

Nanoarchitecting to induce flexibility in $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films for thermoelectric applications



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Aim: The growth of flexible $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films with better mechanical flexibility, while sustaining high thermoelectric efficiency comparable to that of its pristine bulk values.

Motivation behind this study

Organic materials

- Flexible
- Low output power density
- Unstable

Inorganic materials

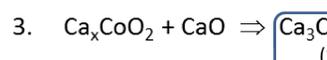
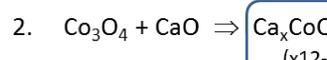
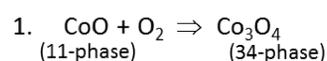
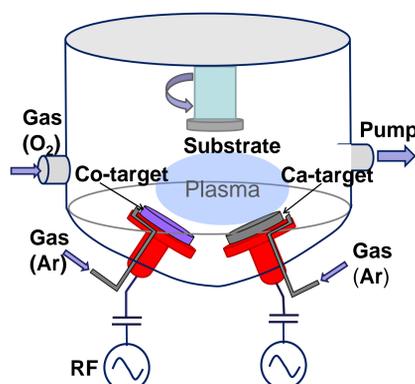
- Stable
- High output power density
- Rigid and brittle

Future demand

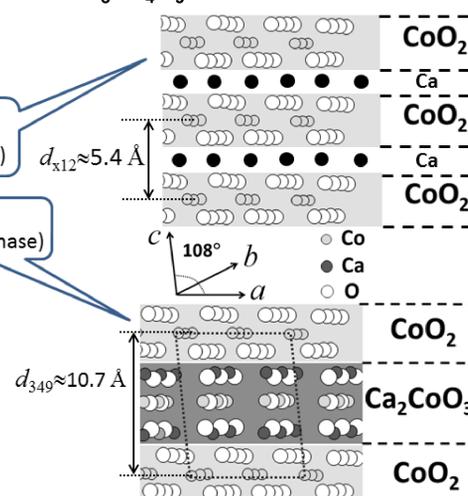
- Stability
- High output power density
- Flexibility

CaO-CoO film deposited by rf-magnetron reactive cosputtering

As-deposited CaO-CoO film reactively annealed to form final phase of $\text{Ca}_3\text{Co}_4\text{O}_9$



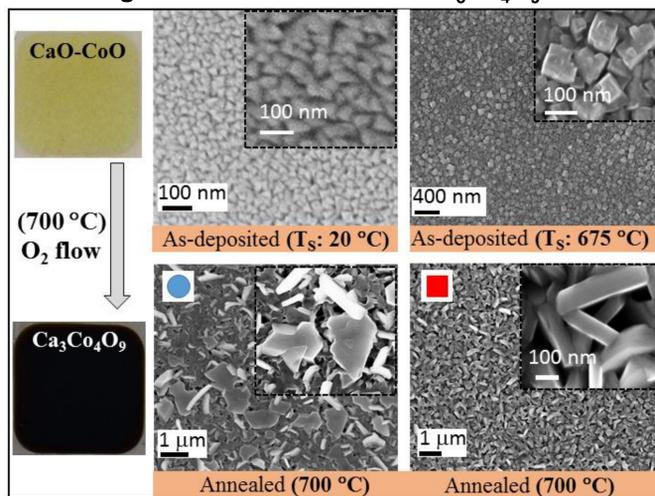
Three stage phase transformation occur during annealing



Advantage of mica as substrate

- Mica can sustain high deposition temperature of 675 °C.
- Mica can serve as flexible substrate.
- Thin film can be transferred onto other flexible platform from mica substrate.

Tailoring of nanoarchitecture of $\text{Ca}_3\text{Co}_4\text{O}_9$ film



- Architecture of the film depends on the nanostructural evolution during thermally induced phase transformation during annealing.
- The pattern of nanostructural evolution depends on the relative arrangements of CaO and CoO phases in the as-deposited films, which is controlled by deposition temperature.

Flexible $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film

Different steps for developing flexible film from sample (T_s : 675 °C)



Step 1: Film is attached to a glass slide by wax



Step 2: Substrate thickness is reduced to 100 μm.



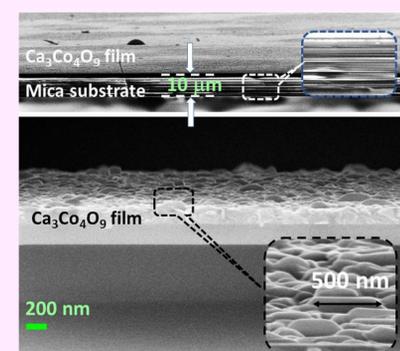
Step 3: Thickness is reduced to 10 μm.



Step 4: Immersed in acetone for 12 h to dissolve wax.



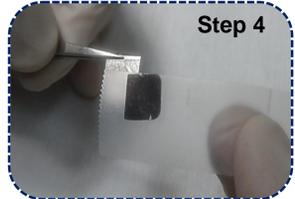
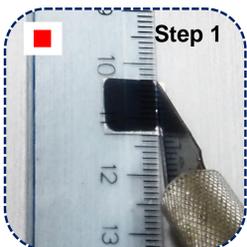
Cross section SEM image of the flexible film



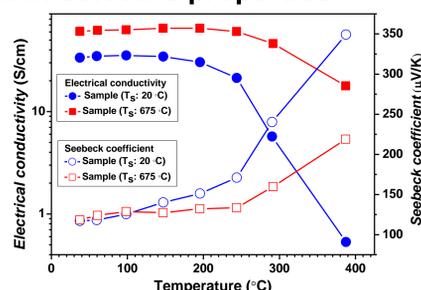
- Vertical alignment of the grains improve the mechanical flexibility of the film.
- Substrate thickness being 10 μm the film is easily bendable.

Transfer of $\text{Ca}_3\text{Co}_4\text{O}_9$ film onto other flexible platform

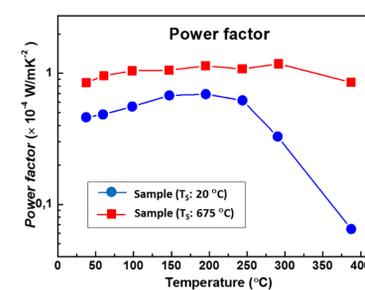
- The film is transferred onto the adhesive tape following the steps shown below.



Thermoelectric properties



- Best value of electrical resistivity is obtained as 16.46 mΩ.cm near room temperature from sample (T_s : 675 °C).
- Power factor above $1 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ is achieved from the same sample.



Conclusion:

- A nanoarchitecting approach has been demonstrated to induce flexibility in $\text{Ca}_3\text{Co}_4\text{O}_9$.
- Mica acts as flexible substrate.
- Maximum power factor $\sim 1.2 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ near 300 °C.

Reference

- B. Paul, J. L. Schroeder, S. Kerdsonpanya, N. V. Nong, N. Schell, D. Ostach, J. Lu, J. Birch, P. Eklund, *Advanced Electronic Materials* **1**, 1400022 (2015).