On-chip thermoelectric module comprised of oxide thin film legs

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Abstract

On-chip thermoelectric thin film modules containing 5 legs of n -type ($\text{Al}_{0.02}\text{Zn}_{0.98}\text{O}$) and 5 legs of p -type ($\text{Ca}_3\text{Co}_4\text{O}_9$) were fabricated on Al_2O_3 , SrTiO_3 single crystal, and fused silica substrates by pulsed laser deposition technique. Performance of modules was evaluated using ad-hoc customized system where the module was set vertically for temperature gradient. The maximum output power (P_{max}) was obtained on Al_2O_3 (0001) single crystal substrate with temperature difference (ΔT) = 230°C (T_h = 300°C): P_{max} = 29.9 pW. The value of maximum output power increases with increase of temperature difference (ΔT). These results are encouraging for the practical applications of

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thermoelectric oxide thin films.

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1. Introduction

In the recent years, oxide materials have increasingly gained attention in the thermoelectric community due to their promising characteristics: high stability at high temperatures (600°C and more), low price, non-toxicity. Consequently, oxides have been started to be regarded as alternative to inter-metallic and alloys for the fabrication of modules to convert waste heat into electricity. Reviews on thermoelectric bulk oxides [1, 2, 3, 4, 5, 6] show that the thermoelectric performance is still poor in comparison with metallic materials and requires improvement. The performance of thermoelectric materials is determined by the dimensionless figure of merit $ZT = \sigma \cdot S^2 \cdot T / \kappa$ (S: Seebeck coefficient; σ : electrical conductivity; κ : thermal conductivity; T: absolute temperature)[7].

Still the thermoelectric performance of the best *n*-type bulk oxide $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$ ($ZT = 0.65$ at 1273 K) [8] and the best *p*-type $\text{Ca}_{2.8}\text{Lu}_{0.15}\text{Ag}_{0.05}\text{Co}_4\text{O}_9$ ($ZT = 0.6$ at 1100 K) [9] is lower than the benchmark $ZT = 1$, which is commonly reached by metallic materials (whose generally decompose or become unsta-

ble at around 600°C). Nevertheless, several contributions related to modules based on ZnO as *n*-type material and Ca₃Co₄O₉ as *p*-type material have been published [9, 10, 11]. Depending on the number of legs and difference of temperature (ΔT), the typical output power (P) of these modules is several milliwatts at high temperatures: $P = 3.7 \sim 423$ mW; $\Delta T = 260 \sim 658$ K, T_h (temperature of hot-end of the module) = 773~1100 K, as summarized in [9].

These values are promising and there is a wide room for improvement related to the reduction of high internal resistance of the module and enhancement of the performance of the materials. As a paradigm for any kind of thermoelectric material [12, 13], the introduction of nano-sized defects leads to improved phonon scattering, consequently decreasing thermal conductivity and improving ZT [14, 15, 16, 17, 18]. This pattern has have been followed successfully in nano-structured BiTe/PbTe multilayers [19], AgPbSbTe alloys embedded with Ag-rich nano-inclusions [20], porous Al-doped ZnO [21], atomically substituted oxides with natural nano-sized precipitates [8, 9], nano-engineering [22, 23], and many more [24, 25]. The main issue is to control the size and distribution of the nano-structures (nano-layers, pores, precipitates, secondary phases) inside the thermoelectric matrix, which have

36 been found quite hard in bulk materials [14, 15, 16, 17]. The control of
 37 nano-structure and defects in epitaxial thin films through strain engineering
 38 and artificial defects are at the advanced stage in several categories of func-
 39 tional oxides such as multiferroics [26], ferroics [27], superconductors [28],
 40 electronics [29], and more [30]. This approach is still at preliminary stage in
 41 thermoelectric oxide thin films [31].

42 Anyway, high thermoelectric performance has been reported by various
 43 groups in *p*-type [32, 33, 34] and *n*-type [35, 36, 37, 38] nano-engineered
 44 oxide thin films, including our previous reports on Al-doped ZnO [39, 40].
 45 The natural consequence is the use of thermoelectric thin films as legs for
 46 planar modules. However, to the date, very few reports on fabrication of
 47 thermoelectric oxide modules based on thin films have been published [41,
 48 42, 43]. According to our best knowledge, only one evaluation of thin films
 49 module performance was reported: $P = 0.4 \text{ pW/K}^2$ in a planar module based
 50 on CuO and ZnO legs obtained by sputtering on Al_2O_3 substrate [43].

51 The aim of this work is to make progress in exploring the field, describing
 52 planar modules based on *n*-type ZnO and *p*-type $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film legs
 53 fabricated by pulsed laser deposition (PLD) technique. The role of substrate
 54 is investigated by evaluating the performance of the module on Al_2O_3 , SrTiO_3

55 (STO) and fused silica.

56 **2. Experimental Technique**

57 The on-chip thermoelectric module was fabricated by pulsed laser deposi-
58 tion (PLD) technique using Nd:YAG laser (266 nm). Two pellets (20 mm in
59 diameter and 3 mm in thickness) of $\text{Zn}_{0.98}\text{Al}_{0.02}\text{O}$ (AZO) and $\text{Ca}_3\text{Co}_4\text{O}_9$ were
60 prepared by spark plasma sintering and used as the targets in PLD chamber
61 for the thin films deposition.

62 At first, laser was focused on $\text{Ca}_3\text{Co}_4\text{O}_9$ target and *p*-type legs were de-
63 posited on 10 mm $\times$ 10 mm substrates by superimposing a custom nickel
64 mask (Ni mask) (Micron Co. Ltd, Osaka) using the following conditions:
65 energy density of about 1.1 J/cm²; deposition period of 30 min; deposition
66 temperature (T_{dep}) = 700°C on Al_2O_3 and fused silica substrates, T_{dep} =
67 650°C on STO substrates; oxygen pressure of 200 mTorr; laser pulse fre-
68 quency 10 Hz; substrate-target distance about 35 mm; rotation speed of the
69 target 30 % rpm. Optimal deposition temperatures for $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films
70 were chosen after screening from 550°C to 850°C: films not showing any X-ray
71 diffraction (XRD) peak were discarded.

72 Then, Al-doped ZnO (AZO) target was moved under the laser beam and

73 ablated to fabricate n-legs after shifting the custom Ni mask. Conditions
 74 used for AZO legs were same as for $\text{Ca}_3\text{Co}_4\text{O}_9$ legs except for higher energy
 75 density (about 4.2 J/cm^2) and lower T_{dep} (400°C on Al_2O_3 substrate, 300°C
 76 on STO and fused silica substrates) as previously tested to produce the best
 77 performance thin films. In both steps, the cooling from deposition temper-
 78 ature to room temperature was accomplished in 300 Torr of oxygen. Gold
 79 electrodes were sputtered using a custom Ni mask at room temperature after
 80 completion of PLD routes in order to achieve the electrical connection of the
 81 p-n couples. The sequence of thin film deposition for on-chip thermoelectric
 82 module has been shown in Fig. 1 (a) along with schematic side view of mod-
 83 ule. The schematic top view of module and a picture of the module surface
 84 are shown in Fig. 1(b) and 1(c), respectively.

85 Due to geometrical constraints in some of the characterization facilities,
 86 the n -type and p -type films were prepared separately on small pieces ($0.4 \times$
 87 $7 \times 0.05 \text{ cm}^3$ slabs) of the three kinds of substrates using the same conditions
 88 described above. Structural characterization was performed by XRD (Bruker
 89 D8 Discover) and morphology was checked by scattering electron microscopy
 90 (SEM) (JEOL, FESEM). The thickness and in-plane roughness were ob-
 91 tained by a Keyence VK-9700 3D microscope. The electrical conductivity

92 was measured in the temperature range 300 K to 600 K by a custom-built
93 four-point-probe technique consisting of a current source (ADCMT 6144), a
94 temperature controller (Cryo-con 32) and a nano voltmeter (Keithley 2182A).
95 Seebeck coefficient was measured in the temperature range 300 K to 600 K
96 with a commercially available system (MMR Technologies Inc.).

97 Performance of modules was evaluated using ad-hoc customized system
98 where the module was set vertically in between alumina (heat source; however
99 heat is generated by hot plate) and aluminum nitride (heat sink) sheet. A
100 schematic of experimental set-up is shown in figure 1 (d), where T_h and
101 T_c are hot-end and cold-end temperature of the module, respectively. The
102 generation of thermoelectric voltage was checked by heating the module from
103 the bottom on a hot plate (T_h up to 300°C) while monitoring voltage (by
104 Keithley 2182A) and temperature by means of two K-type thermocouples
105 controlled by TR-KN units (AS-ONE).

106 This thermoelectric voltage is measured by using a variable resistance (in
107 the range of 10 ohm to 10^6 ohm) as external load and power was evaluated at
108 different temperatures. External variable resistance was set for load purpose
109 and the output power was evaluated at different temperatures for each value
110 of external resistance. The maximum output power at each temperature was

determined as the peak of the polynomial bell-shape fitting the experimental points. A difference of temperature between the two sides of the module was generated by setting a water beaker as a coolant on the top of Aluminum nitride sheet.

3. Results and Discussion

AZO thin films served as an *n*-type leg for the on-chip thermoelectric module. We extensively reported about thermoelectric performance of AZO in our previous works [39, 40, 44]. High-quality *c*-axis oriented films were grown on single crystals (Al_2O_3 and STO) as well as on amorphous fused silica. The optimum conditions of AZO thin films were reported for enhanced thermoelectric performance with respect to the corresponding bulk material. The thermoelectric parameters of AZO thin film on single crystal Al_2O_3 , STO and amorphous fused silica substrates are summarized in table 1 from our previous reports. The AZO thin film deposited on fused silica substrates shows the best thermoelectric performance in temperature range 300 K to 600 K.

We further extended our work to prepare a *p*-type leg for on-chip thermoelectric module. For this purpose, we focused on thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$

thin films on various substrates such as single crystal Al_2O_3 , STO and amorphous fused silica substrates. The deposition condition were screened and, as main difference respect to AZO, deposition temperature was higher while energy density of the laser beam focused on the target was about a quarter. Thin films of $\text{Ca}_3\text{Co}_4\text{O}_9$ are *c*-axis grown as found in XRD patterns reported in Figure 2. The SEM images of films surface are reported in Fig. 3. All films shows randomly disposed elongated grains with similar dimensions on STO and fused silica while size is bigger on Al_2O_3 even if deposition temperature was almost same on the three different substrates.

Within the time-frame of our project, the preliminary thermoelectric parameters for $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films are presented in table 2. The thermoelectric properties of our grown $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films on various substrates are also plotted in Fig. 4. Figure 4(a) shows the electrical conductivity vs temperature (σ -T) characteristics of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films measured by four probes technique. Thin film grown on Al_2O_3 substrates shows the best electrical conductivity about 12 S/cm at 300 K and 18 S/cm at 600 K. The reason of superior performance of the film grown on Al_2O_3 respect to the film on STO may be reached in the lower mismatch: 1.02% on Al_2O_3 and 2.06% on STO. It is possible to calculate the linear concentration of dislocations gener-

148 ated at any film/substrate interface by $L = [(a_f - a_s)/a_{avg}^2]$, where a_f , a_s , and
 149 a_{avg} are the thin film, substrate, and average lattice parameter, respectively
 150 [39]. Assuming a regular distribution, the areal density of dislocations can
 151 be calculated as $N = L^2$. The value of N varies with substrate and crystalline
 152 orientation. In our system, the value of N is $1.74 \times 10^{11} \text{ cm}^{-2}$ on STO and
 153 $2.87 \times 10^{10} \text{ cm}^{-2}$ on Al_2O_3 . The lower amount of dislocations on Al_2O_3
 154 induces a moderate electron scattering, giving higher electrical conductivity.
 155 Another factor to be taken into account is the lower amount of scattering
 156 at grain boundaries due to the bigger size of the grains in the film grown
 157 on Al_2O_3 . The value of electrical conductivity of our $\text{Ca}_3\text{Co}_4\text{O}_9$ samples is
 158 however much lower than our bulk of same composition (108 S/cm at 300 K
 159 and 132 S/cm at 600 K)

160 The Seebeck coefficient vs temperature (S-T) characteristics of $\text{Ca}_3\text{Co}_4\text{O}_9$
 161 thin films are measured in temperature range 300 K to 600 K. The average
 162 response for thin film grown on fused silica shows higher value of Seebeck
 163 coefficient than the thin films grown on single crystal substrates (STO and
 164 Al_2O_3). The expected trend of substrate dependence of Seebeck coefficient
 165 is opposite to electrical conductivity and plotted in Fig. 4(b). The values
 166 of Seebeck coefficients are positive which reflects that the thin films are p -

167 type thermoelectric. The value of Seebeck coefficients at 300 K and 600 K are
168 shown in table 2. The comparison shows that the value of Seebeck coefficient
169 for thin film is higher than the value of our bulk of same composition which
170 is a good indication of the thermoelectric performance of thin film. The best
171 Seebeck coefficients are about $160 \mu\text{V/K}$ at 300 K and $186 \mu\text{V/K}$ at 600 K
172 for thin films grown on fused silica substrates. Values on both crystalline
173 substrates are closer, and all values are in the same range of typical values
174 reported in literature for thin films or bulk $\text{Ca}_3\text{Co}_4\text{O}_9$.

175 The performance of thin film is evaluated by the value of power fac-
176 tor (P.F.) which can be calculated by $\sigma.S^2$. The value of power factor for
177 $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films are plotted in Fig. 4(c) with the function of tempera-
178 ture. The values of power factor for 300 K and 600 K are also summarized in
179 table 2. The values on thin films are about two orders lower than the value
180 of power factor for our bulk of same composition. This can be solely at-
181 tributed to the lower electrical conductivity. The best performance is shown
182 by thin films grown on Al_2O_3 (0001) single crystal substrates due to higher
183 electrical conductivity and the lower mismatch which helps to enhance the
184 properties. The values of power factor are 0.024 mW/m.K^2 at 300 K and
185 0.045 mW/m.K^2 at 600 K. The value of power factor can be improved by op-

timizing the growth condition which includes varying partial oxygen pressure during deposition, deposition temperature and rotation speed of the target.

Further we calculated the figure of merit (ZT) of thin films by $\sigma.S^2.T/\kappa$. We have followed conservative approximation and used two approximations to estimate the value of ZT of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films. i) we have used the thermal conductivity of bulk material of same composition at room temperature other than the thermal conductivity of thin films which is not available in literature at the moment. Due to quantum confinement effect the value of thermal conductivity of thin film will be much smaller than the thermal conductivity of bulk material of same composition; ii) the behavior of ZT at elevated temperatures is estimated using thermal conductivity at room temperature ($\kappa=\kappa_{300}$) which defines ZT as $\sigma.S^2.T/\kappa_{300}$ other than $\sigma.S^2.T/\kappa$: since the thermal conductivity of single crystals decreases with increasing temperature due to increased phonon-phonon scattering, we assert this as a conservative approximation [45].

In the case of AZO films, we were able to measure the value of thermal conductivity at room temperature, then we followed the second approximation [45]. The results for *p*-type $\text{Ca}_3\text{Co}_4\text{O}_9$ can be seen in table 2, including the value of thermal conductivity of corresponding bulk, which decreased

205 from 2.08 W/m.K (at 300 K) to 1.78 W/m.K (at 600 K). The figure of merit
 206 vs temperature (ZT vs T) characteristics is plotted in Fig. 4(d) and summa-
 207 rized in table 2. The best performance is shown by thin films deposited on
 208 Al_2O_3 substrates at 700°C which is ZT about 0.004 at 300 K and 0.013 at 600
 209 K. With reference of our previous reports of AZO thin films, if the thermal
 210 conductivity of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film is an order smaller than the bulk, we will
 211 be able to achieve the value of ZT an order higher than the present values
 212 and that will be about 0.04 at 300 K and 0.13 at 600 K. This prediction will
 213 result, the value of ZT for $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film, an order higher than the bulk
 214 of same composition.

215 Combining the conditions of optimized AZO films and preliminary condi-
 216 tions of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films, we have fabricated the on-chip thermoelectric
 217 module on each substrate. We have used 5 legs of each *n*-type and *p*-type
 218 thermoelectric thin films on Al_2O_3 , STO and fused silica substrates, and then
 219 we compared the performance of the three modules. The real on-chip ther-
 220 moelectric module deposited on Al_2O_3 is shown in Fig. 1(c). Performance of
 221 on-chip thermoelectric module was evaluated using ad-hoc customized sys-
 222 tem where the module was set vertically for temperature gradient (Fig. 1
 223 (d)). Figure 5(a) shows a schematic of the temperature gradient direction

224 and Fig. 5(b) shows the snapshot of the ad-hoc assembly of module mount
 225 together with Al_2O_3 foam. The power generation characteristics of on-chip
 226 thermoelectric module is shown in Fig. 6(a) - 6(c) on various substrates and
 227 temperature difference ($\Delta T = T_h - T_c$) of heat source (T_h) and sink (T_c). The
 228 temperature of heat source varies from 100°C to 300°C and keeping heat
 229 sink temperature near 0°C . In this range of temperature, the load external
 230 resistance was changed from 100 ohm to 1 Mohm. The maximum output
 231 power (P_{max}) increase with increase in ΔT and the highest output power is
 232 achieved while keeping higher ΔT .

233 For $T_h = 300^\circ\text{C}$, the summarized plot is presented in Fig. 6(d) for various
 234 substrates and overall the best performance of on-chip thermoelectric was
 235 obtained on Al_2O_3 . The value of maximum output power, P_{max} , of on-chip
 236 module is about 0.3 pW on FS, 17.9 pW on STO, and 29.9 pW on Al_2O_3
 237 substrates, being at the same level reported by Zappa et. al. on CuO/ZnO
 238 thin film module [43].

239 The output power of our thin film module is still far from typical output
 240 power of modules based on bulk oxides [9], however this result is encouraging
 241 for the practical applications of thermoelectric oxide thin films including the
 242 modules on flexible substrates for ubiquitous harvesting of the waste heat.

243 The future work will be focused on enhancing the performance of on-chip
244 module which can be done by following steps - i) enhancing thermoelectrical
245 performance of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film [32]; ii) improving dimensions of n -type
246 and p -type legs of module [46]; iii) analyzing the material for electrical con-
247 tact of n -type and p -type legs of module.

248 4. Summary

249 The preliminary on-chip thin film thermoelectric module of n -type Al-
250 doped ZnO and p -type $\text{Ca}_3\text{Co}_4\text{O}_9$ has been successfully fabricated. The per-
251 formance of on-chip thermoelectric module is evaluated by ad-hoc customized
252 system where the on-chip module is set vertically. The output power increases
253 with increase in temperature gradient. The best performance is shown by the
254 module which is fabricated on Al_2O_3 single crystal substrates. The largest
255 output power was obtained with temperature gradient $\Delta T = 230^\circ\text{C}$ ($T_h =$
256 300°C): $P_{max} = 29.9 \text{ pW}$ on Al_2O_3 . The further improvement is possible op-
257 timizing the growth condition of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films in such a way that
258 electrical conductivity should enhance.

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Table 1: Electrical and thermal parameters for thin films and bulk pellet of AZO at 300K/600K as n -type leg for on-chip thermoelectric module. All the values were reported in our previous works as referred.

Substrate and T_{dep}	Electrical Conductivity (σ)	Seebeck Coefficient S	Power Factor (PF)	Thermal conductivity (κ)	Figure of Merit (ZT)	Reference
$^{\circ}\text{C}$	S/cm	$\mu\text{V/K}$	10^{-3} W/m.K^2	W/m.K		
STO 300	310/382	-65/-121	0.13/0.55	6.5	0.006/0.05	[31], [39]
Al_2O_3 400	299/291	-58/-126	0.10/0.43	6.897	0.004/0.04	[31], [39]
Fused Silica 300	601/923	-62/-111	0.23/1.2	4.89	0.014/0.13	[31], [40]
Bulk AZO	206/152	-132/-150	0.35/0.34	34	0.0035/0.014	[11]

Table 2: Electrical and thermal parameters for thin films and bulk pellet of $\text{Ca}_3\text{Co}_4\text{O}_9$ at 300K/600K as p -type leg for on-chip thermoelectric module. Bulk values were reported in our previous work as referred.

Substrate and T_{dep}	Electrical Conductivity (σ)	Seebeck Coefficient S	Power Factor (PF)	Thermal conductivity (κ)	Figure of Merit (ZT)	Reference
$^{\circ}\text{C}$	S/cm	$\mu\text{V/K}$	10^{-3} W/m.K^2	W/m.K		
STO 650	0.03/1.23	134/167	$5 \times 10^{-5}/0.003$	2.08	$7.5 \times 10^{-7}/0.001$	This work
Al_2O_3 700	12/18	143/158	$0.02/0.045$	2.08	0.004/0.013	This work
Fused Silica 700	0.11/2.44	160/186	$2.8 \times 10^{-4}/0.008$	2.08	$4 \times 10^{-5}/0.002$	This work
Bulk $\text{Ca}_3\text{Co}_4\text{O}_9$	108/132	129/148	0.18/0.29	2.08/1.78	0.023/0.099	[11]

272 **Figure Captions**

273 **Figure 1:** (a) 3D sketch of the thin film module with sequence of thin
274 films and electrodes deposition; (b) schematic top view of the module and
275 (c) photograph of the module after fabrication of thin films legs and gold
276 contacts; (d) Schematic of module testing set-up with a load resistor (R).

277 **Figure 2:** XRD pattern of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films deposited on STO,
278 Al_2O_3 , and fused silica substrates at corresponding deposition temperature.

279 **Figure 3:** SEM images of the surface of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films deposited
280 on (a) STO; (b) Al_2O_3 ; (c) fused silica.

281 **Figure 4:** Temperature dependent transport and thermoelectric proper-
282 ties of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films deposited on several substrates with correspond-
283 ing deposition temperature (T_{dep}): (a) electrical conductivity; (b) Seebeck
284 coefficient; (c) Power factor; (d) A dimensional figure of merit.

285 **Figure 5:** (a) Flow of heat gradient direction during testing of ther-
286 moelectric module; (b) image of thermoelectric module disposed vertically
287 during the power output test.

288 **Figure 6:** Output power of thin film thermoelectric modules at increasing
289 temperatures (a) on Al_2O_3 ; (b) on STO and (c) on fused silica; (d) output
290 power of the modules fabricated on the three different substrates at $T_h =$

²⁹¹ 300°C.

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Step 4: Electrodes

Step 3: AZO thin film

Step 2: $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film

Step 1: Substrate

(a)

Side View

(b)

Top View

(c)

(d)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

(a)

(b)

(a) On-chip thermoelectric module on Al_2O_3 substrates

(b) On-chip thermoelectric module on F.S. substrates

(c) On-chip thermoelectric module on STO substrates

(d) On-chip thermoelectric module (Th 300°C)

Figure 6