Mechanism of Formation of the Thermoelectric Layered Cobaltate \(\text{Ca}_3\text{Co}_4\text{O}_9\) by Annealing of \(\text{CaO}\text{–CoO}\) Thin Films

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The layered cobaltate \(\text{Ca}_3\text{Co}_4\text{O}_9\) is of interest for energy-harvesting and heat-conversion applications because of its good thermoelectric properties and the fact that the raw materials Ca and Co are nontoxic, abundantly available, and inexpensive. While single-crystalline \(\text{Ca}_3\text{Co}_4\text{O}_9\) exhibits high Seebeck coefficient and low resistivity, its widespread use is hampered by the fact that single crystals are too small and expensive. A promising alternative approach is the growth of highly textured and/or epitaxial \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films with correspondingly anisotropic properties. Here, we present a two-step sputtering/annealing method for the formation of highly textured virtually phase-pure \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films by reactive cosputtering from Ca and Co targets followed by an annealing process at 730 °C under \(\text{O}_2\)-gas flow. The thermally induced phase transformation mechanism is investigated by in situ time-resolved annealing experiments using synchrotron-based 2D X-ray diffraction (XRD) as well as ex situ annealing experiments and standard lab-based XRD. By tuning the proportion of initial CaO and CoO phases during film deposition, the method enables synthesis of \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films as well as \(\text{Ca}_x\text{Co}_y\text{O}_2\). With this method, we demonstrate production of epitaxial \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films with in-plane electrical resistivity of 6.44 mΩ cm and a Seebeck coefficient of 118 μV K\(^{-1}\) at 300 K.

1. Introduction

Thermoelectrics have the potential to play an important role for thermal management and conversion of waste heat into electricity in environmentally friendly energy systems.\(^{[1-3]}\) The power generation efficiency of a thermoelectric materials system is related to the dimensionless figure of merit \(ZT = S^2T/\kappa\rho\), where \(S\), \(T\), \(\kappa\), and \(\rho\) are the Seebeck coefficient, absolute temperature, thermal conductivity, and electrical resistivity, respectively. High power generation efficiencies require high \(ZT\) values, which can be achieved with high-Seebeck materials that readily scatter phonons (low thermal conductivity) without impeding the transport of charge carriers (low electrical resistivity). Such an ideal thermoelectric material is often referred to as a “phonon-glass-electron-crystal.”\(^{[4,5]}\) Materials systems with layered structures are one approach toward realizing a “phonon-glass-electron-crystal.” Alternating layers act as scattering layers for phonons and conducting layers for charge carriers. One class of layered thermoelectric materials are the misfit-layered cobalt oxides, which are described by the general formula \(\text{M}_m\text{A}_n\text{O}_{m+n}\) where \(\text{M} = \text{Ca}, \text{Sr}, \text{Ba}; \text{A} = \text{Co}, \text{Mn}, \text{Ni}, \text{Fe}; \text{m} \geq 1, \text{n} \geq 0, \text{and} m + n \geq 2,\) the misfit-layered cobalt oxides are comprised of alternately stacked layers (along the \(c\) axis) of rocksalt-type \(\text{M}_m\text{A}_n\text{O}_{m+n}\) layers, acting as phonon blocking layers, and \(\text{CdI}_2\)-type \(\text{Co}_x\) layers, acting as charge carrier conducting channels. This class of materials exhibits excellent thermoelectric properties, they are nontoxic, and the raw materials are abundant and inexpensive.\(^{[7]}\)

The most important misfit-layered cobalt oxide is the archetypical \(\text{Ca}_3\text{Co}_4\text{O}_9\) (alternatively expressed as \(\text{Ca}_3\text{Co}_4\text{O}_{3n}\)) which exhibits a high Seebeck coefficient (S) and low electrical resistivity (\(\rho\)).\(^{[8,9]}\) The physical properties of \(\text{Ca}_3\text{Co}_4\text{O}_9\) are anisotropic due to its inherently nanolaminated structure. Less resistive transport of charge carriers (e.g., 2 mΩ cm at room temperature)\(^{[10]}\) is practically realized in the basal plane of single crystalline \(\text{Ca}_3\text{Co}_4\text{O}_9\).\(^{[10,31]}\) Despite these advantages, technical challenges and high cost associated with the growth of larger size \(\text{Ca}_3\text{Co}_4\text{O}_9\) single crystals make them difficult to apply in practice. A more promising approach to exploit the anisotropic properties of \(\text{Ca}_3\text{Co}_4\text{O}_9\) is the growth of textured and/or epitaxial \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films, whose thermoelectric properties may be comparable to that of single crystalline \(\text{Ca}_3\text{Co}_4\text{O}_9\).

Synthesis of \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films has been demonstrated by...
both chemical techniques and physical vapor deposition (PVD) techniques. Chemical synthesis methods include the chemical vapor deposition (CVD) techniques atomic layer deposition (ALD) and metal-organic CVD, as well as chemical solution deposition methods followed by annealing and reactive solid-phase epitaxy by topotactic ion exchange. However, PVD has broad advantages compared to chemical methods since PVD operates far from thermodynamic equilibrium and offers atomistic control of the deposition flux. PVD-based synthesis of Ca$_2$CoO$_4$ thin films has been demonstrated with both pulsed laser deposition and rf-magnetron sputtering from compound targets of Ca–Co–O. However, sputter-deposition from compound targets suffers from two distinct drawbacks: (1) the Ca–Co–O ratio is fixed and the resultant film composition is often different from that of the target and (2) deposition from an oxide target yields low deposition rates. Both of these drawbacks can be overcome by reactive cosputtering from elemental targets (i.e., Ca and Co), thus making this approach more suitable for upscaling.

Here, we report a method for the growth of Ca$_2$CoO$_4$ thin films by a two-step sputtering/annealing method. CaO–CoO films are first deposited by reactive magnetron cosputtering from Ca and Co targets followed by annealing in an oxygen atmosphere to form Ca$_2$CoO$_4$. The phase transformation mechanism is investigated by in situ time-resolved annealing experiments using synchrotron-based X-ray diffraction (XRD) with a 2D-detector as well as ex situ annealing experiments and standard lab-based XRD. The present method carries important advantages in that by tuning the proportion of initial CaO and CoO phases during film deposition, the method enables synthesis of Ca$_2$CoO$_4$ thin films as well as Ca$_2$CoO$_3$. Further advantages include the high deposition rate (compared to deposition from oxide sources) associated with reactive sputter-deposition and the abundant availability of metallic Ca and Co targets. Thus, the present method offers prospects for upscaling and implementation in applications.

2. Results and Discussion

2.1. As-Deposited CaO–CoO and Annealed Ca–Co–O Films

The as-deposited CaO–CoO films are comprised of only CaO and CoO phases irrespective of the Ca:Co ratio in the films. Figure 1a shows a θ–2θ XRD scan for the as-deposited Ca:Co = 0.72 film. θ–2θ scans of as-deposited films with other Ca:Co elemental ratios were similar in appearance (not shown), albeit with varying CaO:CoO peak intensity ratios. The films were annealed at 730 °C for 4 h under O$_2$ gas flow and the resultant phases were dependent on the initial Ca:Co ratio (Figure 1b–e). As expected, the annealed Ca:Co = 0.72 film only shows the presence of Ca$_2$CoO$_3$ since its elemental ratio is closest to stoichiometric Ca$_2$CoO$_3$ (i.e., Ca:Co = 0.75). As discussed below, a small amount of interfacial Ca$_2$CoO$_3$ (with overlapping peaks with Ca$_2$CoO$_3$) is also present. The Ca$_2$CoO$_3$ diffraction peaks occur for 001, 002, 003, 004, 006, and 008 Ca$_2$CoO$_3$. The 005 peak of Ca$_2$CoO$_3$ coincides with the large 006 peak of Al$_2$O$_3$. The Ca:Co = 0.72 film exhibited an epitaxial relationship of (001)Ca$_2$CoO$_3$∥(001)Al$_2$O$_3$, as verified by XRD pole figures (see the Supporting Information).

Films with other Ca:Co ratios show the presence of Ca$_2$CoO$_3$ in varying degrees in addition to other phases, depending on whether the initial film was Ca-rich or Co-rich. For example, the Ca:Co = 0.85 film is Ca-rich and shows the additional presence of CaO (Figure 1e) whereas the Ca:Co = 0.69 is Co-rich and shows the additional presence of Co$_3$O$_4$ (Figure 1c). The Ca:Co = 0.47 film is also Co-rich but exhibits a Ca:Co elemental ratio within the stoichiometric window of Ca$_2$CoO$_3$, where x ranges between 0.26 and 0.5. Therefore, the Ca:Co = 0.47 film is constituted mainly of the Ca$_2$CoO$_3$ phase, which is manifested by strong diffraction peaks at 2θ = 16.425°, 33.275°, 49.275°, and 69.675° from the (001), (002), (003), and (004) planes of the Ca$_2$CoO$_3$ phase, respectively (Figure 1b). The additional low intensity diffraction peaks are attributed to the presence of minor concentrations of Ca$_2$CoO$_3$ and Co$_3$O$_4$ phases. The results from the annealed Ca:Co = 0.47 and Ca:Co = 0.72 films show that the present two-step sputtering/annealing method can be employed to grow two of the known ternary layered phases in the Ca–Co–O system (i.e., Ca$_2$CoO$_3$ and Ca$_2$CoO$_3$).

Identifying the Ca$_2$CoO$_3$ concentration from XRD patterns is difficult since all of the Ca$_2$CoO$_3$ peaks overlap with various Ca$_2$CoO$_3$ peaks. Therefore, we use a simplified approach for monitoring the progress of Ca$_2$CoO$_3$ formation. The peak at 2θ = 8.225° is solely originating from the (001) plane of Ca$_2$CoO$_3$, whereas the peak at 2θ = 16.425° is a convolution.
of the \( \text{Ca}_{3}\text{Co}_{4}\text{O}_{9} \) 002 and \( \text{Ca}_{2}\text{Co}_{2}\text{O}_{5} \) 001 peaks. Defining \( I_1 \) as the integrated peak intensity of the \( 2\theta = 8.225^\circ \) peak and \( I_2 \) as the integrated peak intensity of the \( 2\theta = 16.425^\circ \) peak, the \( I_2/I_1 \) ratio provides a qualitative comparative measure of the \( \text{Ca}_{3}\text{Co}_{4}\text{O}_{9} \) content, with lower \( I_2/I_1 \) values indicating higher \( \text{Ca}_{2}\text{Co}_{2}\text{O}_{5} \) content. Figure 1 displays the \( I_2/I_1 \) values for each of the annealed films. Since the \( \text{Ca}:\text{Co} = 0.72 \) film was verified by transmission electron microscopy (TEM, see next paragraph) to be nearly phase pure, the \( I_2/I_1 \) value for the \( \text{Ca}:\text{Co} = 0.72 \) film is considered the baseline for phase purity. Any decrease from this baseline value indicates the partial presence of the \( \text{Ca}_{2}\text{Co}_{2}\text{O}_{5} \) phase in the off-stoichiometric film.

Figure 2a shows a typical TEM image of an annealed \( \text{Ca}:\text{Co} = 0.72 \) film. The high-resolution TEM (HRTEM) image in Figure 2b shows the layered structure of \( \text{Ca}_{3}\text{Co}_{4}\text{O}_{9} \). The atomic arrangement of \( \text{Ca}, \text{Co}, \) and \( \text{O} \) atoms is schematically presented next to the HRTM image. Compositional analyses and lattice imaging show that a region up to 17 nm from the substrate surface consists of the \( \text{Ca}_{3}\text{Co}_{4}\text{O}_{9} \) phase. The presence of \( \text{Ca}_{2}\text{Co}_{2}\text{O}_{5} \) near the interface is attributed to a \( \text{Ca} \)-deficiency near the substrate surface in the as-deposited films. This \( \text{Ca} \)-deficiency was observed in as-deposited films by energy dispersive X-ray spectroscopy (EDS) mapping of a TEM cross section (see Figure S2, Supporting Information). The \( \text{Ca} \)-deficiency occurs due to the segregation of thermally driven \( \text{Ca} \) near the surface of the as-deposited films, which is caused by substrate heating during sputter deposition. The \( d \) spacing of planes of \( \text{Ca}_{3}\text{Co}_{4}\text{O}_{9} \) along the \( c \) direction is observed to be \( \approx 10.7 \) Å, which is consistent with the \( d \) spacing calculated from the 001 peaks of the \( \theta-2\theta \) scan. The \( d \) spacing of the planes of \( \text{Ca}_{2}\text{Co}_{2}\text{O}_{5} \) in the same direction is calculated to be \( \approx 5.41 \) Å, which is close to the reported value of 5.44 Å. 

2.2. In Situ Time-Resolved Synchrotron-Based XRD Study

A 260 nm \( \text{CaO-CoO} \) film with \( \text{Ca}:\text{Co} = 0.72 \) was characterized by in situ time-resolved synchrotron-based 2D XRD during annealing in order to determine the details of the thermally induced phase transformation process from \( \text{CaO-CoO} \) films into \( \text{Ca}_{3}\text{Co}_{4}\text{O}_{9} \). The film was annealed in a pure oxygen atmosphere with a continuous flow of pure oxygen (100 sccm). The annealing time/temperature profile is shown in Figure 3b. In brief, the film was ramped (8 K min\(^{-1}\)) to 720 °C, held at 720 °C for 135 min, ramped to 800 °C, held for 60 min, ramped to 880 °C, held for 10 min, ramped to 960 °C, held for 6 min, ramped to 1040 °C, held for 6 min, ramped to 1120 °C, and held for 5 min.

Figure 3a shows relevant sections of the 2D synchrotron-based XRD images during annealing, in which \( \text{CaO}, \text{CoO}, \text{CoO}_2, \text{Ca}_2\text{Co}_2\text{O}_5, \text{and Ca}_3\text{Co}_4\text{O}_9 \) are present at various stages of the annealing process (a time-resolved video is also available as Supporting Information). The diffraction images show that \( \text{CoO} \) first oxidizes to the intermediate \( \text{CoO}_2 \) phase, which then reacts with \( \text{CaO} \) to form \( \text{Ca}_2\text{Co}_2\text{O}_5 \). \( \text{Ca}_2\text{Co}_2\text{O}_5 \) subsequently reacts with \( \text{CaO} \) to form the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) phase. As the 001 diffraction spots of \( \text{Ca}_2\text{Co}_2\text{O}_5 \) coincide with those of \( \text{Ca}_3\text{Co}_4\text{O}_9 \), they are indistinguishable in the 2D diffraction images. The formation of \( \text{Ca}_2\text{Co}_2\text{O}_5 \) as an intermediate phase via the reaction of \( \text{CoO}_2 \) with \( \text{CaO} \) was verified by ex situ annealing and XRD experiments as described in the next section. It is apparent that those 2D diffraction spots will initially be from the (001) and (002) planes of \( \text{Ca}_2\text{Co}_2\text{O}_5 \) and at the end from the (002) and (004) planes of \( \text{Ca}_3\text{Co}_4\text{O}_9 \). Annealing temperatures above 880 °C led to the loss of calcium from \( \text{Ca}_3\text{Co}_4\text{O}_9 \) and the formation of \( \text{CoO} \) and \( \text{CoO}_2 \) cobalt oxide phases.

**Figure 2.** a) TEM image of \( \text{Ca}:\text{Co} = 0.72 \) thin film showing the layered \( \text{Ca}_3\text{Co}_4\text{O}_{9} \) structure with a 17 nm region from the interface comprised of \( \text{Ca}_2\text{Co}_2\text{O}_{5} \). b) Lattice-resolved TEM image and schematic of the atomic arrangement of the layers.
whereby CoO transforms into CoO₂ while Co₂O₃ is simultaneously being consumed by the reaction with CaO to form Ca₂CoO₄. The consumption rate of Co₂O₃ is higher in zone 3 as evidenced by the downward trend of the Co₂O₃ integrated peak intensity. The onset of zone 4 is characterized by the CoO phase being exhausted, which results in the cessation of Co₂O₃ formation. The supply of Co₂O₃ is now limited, so the rate of Ca₄Co₂O₇ / Ca₄CoO₆ formation decreases as evidenced by the decreasing slopes in the Ca₄Co₂O₇ / Ca₄CoO₆ and CaO curves in zone 4. The Ca₄Co₂O₇ and Ca₄CoO₆ phases coexist in zone 4 and the complete phase transformation to Ca₃CaO₂O₈ is not yet finished. Zone 5 starts when the temperature is increased to 800 °C. The increased temperature leads to increased reaction rates as shown by the changes in slope for all curves. In zone 5, the consumption rate of Ca₄Co₂O₇ by the reaction with CaO to form Ca₃CaO₂O₈ becomes higher than its formation rate by the reaction of CaO and Co₂O₃ since the Co₂O₃ is gradually disappearing. In zone 6, the phase transformation to Ca₃CaO₂O₈ comes to its end, which is evident from the decreasing slope of Ca₃CaO₂O₈ integrated peak intensity. Further increases in temperature to 880, 960, 1040, and 1120 °C (zone 7) lead to the evaporation of Ca from the lattice and the formation of CoO and Co₂O₃. Therefore, the Ca₃CaO₂O₈ films are not stable at temperatures above 880 °C.

From the in situ time-resolved synchrotron-based XRD study it is concluded that the formation of Ca₄Co₂O₇ and Ca₄CoO₆ is initiated by the formation of Co₂O₃. Complete transformation to the final phase of Ca₃CaO₂O₈ occurs in the temperature range 720 < T < 880 °C. Annealing at temperature at or above 880 °C leads to the decomposition of Ca₃CaO₂O₈.

2.3. Ex Situ Study of Phase Transformation

Ex situ studies provide complementary information to the synchrotron-radiation studies. A CaO–CoO film with Ca:Co = 0.72 was characterized by ex situ annealing and XRD experiments in order to distinguish the Ca₄Co₂O₇ and Ca₄CoO₆ phases. The film was subjected to different annealing conditions in six sequential steps, as illustrated in Figure 4. Figure 5a shows the θ–2θ XRD scan for the as-deposited film while Figure 5b–g shows θ–2θ scans after each annealing step.

After annealing step 1 (Figure 5b), the appearance of Co₂O₃ peaks with a concomitant decrease in the peak intensity of CoO indicates the reaction of CoO with oxygen to form Co₂O₃. The Co₂O₃ has also reacted with CaO to form the Ca₄Co₂O₇-phase as confirmed by the peaks at 2θ = 16.425°, 33.275°, and 69.675°, which are the Ca₄Co₂O₇ 001, 002, and 004 peaks, respectively.
The results indicate a competition between the formation and consumption of Ca$_3$CoO$_5$

After annealing step 2 (Figure 5c), the Ca$_3$CoO$_2$ phase becomes more intense, the CoO phase has disappeared, and the Ca$_3$CoO$_4$ phase has begun developing as evidenced by the Ca$_3$CoO$_9$ 001 and Ca$_3$CoO$_{5.8}$ 003 reflections (2θ = 8.225° and 2θ = 24.925°, respectively). It should be noted that the d spacing of the c planes in Ca$_3$CoO$_2$ (≈5.41 Å) is almost half of the c lattice parameter of Ca$_3$CoO$_{5.8}$ (≈10.8 Å), resulting in the near-coincidence of some of the Ca$_3$CoO$_9$ 001 peaks with the Ca$_3$CoO$_2$ 001 peaks, thus making it difficult to distinguish these two phases. However, the Ca$_3$CoO$_3$ 001 (2θ = 8.225°) and Ca$_3$CoO$_{5.8}$ 003 (2θ = 24.925°) peaks do not overlap with any Ca$_3$CoO$_2$ peaks.

The I$_f$/I$_0$ integrated peak intensity ratio in Figure 5c is much larger than the I$_f$/I$_0$ ratio for the Ca$_3$CoO$_9$ film in Figure 1c, indicating that Ca$_3$CoO$_2$ is the dominant phase. The Ca$_3$CoO$_2$ and Ca$_3$CoO$_4$ phases exhibit overlapping peaks at 2θ angles of 16.425°, 33.275°, 51.025°, and 69.675°. The Ca$_3$CoO$_4$ phase appears at slightly larger 2θ values than the Ca$_3$CoO$_2$ phase. Therefore, small shifting of the overlapping peaks towards higher 2θ values with increased annealing time provides further evidence of the phase transformation from Ca$_3$CoO$_2$ to Ca$_3$CoO$_9$.

Figure 6 shows enlarged θ–2θ scans for the peaks labeled as I$_1$ and I$_2$. The I$_1$ peak is the Ca$_3$CoO$_2$ 001 reflection and increased annealing time leads to increased intensity but no peak shift. On the other hand, the I$_2$ peak is a convolution of the Ca$_3$CoO$_3$ 001 and Ca$_3$CoO$_{5.8}$ 002 reflections, which have slightly different d spacings. Therefore, increased annealing time leads to increased Ca$_3$CoO$_4$ intensity, decreased Ca$_3$CoO$_2$ intensity, and an associated shift in the I$_2$ peak towards higher 2θ values. From these results, we conclude that three different phase transformation processes (i.e., CoO + O$_2$ ⇌ Co$_3$O$_4$; Co$_3$O$_4$ + CaO ⇌ Ca$_3$CoO$_5$; and Ca$_3$CoO$_2$ + CaO ⇌ Ca$_3$CoO$_9$) are simultaneously occurring at temperatures above 520 °C and the reaction process can be monitored through the I$_f$/I$_0$ ratio.

After annealing step 3 (Figure 5d), the Ca$_3$CoO$_{5.8}$ phase becomes more intense, the CoO phase has disappeared, and the CaO phase intensity begins decreasing. The phase
transformation process continues to proceed with increased annealing time (step 4, Figure 5e), but the presence of CaO peaks indicates that the phase transformation process is not yet completed. Further annealing at higher temperature (step 5, Figure 5f) shows complete consumption of CaO and a further decrease of the I2/I1 ratio. The only peaks remaining are associated with the Ca4Co2O7 phase, indicating completion of the phase transformation. Finally, annealing at 800 °C (step 6, Figure 5g) results in decomposition of Ca4Co2O7 into Co3O4 and CaO.

Ex situ annealing and XRD experiments thus confirm that the transformation of CaO–CoO films into a layered Ca4Co2O7 structure occurs via the intermediate formation of a layered Ca4CoO2 structure. Ca4Co2O7 is the most stable phase in the temperature range of 700–775 °C for a Ca:Co elemental ratio of 0.72. In contrast, the Ca4CoO2 phase is stable from 500 to 775 °C for lower Ca content (cf., Figure 1).

2.4. Thermoelectric Properties

Figure 7a–c shows the electrical resistivity, Seebeck coefficient, and power factor, respectively, as a function of temperature for samples with different Ca:Co ratio. The electrical resistivity (Figure 7a) of the Ca:Co = 0.72 film is lower than that of the Ca-rich and Co-rich samples throughout the measured temperature range, owing to its phase purity. The room temperature electrical resistivity of the phase pure sample (6.44 mΩ cm) is comparable to most Ca4Co2O7 thin films grown by different techniques, but somewhat higher than the lowest reported electrical resistivity value for Ca4Co2O7 thin films deposited on glass substrates (≈4 mΩ cm). The electrical resistivity of the Ca-rich and Co-rich samples increases with increasing deviation of the Ca:Co ratio from the stoichiometric limit, which is attributed to enhanced scattering of charge carriers by the grains of impurity oxide phases. The electrical resistivity of the Ca4Co2O7 thin films is temperature independent up to about 275 °C followed by a systematic increase with increasing temperature. The increasing electrical resistivity beyond 275 °C is attributed to the release of oxygen from the films at high temperature. This is a known effect for Ca4Co2O7 thin films when the measurements are performed in a low-pressure helium atmosphere and not in regular atmosphere.

The room-temperature electrical resistivity of Ca4Co2O7 film with Ca:Co = 0.47 is 208 mΩ cm, which is higher than the reported value of 5 mΩ cm for epitaxial phase-pure films, as well as the value of 60.8 mΩ cm for bulk polycrystalline Ca4Co2O7 (α = 0.47). The presence of Ca4Co2O7 and Co3O4 phases in Ca4CoO2 (α = 0.47) film, as confirmed by XRD,
explains the relatively high in-plane resistivity of the Ca$_2$CoO$_2$ film, which is attributed to the scattering of charge carriers at Ca$_2$CoO$_2$/Ca$_2$CoO$_3$ and Ca$_2$CoO$_2$/CoO$_3$ interfaces in the film.

The Seebeck coefficient (Figure 7b) follows the same trends as electrical resistivity. The room temperature Seebeck coefficient of the Ca$_2$CoO$_2$ (x = 0.47) film is 135 μV K$^{-1}$, which is higher than the reported value of in-plane Seebeck coefficient 60 μV K$^{-1}$ for Ca$_2$CoO$_2$ epitaxial thin films$^{33}$ and comparable to the value of 145 μV K$^{-1}$ for bulk polycrystalline Ca$_2$CoO$_2$ (x = 0.47).$^{33}$ The room temperature Seebeck coefficient of the phase pure CaCoO$_2$ = 0.72 film is 118 μV K$^{-1}$, which is consistent with reported values for Ca$_2$CoO$_3$ thin films.$^{34,35}$ The power factor (Figure 7c) of the phase pure CaCoO$_2$ = 0.72 film is substantially higher (above 2 × 10$^{-4}$ W m$^{-1}$ K$^{-2}$ throughout the measured temperature range) than the other samples due to its lower electrical resistivity. The maximum power factor is 3 × 10$^{-4}$ W m$^{-1}$ K$^{-2}$ at about 350 °C for the phase pure CaCoO$_2$ = 0.72 film. Figure 7d shows the integrated peak intensity ratio I$_{2}$/I$_{3}$ and the room temperature power factor as a function of the CaCo elemental ratio. The power factor is highest for the CaCoO$_2$ = 0.72 film and falls when the Ca:Co ratio deviates from near-stoichiometry.

3. Conclusion

We have demonstrated a two-step sputtering/annealing method for the formation of highly textured Ca$_2$CoO$_3$ thin films from reactively co-sputtered CaO–CoO thin films. The same method was also demonstrated to enable the growth of Ca$_2$CoO$_2$ thin films. With this method, individual compositional control is possible by tuning the Ca:Co ratio. The in situ time-resolved annealing experiments using synchrotron-based XRD as well as ex situ annealing experiments revealed that the thermally induced phase transformation into Ca$_2$CoO$_3$ starts from the following steps:

$$\text{CoO} + \text{O}_2 \rightarrow \text{Co}_2\text{O}_3$$

(1)

$$\text{Co}_2\text{O}_3 + \text{CaO} \rightarrow \text{Ca}_2\text{CoO}_3$$

(2)

$$\text{Ca}_2\text{CoO}_3 + \text{CoO} \rightarrow \text{Ca}_2\text{CoO}_3$$

(3)

Highly textured Ca$_2$CoO$_3$ thin films exhibit good thermoelectric properties, which may be further improved by ensuring uniform distribution of CaO and CoO phases in the as-deposited film, e.g., by sequential deposition. Apart from the high degree of control over phase composition and chemical composition, the abundant availability of the metallic Ca and Co targets and the high rate deposition rate of reactive sputtering imply the suitability for industrial upscaling and implementation in applications.

4. Experimental Section

Ca$_2$CoO$_3$ thin films were prepared by a two-step deposition and annealing process. Prior to deposition, Al$_2$O$_3$(001) substrates were held at 700 °C for 1 h. Then, Co–CoO films were reactively co-sputtered from Ca and Co targets onto the Al$_2$O$_3$(001) substrates by rf-magnetron sputtering at 0.27 Pa (2 mTorr) in an oxygen (1.5%)–argon (98.5%) mixture. The deposition system is described in refs. [36] and [37]. Five series of samples with varying Ca:Co elemental ratio were deposited (Ca:Co = 0.85, 0.81, 0.72, 0.69, and 0.47) and a second series of Ca:Co = 0.72 films was deposited to ensure process reproducibility. The structural properties of these Ca$_2$CoO$_2$ = 0.72 films were essentially the same and the Ca:Co elemental ratio corresponds to stoichiometric Ca$_2$CoO$_3$ within the error of the composition analysis. The composition of the films was determined at different regions of the film surface by EDS, with an accuracy of ±5%. The samples with Ca:Co = 0.85 and 0.81 are Ca-rich, samples with Ca:Co = 0.72 are near-stoichiometric, and samples with Ca:Co = 0.69 and 0.47 are Co-rich. The crystal structure and morphology of the films were characterized by θ–2θ XRD and pole figure analyses using monochromatic Cu Kα radiation (λ = 1.5406 Å), TEM, and scanning electron microscopy. The θ–2θ XRD scans were performed with a Philips PW 1820 diffractometer while the pole figures were performed with a Philips X’pert materials research diffractometer operated with a point focus, primary optics of 2 × 2 mm$^2$ cross slits, and secondary optics with parallel-plate collimator.

In situ annealing experiments using time-resolved synchrotron-based 2D XRD were performed at the High Energy Materials Science Beamline (P07) at PETRA III (Positron-Electron Twin Ring Accelerator), DESY (Deutsches Elektronen-Synchrotron), Hamburg, with 33.7 keV monochromatic X-rays and a slit-determined spot size of 0.5 mm × 2 mm. The 2D detector used was a Perkin Elmer 1621 Flat Panel, with 200 × 200 μm$^2$ pixel size and 2048 × 2048 array field of view.$^{38}$

Ex situ annealing and XRD experiments were performed on a single CaO–CoO thin film with Ca:Co = 0.72. The CaCoO$_2$ = 0.72 film was subjected to six sequential annealing steps and θ–2θ XRD scans were performed after each annealing step. The annealing furnace was stabilized at a given set-point temperature prior to inserting the sample for a specified time period. The sample temperature was monitored as a function of time via a thermocouple in contact with the film substrate. The sample was removed from the furnace after the specified annealing time and cooled in ambient air at room temperature, as illustrated in Figure 4. In steps 1–4, the furnace temperature was set at 710 °C and the sample was annealed for 3, 5, 6, and 40 min corresponding to final sample temperatures of 520, 640, 680, and 700 °C, respectively. In step 5, the furnace temperature was set at 790 °C and the sample was annealed for 29 min corresponding to a temperature of 775 °C. Finally, in step 6 the furnace temperature was set at 850 °C and the sample was annealed for 10 min corresponding to a temperature of 800 °C. The temperature dependent in-plane electrical resistivity and Seebeck coefficient were simultaneously characterized using an ULVAC-RIKO ZEM3 system in a low-pressure helium atmosphere.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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