Nanostructural Tailoring to Induce Flexibility in Thermoelectric Ca₃Co₄O₉ Thin Films

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Supporting Information

**ABSTRACT:** Because of their inherent rigidity and brittleness, inorganic materials have seen limited use in flexible thermoelectric applications. On the other hand, for high output power density and stability, the use of inorganic materials is required. Here, we demonstrate a concept of fully inorganic flexible thermoelectric thin films with Ca₃Co₄O₉-on-mica. Ca₃Co₄O₉ is promising not only because of its high Seebeck coefficient and good electrical conductivity but also because of the abundance, low cost, and nontoxicity of its constituent raw materials. We show a promising nanostructural tailoring approach to induce flexibility in inorganic thin-film materials, achieving flexibility in nanostructured Ca₃Co₄O₉ thin films. The films were grown by thermally induced phase transformation from CaO–CoO thin films deposited by reactive rf-magnetron cosputtering from metallic targets of Ca and Co to the final phase of Ca₃Co₄O₉ on a mica substrate. The pattern of nanostructural evolution during the solid-state phase transformation is determined by the surface energy and strain energy contributions, whereas different distributions of CaO and CoO phases in the as-deposited films promote different nanostructuring during the phase transformation. Another interesting fact is that the Ca₃Co₄O₉ film is transferable onto an arbitrary flexible platform from the parent mica substrate by etch-free dry transfer. The highest thermoelectric power factor obtained is above 1 × 10⁻⁴ W m⁻¹ K⁻² in a wide temperature range, thus showing low-temperature applicability of this class of materials.

**KEYWORDS:** Ca₃Co₄O₉, thermoelectrics, nanostructure, flexible film, transferable film

1. **INTRODUCTION**

Microscale electronic components tend to operate on battery power,¹ which has limitations on their lifetime and requirement for recharging. This is not desired for wearable devices, where a possible solution could be the scavenging of body heat for electrical power generation by flexible thermoelectric converters (TEC).² However, for wearable and other flexible applications, a technology transformation is required from rigid thermoelectrics to flexible thermoelectrics.

Organic materials, because of their inherent flexibility, have been preferred over inorganic materials for this purpose. Extensive investigations have been done on organic materials,³–⁵ with high thermoelectric performance reported for the conjugated polymer, PEDOT:PSS, with a thermoelectric figure of merit, ZT, of 0.25.⁶ Despite the advantages of low material cost and solution-synthesis possibility, polymer materials typically have low output power density and stability.⁷ For high output power density and reliable performance over longer period of time, particularly in hostile environments, the use of inorganic materials is inevitable. However, it then becomes necessary to overcome the problem of material rigidity.

Recently, there have been some investigations on developing flexible TEC based on inorganic materials.⁹,¹⁰ In these investigations, flexible platforms are used to hold the thermocouples of inorganic materials, and the legs of the thermocouples are subjected to temperature gradient in an out-of-plane direction of the flexible platform. The disadvantage of such thermocouple arrangements (vertical arrangements), leg height of the thermocouples being in the micrometer range, is that the temperature gradient along the active materials is low, resulting in a low output voltage from the modules. Further, maximum power output from a wearable thermoelectric device requires thermal matching between the body skin and air, and for that 3–5 mm leg height is investigated to be appropriate.¹¹ Achieving such a leg height in a flexible module with vertical leg arrangements is quite challenging. An alternative option can be the lateral arrangement of thermocouples, where the thickness of the leg materials is not important as they are subjected to temperature gradient along their length, in parallel with the substrate plane.¹² The additional advantage of such arrangements is that a large number of thermocouples can be accommodated in a small area. However, with such lateral arrangements of thermocouples, both the substrate and the thin leg materials need to be mechanically flexible.

There have been some attempts for developing flexible thermoelectric devices with such lateral arrangements of
thermocouples. For that, thin legs of inorganic materials are deposited on flexible polymer substrates by the printing method, for example, screen printing, inkjet printing, and dispenser printing. However, the problem with these printing techniques is that the low processing temperature of the film, restricted by low-temperature sustainability of the polymer substrate, causes rough interfaces of the grains in the film, resulting in the scattering of charge carriers and thus a drastic reduction in the electrical conductivity. To reduce the grain boundary scattering of charge carriers, the thermocouple legs can be deposited by sputter-deposition on flexible substrates. However, the mechanical flexibility of the leg materials is still a challenge, which needs to be addressed by inducing mechanical flexibility in inorganic thin films but with no deterioration of their electronic properties. Recently, Zhou et al. have developed carbon nanotube-based flexible TEC for room-temperature wearable applications; however, its applicability above room temperature has not been examined.

Tailoring the structure on the nanoscale can induce new mechanical properties in inorganic materials. For example, pristine Al2O3 is rigid in nature, but hierarchical nanoarchitectures have been reported to produce squeezable Al2O3 with 50% recoverability. Nanostructural engineering has been used to tailor the electronic and phononic properties of inorganic thermoelectric materials for the enhancement of their thermoelectric efficiency. However, such experiments to induce mechanical flexibility in these materials are unexplored. Here, we report the growth of flexible Ca3Co4O9 thin films on a flexible mica substrate. A novel nanostructural tailoring approach has been demonstrated to induce flexibility in Ca3Co4O9 thin films without significant effects on their electronic properties. Flexible Ca3Co4O9 films can be applicable in a wide temperature range from room-temperature wearable applications to waste-heat recovery from hot curved surfaces (e.g., hot pipes) and for applications in hostile environments. Thermoelectric performance of the investigated films has been evaluated in terms of their power factors. High power factor (\(\approx S^2/\rho\), where \(S\) is the Seebeck coefficient and \(\rho\) is the electrical resistivity) is more important than low thermal conductivity to achieve a high output power, in particular, for low-power applications, such as wearable applications. However, sustaining a high power factor in flexible materials comparable to their pristine bulk values is quite challenging. The formation of nanolaminar platelets is typical of Ca3Co4O9 because of its inherently layered structure. We show that the size and orientation of these platelet-like grains can be controlled to achieve flexible mechanical properties of the films without compromising with their thermoelectric performance. The nanostructured Ca3Co4O9 films are produced by thermally induced phase transformation from CaO–CoO thin films deposited on mica substrates by reactive rf-magnetron cosputtering from elemental targets of Ca and Co. Muscovite mica is chosen as the substrate as it can act as a flexible substrate and at the same time can sustain high processing temperature of 700 °C. Muscovite mica forms a layered structure, where aluminosilicate layers are loosely bound by the boundary layer of potassium (K⁺) ions, which is bendable and easily cleaved along the boundary layer. Further, the film is easily transferable from mica by dry transfer, that is, mica can also act as a sacrificial layer for the transferable film.

2. EXPERIMENTAL SECTION

Ca3Co4O9 thin films were prepared by a two-step sputtering/annealing process. In this process, first, CaO–CoO films were reactively cosputtered from Ca and Co targets onto the muscovite mica (001) substrates by rf-magnetron sputtering at 0.27 Pa (2 mTorr) in an oxygen–argon mixture with oxygen 1.5%; second, the as-deposited films were annealed at 700 °C in an O2 gas flow to form the final phase of Ca3Co4O9. Four series of samples, namely, (T; 20 °C), (T; 225 °C), (T; 375 °C), and (T; 675 °C), were deposited with varying substrate temperatures from room temperature to 675 °C but with the same oxygen percentage (1.5%) in the gas mixture. The total gas pressure during the sputtered deposition is kept low, 2 mTorr, so as to avoid the scattering of the ionized species. On the other hand, to ensure the deposition rate of ~10 nm/min, the oxygen content in the gas mixture is maintained at a minimum possible value of 1.5% before it oxidizes the elemental targets of Ca and Co. Above 1.5% oxygen, the surface of the Ca and Co targets is found to be rapidly oxidized, resulting in a drastic reduction in the deposition rate. The crystal structure and morphology of the films were characterized by \(\theta\)–2\(\theta\) X-ray diffraction (XRD) analyses using monochromatic Cu Kα radiation (\(\lambda = 1.5406 \text{ Å}\), transmission electron microscopy (TEM) 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 \(\theta\)–2\(\theta\) XRD scans were performed with a Philips PW 1820 diffractometer. The samples for TEM were prepared by ion-beam thinning method. For cross-sectional TEM, two pieces of the sample 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 at an Ar⁺ energy of 5 kV and a gun angle of 5°, with a final polishing step at 2 kV Ar⁺ energy. For the TEM analysis of the film from its top, it was cut into 3 mm diameter disks, and then, the sample was thinned to 50 μm. Finally, the samples were ion-milled from the substrate side until electron-transparent. The composition of the films was determined by energy-dispersive X-ray spectroscopy (EDS), with an accuracy of ±5%. 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.

3. RESULTS AND DISCUSSION

3.1. Structure of the Films. Figure 1a shows an optical image of an as-deposited film, which was deposited with no substrate heating, that is, the substrate was kept at room temperature 20 °C during sputtering deposition, and hence, the film is denoted (T; 20 °C). Similarly, a series of other films (T; 225 °C), (T; 375 °C), and (T; 675 °C) are named after their deposition temperatures 225, 375, and 675 °C, respectively. The as-deposited film is yellow in color. This appearance is similar for the rest of the samples (not shown). The as-deposited films consist of CaO–CoO phases, which is consistent with the observations on a sapphire substrate. Figure 1b shows the postannealed film (T; 20 °C). After annealing, all samples turn dark, as shown in Figure 1b. This change in color is attributed to the phase transformation from the CaO–CoO phase to the final phase of Ca3Co4O9. In our previous study, we demonstrated the occurrence of three-stage phase transformation during annealing, leading to the formation of the final phase of Ca3Co4O9.

Figure 1c shows the \(\theta\)–2\(\theta\) XRD scan for the postannealed film (T; 20 °C). Broadened peaks at around 2\(\theta\) = 8.66°, 17.51°, 26.62°, and 35.85° occur from the (001) planes of muscovite mica. Diffraction peaks at 2\(\theta\) = 16.42°, 24.73°, and 33.25° are observed, originating from the (002), (003), and (004) planes of Ca3Co4O9. The peak from the (001) plane of Ca3Co4O9 is not visible here as it coincides with the broadened
peak of mica at 2θ = 8.66°. Apart from the (00l) planes of Ca₃Co₄O₉, one low intense peak from the (−201) plane is visible in Figure 1c, which indicates that the film (Tₛ: 20 °C) is not singly oriented, but it has grains with a mixed orientation. The XRD peaks in the θ−2θ XRD scan of the annealed films (Tₛ: 225 °C), (Tₛ: 375 °C), and (Tₛ: 675 °C) are so weak that they almost coincide with the background (see Figure S-1 of Supporting Information). This is because the orientation of the Ca₃Co₄O₉ film might not satisfy Bragg’s condition in the out-of-plane direction, which is consistent with the previous observation for the CaCo₄O₉ film grown on SrTiO₃(111).²⁷ The orientation and the crystal structure of the films were investigated by TEM and SEM and are discussed later.

Figure 2a−d shows the SEM images of the as-deposited films (Tₛ: 20 °C), (Tₛ: 225 °C), (Tₛ: 375 °C), and (Tₛ: 675 °C), and Figure 2e−h shows the SEM images of the postannealed films. The morphology of the as-deposited films changes from sample to sample, which is attributed to the different deposition temperatures of the films. The morphology of the annealed films also varies from sample to sample. The formation of platelet-like grains in the postannealed films is evident from Figure 2. Because of the inherently layered structure, the formation of nanolaminated platelets is typical for Ca₃Co₄O₉. Controlling the size and orientation of these nanolaminar platelets is not trivial in the films.²⁹−³² Here, we have modified the orientation of the nanolaminated grains in the films independent of the substrate by controlling the growth condition. Figure 2a shows the SEM image of the annealed film (Tₛ: 20 °C), showing both the in-plane and out-of-plane orientations of the nanolaminated grains of Ca₃Co₄O₉. In the films (Tₛ: 225 °C), (Tₛ: 375 °C), and (Tₛ: 675 °C), the nanolaminated grains tend to align nearly vertically (as shown in Figure 2f−h), that is, the c-axis of the grains is along the in-plane direction of the sample. The phase of these films has been confirmed by TEM analysis and is discussed later. The thickness of the nanolaminated grains in the film (Tₛ: 225 °C) is found not to be uniform; certain distribution in the grain thickness is evident from the SEM image. The thickness of the nanolaminated grains in the sample (Tₛ: 375 °C) is found to be almost uniform (also evident from Figure 2g) and estimated to be around 50 nm. When the deposition temperature is increased to 675 °C, a distribution in the grain thickness is observed in the film (Tₛ: 675 °C). SEM images of the larger area of all as-deposited and postannealed films are provided in Figures S-2 and S-3 in the Supporting Information.

Different arrangements of the nanolaminated grains in the annealed films is due to the different self-arrangements of the grains during nanostructural evolution during phase transformation, which is likely to be influenced by the initial
arrangements of CaO and CoO phases in the as-deposited CaO–CoO films. The energetic constraints that guide the self-arrangements are anticipated to include the surface and interface energy minimizations, as well as strain energy minimization. The self-assembly growth of the layered cobaltate in the chemical solution deposition (CSD) technique was studied before. The oriented growth of the films was explained as owing to the external stress due to solvent evaporation. In another study, Fu et al. reported the $c$-orientation of the Ca$_3$Co$_4$O$_9$ film grown on a polycrystalline Al$_2$O$_3$ substrate by the CSD technique. They argued that the interactive force of the $(00\overline{1})$ plane of Ca$_3$Co$_4$O$_9$ with the Al$_2$O$_3$(00$\overline{1}$) plane is stronger than that in other planes, and hence, the Ca$_3$Co$_4$O$_9$(00$\overline{1}$) plane tends to nucleate onto the Al$_2$O$_3$(00$\overline{1}$) plane serving as seeds for $c$-axis-oriented growth, resulting in the $c$-axis self-assembled orientation. Therefore, the substrate is believed to have a stronger impact on the selection of the film orientation. However, in our study, the various orientations of the grains of polycrystalline Ca$_3$Co$_4$O$_9$ on the same substrate under different deposition conditions negate the argument on substrate influence on the texture selection of the film. In our case, it is rather so that the distribution of crystallographic orientations of the grains in a polycrystalline film evolves during postdeposition annealing through a number of kinetic processes. The final texture of the film depends on which texture-selection mechanism and driving force dominates. In the present case, the different arrangements of CaO and CoO nanophases in the as-deposited films drive the strain force in different directions, leading to different nanostructures of the postannealed films.

Figure 3a shows a typical cross-sectional TEM image of an annealed film ($T_s$: 675 °C). The near vertical orientation of the nanolaminated grains in Figure 3a is consistent with the observation from the SEM image analyses. The compositional analyses by EDS confirm the Ca to Co ratio to be $\approx 0.73$, which corresponds to the Ca/Co ratio of 0.75 in Ca$_3$Co$_4$O$_9$. The presence of an amorphous layer of thickness $\approx 50$ nm between the substrate and the film is evident from Figure 3a. The amorphous layer is formed because of the high-temperature treatment during annealing. In the amorphous layer, the presence of Ca (21.3 at %) along with the elements from the mica substrate, O (55.7 at %), Al (7.9 at %), Si (9.9 at %), and Fe (4.2 at %), is confirmed by EDS analyses, however, with no trace of Co. The proportion of O, Al, Si, K, and Fe in the amorphous layer is found to be equivalent to that of the mica substrate. This indicates that at 700 °C, the layered structure of mica near the interfacial region collapses, forming an amorphous layer through the absorption of Ca. The formation of such an interfacial layer was confirmed for all annealed films (not shown). Figure 3b shows the top view of the TEM image of the annealed film ($T_s$: 675 °C). The grains are found to form a closed network, which is consistent with the observation from the SEM analyses. Such a network formation is desirable for avoiding any disruption of transport of charge carriers during flexible applications. The presence of void spaces between the grains is visible in Figure 3b, which indicates that the film ($T_s$: 675 °C) is not 100% dense. This is consistent with the SEM observation in Figure 2h. A high-resolution TEM image in the inset of Figure 3b shows the lattice imaging of the nanolaminated grains. From the TEM image analyses, it is clear that the nanolaminated grains are not perfectly vertically aligned (see Figure 3a), that is, the $c$-axis of the grains makes a certain angle of inclination ($5^\circ$–$25^\circ$) with the substrate plane. Because of such an out-of-plane alignment of the nanolaminated grains, Bragg’s condition is not satisfied, and hence, the XRD peaks are weak in the $\theta$–$2\theta$ XRD scan.

3.2. Flexibility and Transferability of the Film. Figure 4a shows a typical flexible film prepared from the sample ($T_s$: 675 °C). Figure 4b shows the different steps leading to the thin flexible film. In step 1, the film is attached to a glass slide by wax in an upside down position. In step 2, the thickness of the mica substrate is reduced to 100 μm by the physical delamination process. To further reduce the substrate thickness, mica is delaminated by a sticky tape, as shown in step 3. After repeating such delamination several times, the substrate thickness is reduced to 20 μm, as shown in step 4. In step 5, the glass slide is kept in acetone for 12 h so that the wax is completely dissolved and a thin flexible film can be isolated. The film is bendable to a bending radius of 14 mm without any deterioration of its physical properties.

Figure 5a shows a cross-sectional SEM image of the flexible film ($T_s$: 675 °C). The inset of Figure 5a shows the magnified
image of a small cross-sectional portion of the film. The substrate thickness is around 20 μm. Figure 5b shows a magnified image of the small portion of the film. The average film thickness is 250 nm. The inset of Figure 5b shows the magnified image of a small portion of the film. The arrangement of the nanolaminated grains of Ca₃Co₄O₉ is clearly visible in the image. Such grain arrangements enable the film (Tc: 675 °C) to withstand higher stress (tensile and compressive stress) developed due to bending. The epitaxially grown oriented Ca₃Co₄O₉ films do not allow such bending without developing cracks. Therefore, we grow polycrystalline films with nanolaminated grains with their c-axis randomly oriented in the sample plane (i.e., standing basal planes). This arrangement of the grains results in a network formation with gaps between the grains (as shown in Figure 3b), which allow the relative motion and grain boundary/dislocation glide during bending, thus sustaining bending stress. In a fully dense oriented film, this relative motion is not possible and thus develops cracks to release the bending stress. Observation by an optical microscope confirms the absence of cracks in the film even after the repeated bending of the film to the bending radius of 14 mm in both directions. Figure 5c shows an optical image of a small area (3.2 × 2.4 mm²) of the film before and after bending. The film surface before bending is seemingly flat; however, after bending, some local curvatures in the film are developed from the compressive stress due to bending (evident from Figure 5c) but with no crack on the surface of the bended film. Thus, it is confirmed that the film is able to sustain both tensile stress and compressive stress when it is subjected to a bending radius of 14 mm and thus has no effect on the thermoelectric properties of the film (see section 3.3 for more details on thermoelectric properties). Because of similar grain arrangements, the films (Tc: 225 °C) and (Tc: 375 °C) have been found to withstand bending stress when they are subjected to bending.

Another promising aspect of the present study is the transferability of the film to other flexible platforms. With the emergence of flexible thermoelectrics, transfer of the films from the rigid substrate onto a flexible platform is a major challenge. Strategies such as 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 a monolayer or a few atomic layers of metal sulfide onto flexible polymer platforms; however, these strategies have not yet been examined on thick films (say thickness of several hundred nanometers). Recently, Lu et al. have demonstrated the possibility of transfer of thick films by etching of sacrificial water-soluble layers.

In the present study, we examined if a 250 nm thick Ca₃Co₄O₉ film can be mechanically transferred from the parent mica substrate to another flexible platform. The transferability of the film was examined by transferring the film on a sticky tape. The different steps of film transfer are shown in Figure 6a. In step 1, one side of the film is marked by a sharp blade. In the second step, a tape was stuck to the film. After that, the film was isolated from the mica substrate by stripping (step 3). Figure 6b shows the optical image of the back surface of the mechanically stripped film. Some leftover thin mica layers were still seen sticking to the back surface of the stripped film (Figure 6b). This, however, does not affect the functionality of the film as one exposed surface is sufficient for TEC.

However, the functionality of the film can be effected by the microcracks. Figure 6c shows the optical image of a small area (3.2 × 2.4 mm²) of the back surface of the stripped film. The presence of microcracks on the exposed part of the film is evident from Figure 6c. To avoid microcracks, we instead remove the mica from the substrate side in a way similar to that demonstrated before in Figure 4a, however, with one exception. The film, instead of sticking to a glass slide, is adhered to a flat and sticky surface of a sticky tape (as shown in Figure 7a). Figure 7b shows the back surface of the film after the removal of mica. Partial presence of the mica layers is still observed as before, but no microcracks are observed by optical microscopic

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**Figure 5.** (a) Cross-sectional SEM image of the flexible film (Tc: 675 °C), (b) magnified cross-sectional SEM image of the flexible film (Tc: 675 °C) and (c) optical image of a small area of the film (Tc: 675 °C) before and after bending.

**Figure 6.** (a) Demonstration of the transformation of the film onto a sticky tape, (b) optical image of the back surface of the stripped film, and (c) optical image of the small portion of the back surface of the stripped film.
analyses. Figure 7c is a typical optical image of a small area (∼3.2 × 2.4 mm²) of the back surface of the film, which shows no cracks on the film.

3.3. Thermoelectric Properties. Figure 8a shows the temperature-dependent electrical resistivity of all annealed films. The electrical resistivity of all films does not vary much as a function of temperature until 250 °C. Beyond 250 °C, a rapid increase in the electrical resistivity is observed with temperature, which is attributed to the release of oxygen from the films.41−44 The rate of increase in the electrical resistivity of all films is not the same. Above 250 °C, the ρ versus T curve of the film (T₀: 20 °C) is much steeper than those of other films. A nominal increase in the electrical resistivity with the temperature of the film (T₀: 675 °C) as compared to other films is likely due to the fact that it prevents the release of oxygen to a greater extent at high temperatures. The lower tendency of oxygen release from the film (T₀: 675 °C) is attributed to its larger grain size than that of the film (T₀: 375 °C) (see Figure 3g,h for comparison). This is because the release of oxygen is more probable from the region near the surface of the grains, and with the increase in the size of the grains, the surface-to-volume ratio decreases, which in turn reduces the effect of oxygen release. Note that the electrical resistivity measurement was performed in low-pressure helium gas, increasing the tendency of oxygen release at high temperatures. The oxygen release will be very limited under an atmospheric condition. However, the main focus of the present study is the low-temperature applicability of Ca₃Co₄O₉ films, particularly for wearable applications, and hence, high-temperature stability is of limited importance. Near room temperature, the electrical resistivity of the films (T₀: 20 °C), (T₀: 225 °C), (T₀: 375 °C), and (T₀: 675 °C) is 29.73, 25.00, 20.30, and 16.46 mΩ cm, respectively. The highest electrical resistivity of the film (T₀: 20 °C) is attributed to both out-of-plane and in-plane orientations of the grains in the film. Because of the inherently layered structure, the physical properties of Ca₃Co₄O₉ are anisotropic in nature. The electrical resistivity along the c-direction of Ca₃Co₄O₉ is higher than that in the (a,b) plane. Because of both out-of-plane and in-plane orientations of the grains, the resistivity of the film (T₀: 20 °C) is higher. The room-temperature value of the electrical resistivity of the film (T₀: 675 °C), although several times higher than textured Ca₃Co₄O₉ thin films,45 is comparable with the values obtained from undoped polycrystalline bulk Ca₃Co₄O₉.46−51 As previously mentioned, the vertical arrangement of the nanolaminated grains of Ca₃Co₄O₉ is favorable for flexible applications. Repeated bending (100 times) of the film (T₀: 675 °C) shows no

Figure 7. (a) Optical image of the film (T₀: 675 °C) from the substrate side after the film is adhered to a sticky tape, (b) image of the film after the removal of mica from the substrate side, (c) optical image of the small portion of the film after the removal of mica, and (d) image of the bended film after it is transferred to the sticky tape.

Figure 8. Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, and (c) power factor of all films from room temperature to 400 °C before bending. Comparison graph of (d) electrical resistivity, (e) Seebeck coefficient, and (f) power factor of the film (T₀: 675 °C) before and after bending.
deterioration of electrical conductivity. It was the same for the films ($T_1: 225 \, ^{\circ}C$) and ($T_2: 375 \, ^{\circ}C$).

Figure 8b shows the temperature-dependent Seebeck coefficient ($S$) of all annealed films. Seebeck coefficient of all films varies with temperature following the same manner as electrical resistivity. The highest value of Seebeck coefficient near room temperature is obtained as 118 $\mu V/K$ from the film ($T_1: 675 \, ^{\circ}C$). Near room temperature, not much variation of Seebeck values is observed for different films and remains within $111-118 \, \mu V/K$, which is comparable to the reported values for bulk Ca$_3$Co$_4$O$_9$.

Small bending in both directions; however, no notable change in the Seebeck coefficient is observed among the films.

Figure 8c shows the power factor ($PF = S^2/\rho$) of all films as a function of temperature. Near room temperature, power factors of $\sim 1 \times 10^{-4} \, \text{W m}^{-1} \text{K}^{-2}$ are obtained from the films ($T_1: 675 \, ^{\circ}C$), achieving the highest value of $1.18 \times 10^{-4} \, \text{W m}^{-1} \text{K}^{-2}$ near 300 $^{\circ}C$. The power factor in the film ($T_1: 675 \, ^{\circ}C$), unlike the bulk sample, is nearly flattened with temperature. It is remarkable for flexible oxide thin films to exhibit such a high power factor near room temperature. Liu et al. demonstrated a free-standing Ca$_3$Co$_4$O$_9$/PEDOT:PSS composite thin film; however, the room-temperature value of power factor was almost 7 times lower than the value obtained from the flexible film ($T_1: 675 \, ^{\circ}C$). Near room temperature, the power factor of the flexible film ($T_1: 675 \, ^{\circ}C$) is comparable to the values reported for undoped bulk polycrystalline Ca$_3$Co$_4$O$_9$ and further enhancement of power factor of the film is possible by optimal doping.

To examine the bending effect on the thermoelectric properties of the flexible film ($T_1: 675 \, ^{\circ}C$), its Seebeck measurement was performed after it was subjected to 100 times bending in both directions; however, no notable change in the results is observed; whatever variation in the Seebeck coefficient and electrical resistivity is found, it is well below the error limit specified by the ULVAC-RIKO ZEM3 system.

Figure 8d–f compares the electrical resistivity, Seebeck coefficient, and power factor, respectively, of the film ($T_1: 675 \, ^{\circ}C$) before and after bending. No remarkable change in the values of the Seebeck coefficient, electrical resistivity, and power factor is observed. Small fluctuation in the values is well below the error limit. For flexible applications, the flexibility of the substrate is necessary but not sufficient; the film also needs to be flexible. Considering both the mechanical flexibility and thermoelectric properties, the presently developed Ca$_3$Co$_4$O$_9$ films thus improve on other reports on flexible films.

4. CONCLUSIONS

A fully inorganic flexible film, Ca$_3$Co$_4$O$_9$-on-mica, has been developed. A nanostructural tailoring approach has been demonstrated to induce mechanical flexibility in Ca$_3$Co$_4$O$_9$ thin films. The nanostructured Ca$_3$Co$_4$O$_9$ film is obtained by thermally induced phase transformation from the CaO–CoO thin film deposited on the mica substrate by reactive rf-magnetron cosputtering to the final phase of Ca$_3$Co$_4$O$_9$. Mica acts as a flexible substrate and at the same time as a sacrificial layer for the film transfer onto other flexible platforms. The nanostructure of the film is influenced by the initial arrangements of the CaO and CoO phases in the as-deposited films, which is controlled by controlling the deposition conditions: deposition temperature and percentage of oxygen in the gas mixture. Flexible films are bendable to the bending radius of 14 mm without any deterioration of thermoelectric performance. The maximum power factor of the flexible film is $1.18 \times 10^{-4} \, \text{W m}^{-1} \text{K}^{-2}$ near 300 $^{\circ}C$ and does not change much as a function of temperature within the temperature range measured. With this high power factor and mechanical flexibility, the present films can be promising in the area of flexible thermoelectrics. Further enhancement of the power factor is possible by optimal doping. The present approach can also be applicable to grow flexible films of other compounds in layered cobaltate family.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b06301.

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