures with high-quality conformal thin films.^{12,13,17,18} We were the first to report the ALD of $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$ (or $\text{Ca}_3\text{Co}_4\text{O}_9$) films with good thermoelectric properties already a decade ago.²⁰ More recently, we attempted to grow Sr-based $[\text{Sr}_2\text{O}_2]_{0.5}\text{CoO}_2$ films but without success. On the other hand, well-behaving ALD processes for the perovskite SrCoO_3 and $(\text{La},\text{Sr})\text{CoO}_3$ films could be developed.^{21,22} The only material of A_xCoO_2 type deposited by ALD thus far has been LiCoO_2 ,²³ while a feasible ALD process for Na_xCoO_2 would be desirable due to its excellent TE properties. It is important to

notice that the deposition of Na_xCoO_2 thin films with other techniques has turned out to be challenging. For example, Ohta *et al.*²⁴ needed to employ a multistep process for growing epitaxial Na_xCoO_2 films. First, they deposited CoO on sapphire using pulsed laser deposition (PLD). Then, they capped the layer with a thin yttria-stabilized zirconia plate for protection, put NaHCO_3 powder onto the stack, and finally annealed the sample at 700 °C in air. The reason for this quite unconventional procedure was the high vapor pressure of sodium which made the direct PLD process difficult.

Sodium has been a kind of white spot among the elements used in ALD processes, except in the pioneering works exploring sodium *tert*-butoxide, sodium hexamethyldisilazide, and sodium trimethylsilanolate precursors of limited stability for the ALD of sodium aluminates, silicates, niobates, and tantalates;^{25,26} the ALD of Na oxide was not challenged due to its hygroscopic nature. Our group then challenged combined ALD and molecular layer deposition processes for Na-containing inorganic-organic hybrid thin films using Na-2,2,6,6-tetramethyl-3,5-heptanedionate as the precursor for sodium;^{27–29} thermal stability of that precursor enabled reproducible depositions at temperatures as high as 300 °C. The ALD of cobalt oxides is still an active matter of research as can be seen from the list in Table I.

In this work, we challenge the ALD of Na_xCoO_2 for the first time. We characterize the films with X-ray diffraction and various microscopy techniques; the results reveal a highly controlled but peculiar type of growth mode resulting in unique channel-like island structures. We compare the results with those obtained for ALD $\text{Ca}_3\text{Co}_4\text{O}_9$ films grown under similar conditions to find out that the growth modes are strikingly different for these two highly related thermoelectric compounds. Moreover, we thoroughly characterize our $\text{Ca}_3\text{Co}_4\text{O}_9$ films for their chemical composition, depth profile, and physical properties.

TABLE I. ALD processes reported for cobalt oxides. [†]Pr-MeAMD, isopropyl-acetamidinate; AMD, *N*-*tert*-butyl-*N*-ethylpropionamidinate; TMEDA, tetramethylethylenediamine; [‡]Bu-DAD, 1,4-di-*tert*-butyl-1,3-diazadienate; dpdab, 1,4-di-iso-propyl-1,4-diazabutadienyl; and [§]BuAc, *tert*-butylacetylene.

Precursor	Reactant	Deposition temp. (°C)	Reference
Co(thd) ₂	O ₃	115–300	30–32
Co(acac) ₃	Air	180	33
Co(Cp) ₂	O ₃	137–331	34
Co(Cp) ₂	O ₂ plasma	100–400	35
(CO) ₂ -Co(Cp)	O ₃	50–150	36
Co([†] Pr-MeAMD) ₂	H ₂ O	170–180	37
Co(AMD) ₂	H ₂ O	180–270	38
TMEDA-CoCl ₂	H ₂ O	225–300	39
Co([‡] Bu-DAD) ₂	O ₃	100–150	40
Co(dpdab) ₂	O ₂	125–300	41
[Co ₂ (CO) ₈]	O ₃	50	42
[§] BuAc-(CO) ₆ -Co ₂	O ₃	70–140	43
CoI ₂	O ₂	475–650	44

II. EXPERIMENT

Na_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films were grown with an ASM Microchemistry F120 ALD reactor operated at a pressure of about 1 Torr. In all depositions, O₃ generated from O₂ (grade 5.0, AGA) with a Fischer Modell 502 generator was used as the reactant (i.e., third precursor). The Na_xCoO_2 films were grown from Na(thd) and Co(acac)₃ (acac = acetylacetonate) metal precursors, while the $\text{Ca}_3\text{Co}_4\text{O}_9$ films were grown with Ca(thd)₂ and Co(thd)₂ to be consistent with our earlier work.²⁰ The metal-thd precursors were prepared using the method described by Hammond *et al.*,⁴⁵ and Co(acac)₃ was purchased. The solid metal precursors were sublimated from open boats at the following temperatures: Na(thd) at 170 °C, Co(acac)₃ at 130 °C, Ca(thd)₂ at 180 °C, and Co(thd)₂ at 90 °C. The replacement of Co(thd)₂ with Co(acac)₃ for the Na_xCoO_2 process had the advantage that the sublimation temperature is closer to that of the second precursor. It is important to note that we also performed depositions for $\text{Ca}_3\text{Co}_4\text{O}_9$ using the Co(acac)₃ precursor and observed very little differences to the depositions carried out with Co(thd)₂. The Na_xCoO_2 films were deposited with a total of 2400 single-metal cycles, and the $\text{Ca}_3\text{Co}_4\text{O}_9$ films with 2800 single-metal cycles, unless stated otherwise. The single-metal cycles were combined to supercycles to adequately obtain the desired stoichiometry; for example, the $\text{Ca}_3\text{Co}_4\text{O}_9$ supercycle consisted of a combination of seven single-metal cycles as follows: [3 × (Co + Ca) + Co]. The precursor/N₂ purge times were fixed to the following values based on preliminary tests: 4, 10, 3, and 12 s for the metal precursor exposure, precursor purge, O₃ exposure, and O₃ purge, respectively, in the Na_xCoO_2 process, and 5.5, 8, 3, and 8 s for the Ca precursor exposure, precursor purge, O₃ exposure, and O₃ purge, respectively, in the $\text{Ca}_3\text{Co}_4\text{O}_9$ process. The Co(thd)₂ exposure time in the latter case was 4.5 s.

The as-deposited films were heat-treated in O₂ atmosphere for crystallization using an ATV PEO 601 rapid-thermal-processing oven. The annealing temperature was held for 15 min while the ramp times were set to 40 min. The crystal phases in the films were identified with grazing-incidence X-ray diffraction (GIXRD) and XRD in Bragg–Brentano geometry using a Panalytical X'Pert Pro MPD diffractometer (Cu-Kα source). The same tool was employed for determining the film thicknesses with X-ray reflection (XRR). A J. A. Woollam CompleteEase ellipsometer was used to confirm these thickness values and to determine optical dispersion. Furthermore, the morphology of the films was investigated with atomic force microscopy (AFM) using a Dimension5000 Nanoscope. Elemental compositions of the films were determined with X-ray photoelectron spectroscopy (XPS) using a Thermo-Scientific K-alpha spectrometer.

III. RESULTS AND DISCUSSION

The best TE properties for bulk Na_xCoO_2 samples are realized for *x* values between ~0.5 and 0.75.^{2,3} We started our ALD studies on the Na_xCoO_2 system targeting *x* = 0.5 stoichiometry. Figure 1(a) presents the GIXRD patterns for an as-deposited *x* = 0.5 Na_xCoO_2 film grown at 220 °C and for the same thin film after annealing at 500 and 900 °C in O₂. The as-deposited film is weakly crystalline with most peaks consistent with the presence of the spinel Co₃O₄ phase. After annealing at 500 °C, the layered Na_xCoO_2 phase can

FIG. 1. GIXRD patterns for postdeposition heat-treated Na_xCoO_2 films: (a) $x = 0.5$ films heat-treated at different temperatures and (b) films with different x values heat-treated at 600°C ; all heat-treatments are carried out in O_2 .

FIG. 2. Morphology of Na_xCoO_2 deposits ($x = 0.33$): (a) optical micrograph and (b) AFM image.

be readily identified from the presence of the most prominent (002) peak at 16° . This phase remains remarkably stable over a wide temperature range until a new phase appears after annealing at 900°C , as is evident from the disappearance of the Na_xCoO_2 (002) peak and the appearance of a new peak at 22° . There is no straightforward identification of this high-temperature phase, but one possibility is $\text{Co}(\text{OH})_2$.

The Na_xCoO_2 phase forms (upon postdeposition annealing at 600°C in O_2) in a remarkably wide nominal x range; Fig. 1(b) shows GIXRD patterns for a series of films with the nominal x value ranging from 0.33 to 2. Only for the sample with a clear Na excess ($x = 2$), diffraction peaks due to other phase(s) than Na_xCoO_2 are observed [Fig. 1(b)].

Interestingly, even though the layered Na_xCoO_2 phase could be readily and very reproducibly grown with our ALD process, the resultant films were not continuous but exhibited a unique channel-like island structure. As an example, Fig. 2(a) shows a micrograph for an as-deposited Na_xCoO_2 film with $x = 0.33$ grown with 2400 ALD cycles. This micrograph was recorded with a simple optical microscope using a $10\times$ magnification lens. It is clear that even after the high number of deposition cycles applied, the peculiar island pattern persists. Parallel results were systematically observed for the other x values too ($0.33 \leq x \leq 1$). Unfortunately, this morphology made the films insulating, at least on the macroscopical scale. So, it was not possible to determine the electrical resistivity or the Seebeck coefficient. Previously, somewhat similar channel-like structures have been seen for ALD-grown metallic Cu films and then attributed to the coalescence of the

islands.⁴⁶ However, the length scales are quite different in the two cases; the island pattern structures of the size observed here for our Na_xCoO_2 films have not been reported thus far for any ALD-grown materials, to the best of our knowledge.

We investigated the deposits in more detail using AFM [Fig. 2(b)]. For this sample with $x = 0.33$, these measurements show a height of the features of about 120 nm and a width on the order of magnitude of $10\text{--}20\mu\text{m}$, indicating that indeed all the deposited materials are in the lamellas with the bare substrate surface in between. Given the limited coverage, a growth per cycle (GPC) between 0.23 and $0.30\text{ \AA/cycle}$ can be estimated, which is consistent with the GPC values expected from the single-metal processes. Similar island heights were measured for the sample with $x = 1$.

It was also interesting to compare this morphology with those seen for the films yielded under similar conditions from the two parent binary processes. First, the present morphology of the Na_xCoO_2 films is in sharp contrast to our earlier research on ALD of Co_3O_4 films, where very smooth continuous films were straightforwardly achieved.³² Second, in the present study, we carried out a series of initial $\text{Na}(\text{thd}) + \text{O}_3$ depositions for the optimization of sublimation conditions and pulse length of the $\text{Na}(\text{thd})$ precursor. These amorphous films were smooth and homogeneous and could be readily characterized with XRR for film thickness; the GPC calculated from the film thickness and the number of ALD cycles applied was $0.23\text{ \AA/cycle}$, thus very similar to that for the Co_3O_4 films.

The island formation was also something not seen in our earlier work for $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2(\text{Ca}_3\text{Co}_4\text{O}_9)$ thin films, which

were found smooth and continuous.²⁰ Therefore, we repeated this process here for investigating the differences between the ALD growths of these apparently quite similar materials in more detail. Figure 2(a) shows XRR curves for a $\text{Ca}_3\text{Co}_4\text{O}_9$ film deposited with 2800 cycles and a nominal Ca/Co ratio of 3:4 at 250 °C. For the as-deposited thin film, the pronounced fringes indicate a smooth film with a thickness of 95 nm corresponding to a GPC of 0.34 Å/cycle, which is a typical value for ALD metal oxide films from diketone precursors.^{42,47} After annealing, the film became much rougher as demonstrated in Fig. 3(a) for a sample heat-treated at 750 °C in O_2 .

The increased roughness is caused as commonly observed for ALD films by crystallization of the material; from the GIXRD patterns shown in Fig. 3(b), the presence of the crystalline $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$ phase is seen for samples heat-treated at 600 °C or above. It is worth noticing that the appearance of diffraction peaks in the GIXRD geometry implies the presence of randomly oriented grains. On the other hand, in the XRD patterns measured in

Bragg–Brentano geometry, the (001) peaks dominated, as in our previous study.²⁰

We confirmed the composition of the “ $\text{Ca}_3\text{Co}_4\text{O}_9$ ” films with XPS depth profiling for both the as-deposited and heat-treated films. As can be seen in Fig. 4(a), the composition of the as-deposited film is quite constant throughout the profile with a slight excess of Ca and a relatively high C content of about 10%. After annealing at 750 °C, diffusion of Ca to the interface with Si can be observed in Fig. 4(b), while the composition of the main film is now close to the targeted $\text{Ca}_3\text{Co}_4\text{O}_9$ composition.

The films were further characterized using spectroscopic ellipsometry. For the film that was annealed at 750 °C, we assumed that the deposit consists of two layers both modelled with the combination of a Lorentz and a Cody–Lorentz oscillator. A good fit was obtained for 74 and 8 nm thicknesses of the upper and the lower layer, respectively, which is in accordance with the XPS results. The dispersion of the real and imaginary parts of the refractive indices n and k is shown in Fig. 5. The most pronounced feature of the optical dispersion curves is an absorption peak starting at ~500 nm. The optical measurements reported in the literature typically show significant absorption throughout the visible spectrum.^{13,48} Absorption peaks at similar wavelengths as reported here have been attributed to charge transfer transition between the O^{2-} and Co^{3+} ions,⁴⁸ and the transition between the crystal-field splitted t_{2g} and e_g Co 3d bands.⁴⁹ This is consistent with the observations made by Chambrier *et al.*,⁵⁰ who observed an absorption onset at similar wavelengths for their $\text{Ca}_3\text{Co}_4\text{O}_9$ films fabricated with PLD.

Finally, we characterized our $\text{Ca}_3\text{Co}_4\text{O}_9$ films for their electrical transport properties. The electrical sheet resistance of the as-deposited film was 83 kΩ/□, which corresponds to a resistivity of 790 mΩ cm. After annealing at 600 °C, the sheet resistance decreased to 17 kΩ/□, and after annealing at 750 °C, it decreased to 2.2 kΩ/□, while a further increase in the

FIG. 3. (a) XRR patterns for as-deposited and heat-treated (750 °C) $\text{Ca}_3\text{Co}_4\text{O}_9$ films; (b) GIXRD patterns of $\text{Ca}_3\text{Co}_4\text{O}_9$ films heat-treated at different temperatures; all heat-treatments are carried out in O_2 .

FIG. 4. XPS depth profiles for $\text{Ca}_3\text{Co}_4\text{O}_9$ films: (a) as-deposited and (b) heat-treated at 750 °C.

FIG. 5. Optical constants n and k for $\text{Ca}_3\text{Co}_4\text{O}_9$ films: as-deposited (dashed lines) and heat-treated at 750°C (solid lines).

annealing temperature to 850°C increased the sheet resistance to $3.8\text{ k}\Omega/\square$. Using the film thickness measured for the as-deposited film, these values correspond to resistivities of 160, 20, and $36\text{ m}\Omega\text{ cm}$. The resistivity value obtained for the film annealed at 750°C is very close to the value ($12\text{ m}\Omega\text{ cm}$) we previously measured for optimized (in terms of oxygen content) ALD $\text{Ca}_3\text{Co}_4\text{O}_9$ films.²⁰

IV. SUMMARY AND CONCLUSIONS

We have investigated and compared the ALD of two important thermoelectric layered cobalt oxide materials, Na_xCoO_2 and $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$ or “ $\text{Ca}_3\text{Co}_4\text{O}_9$.” The former ALD process was new, while the latter we had developed earlier.

In both cases, obtaining the targeted thermoelectric material in crystalline form required a postdeposition heat-treatment; importantly, for Na_xCoO_2 , the layered phase was obtained as the single crystalline phase for a wide range of Na contents x . Then, comparing the heat-treated Na_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ films, the film morphologies were found amazingly different. While the $\text{Ca}_3\text{Co}_4\text{O}_9$ films were smooth and continuous, the Na_xCoO_2 films independent of x exhibited an intriguing morphology consisting of virtually macroscopic island structures. This may not be only a negative aspect as it could provide us with interesting possibilities once properly elaborated to design/fabricate unique nano-/microstructures for enhanced thermoelectric characteristics.

Finally, we characterized our ALD $\text{Ca}_3\text{Co}_4\text{O}_9$ films in more detail than was previously accomplished.²⁰ The presence of polycrystalline $\text{Ca}_3\text{Co}_2\text{O}_9$ was proven with GIXRD for films annealed in O_2 at 600°C or higher; the elemental-composition profile was measured with XPS; and the optical dispersion was determined with spectroscopic ellipsometry. Moreover, the robustness of this process was demonstrated by an unintentional Ca excess; here, the stoichiometric $\text{Ca}_3\text{Co}_4\text{O}_9$ was obtained after annealing through diffusion of Ca to the interface with the substrate.

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