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V. Rogé, A. Stolz, N Dumuis, Fabian Delorme, Fabien Giovannelli, et al.. Synthesis and characterisation of a planar thermoelectric generator based on $\text{Ca}_3\text{Co}_4\text{O}_9$ and SrTiO_3 thin-films. Journées Nationales sur les Technologies Emergentes en micronanofabrication (JNTE), Nov 2017, Orléans, France. hal-01920288

HAL Id: hal-01920288

<https://hal.science/hal-01920288v1>

Submitted on 13 Nov 2018

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Synthesis and characterisation of a planar thermoelectric generator based on $\text{Ca}_3\text{Co}_4\text{O}_9$ and SrTiO_3 thin-films.

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Topic: Synthesis of materials

Abstract: We propose the fabrication of a planar thermoelectric generator based on the serial alignment of p-type $\text{Ca}_3\text{Co}_4\text{O}_9$ and n-type SrTiO_3 thin films. The physico-chemical characterization of each material, grown by pulsed-laser deposition, as well as the thermoelectric performances of the device, are presented and discussed.

I. INTRODUCTION

With the worldwide increasing concern about renewable energy production, thermoelectric generators have attracted much attention due to their remarkable properties to directly convert heat into electricity through the Seebeck effect. The Seebeck effect is the conversion of heat into electricity due to the charge carriers migration in materials induced by a temperature gradient. The Seebeck effect (S) can be expressed as follow:

$$S = \frac{\Delta V}{\Delta T} \quad (1)$$

Where ΔV corresponds to the potential difference induced by the charge carriers migration, and ΔT the temperature difference across the material. Currently, the use of thermoelectric generators is limited to applications where their high cost and low efficiency are balanced with their reliability and long lifetime, like spacecraft power supply or other niche applications [1]. A thermoelectric generator is consists in multiple thermoelectric modules themselves composed of a p-type and n-type material connected in series.

Up to now, the most performing thermoelectric generators are based on semi-conductor materials such as Bi_2Te_3 , PbTe , SiGe , or Skutterudite phases [2]. Their performances are defined by the dimensionless figure of merit (ZT), expressed as follow:

$$ZT = \frac{\sigma S^2 T}{\kappa} \quad (2)$$

Where σ corresponds to the electrical conductivity, S the Seebeck effect, T the temperature and κ the thermal conductivity. The most performing commercialized thermoelectric materials are composed of harmful element for the flora and fauna, and elements like tellurium or germanium are rare and expensive. Increasing the thermo-power conversion efficiency in large temperature windows

(close to ambient up to high temperatures) with cheaper and safer materials are the main obstacles to overcome for the large-scale use of thermoelectric generators. A figure of merit around 2 would lead approximately to a 10% efficiency [3]. Thus, intensive research is needed for new materials development and thermoelectric generators design.

Among the promising new material families, misfit layered metal oxides like cobaltite appear as good candidates for safer and competitive p-type thermoelectric materials. The misfit structure helps scattering phonons without impairing the electrical conductivity [4]. For this reason, they are also called phonon glass-electron crystal structures. $\text{Ca}_3\text{Co}_4\text{O}_9$ is particularly interesting due to its stability at high temperature and low cost. It is a p-type semi-conductor with high Seebeck coefficient ($S \approx 130 \mu\text{V.K}^{-1}$) and low electrical resistivity (60 S.cm^{-1}) [5]. Concerning n-type metal oxides, researches focus mainly on the electron-doped SrTiO_3 perovskite. SrTiO_3 is a cubic perovskite stable at high temperature and relatively inexpensive, composed of element easily available in natural resources. The electrical properties of SrTiO_3 can be tuned by incorporating oxygen vacancies in the crystal lattice, or by substituting the Sr^{2+} or Ti^{3+} ions with other cations like La^{3+} or Nb^{5+} respectively [6],[7]. The undoped SrTiO_3 stoichiometric crystal exhibits insulating properties, while a metallic behavior appears in oxygen deficient or La^{3+} and Nb^{5+} doped crystal.

To achieve the synthesis of $\text{Ca}_3\text{Co}_4\text{O}_9$ and SrTiO_3 thin films, the pulsed-laser deposition (PLD) process has been chosen for its capability to produce high quality thin films with controlled stoichiometric composition, morphologies and thickness.

In this work, we study the feasibility of $\text{Ca}_3\text{Co}_4\text{O}_9$ and SrTiO_3 thin films based thermoelectric generators in planar configuration. First, we would like to emphasize the $\text{Ca}_3\text{Co}_4\text{O}_9$ films growth and characterization by PLD, especially the effect of pressure, substrate temperature and the role of the thermal annealing after deposition. Secondly, we present the thermoelectric generator characterization on a home-made ZT meter equipment.

II. EXPERIMENTAL SECTION

One side polished (100) silicon wafers with thermal SiO_2 layers (600 nm) grown on top of the surface, as well as one side polished c-cut sapphire were used as substrates. The $\text{Ca}_3\text{Co}_4\text{O}_9$ (99.9%) and La-doped SrTiO_3 (0.05% La) PLD targets were provided by the GREMAN laboratory. The

pure SrTiO₃ (99.9%) PLD target was purchased from NEYCO. The PLD process was performed in a homemade reactor with a Nd-YAG laser from Continuum company, operating at 10 Hz, 25 mJ (4 J.cm⁻² on the target), 10 ns and 266 nm. The deposition parameters for Ca₃Co₄O₉ and SrTiO₃ films varied from 1.10⁻⁶ mbar to 1.10⁻¹ mbar for the pressure, and from 20 to 750 °C for the temperature. When annealing steps were necessary for Ca₃Co₄O₉ films, it was performed in an oven working at atmospheric pressure (air) at 600 °C. Thermoelectric characterizations were performed in a home-made ZT-meter, working with a CO₂ laser as heating source and a Keitley 2700 multimeter for the potential difference measurement (this ZT meter equipment will be described in further details in the final publication during the conference).

III. RESULTS AND DISCUSSION

As depicted in the Figure 1, the thermoelectric generator is composed of three Ca₃Co₄O₉ p-type “legs” and three SrTiO₃ n-type “legs” connected in series with platinum contacts.

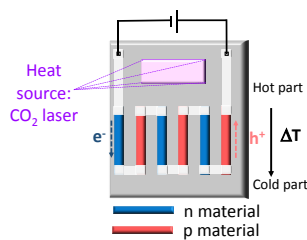


Figure 1. Representative schema of planar thermoelectric generator.

In order to achieve homogeneous, compact, smooth and crystalline Ca₃Co₄O₉ thin films, it requires the growth of an amorphous Ca₃Co₄O₉ at relatively low temperature of 500 °C and pressures below 1.10⁻² mbar. The highest pressures and temperatures lead to Ca₃Co₄O₉ crystalline films, whereas low pressures and temperatures lead to amorphous structures. However, the SEM pictures (not shown here) reveal rough surfaces for high growth temperatures whereas the low temperatures lead to smoother surfaces.

After the thermal annealing (600 °C, air) of a smooth amorphous film (i.e. the one grown at 500 °C, 1.10⁻² mbar), we observe a clear textured crystallization into the Ca₃Co₄O₉ phase, with a surface roughness better than the films grown at 700 °C during the PLD process (Figure 2).

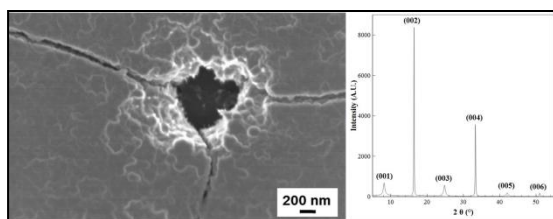


Figure 2. SEM image and XRD diffractogram of Ca₃Co₄O₉ thin film annealed at 600 °C at air.

Concerning the SrTiO₃ films, we pointed out that low pressures are mandatory to achieve the best conductive films, whereas the temperature range to reach the crystalline cubic phase was less critical (between 500°C and 750 °C) compared to Ca₃Co₄O₉ films. Further characterizations

(electrical resistivity, Rutheford backscattering, Hall effect, Seebeck coefficient) of the two materials will be presented during the conference.

Based on these results, we designed a thermoelectric generator proof of concept, as presented on the Figure 1, using masks during the Ca₃Co₄O₉ and SrTiO₃ deposition to obtain “legs”. On Figure 3, we can observe a SEM picture of one Ca₃Co₄O₉ leg.

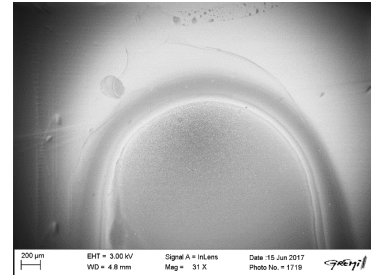


Figure 3. SEM picture of a Ca₃Co₄O₉ thin film deposited on SiO₂/Si with a mask .

The thermoelectric power generation of this device will be tested on the ZT meter to characterize its performances as thermoelectric generator for microelectronic operating at low temperature (bellow 200 °C).

IV. CONCLUSION

The synthesis and characterization of a thermoelectric generator based on Ca₃Co₄O₉ and SrTiO₃ thin films grown by pulsed-laser deposition are presented. We want to describe the complex growth of Ca₃Co₄O₉ thin films and propose a solution to reach films with the best properties for thermoelectric applications. After mastering the growth of both Ca₃Co₄O₉ and SrTiO₃ by PLD, we would like to present the proof of concept for the thermoelectric generator device and its associated thermoelectric properties.

V. ACKNOWLEDGMENT

The authors would like to thank the French Région Centre for the financial support of the METEO project.

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