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Growth of $\text{Ca}_3\text{Co}_4\text{O}_9$ films: Simple chemical solution deposition and stress induced spontaneous dewetting

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Growth of $\text{Ca}_3\text{Co}_4\text{O}_9$ films: Simple chemical solution deposition and stress induced spontaneous dewetting

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Chemical solution deposition as a simple method for preparation of oxide films is used to fabricate misfit structured $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric films using cheap precursors, Ca and Co acetates, which opens up a simple route to fabricate large-area Co-based oxide thermoelectric films. The results show that when the annealing temperature is higher than 800 °C crystallized $\text{Ca}_3\text{Co}_4\text{O}_9$ films can be obtained on single-crystal LaAlO_3 substrates, whereas the $\text{Ca}_3\text{Co}_4\text{O}_9$ films are amorphous for lower annealing temperatures. Experimental evidence shows that the amorphous $\text{Ca}_3\text{Co}_4\text{O}_9$ films behave like semiconductors with enhanced resistivity and Seebeck coefficient within the measured temperature range. The magnetoresistance is positive indicating the absence of long-range order of the Co-ion spins. For the crystallized $\text{Ca}_3\text{Co}_4\text{O}_9$ films, it can be seen that the thinner films show the characteristics of spontaneous dewetting induced by the stress, which suggests that it is possible to prepare nanostructured $\text{Ca}_3\text{Co}_4\text{O}_9$ films through tailoring the film thickness and the lattice mismatch; whereas, for the thicker films the temperature dependence of the resistivity and the Seebeck coefficient shows that it is possible to prepare excellent $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric films using chemical solution deposition route, which will broaden the range of preparation methods for misfit structured Co-based thermoelectric films.

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I. INTRODUCTION

Thermoelectric (TE) generation systems can convert heat energy directly into electrical energy, irrespective of the source size, which provides an effective route to use the waste heat from automobiles, factories, and so on. The TE generation systems require that the TE materials should possess high conversion efficiency and also be composed of nontoxic and abundantly available elemental materials having high chemical stability in air, even at temperatures of 800–1000 K. As compared with the Bi–Te based TE materials, recently, the layered cobalt-based oxide TE materials have been widely studied because of their excellent TE properties, especially for applications involving higher temperatures and an oxidizing atmosphere. Among various cobalt-based oxide TE materials, $\text{Ca}_3\text{Co}_4\text{O}_9$ (CCO349) has its dimensionless figure of TE merit $ZT=S^2T/\rho\kappa$ (where S is the Seebeck coefficient, T is the temperature, ρ is the electrical resistivity, and κ is the thermal conductivity) about 1 near 1000 K, which suggests that the CCO349 can be considered as a very important candidate for TE applications.^{1–3} The

CCO349 is built up by stacking along the c -axis of triple rock salt-type layer Ca_2CoO_3 and single CdI_2 -type CoO_2 layers, which both have monoclinic symmetry with identical a , c , and β , but different b parameters (for the Ca_2CoO_3 layer, $a=4.8376$ Å, $c=10.833$ Å, $\beta=98.06^\circ$, and $b_1=4.5565$ Å, while for the CoO_2 layer, $b_2=2.8189$ Å).⁴

As for the fabrication of CCO349 films, which can be used in various applications⁵ such as thermochemistry-on-a-chip, biothermoelectric chips, active cooling for microelectronic processors, and localized cooling/heating at points of interest, the commonly used method is pulsed laser deposition (PLD),^{6–8} and there have few reports about the chemical solution deposition (CSD) route,⁹ which is a simple, low-cost method for large-area films. Moreover, in the processes of preparing films, the interfacial strain in the films is a key parameter controlling many physical properties, which has stimulated considerable efforts towards understanding the relaxation mechanisms.^{10,11} Furthermore, the interfacial strain is the driving force for the generation of low-dimensional self-assembled nanostructures or for the spontaneous formation of discontinuous films through temperature-induced dewetting phenomena, which is considered as a promising

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methodology for the fabrication of new devices based on nanostructures such as nanodots or nanowires.^{12–16}

In this article, we report on CSD of CCO349 films on LaAlO₃ (LAO) single crystal substrates and the dewetting effects associated with strains are also studied. The results show that CCO349 films can be prepared using the simple CSD method on LAO substrates, although the mismatch is several tens of percentage points, which can broaden selection of substrates, as well as opening up a simple route for the preparation of CCO349 films, especially for large-scale production.

II. EXPERIMENTAL

CCO349 films were prepared by the CSD method. Ca-acetate (Alfa Aesar) and Co-acetate (Alfa Aesar) were dissolved in propionic acid at 70 °C and stirred at this temperature for 20 min, and then the solution was stirred at room temperature for more than 10 h in order to get a well mixed precursor solution. The solution was diluted only by propionic acid to 0.7M in cations. At this stage the obtained solution can be kept for several months in atmosphere.

Before the process of deposition, the LAO substrates were ultrasonically cleaned with acetone for 15 min and then annealed at 900 °C for 60 min in air in order to obtain a well-crystallized LAO substrate surface. The films were prepared by the spin-coating method on LAO (*h*00) substrates using a rotation speed of 4500 rpm and a time of 60 s. The deposited films were then dried at 350 °C for 30 min in order to expel the organics. In order to obtain films with different thicknesses as well as study the dewetting phenomena, the spin-coating and drying procedures were repeated for different times from one to four times. Finally, the dried films with different thickness were annealed at different temperatures from 400 to 900 °C for 2 h under flowing oxygen with a flux of 450 SCCM (SCCM denotes cubic centimeter per minute at STP).

In order to study the kinetic process in the CSD for CCO349 films, films with two coatings were annealed at 900 °C for different times from 1 to 4 h. Additionally, in order to give further images about the thickness effect on the dewetting phenomena, thinner CCO349 films were fabricated using more diluted solution with 0.3M in cations and annealed at 800 and 900 °C for 2 h.

In order to briefly study the mismatch effect on the dewetting, one CCO349 film with two coatings was fabricated on the γ -cut Al₂O₃ (0001) substrate and annealed at 850 °C for 2 h. The lattice mismatch between the Al₂O₃ and CCO349 is 1.5% for the CoO₂ layer/Al₂O₃ and 4.5% for the Ca₂CoO₃ layer/Al₂O₃.⁶

The CCO349 film was also prepared on Si (100) substrate with native SiO₂ layer using the solution with concentration of 0.7M in cations and 850 °C annealing temperature for 2 h in order to study the substrate-induced stress effect on the metal-insulator transition.

Thermogravimetric (TG) measurements on the CCO349 powder obtained from the solution dried at 100 °C were carried out on a Perkin-Elmer designed Pyris Diamond differential scanning calorimeter (DSC). X-ray diffraction (XRD)

FIG. 1. TG and DTA results on CCO349 powders in air.

was carried out at different temperatures using a Philips X'pert Pro diffractometer with Cu $K\alpha$ radiation to check the crystallization and orientation both for out of plane and in-plane. Field-emission scanning electronic microscopy (FE-SEM) (FEI Sirion 200) and atomic force microscopy (AFM) (Park Scientific Instruments Autoprobe CP) were carried out to check the microstructure and the thickness. The thickness was checked by the cross section of the FE-SEM, and it was observed that the one layer CCO349 film was consisted of discontinuous CCO349 islands with the height from 50 to 100 nm; while, the island height of CCO349 film was about 100–200 nm for the two layer and three layer CCO349 films, however, the island distance was decreased with the increasing of the layers; and the thickness of the four layer CCO349 film was about 200–220 nm. The resistivity data were obtained using a physical properties measurement system (PPMS) (Quantum Design) with a standard four-point probe method, and the Seebeck coefficient was measured using PPMS in the four-probe steady state mode.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the TG and the derivative of the TG (DTA) results within the measured temperature range of 50–750 °C. It can be seen that at 300 °C the weight is greatly decreased, which can be attributed to the volatilization of the organic solvents. When the temperature is increased to 700 °C the weight loss is slight. From Fig. 2, it can be seen that the film annealed at 750 °C in oxygen is amorphous without any CCO349 diffraction peaks. Moreover, no intermediate phases are detected by synchronous XRD measurements from room temperature to 750 °C. When the annealing temperature is increased to 800 °C, one can clearly see that the derived films are highly *c*-axis oriented without any other undesired diffraction peaks. However, when the annealing temperature is increased to 925 °C, some undesired peaks appear, which suggests that in our experiments the stable annealing temperature range for crystallized CCO349 films is 800–900 °C. Additionally, the *c*-axis lattice constant is about 10.70 Å for all the crystallized films, which is smaller than that of the bulk material lattice constant ($\sim$ 10.83 Å) (Ref. 4) and approaches the lattice constant of the CCO349 films prepared by PLD (10.70 Å), indicating

FIG. 2. XRD of CCO349/LAO annealed at different temperatures: (a) 700 °C, (b) 800 °C, (c) 850 °C, and (d) 900 °C. The inset (A) shows the (004)-plane rocking curves for films annealed at different temperatures: (a) 800 °C, (b) 850 °C, and (c) 900 °C. The inset (B) is the typical Φ -scanning result on the 900 °C-annealed CCO349 film with two coatings.

that the derived CCO349 films are in-plane tensile strained.^{5,7} A similar shortening of the c -axis lattice constant for all the films suggests that there have been the same in-plane tensile stress for all derived films, which can be attributed to the dewetting and will be discussed below.

The lattice mismatch $\Delta a = (a_f - a_s) / a_s \times 100\%$, where a_f and a_s are the CoO₂-layer and the substrate lattice constants, respectively, and is +21% and -36% for the a -axis and b -axis, respectively. It is interesting to observe that highly c -axis oriented CCO349 films can be obtained on even such largely lattice-mismatched substrates, which will broaden the choice of substrates and can be explained according to the near coincidence site lattice (NCSL) theories.¹⁷

In order to check the out-of-plane orientation of the prepared CCO349 films, rocking curve measurements were carried out for the films with one coating but annealed at different temperatures, and the results are shown in the inset (A) of Fig. 2. It can be clearly seen that with increasing annealing temperature the full width at half maximum (FWHM) of the rocking curve is decreased from 0.20° to 0.15°, meaning an improvement in the out-of-plane orientation, which can be attributed to an increase in the driving energy for epitaxial/oriented growth.¹⁵

Figure 3 presents the FE-SEM results on films with two coatings that were annealed at different temperatures. It can be observed that when the annealing temperature is lower than 800 °C the films are dense and show amorphous characteristics, which is the same as the XRD results. When the annealing temperature is increased to 800 °C, it is observed that the films are dewetting. Moreover, as the annealing temperature increases, the dewetting area appeared as white color in the FE-SEM results and is also increased. The energy dispersive spectroscopy (EDS) analysis unambiguously indicates that the dewetting area lacks the Ca and Co elements, and only the La and Al elements of the LAO substrate are present. Moreover, the ratio of Ca/Co in the wetting area is about 1.3, implying that the derived films are stoichio-

FIG. 3. FE-SEM results on CCO349 films annealed at different temperatures: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 850 °C, and (f) 900 °C.

metric. Figures 4(a)–4(c) present the three-dimensional (3D) AFM results on several typical films that show dewetting. It can be seen that as the annealing temperature increases, the dewetting is obviously enhanced, which is same as the results from FE-SEM. Moreover, from Fig. 4(d) one can see that the wetting area is about 100–200 nm in thickness and that the lateral face is nearly normal to the substrate and can be attributed to the {100} planes of CCO349. It is believed that the dewetting phenomena should be appeared in the epitaxial films or biaxially textured film. In order to check the in-plane orientation of the derived films, XRD phi-scanning measurements⁶ were carried out for the CCO349 films with two coatings but annealed at different temperatures. It is observed that all films are biaxially textured and six diffraction

FIG. 4. 3D-AFM results on CCO349 films with two coatings annealed at different temperatures: (a) 800 °C, (b) 850 °C, (c) 900 °C, and (d) profile image for 900 °C-annealed film along the line in (c).

FIG. 5. XRD θ - 2θ results on CCO349 films annealed at 900 °C but different coatings: (a) one coating, (b) two coatings, (c) three coatings, and (d) four coatings. The inset shows the (004)-plane rocking curves of CCO349 films annealed at 900 °C but composed of different coatings: (a) one coating, (b) two coatings, (c) three coatings, and (d) four coatings.

peaks are clearly observed. The typical phi-scanning result for the 900 °C-annealed CCO349 film with two coatings are shown in the inset (B) of Fig. 2, which clearly suggests that the derived films have in-plane orientation.

In order to study the thickness effects on the dewetting, we carried out the preparation of CCO349 films with different coatings. The XRD results on the 900 °C-annealed films with different coatings are shown in Fig. 5. It can be seen that all the obtained films are also highly *c*-axis oriented without any undesired diffraction peaks. The *c*-axis lattice constants are also 10.70 Å for all the films despite the thickness variations, meaning that the interface stress is also the same for all the films. The out-of-plane orientation of the CCO349 films annealed at 900 °C with different coatings was also investigated through rocking curve measurements, and the results are also shown in Fig. 5. The results clearly suggest that the out-of-plane orientation of the film is decreased as the film thickness increases, which can be attributed to the improved bulk nucleation within the bulk films.¹⁵

Figures 6(a)–6(d) presents the FE-SEM results on the films annealed at 850 °C with different coatings. It is found that with increasing thickness the dewetting area is decreased, and the films with four coatings are dense without dewetting. Moreover, for the films with four coatings, many hexagonal grains stay on the bottom layer with sharply flat morphology. The mean size of the hexagonal grains in the 900 °C-annealed film as shown in Fig. 6(f) is larger than that of the 850 °C-annealed film as shown in Fig. 6(e), which can be attributed to the enhanced atomic diffusion.

In order to further study the influence of the thickness on the dewetting effect, thinner CCO349 films derived from a diluted solution (0.3M in cations) were prepared using 800 and 900 °C annealing temperatures. The FE-SEM results are shown in Figs. 7(a) and 7(b). It can be clearly seen that the dewetting area is increased as compared with the thicker films. Moreover, it is observed that the grain size of the film annealed at 900 °C is larger than that of the film annealed at 800 °C, proving that the grain size increases with increasing annealing temperatures. From the above results, it is expected that if the solution concentration is further decreased, one can obtain highly oriented CCO349 films with nano-

FIG. 6. FE-SEM results on CCO349 films annealed at 850 °C but with different coatings: (a) one coating, (b) two coatings, (c) three coatings, and (d) four coatings. (e) and (f) are FE-SEM with high magnification for four coatings annealed at 800 and 900 °C, respectively.

FIG. 7. (a) and (b) are the FE-SEM results on films derived from a 0.3M solution and annealed at 800 and 900 °C, respectively. (c)–(e) are the FE-SEM results on films with two coatings that were annealed at 900 °C but for different times: (c) 1 h, (d) 2 h, and (e) 4 h. (f) is the FE-SEM result for a CCO349 film annealed at 850 °C with two coatings on Al₂O₃.

structured particles on LAO substrates, which will open up a simple route to CCO349 films with nanostructures.

We should now consider if the spontaneously generated surface structures described above are in a quasiequilibrium state or, instead, if they are kinetically limited structures. This is a key issue because it is intimately related to the basis for modeling the observed behavior. In addition, it will open up the possibility to generate different nanostructures controlled by growth kinetics and coarsening effects. Based on the above consideration, we have investigated the influence of the annealing times on the surface structure of the CCO349 films. The FE-SEM results on the 900 °C-annealed films with two coatings but different annealing times are shown in Figs. 7(c)–7(e). It can be clearly seen that the dewetting area increases with the annealing time. It can be then concluded that the structure of the CCO349 film with two coatings is a metastable state that evolves toward a new equilibrium state through atomic diffusion process. That is to say, during the growth process of the CCO349 films, the nucleation and growth of pinholes or cracks, which are the origin of the dewetting, are propagated. Moreover, there is no dewetting for thicker films with four coatings, even if the annealing period is prolonged to longer than 4 h.

In order to investigate the lattice mismatch effects on the dewetting, CCO349 films on γ -cut Al_2O_3 (0001) substrates were prepared and the lattice mismatch between the Al_2O_3 and CCO349 is 1.5% for the CoO_2 layer/ Al_2O_3 and 4.5% for the Ca_2CoO_3 layer/ Al_2O_3 , which is obviously smaller than that of the CCO349 films on LAO substrates. Figure 7(f) is the typical FE-SEM result for the CCO349 film/ Al_2O_3 with two coatings and annealed at 850 °C for 2 h; it is seen that the film shows no characteristics of dewetting, which suggests that the lattice mismatch plays an important role on the determination of the dewetting phenomena.

It is often observed that the dewetting occurs only when the thickness of a film is lower than a critical value.¹⁸ For our experiments, if we define the island geometry as parallelepipedic and the crystal structure of the CCO349 is monoclinic, we can define the relevant interfacial and surface energies as follows: γ_{001} , γ_{100} , γ_i , and γ_s are the corresponding energies for the surface energy of the CCO349 (001) plane, the surface energy of the CCO349 {100} plane, the interfacial energy of the film/substrate, and the surface energy of the substrate, respectively. Then, performed the same as in Ref. 14, we can write the total energy E_0 for a homogeneous continuous film (without dewetting such as the four layer CCO349 films) with a surface $A=a^2$ and the total energy E for a dewetted film. The E/E_0 as a function of the normalized dimension x of the dewetted areas in the film having an initial thickness h_0 can be normalized to γ_{001} , and the obtained equation is as follows:

$$\begin{aligned} \frac{E}{E_0} = (1-x^2) + \frac{xh_0}{a(1-x^2)} \left(\frac{(\gamma_{100}/\gamma_{001})}{1 + \gamma_i/\gamma_{001}} \right) \\ + x^2 \left(\frac{(\gamma_s/\gamma_{001})}{\gamma_i/\gamma_{001}} \right) \end{aligned}$$

Since we have no detailed datum about the γ_s/γ_{001} and $\gamma_{100}/\gamma_{001}$, considering the layered structure of the CCO 349,

FIG. 8. (a) is the typical case for E/E_0 with fixed $\gamma_i/\gamma_{001}=0.5$ but different initial thicknesses h_0/a ; (b) shows the typical case for E/E_0 with fixed $h_0/a=0.125$ but different γ_i/γ_{001} .

we assume that $\gamma_s/\gamma_{001} \approx 1$ and $\gamma_{100}/\gamma_{001} \approx 10$, then we can estimate the relative stability of the different surface configurations. Figure 8(a) is the typical case for E/E_0 with fixed $\gamma_i/\gamma_{001}=0.5$ but different initial thicknesses h_0/a , and Fig. 8(b) shows the typical case for E/E_0 with fixed $h_0/a=0.125$ but different γ_i/γ_{001} . From Fig. 8(a) it can be seen that when the thickness is below a certain value, the CCO349 film becomes unstable, i.e., $E/E_0 < 1$; moreover, the $x_{\min}$ increases for thinner films, meaning that the CCO349 film becomes less stable when the thickness is decreased, which corresponds to the CCO349 films on LAO substrates with different coatings. From Fig. 8(b) it can be seen that when γ_i/γ_{001} is higher than a certain value, the CCO349 film becomes unstable; moreover, with the increase of γ_i/γ_{001} the $x_{\min}$ increases, which suggests that the dewetting area is improved when the interfacial energy is increased, corresponding to the conditions of CCO349 films on LAO and Al_2O_3 substrates. The above results clearly suggest that it is possible to prepare nanostructured CCO349 films through tailoring the film thickness and the lattice mismatch.

As a final experimental investigation intending to quantify the prepared CCO349 films, we have carried out measurements of the temperature dependence of the resistivity (ρ - T) and Seebeck coefficient (S - T). Figure 9 presents the typical ρ - T results for the films without dewetting. It can be seen that the amorphous film behaves as a semiconductor

FIG. 9. ρ - T results on different films. (a) 700 °C-annealed film with two coatings; the inset contains the corresponding magnetoresistance results. (b) 800 °C-annealed film with four coatings; the inset shows the enlarged result. (c) 850 °C-annealed film with four coatings; the inset contains the corresponding magnetoresistance. (d) 900 °C-annealed film with four coatings; the inset shows the enlarged results at higher temperatures.

with enhanced resistivity; whereas, all the crystallized films have an insulator-metal (IM) transition near 100–200 K, as shown in the inset of Fig. 9(b), which is similar to the results on single crystals,¹⁹ bulk ceramics,⁴ and films prepared by PLD (Refs. 6–8) and can be attributed to the spin-density-wave (SDW) effects. However, the IM transition temperature is higher than that of the bulk CCO349 samples,⁴ which may be related to the residual stress in the derived films.²⁰ In order to verify this presumption we have prepared CCO349 films on Si substrates with a native SiO₂ amorphous layer. The XRD results on the CCO349/SiO₂/Si film annealed at 850 °C with four coatings is shown in inset (a) of Fig. 10, which gives the evidence that the film is randomly oriented,

meaning that there is no residual stress in this sample. The ρ - T result for the CCO349/SiO₂/Si film is shown in inset (b) of Fig. 10, which shows that the IM transition temperature is about 85 K, similar to the results on CCO349 ceramics⁴ or single crystals,¹⁹ meaning that the enhanced IM temperature of the CCO349 films on LAO substrate can be attributed to the residual stress effects. Moreover, for all the crystallized films it is observed that the resistivity at 300 K is about 10–20 $\text{m}\Omega\text{ cm}$, which is slightly larger than that of the films derived by PLD, but is similar to that of the films prepared by CSD,⁹ which can be attributed to large amounts of defects in the CSD-derived films. For the CCO349/LAO films with different layers, it should be pointed out that the resistivity is very large and cannot be measured in the PPMS for the one layer film, and the resistivity at 300 K of the two and three layer films is ~ 50 –100 and 30–50 $\text{m}\Omega\text{ cm}$, respectively, which means that the percolation effect also plays an important role on the resistivity. Moreover, from the enlarged ρ - T curve as shown in the inset of Fig. 9(d), one can also observe that there is a transition located at T_{cross} that is attributed to the Co-ion spin state crossover.⁴ Additionally, above T_{cross} , there is another IM transition denoted as T^* , which corresponds roughly to the Mott limit $k_F l = (\hbar/e^2)c/\rho$, with the Fermi wave vector k_F and the mean free path l ($c = 10.70 \text{ \AA}$).¹⁹

In order to check the effects of the applied magnetic field on the properties of the prepared films, the ρ - T under 7 T was measured. The temperature dependence of the magnetoresistance (MR) $[(\rho_{7T} - \rho_{0T})/\rho_{0T} \times 100\%]$ for typical films is plotted in the inset of Fig. 9(a) and the inset of Fig. 9(c). It can be seen that for the film annealed at 850 °C the MR is

FIG. 10. S - T results on different films. Inset (a) contains the XRD results on CCO349/SiO₂/Si, and inset (b) is the ρ - T results on CCO349/SiO₂/Si.

negative and positive for $T < 20$ K and $T > 20$ K, respectively, which is related to the ferrimagnetism and the Lorentz force, respectively.⁴ For the amorphous film, the results show that the MR is positive within the whole measured temperature range, which suggests that the ferrimagnetic order cannot be formed in amorphous film.

For TE materials, one important parameter is the Seebeck coefficient S . In our experiments, S is measured using the four-probe steady state mode on PPMS, and the results are shown in Fig. 10. It can be seen that for the crystallized films, the $S(T)$ behaves as metals, whereas, for the amorphous film the $S(T)$ is semiconductorlike. Moreover, the $S(300$ K) is ~ 154 and ~ 80 $\mu\text{V/K}$ for the films annealed at 850 and 900 $^{\circ}\text{C}$ on LAO, respectively; the S value at low temperatures is improved larger than 300 $\mu\text{V/K}$ for the amorphous film, which can be attributed to the enhanced effective mass.⁹ In cobalt-based TE materials, it is usual to find that the S is intimately relative to the Co-ion spin states. In NaCo_2O_4 , if the low-spin (LS) states of Co^{3+} and Co^{4+} are stable, the g_3 and g_4 will be 1 and 6, where g_3 and g_4 are the numbers of the configurations of the Co^{3+} and Co^{4+} ions, respectively; when the LS states of a Co^{3+} are stable and the LS and high-spin (HS) states of Co^{4+} are close in energy, the g_3 and g_4 will be 1 and 12.²¹ Additionally, a photoemission study has revealed that the ratio of $\text{Co}^{3+}/\text{Co}^{4+}$ is 1:2.²² If the above two spin states are possible, then the S can be estimated using the Heikes formula, and the results are 94 and 154 $\mu\text{V/K}$, which is close to our results on CCO349/LAO film annealed at 900 and 850 $^{\circ}\text{C}$, respectively, suggesting that it is possible to tune the S values through control of the annealing temperature in the CSD processing.

IV. CONCLUSION

A simple chemical solution deposition using cheap precursors was used to prepare $\text{Ca}_3\text{Co}_4\text{O}_9$ films on LaAlO_3 single-crystal substrates. The results showed that when the thickness was lower than a certain value the dewetting phenomenon occurred, which originates from the large interface stress between the film and the substrate. The simulation results showed that it was possible to fabricate nanostructured $\text{Ca}_3\text{Co}_4\text{O}_9$ films through tailoring the film thickness

and the lattice mismatch. The microstructures and physical properties of the wetting films clearly suggest that chemical solution deposition can be used to prepare $\text{Ca}_3\text{Co}_4\text{O}_9$ films, which opens up a simple route to fabricate large-area Co-based oxide thermoelectric films.

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- ¹K. Koumoto, I. Terasaki, and R. Funahashi, *MRS Bull.* **31**, 206 (2006).
- ²T. M. Tritt and M. A. Subramanian, *MRS Bull.* **31**, 188 (2006).
- ³R. Funahashi, I. Matsubara, H. Ikuta, T. Takeuchi, U. Mazutani, and S. Sodeoka, *Jpn. J. Appl. Phys., Part 2* **39**, L1127 (2000).
- ⁴A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, and B. Raveau, *Phys. Rev. B* **62**, 166 (2000).
- ⁵Y. F. Hu, W. D. Si, E. Sutter, and Q. Li, *Appl. Phys. Lett.* **86**, 082103 (2005).
- ⁶H. W. Eng, W. Prellier, S. Herbert, D. Grebille, L. Michin, and B. Mercey, *J. Appl. Phys.* **97**, 013706 (2005).
- ⁷Y. F. Hu, W. D. Si, E. Sutter, and Q. Li, *Appl. Phys. Lett.* **87**, 171912 (2005).
- ⁸A. Pautrat, H. W. Eng, and W. Prellier, *Phys. Rev. B* **72**, 233405 (2005).
- ⁹I. Matsubara, R. Funahashi, M. Shikano, K. Sasaki, and H. Enomoto, *Appl. Phys. Lett.* **80**, 4729 (2002).
- ¹⁰K. Brunner, *Rep. Prog. Phys.* **65**, 27 (2002).
- ¹¹J. P. Locquet, J. Perret, J. Fompeyrine, E. Machler, J. W. Seo, and G. Van Tendeloo, *Nature (London)* **394**, 453 (1998).
- ¹²V. A. Schukin and D. Bimberg, *Rev. Mod. Phys.* **71**, 1125 (1999).
- ¹³C. Teichert, *Phys. Rep.* **365**, 335 (2002).
- ¹⁴M. Coll, K. Gazquez, A. Pomar, K. Sandiumenge, and X. Obradors, *Phys. Rev. B* **73**, 075420 (2006).
- ¹⁵R. W. Schwartz, T. Schneller, and R. Waser, *C. R. Chim.* **7**, 433 (2004).
- ¹⁶I. Szafraniak, C. Harnagea, R. Scholz, S. Bhattacharyya, D. Hesse, and M. Alexe, *Appl. Phys. Lett.* **83**, 2211 (2003).
- ¹⁷P. A. Langjahr, T. Wagner, F. F. Lang, and M. Ruhle, *J. Cryst. Growth* **256**, 162 (2003).
- ¹⁸J. H. Kim and F. F. Lange, *J. Mater. Res.* **14**, 1626 (1999).
- ¹⁹B. C. Zhao, Y. P. Sun, W. J. Lu, X. B. Zhu, and W. H. Song, *Phys. Rev. B* **74**, 144417 (2005).
- ²⁰P. Limelette, V. Hardy, P. Auban-Senzier, D. Jerome, D. Flahaut, S. Herbert, R. Fresard, Ch. Simon, J. Nouderm, and A. Maignan, *Phys. Rev. B* **71**, 233108 (2005).
- ²¹W. Koshibae, K. Tsutsui, and S. Maekawa, *Phys. Rev. B* **62**, 6869 (2000).
- ²²S. Hirata, M.S. Thesis, University of Tokyo, 2004.