Nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ Thin Films for Transferable Thermoelectrics

Biplab Paul, Emma M. Björk, Aparabal Kumar, Jun Lu, and Per Eklund

†Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), and ‡Nanostructured Materials, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden
§Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

ABSTRACT: The development of high-performance and transferable thin-film thermoelectric materials is important for low-power applications, e.g., to power wearable electronics, and for on-chip cooling. Nanoporous films offer an opportunity to improve thermoelectric performance by selectively scattering phonons without affecting electronic transport. Here, we report the growth of nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films by a sequential sputtering-annealing method. $\text{Ca}_3\text{Co}_4\text{O}_9$ is promising for its high Seebeck coefficient and good electrical conductivity and important for its nontoxicity, low cost, and abundance of its constituent raw materials. To grow nanoporous films, multilayered CaO/CoO films were deposited on sapphire and mica substrates by rf-magnetron reactive sputtering from elemental Ca and Co targets, followed by annealing at $700 \, ^\circ\text{C}$ to form the final phase of $\text{Ca}_3\text{Co}_4\text{O}_9$. This phase transformation is accompanied by a volume contraction causing formation of nanopores in the film. The thermoelectric properties of the nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ films can be altered by controlling the porosity. The lowest electrical resistivity is $\sim 7 \, \text{m}^\Omega\,\text{cm}$, yielding a power factor of $2.32 \times 10^{-4} \, \text{Wm}^{-1}\text{K}^{-2}$ near room temperature. Furthermore, the films are transferable from the primary mica substrates to other arbitrary polymer platforms by simple dry transfer, which opens an opportunity of low-temperature use these materials.

KEYWORDS: thin film, nanoporous, transferable, thermoelectrics, $\text{Ca}_3\text{Co}_4\text{O}_9$

1. INTRODUCTION

Nanoporous materials are promising in the area of thermoelectricity, as they can enable simultaneous tailoring of electronic and phononic properties in a single material system, leading to multifold enhancement of thermoelectric efficiency. The thermoelectric efficiency of any material system is related to dimensionless thermoelectric figure of merit $ZT = (S^2T/\rho\kappa)$, where $S$, $\rho$, $\kappa$, and $T$ are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. High thermoelectric efficiency requires high Seebeck coefficient simultaneously with low electrical resistivity and thermal conductivity. However, design of such materials is quite challenging because these parameters are interdependent with electrically conducting materials having low Seebeck coefficient and high thermal conductivity, and vice versa.

Bulk nanostructured thermoelectric materials can be used to achieve low phonon thermal conductivity, while retaining good electronic properties. Nanoscale features with dimension comparable to the phonon mean free path have been incorporated to preferentially scatter the phonons to reduce thermal conductivity and thus enhance $ZT$. An alternative approach for selective scattering of phonons can be the incorporation of nanopores with controlled size and periodicity. The average mean free path of electrons in most materials is typically 1 order of magnitude lower than phonon mean free path. For example, the mean free path of electrons in silicon (Si) is in the range $1–10 \, \text{nm}$ for heavily doped Si with carrier concentration of the order of $1 \times 10^{20} \, \text{cm}^{-3}$, while the phonon mean free path is $300 \, \text{nm}$ at $300 \, ^\circ\text{K}$. Thus, the reduction in thermal conductivity of nanoporous materials is possible without adversely affecting electronic properties, by controlling the characteristic length scale of the porous structure in the range in-between electronic and phonon mean free path. For example, the thermal conductivity of thin holey silicon with $55 \, \text{nm}$ pitch (periodicity of pores) can be reduced by almost 2 orders of magnitude as compared to the pristine bulk value, while retaining a high power factor, resulting in enhanced $ZT \approx 0.4$ at $300 \, ^\circ\text{K}$. Others have reported drastic reduction of thermal conductivity in Si-based 2D phononic crystals due to the suppression of phonon mean free path, however, with no report on their electronic or thermoelectric properties.

$\text{Ca}_3\text{Co}_4\text{O}_9$ is a promising thermoelectric material because of low cost, abundance, and nontoxicity of its constituent raw materials. However, the best performance of this class of materials typically occurs at high temperatures near 1000 K. Investigations on bulk nanostructured $\text{Ca}_3\text{Co}_4\text{O}_9$ have not reported significant improvement of power factor near room temperature. Because of the inherently layered structure, the electronic properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ are anisotropic in nature, and less resistive electronic transport is found to occur in ($a$, $b$) plane of $\text{Ca}_3\text{Co}_4\text{O}_9$. Thus, for achieving high power factors in this material system, oriented thin films can be used for exploitation of anisotropic properties. We have previously...
Figure 1. (a) Schematic representation of sequential CaO/CoO films with periodicities 10 and 20 nm, (b) cross-sectional TEM image of as-deposited films SAl2O3: 5.5/4.5 and SAl2O3: 11/9 on sapphire substrate, (c) EDS mapping of the layered structure of the films, (d, e) magnified image of small portion of the cross-section of the films.

The method requires neither templates nor etching steps like previous reports on the growth of thin nanoporous films. Thermoelectric properties of the films are characterized in terms of their power factors. A retained high power factor near room temperature is important for mechanically flexible applications, where the output power is more important than the efficiency. For high output power, a high power factor is more important than achieving high ZT. Even with large number of pores, a high power factor of 2.32 × 10−4 W m−1 K−2 is obtained near room temperature from undoped nanoporous Ca3Co4O9 thin films. Furthermore, the nanoporous films are transferable onto arbitrary flexible platforms by mechanical stripping, thus opening a new opportunity for transferable thermoelectrics.

2. EXPERIMENTAL SECTION

Nanoporous Ca3Co4O9 thin films were prepared by a two-step sputtering/annealing method. First, CaO/CoO films were sequentially deposited by rf-magnetron reactive sputtering from metallic targets of Ca and Co onto muscovite mica (001) and sapphire (001) substrates at 0.27 Pa (2 mTorr) in an oxygen–argon mixture with oxygen 0.5%, while maintaining the substrate temperature at 300 °C for sapphire substrates and 600 °C for mica substrates. The target powers were controlled to maintain deposition rate of 5.5 nm/min for CaO and 4.5 nm/min for CoO. In second step the as-deposited CaO/CoO films were annealed at 700 °C in O2 gas flow to form the final phase of Ca3Co4O9. The crystal structure and morphology of the films were characterized by ϸ–2ϴ X-ray diffraction (XRD) analyses using monochromatic Cu Kα radiation (λ = 1.5406 Å), transmission electron microscopy by using a FEI Tecnai G2 TF20 UT instrument with a field emission gun operated at 200 kV and with a point resolution of 1.9 Å, and scanning electron microscopy (SEM, LEO 1550 Gemini). The ϸ–2ϴ XRD scans were performed with a Philips PW 1820 diffractometer. For cross-sectional TEM, two pieces of the samples were glued together face to face and clamped with a Ti grid and then polished down to 50 μm thickness. Finally, the polished sample was ion milled in a Gatan Precision Ion Polishing System (PIPS) at Ar+ energy of 5 kV and a gun angle of 3°, with a final polishing step with 2 kV Ar+ energy. The composition of the films was determined by EDS attached to TEM, with an accuracy ±5%. The temperature dependent in-plane electrical resistivity and Seebeck coefficient were simultaneously characterized using an ULVAC-RIKO ZEMS system in a low-pressure helium atmosphere. The available surface area of the films was measured by Kr-sorption at 77 K using an ASAP2020. The samples, i.e., film on a substrate, were degassed at 100 °C for 17 h prior to the measurements. The BET surface area was determined at P/P0 = 0.12−0.20. The BET surface was recalculated to available surface area/film volume using the following equation:

\[
\text{available surface area/film volume} = \frac{(\text{BET surface area sample mass})}{(\text{area of film coated substrate film thickness})}
\]

where the film thickness was estimated from TEM, and the area of the film-coated substrate was determined by optical imaging. It was assumed that all contribution to the specific surface area originated from the films since the reference measurements on bare substrates did not provide any measurable value.

3. RESULTS AND DISCUSSION

Figure 1a is a scheme of sequentially deposited CaO/CoO films with two different periodicities of the layers. Four samples, namely SAl2O3: 5.5/4.5, Smica: 5.5/4.5, SAl2O3: 11/9, and Smica: 11/9, have been deposited. The films are named after the type of substrates and thickness of individual CaO and CoO layers in the as-deposited films. For example, SAl2O3: 5.5/4.5 and Smica: 5.5/4.5 films were deposited on sapphire Al2O3(001) and mica (muscovite mica (001)) substrates, respectively, and the thicknesses of sequential CaO and CoO layers are 5.5 and 4.5 nm, respectively. In SAl2O3: 11/9 and Smica: 11/9, the thicknesses of CaO and CoO layers are 11 and 9 nm, respectively.

Figure 1b shows a cross-sectional transmission electron microscopic (TEM) image of as-deposited CaO/CoO films SAl2O3: 5.5/4.5 and SAl2O3: 11/9, respectively. Figure 1c shows an EDS map of a small portion of the as-deposited films SAl2O3: 5.5/4.5 and SAl2O3: 11/9. EDS mapping confirms that the dark lines in Figure 1b are from CoO phase, and bright lines are...
from CaO phase. Figure 1d, e show magnified images of small portions of the as-deposited films $S_{\text{Al}_2\text{O}_3}: 5.5/4.5$ and $S_{\text{Al}_2\text{O}_3}: 11/9$, respectively. In the as-deposited film $S_{\text{Al}_2\text{O}_3}: 5.5/4.5$ the period is 10 nm (i.e., $5.5 \text{ nm} + 4.5 \text{ nm}$) and with 20 alternating layers. The total thickness of the film is 100 nm. In the as-deposited film $S_{\text{Al}_2\text{O}_3}: 11/9$ the period is 20 nm and with 20 alternating layers. The total thickness of the film is 200 nm. The layered structure of as-deposited films on the two different substrates are very similar (not shown here).

Figure 2a shows $\theta−2\theta$ XRD scans of the as-deposited films $S_{\text{Al}_2\text{O}_3}: 5.5/4.5$ and $S_{\text{Al}_2\text{O}_3}: 11/9$ on sapphire substrates, (b) as-deposited films $S_{\text{mica}}: 5.5/4.5$ and $S_{\text{mica}}: 11/9$ on mica substrates, (c) postannealed films $S_{\text{Al}_2\text{O}_3}: 5.5/4.5$ and $S_{\text{Al}_2\text{O}_3}: 11/9$ on sapphire substrates, (d) postannealed films $S_{\text{mica}}: 5.5/4.5$ and $S_{\text{mica}}: 11/9$ on mica substrates.

Figure 2. $\theta−2\theta$ XRD scan of (a) as-deposited films $S_{\text{Al}_2\text{O}_3}: 5.5/4.5$ and $S_{\text{Al}_2\text{O}_3}: 11/9$ on sapphire substrates, (b) as-deposited films $S_{\text{mica}}: 5.5/4.5$ and $S_{\text{mica}}: 11/9$ on mica substrates, (c) postannealed films $S_{\text{Al}_2\text{O}_3}: 5.5/4.5$ and $S_{\text{Al}_2\text{O}_3}: 11/9$ on sapphire substrates, (d) postannealed films $S_{\text{mica}}: 5.5/4.5$ and $S_{\text{mica}}: 11/9$ on mica substrates.

Figure 3. SEM image of postannealed film (a) $S_{\text{Al}_2\text{O}_3}: 5.5/4.5$ and (b) $S_{\text{Al}_2\text{O}_3}: 11/9$ on sapphire substrate, and (c) $S_{\text{mica}}: 5.5/4.5$ and (d) $S_{\text{mica}}: 11/9$ on mica substrate.
film. The d-spacings of the annealed Ca$_3$Co$_4$O$_9$ films S$_{Al2O3}$: 5.5/4.5, S$_{Al2O3}$: 11/9, S$_{mica}$: 5.5/4.5, and S$_{mica}$: 11/9 are calculated to be 10.7218, 10.7297, 10.7404, and 10.7337 Å, respectively, which are consistent with the reported d-spacing for Ca$_3$Co$_4$O$_9$ single crystal. The corresponding out-of-plane lattice parameters (c-parameter) are 10.8306, 10.8386, 10.8494, and 10.8426 Å for S$_{Al2O3}$: 5.5/4.5, S$_{Al2O3}$: 11/9, S$_{mica}$: 5.5/4.5, and S$_{mica}$: 11/9, respectively, and consistent with the reported c-parameter of bulk Ca$_3$Co$_4$O$_9$.

From the above results, it is clear that the final phase of Ca$_3$Co$_4$O$_9$ is obtained from all sequentially deposited CaO/CoO films irrespective of substrate. During annealing, a three-stage phase transformation from sequential CaO/CoO films to the final phase of Ca$_3$Co$_4$O$_9$ occurs, as shown by our previous study on cosputtered CaO-CoO thin films on sapphire substrates. All annealed Ca$_3$Co$_4$O$_9$ films are c-axis-oriented irrespective of substrate. The advantage of mica as substrate is that even with excess Ca in the as-deposited films, the postannealed Ca$_3$Co$_4$O$_9$ films on mica substrates are phase-pure. In this case, excess Ca is incorporated in an amorphous interfacial layer between the mica substrate and the film (this is discussed later in detail).

Figures 3a–d show SEM images of the annealed films S$_{Al2O3}$: 5.5/4.5, S$_{Al2O3}$: 11/9, S$_{mica}$: 5.5/4.5, and S$_{mica}$: 11/9, respectively. The presence of horizontal grains with dimension of several hundred nanometers in the postannealed film S$_{Al2O3}$: 5.5/4.5 is seen in Figure 3a. Visible bright spots on the film surface are from grains of different orientation. These grains are not observed in XRD, since they do not satisfy Bragg’s condition in the out-of-plane direction, which is consistent with previous observations for the Ca$_3$Co$_4$O$_9$ films grown on SrTiO$_3$(111) and on muscovite mica. In contradiction, SEM of the postannealed film S$_{Al2O3}$: 11/9 does not show the presence of any of these grains (see Figure 2b), which is also confirmed by TEM image analyses (discussed later). The surface of the film S$_{Al2O3}$: 11/9 is relatively smoother than the surface of the film S$_{Al2O3}$: 5.5/4.5. The visible black spots on the surface of the film S$_{Al2O3}$: 11/9 are from randomly distributed pores in the film having dimension in the range from few nanometers to several hundred nanometers. Nanopores in the annealed film S$_{mica}$: 5.5/4.5 are irregular in shape, but distributed rather homogeneously in the film. The nanopores in the film S$_{mica}$: 11/9 are polygonal in shape, and having dimension in the range from a few tens of nanometers to several hundred nanometers. The nanopores in the film S$_{mica}$: 11/9 have visible openings with sharp edges, in contrast to the film S$_{Al2O3}$: 11/9.

It is clear from Figure 3 that the porosity varies from film to film. The porosity of the films is compared in terms of their available surface area per unit volume, where a high available surface indicates a large porosity since the pore sizes in all films are in the same range. The available surface areas of the films per unit volume are calculated to be 0.11, 0.68, and 0.26 m$^2$/mm$^3$ for the films S$_{Al2O3}$: 11/9, S$_{mica}$: 5.5/4.5, and S$_{mica}$: 11/9, respectively. The highest value of available surface area per unit volume of the film S$_{mica}$: 5.5/4.5 is attributed to its higher porosity than the rest films. On the other hand, the lowest value of available surface area per unit volume of the film S$_{Al2O3}$: 11/9 is due to its low porosity, which is consistent with the SEM observations. The distinct variation of the surface morphology and porosity of the films on different substrates indicates the difference in substrate influence on thin film growth of nanoporous Ca$_3$Co$_4$O$_9$.

The bright spot in Figure 4a is a void because of a pore in the film. Figure 4b shows a magnified image of a small region, where the layered structure of Ca$_3$Co$_4$O$_9$ and its orientation along c-axis is apparent. The average thickness of this film is 160 nm, a reduction by nearly 20% compared to the as-deposited film. A similar reduction in thickness was observed for the film S$_{Al2O3}$: 5.5/4.5 after annealing, with a final thickness of 80 nm. The presence of voids at the interface between the substrate and the annealed film S$_{Al2O3}$: 11/9 is confirmed by TEM imaging (Figure 4c).

Figure 5a shows a cross-sectional TEM image of the annealed film S$_{mica}$: 11/9. The average thickness of the S$_{mica}$: 11/9 film is ~150 nm, which is 10 nm lower than the thickness of corresponding annealed film on sapphire. This reduction in film thickness is attributed to the incorporation of excess Ca in an amorphous interfacial layer, as confirmed by EDS analyses (see below), which is consistent with our previous observation on the growth of flexible Ca$_3$Co$_4$O$_9$ films on mica substrates. In Figure 5a, voids are visible throughout the interfacial region of the annealed film on mica, in contrast to corresponding film on sapphire. As a consequence, Ca$_3$Co$_4$O$_9$ film is weakly
bonded to the mica substrate via nanopillars. Figure 5b shows a magnified image showing that the film is supported by nanopillars on the mica substrate. The interfacial layer between the film and mica substrate is amorphous in nature, and by EDS analyses the amorphous layer is determined to be Ca-rich (Ca: 31.3 at %). This is because the excess Ca in the film is incorporated in the amorphous layer. The other elements: O (48.8 at %), Al (6.8 at %), Si (8.5 at %), K (0.9 at %), and Fe (3.7 at %) in the amorphous layer retain the same proportion as that in the mica substrate. Figure 5c shows the HRTEM image of a nanopillar of width of around 25 nm. The layered structure of the Ca₃Co₄O₉ phase in the nanopillar is visible.

From the above SEM and TEM results, it is clear that the mica and sapphire substrates affect the growth of Ca₃Co₄O₉ thin films differently, leading to variations in the resulting nanoporous structures. The formation of nanopores in the films is likely caused by the volume contraction of the films after annealing. As mentioned above, the thickness of the annealed films is reduced by around 20% as compared to the as-deposited CaO/CoO films. This volume contraction is due to the increase in density of the films after thermally induced phase transformation. This densification develops compressive stress in the films. As a consequence, the films are subjected through the formation of nanopores for releasing stress. Mica is likely more favorable than sapphire for such stress release because of weaker adhesion of the film with mica.

4. TRANSFERABILITY OF THE FILMS

The transferability of the nanoporous films was investigated by transferring the nanoporous film S_mica: 11/9 on to polydimethylsiloxane (PDMS) platform. The different stages of the transfer process are illustrated in Figure 6. Initially, the mica substrate is isolated from the film following the steps as shown in Figure 6a–d. First, a glass slide is coated with a thin layer of wax. In the next step, the film is attached to the glass slide upside down, and then the thickness of the mica substrate is reduced to below 20 μm by isolating the mica layers from the back by mechanical force (Figure 6b). For further thickness reduction, thin layers of mica are repeatedly removed by adhesive tape as shown in Figure 6c. Figure 6d shows the back surface of the film after the complete removal of mica. After the removal of mica, no cracks in the film were observed by optical microscopy. After that, the back surface of the film is coated with a thin layer of PDMS following the step in Figure 6e. In the next step, the coated film was heated to 80 °C for 3 h for the solidification of PDMS layer. The small area of the coated layer is isolated from the rest using a blade (Figure 6f). This is followed by heating to 150 °C to melt the thin layer of wax between the glass slide and the PDMS layer. Then, the PDMS layer is isolated from glass slide as shown in Figure 6g. To dissolve the wax, the transferred film is immersed in acetone for 10 min. Figure 6h, i show the images of the film after transfer onto PDMS.

Several strategies, e.g., surface-energy-assisted transfer, water penetration- assisted mechanical transfer, film transfer by using ultrasonic water bath, and carrier-polymer-assisted transfer, have been demonstrated to transfer the 2D metal sulfide onto flexible polymer platforms. However, reports on transfer of thick films are less common, a notable exception being the work of Lu et al. on the transfer of thick films by etching of sacrificial water-soluble layers. The present study is important as it demonstrates an alternative method for the damage free dry transfer of thick nanoporous films.

5. THERMOELECTRIC PROPERTIES

Figure 7a shows the temperature-dependent electrical resistivity of all films from room temperature to 400 °C. The room-temperature electrical resistivity of the films S_{Al2O3}: 5.5/4.5, S_{Al2O3}: 11/9, S_{mica}: 5.5/4.5, and S_{mica}: 11/9 is measured to be ∼32, 13, 25, and 7 mΩcm, respectively. No significant variation of electrical resistivity with temperature is observed for all the films until 250 °C, however above 250 °C sharp increase in electrical resistivity is clearly visible in Figure 7a. This sharp increase in electrical resistivity is attributed to the release of oxygen from the film above 250 °C because the measurements are performed in vacuum. This is consistent with the observations on thin films reported elsewhere. Despite the higher porosity of the film S_{mica}: 11/9 than the S_{mica}: 5.5/4.5, the former offers the lowest electrical resistivity throughout the temperature range measured. This indicates that the presence of nanopores in the film S_{mica}: 11/9 does not hamper the transport of charge carriers. The scattering of charge carriers can be avoided in the nanoporous films if the characteristic length-scale of the porous structure is lower than the electronic mean free path, and this is supposed to be the case with the film S_{mica}: 11/9. The room temperature value of electrical resistivity of the film S_{mica}: 11/9 is as low as that is comparable to the values reported for solid thin films, and lower than the values reported for bulk polycrystalline Ca₃Co₄O₉. The electrical resistivity of the film S_{mica}: 5.5/4.5 is more than three times larger than that of the film S_{Al2O3}: 11/9, which is attributed to its higher porosity. With the increase in porosity, the characteristic length scale of the nanoporous structure in the film S_{mica}: 5.5/4.5 might have been reduced below the electronic mean free path, resulting in enhanced scattering of charge carriers. That is, nanopores in the film S_{mica}: 5.5/4.5 strongly scatter the charge carriers leading to the increase in electrical resistivity. Even with lower porosity,
the electrical resistivity of the film \(S_{\text{Al}_2\text{O}_3}: 11/9\) is nearly half that of the film \(S_{\text{mica}}: 5.5/4.5\); however, it is almost twice that of the film \(S_{\text{mica}}: 11/9\). This indicates that the quality of the films on mica substrates is better than that of the films on sapphire substrates. The highest electrical resistivity of the film \(S_{\text{Al}_2\text{O}_3}: 5.5/4.5\) is due to the presence of disoriented grains in the film, which acts as scattering center for charge carriers. Except a slightly lower value of the near-room-temperature power factor, above 2 \(\times\) \(10^{-4}\) \(\mu\text{V/K}\), the highest power factor, above 2 \(\times\) \(10^{-4}\) \(\mu\text{V/K}\), is achieved the temperature range (from room temperature to 350 °C), and the room-temperature value (2.32 \(\times\) \(10^{-4}\) \(\mu\text{V/K}\)) is comparable to previous reports on undoped \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films.28,44,45 The power factor of the films grown on mica substrates than that of the films grown on the sapphire substrates is that the power factors in the former case are less temperature-dependent.

The above results show that the power factor of the films on mica substrates is different depending on the porosity of the films, in contrast to the films on sapphire substrates. This is because, with the increase in porosity the average distance between the pores decreases, resulting in a reduction in electronic mean free path. Because the pores in the film \(S_{\text{mica}}: 5.5/4.5\) are not of regular shape, the average separation of the pores cannot be readily estimated, but should be comparable to the electronic mean free path, resulting in a drastic increase in electrical resistivity. Furthermore, the pores in \(S_{\text{mica}}: 5.5/4.5\) seem to form a network-like structure, which restricts the passage of charge carriers, leading to the increased electrical resistivity. On the other hand, the interpore separation in the film \(S_{\text{mica}}: 11/9\) have a distribution in the range 50–500 nm, that is characteristic length scale of the nanoporous structure is higher than electronic mean free path, resulting in the reduced electrical resistivity and thus enhanced power factor of the film. The electronic mean free path in the most materials is less than 10 nm.46 Recently, high power factor simultaneously with reduced thermal conductivity have been realized in thin films with ordered pores/holes; however, there has been no report on the power factor of the films with disordered pores. The present work thus reveals that the scattering of charge carriers can be avoided in the nanoporous film with disordered pores by controlling the porosity, and thus a high power factor is possible. On the other hand, because of the presence of a large number of pores the thermal conductivity of the film is expected to be reduced. Because of the irregular shape and size and random distribution of nanopores, the direct evaluation of in-plane thermal conductivity of the nanoporous film is not possible. Recently, Kashiwagi et al. theoretically derived in-plane thermal conductivity of the nanoporous \(\text{Bi}_{0.9}\text{Te}_{0.1}\text{Sb}_{1.6}\) thin film from its measured cross-plane value by considering the
The weak bonding of the primary mica substrate onto polymer platforms. With this presence of nanopillars, the obtained from the nanoporous demonstrated. The volume contraction caused by densification and size and random distribution of nanopores. However, reduction in cross-plane thermal conductivity by 1 order of magnitude was realized by Song et al. in nanoporous Bi thin films with random nanopores.\textsuperscript{38,49} The effect of porosity on thermal conductivity of bulk Ca$_3$Co$_4$O$_9$ is also investigated\textsuperscript{48,49} and thermal conductivity of 0.63 W m$^{-1}$ K$^{-1}$ at 373 K is reported by Bittner et al. for \textgreater32\% porous Ca$_3$Co$_4$O$_9$.\textsuperscript{48} Note that the present Ca$_3$Co$_4$O$_9$ films are undoped, and yet a high power factor 2.32 × 10$^{-4}$ W m$^{-1}$ K$^{-2}$ near room temperature is obtained from the film $S_{\text{micro}}$; 11.9. Further enhancement of the power factor is still possible by doping.\textsuperscript{18,50–52} With this power factor combined with transferability, the nanoporous Ca$_3$Co$_4$O$_9$ films are candidates for near-room-temperature thermoelectric applications.

6. CONCLUSION

A sequential sputtering-annealing method, for the growth of nanoporous and transferable Ca$_3$Co$_4$O$_9$ films, has been demonstrated. The volume contraction caused by densification during the thermally induced phase transformation from sequential CaO/CoO film to the final phase of Ca$_3$Co$_4$O$_9$ promotes the formation of nanopores in the film. The porosity of the films is tunable by controlling the thickness of sequential CaO and CoO layers in the initial sputtered deposited films. A high power factor, above 2 × 10$^{-4}$ W m$^{-1}$ K$^{-2}$ in a wide temperature range (from room temperature to 350 °C), is obtained from the nanoporous film on mica substrate. Because of the weak bonding of the film with the mica substrate and the presence of nanopillars, the film is easy transferable from the primary mica substrate onto polymer platforms. With this transferability and high power factor, the nanoporous Ca$_3$Co$_4$O$_9$ films can be a candidate for near-room-temperature thermoelectric applications. Additionally, the film growth method is suitable for upscaling.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: biplab.paul@liu.se.
*E-mail: per.eklund@liu.se.

ORCID

Biplab Paul: 0000-0003-0858-3792
Emma M. Björk: 0000-0001-6609-6779
Aparabal Kumar: 0000-0003-1127-2020
Per Eklund: 0000-0003-1785-0864

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The research leading to these results has received funding from the European Research Council (ERC) under the European Community’s Seventh Framework Programme (FP/2007-2013)/ERC Grant 335383, the Swedish Research Council (VR) under Projects 2016-03365 and 2015-00624, the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU 2009 00971), the Knut and Alice Wallenberg foundation through the Academy Fellow program, the Eurostars project E18892 T-to-Power, the Swedish Foundation for Strategic Research (SSF) through the Future Research Leaders S program, and funding from the Åforsk foundation.

■ REFERENCES

(1) Lee, J.-H.; Galli, G. A.; Grossman, J. C. Nanoporous Si as an efficient thermoelectric. Nano Lett. 2008, 8, 3750–3754.
(2) Tang, J.; Wang, H. – T.; Lee, D. H.; Fardy, M.; Huo, Z.; Russell, T. P.; Yang, P. Holey silicon as an efficient thermoelectric material. Nano Lett. 2010, 10, 4279–4283.
(3) Perez-Taborda, J. A.; Munoz Rojo, M.; Neophytou, J. M. N.; Martin-Gonzalez, M. Ultra-low thermal conductivities in large-area Si-Ge nanomeshes for thermoelectric applications. Sci. Rep. 2016, 6, 32778.
(4) Ren, G. – K.; Lan, J.-L.; Ventura, K. J.; Tan, X.; Lin, Y. – H.; Nan, C. – W. Contribution of point defects and nano-grains to thermal transport behaviours of oxide-based thermoelectrics. NPJ Comput. Mater. 2016, 2, 16023.
(5) Yin, Y.; Tudu, B.; Tiwari, A. Recent advances in oxide thermoelectric materials and modules. Vacuum 2017, 146, 356–374.
(6) He, J.; Tritt, T. M. Advances in thermoelectric materials research: Looking back and moving forward. Science 2017, 357, 1369.
(7) Tan, G.; Zhao, L. – D.; Kanatzidis, M. G. Rationally designing high-performance bulk thermoelectric materials. Chem. Rev. 2016, 116, 12123–12149.
(8) Zieger, G.; Zevalkink, A.; Gibbs, Z. M.; Hautier, G.; Kanatzidis, M. G.; Snyder, G. J. Thinking like a chemist: Intuition in thermoelectric materials wolfgang. Angew. Chem., Int. Ed. 2016, 55, 6826–6841.
(9) Biswas, K.; He, J.; Blum, I. D.; Wu, C. – I.; Hogan, T. P.; Seidman, D. N.; Dravid, V. P.; Kanatzidis, M. G. High-performance bulk thermoelectrics with all-scale hierarchical architectures. Nature 2012, 489, 414–418.
(10) Paul, B.; Banerji, P. Grain structure induced thermoelectric properties in PbTe nanocomposites. Nanosci. Nanotechnol. Lett. 2009, 1, 208–212.
(11) Paul, B.; Kumar, A. V.; Banerji, P. Embedded Ag-rich nanodots in PbTe: Enhancement of thermoelectric properties through energy filtering of the carriers. J. Appl. Phys. 2010, 108, 064322.
(12) Rawat, P. K.; Paul, B.; Banerji, P. Thermoelectric properties of Pb$_5$Sb$_3$(Te$_{0.2}$Pb$_{0.8}$)$_3$ with endotaxial nanostructures: A promising n-type thermoelectric material. Nanotechnology 2013, 24, 215401.
(13) Ju, Y.; Sos, K.; E. Phonon scattering in silicon films with thickness of order 100 nm. Appl. Phys. Lett. 1999, 74, 3005.
(14) Wagner, M. R.; Grzackiwski, B.; Reparaz, J. S.; El Sachat, A.; Sedlizska, M.; Alzina, F.; Sotomayor Torres, C. M. S. Two-dimensional phononic crystals: Disorder matters. Nano Lett. 2016, 16, 5661–5668.
(15) Ma, J.; Sadhu, J. S.; Ganta, D.; Tian, H.; Sinha, S. Thermal transport in 2- and 3-dimensional periodic “holey” nanostructures. AIP Adv. 2014, 4, 124502.
(16) Huang, C. S.; Zhang, F. P.; Zhang, X.; Lu, Q. M.; Zhang, J. X.; Lai, Z. Y. Enhanced thermoelectric figure of merit through electrical and thermal transport modulation by dual-doping and texture modulating for Ca$_3$Co$_4$O$_9$$_{0.85}$ oxide materials. J. Alloys Compd. 2016, 687, 87–94.
(17) Wu, N. Y.; Van Nong, N.; Plyds, N.; Linderoth, S. Effects of yttrium and iron co-doping on the high temperature thermoelectric properties of Ca$_3$Co$_4$O$_9$$_{0.85}$. J. Alloys Compd. 2015, 638, 127–132.
(18) Saini, S.; Yaddanapudi, H. S.; Tian, K.; Yin, Y.; Maggiorotti, D.; Tiwari, A. Terbium ion doping in Ca$_3$Co$_4$O$_9$: A step towards high-performance thermoelectric materials. Sci. Rep. 2017, 7, 44621.
(19) Madre, M. A.; Costa, P. M.; Ferreira, N. M.; Sotelo, A.; Torres, M. A.; Constantinescu, G.; Rasekh, S.; Diez, J. C. Preparation of high performance Ca$_3$Co$_4$O$_9$ thermoelectric ceramics produced by a new two-step method. J. Eur. Ceram. Soc. 2013, 33, 1747–1754.
(20) Obata, K.; Chonan, Y.; Komiyama, T.; Aoyama, T.; Yamaguchi, H.; Sugiyama, S. Grain-oriented Ca$_3$Co$_4$O$_9$ thermoelectric oxide ceramics prepared by solid-state reaction. J. Electron. Mater. 2013, 42, 2221–2226.
(21) Lin, Y.-H.; Lan, J.; Shen, Z.; Liu, Y.; Nan, C.-W.; Li, J.-F. High-temperature electrical transport behaviors in textured CaCo4O9 based polycrystalline ceramics. Appl. Phys. Lett. 2009, 94, 072107.
(22) Kenfai, D.; Chateigner, D.; Gomina, M.; Noudem, J. G. Texture, mechanical and thermoelectric properties of CaCo4O9 ceramics. J. Alloys Compd. 2010, 490, 472–479.
(23) Prevel, M.; Lemonnier, S.; Klein, Y.; Hébert, S.; Chateigner, D.; Ouladifiaf, B.; Noudem, J. G. Textured CaCo4O9 thermoelectrics by thermoforging process. J. Appl. Phys. 2005, 98, 093706.
(24) Zhang, Y.; Zhang, J.; Lu, Q. Synthesis of highly textured CaCo4O9 ceramics by spark plasma sintering. Ceram. Int. 2007, 33, 1305–1308.
(25) Paul, B.; Schroeder, J. L.; Kerdsoongpanya, S.; Van Nong, N.; Schell, N.; Ostach, D.; Li, J.; Birch, J.; Eklund, P. Mechanism of formation of the thermoelectric layered cobaltate CaCo4O9 by annealing of CaO-CoO thin films. Adv. Electron. Mater. 2015, 1, 1400202.
(26) An, H. P.; Zhu, C. H.; Ge, W. W.; Li, Z. Z.; Tang, G. D. Growth and thermoelectric properties of CaCo4O9 thin films with c-axis parallel to Si substrate surface. Thin Solid Films 2013, 545, 229–233.
(27) Zhu, S.; Shi, D.; Dou, S.; Sun, Y.; Li, Q.; Wang, L.; Li, W.; Yeo, W.; Zheng, R.; Chen, Z.; Kong, C. 0 (0 0 1)-oriented BiSr2Co2Oy and CaCo4O9 films: Self-assembly orientation and growth mechanism by chemical solution deposition. Acta Mater. 2010, 58, 4281–4291.
(28) Kang, M. – G.; Cho, K. – H.; Oh, S. – M.; Kim, J. – S.; Kang, C. – H.; Nahm, S.; Yoon, S. – J. High-temperature thermoelectric properties of nanostructured CaCo4O9 thin films. Appl. Phys. Lett. 2011, 98, 142102.
(29) Sun, T.; Ma, J.; Yan, Q. Y.; Huang, Y. Z.; Wang, J. L.; Hng, H. H. Influence of pulsed laser deposition rate on the microstructure and thermoelectric properties of CaCo4O9 thin films. J. Cryst. Growth 2009, 311, 4123–4128.
(30) Kashiwagi, M.; Hirata, S.; Harada, K.; Zheng, Y.; Miyazaki, K.; Yahiro, M.; Adachi, C. Enhanced figure of merit of a porous thin film of bismuth antimony telluride. Appl. Phys. Lett. 2011, 98, 023114.
(31) Liu, W.; Kim, H. S.; Jie, Q.; Ren, Z. Importance of high power factor in thermoelectric materials for power generation application: A perspective. Scr. Mater. 2016, 111, 3–9.
(32) Wu, L.; Meng, Q.; Jooss, C.; Zheng, J. – C.; Inada, H.; Su, D.; Li, Q.; Zhu, Y. Origin of phonon glass–electron crystal behavior in thermoelectric layered cobaltate. Adv. Funct. Mater. 2013, 23, 5728–5736.
(33) Miyazaki, Y.; Onoda, M.; Oku, T.; Kikuchi, M.; Ishii, Y.; Ono, Y.; Morii, Y.; Kajitani, T. Modulated structure of the thermoelectric compound [CaCo4O9]δ[CoO2]y. J. Phys. Soc. Jpn. 2002, 71, 491–497.
(34) Paul, B.; Lu, J.; Eklund, P. Nanostructural tailoring to induce flexibility in thermoelectric CaCo4O9 thin films. ACS Appl. Mater. Interfaces 2017, 9, 25308–25316.
(35) Gurarslan, A.; Yu, Y.; Su, L.; Yu, Y.; Suarez, F.; Yao, S.; Zhu, Y.; Ozturk, M.; Zhang, Y.; Cao, L. Surface-energy-assisted perfect transfer of centimeter-scale monolayer and few-layer MoS2 films onto arbitrary substrates. ACS Nano 2014, 8, 11522–11528.
(36) Lai, S.; Jeon, J.; Song, Y.-J.; Lee, S. Water-penetration-assisted mechanical transfer of large-scale molybdenum disulide onto arbitrary substrates. RSC Adv. 2016, 6, 57497–57501.
(37) Ma, D.; Shi, J.; Ji, Q.; Chen, K.; Yin, J.; Lin, Y.; Zhang, Y.; Liu, M.; Feng, Q.; Song, X.; Guo, X.; Zhang, J.; Zhang, Y.; Liu, Z. A universal etching-free transfer of MoS2 films for applications in photodetectors. Nano Res. 2015, 8, 3662–3672.
(38) Bansal, N.; Cho, M. R.; Brahekk, M.; Koirala, N.; Horibe, Y.; Chen, J.; Wu, W.; Park, Y. D.; Oh, S. Transferring MBE-grown topological insulator films to arbitrary substrates and metal–insulator transition via dirac gap. Nano Lett. 2014, 14, 1343–1348.
(39) Lu, D.; Baek, D.; Hong, S. S.; Kourkoutis, L. F.; Hikita, Y.; Hwang, H. Y. Synthesis of freestanding single-crystal perovskite films and heterostructures by etching of sacrificial water-soluble layers. Nat. Mater. 2016, 15, 1255–1260.
(40) Schrade, M.; Fjeld, H.; Finstad, T. G.; Norby, T. Electronic transport properties of [CaCo4O9]δ[CoO2]y. J. Phys. Chem. C 2011, 1180, 2908–2918.
(41) Van Nong, N.; Samson, A. J.; Pryds, N.; Linderoth, S. Microstructure and thermoelectric properties of screen-printed thick films of misfit-layered cobalt oxides with Ag addition. J. Electron. Mater. 2012, 41, 1280–1285.
(42) Madre, M. A.; Costa, F. M.; Ferreira, N. M.; Sotelo, A.; Torres, M. A.; Constantinescu, G.; Rasekh, S.; Diez, J. C. Preparation of high-performance CaCo4O9 thermoelectric ceramics produced by a New two-step method. J. Eur. Ceram. Soc. 2013, 33, 1747–1754.
(43) Hu, Y. F.; Si, W. D.; Sutter, E.; Li, Q. In situ growth of c-axis-oriented CaCo4O9 thin films on Si (100). Appl. Phys. Lett. 2005, 86, 082103.
(44) An, H. P.; Zhu, C. H.; Ge, W. W.; Li, Z. Z.; Tang, G. D. Growth and thermoelectric properties of CaCo4O9 thin films with c-axis parallel to Si substrate surface. Thin Solid Films 2013, 545, 229–233.
(45) Lybeck, J.; Valkeapää, M.; Shibasaki, S.; Terakas, I.; Yamauchi, H.; Karppinen, M. Thermoelectric properties of oxygen-tuned ALD-grown [CaCo4O9]δ[CoO2]y thin films. Chem. Mater. 2010, 22, 5900–5904.
(46) Fuentes, G. G.; Elizalde, E.; Yubero, F.; Sanz, J. M. Electron inelastic mean free path for Ti, TiC, TiO and TiO2 as determined by quantitative reflection electron energy-loss spectroscopy. Surf. Interface Anal. 2002, 33, 230.
(47) Song, D. W.; Shen, W.-N.; Dunn, B.; Moore, C. D.; Goorsky, M. S.; Radetic, T.; Gronsky, R.; Chen, G. Thermal conductivity of nanoporous bismuth thick films. Appl. Phys. Lett. 2004, 84, 1883.
(48) Bittner, M.; Helmich, L.; Nietschke, F.; Geppert, B.; Oeckler, O.; Feldhoff, A. Porous CaCo4O9 with enhanced thermoelectric properties derived from Sol–Gel synthesis. J. Eur. Ceram. Soc. 2017, 37, 3909–3915.
(49) Presečnik, M.; de Boor, J.; Bernik, S. Synthesis of single-phase CaCo4O9 ceramics and their processing for a microstructure-enhanced thermoelectric performance. Ceram. Int. 2016, 42, 7315–7327.
(50) Sun, T.; Hng, H. H.; Yan, Q. Y.; Ma, J. Enhanced high temperature thermoelectric properties of Bi-doped c-axis oriented CaCo4O9 thin films by pulsed laser deposition. J. Appl. Phys. 2010, 108, 083709.
(51) Butt, S.; Xu, W.; He, W. Q.; Tan, Q.; Ren, G. K.; Lin, Y.; Nan, C. – W. Enhancement of thermoelectric performance in Cd-doped CaCo4O9 via spin entropy, defect chemistry and phonon scattering. J. Mater. Chem. A 2014, 2, 19479.
(52) Zhu, C.; An, H.; Ge, W.; Li, Z.; Tang, G. Enhancing the thermoelectric properties of CaCo4O9 thin films by Nb ion injection. J. Alloys Compd. 2013, 567, 122–126.