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Material optimization via combinatorial deposition and analysis for thermoelectric thin films

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ABSTRACT

This work presents a custom, high-throughput combinatorial approach for the optimization of thermoelectric thin films consisting of materials with complex chemistry and structures (e.g., the layered misfit cobaltite, $Ca_3Fe_xCo_{4-x}O_9$). Combinatorial thin films with graded compositions are produced on 100 mm Si wafers from multiple target materials using pulsed laser deposition. Film thickness and composition are mapped as a function of wafer location. Crystal structures are determined using x–y mapping XRD analysis with specially designed algorithms for automated peak location and analysis. Thermoelectric properties, specifically the Seebeck coefficient and the electrical resistivity, are screened using a custom designed automated probe system. By combining the rapid synthesis of many compositions and structures simultaneously using combinatorial deposition and automated analytical tools capable of spatial mapping, trends in material performance are shown to be quickly obtained primarily due to the elimination of one-at-a-time synthesis and analysis. The possible approaches for such complex multivalent combinatorial optimization of thin films are identified and discussed.
For the $Ca_3Fe_xCo_{4-x}O_9$ system presented, variations to the thermoelectric power factor are dominated by changes in the electrical resistivity. Enhancements to the Seebeck coefficient are observed due to the incorporation of Fe into the $Ca_3Fe_xCo_{4-x}O_9$ structure; however, this improvement is overshadowed by increases in the electrical resistivity due to variations in film thickness and the presence of secondary phases (Co_3O_4 and $Ca_2Fe_2O_5$) which result from increasing Fe content and off-axis pulsed laser deposition.

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1. Introduction

Thermoelectric materials convert thermal energy to electrical energy and vice versa via the Seebeck effect. Generators based on thermoelectric materials are unique in that the conversion of energy is a solid-state process; there are no moving parts or chemical reactions. This allows thermoelectric generators to be used in harsh environments. One primary example is the radioisotope thermoelectric generators used in deep space probes. The Cassini and Voyager missions have used thermoelectric power generation for 100,000+ h of continuous operation without failure or maintenance.

Thermoelectric generators can also be used for waste heat recovery in automotive, aerospace, and industrial applications. In each of these areas, significant amounts of energy are lost to the environment in the form of heat. This represents a tremendous opportunity for system-level efficiency gains as thermoelectric generators can be used to convert a portion of that wasted heat into electricity. The key is to identify efficient thermoelectric materials that can operate in the required temperature range.

Oxide thermoelectric materials, such as $Ca_3Co_4O_9$, Na_xCoO_2, ZnO, and $CaMnO_3$, are made of low cost, abundant elements with low toxicity and are stable in air at high temperatures [1–4]. Unfortunately, these materials generally possess low carrier mobilities and high lattice thermal conductivities due to the ionic bonding of light atoms [5]. However, doping $Ca_3Co_4O_9$ with Fe has been shown to simultaneously improve all three thermoelectric properties [6–9]. Adding small amounts of Fe ($x \le 0.25$) to misfit cobaltite $Ca_3Fe_xCo_{4-x}O_9$ has been shown not only to decrease the electrical resistivity by increasing carrier concentration, but also simultaneously increase the Seebeck coefficient through effective mass enhancement and decrease the thermal conductivity through phonon scattering [7]. This results in an improvement in the figure-of-merit (zT) leading to a more efficient thermoelectric material. Fe has a limited solubility in $Ca_3Co_4O_9$ and bulk samples with concentrations as low as $x = 0.25$ contain secondary phases, specifically $CaFe_2O_5$ and Co_3O_4, which negatively impact the thermoelectric properties, specifically electrical resistivity [6].

Exploring the complex structure–composition-property relationship of oxide phase thermoelectrics using bulk materials generally requires

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time-consuming one-at-a-time syntheses and analyses of myriad compositions using solid-state techniques. Alternatively, the combinatorial screening approach, described in this work, combines combinatorial deposition of a wide variety of compositions on a single wafer and rapid analytical techniques to determine material composition, structure, and properties. This technique drastically increases research speed and efficiency.

1.1. Figure-of-merit and power factor

Thermoelectric material research has focused primarily on improving energy interconversion efficiency via improvements to the thermoelectric material properties. Ioffe proposed a figure-of-merit parameter, z, shown in Eq. (1), to describe the relationship among the relevant material properties: electrical conductivity, thermal conductivity, and Seebeck coefficient [10].

$$zT = \frac{\alpha^2 T}{\rho(\kappa_L + \kappa_e)} \quad (1)$$

Where zT is the material figure-of-merit, ρ is the electrical resistivity, κ_L is the lattice thermal conductivity, κ_e is the electronic thermal conductivity, α is the Seebeck coefficient, and T is the absolute temperature.

The figure-of-merit allows thermoelectric materials with widely varying properties to be compared and can be used to determine the efficiency with which a material can convert thermal energy into electrical energy. The conversion efficiency of a thermoelectric material increases not only when the zT increases due to material property improvements but also when the temperature gradient increases [10]. Therefore, thermoelectric materials that are stable at high temperatures and capable of maintaining large temperature gradients are desirable.

While there is considerable discussion about thermal property measurement, particularly for thin films, measurements of the Seebeck coefficient and the electrical resistivity are more straightforward [10]. These two parameters can be combined into the power factor (α^2/ρ). While not a complete picture of thermoelectric performance, the power factor can be used to quickly screen promising thermoelectric phases for further study.

Generally, materials with improved thermoelectric performance exhibit enhanced properties throughout a broad temperature range. This means that for a given material system the changes observed in the thermoelectric performance at room temperature will be similar to the trends at elevated temperatures. Not only is this shown to be true for the oxide material system [7,9,11,12], but also shown for other high temperature systems including skutterudites [13], half-Heusler [14], Zintl [15–17] and $Na_{1-x}Pb_mSb_yTe_{m+2}$ [18] material systems. While exceptions may occur, the emphasis of this method is to rapidly determine material compositions on which to focus further research efforts, including characterization of the thermoelectric performance throughout the entire temperature range.

1.2. Pulsed laser deposition

Pulsed laser deposition (PLD) is used to deposit gradated films to locate promising compositions of thermoelectric materials for further analysis. The biggest advantage of PLD for combinatorial studies over other thin film deposition techniques, such as chemical vapor deposition or molecular beam epitaxy, is the ability to transfer complex stoichiometries from a target material to the film [19]. PLD also provides unique nanostructuring in thin films, including texturing and dimensional reduction, which can further enhance the TE performance [20]. The electrical resistivity of $Ca_3Co_4O_9$ is anisotropic with respect to the crystallographic orientation [21]. Highly textured $Ca_3Co_4O_9$ thin films have been successfully deposited on a wide variety of substrates yielding power factors which are improved with respect to cold pressed and sintered bulk materials primarily due to the reduction of electrical resistivity [22,23]. Several groups are working on transitioning these thin films directly into thermoelectric generators [1,20,24]; however, this enhancement via texturing can also be realized in bulk $Ca_3Co_4O_9$ via hot pressing, spark plasma sintering [25], or tape casting [26–28].

As shown in Fig. 1, the combinatorial deposition proceeds with a small amount (less than a unit cell) of each of the target materials being deposited sequentially. Generally, after one rotation through all of the targets, the amount deposited at all locations in the combinatorial spread area should be around 1 unit cell in thickness. This is repeated until the desired film thickness is achieved.

This style of deposition closely resembles interval PLD growth mode as the amount of material deposited in each pass is less than a unit cell [19]. The kinetic energy of the species in the plume should be kept relatively high to encourage ballistic mixing [19,29,30]. This will create a strong interfacial bond between the film and the substrate and allow for homogenization of sequentially deposited sub-unit cell layers.

2. Experimental details

2.1. Combinatorial film preparation

PLD targets for pulsed laser deposition were created using solid state ceramic processing techniques. For the $Ca_3Co_4O_9$ and $Ca_3Fe_{0.25}Co_{3.75}O_9$ PLD targets, stoichiometric amounts of $CaCO_3$, Co_3O_4, and Fe_2O_3 (Alfa Aesar, 99.95%+ metals basis) were combined prior and the mixtures were reacted at 1163 K in air for 210 h with 3 intermediate grindings. Cold pressed targets were annealed at 1073 K for 2 h in flowing O_2. The relative density of both sintered oxide targets was greater than 70%.

Combinatorial pulsed laser depositions were conducted using an LPX210i excimer laser ($\lambda = 248$ nm, 20 ms pulse) with a fixed target to substrate distance of ~50 mm. $Ca_3Fe_xCo_{4-x}O_9$ combinatorial films were deposited using 1.7 J/cm^2 laser fluence, 4 Hz, 973 K substrate temperature, and 40 Pa (300 mTorr) O_2 background gas. Films were deposited on 100 mm Si(100) wafers (n-type, 0–100 Ω-cm, 500 μm thick). The film was created by alternating depositions of two targets — $Ca_3Co_4O_9$ at wafer position 0°, followed by $Ca_3Co_{3.75}Fe_{0.25}O_9$ at wafer position 180°. This was repeated to make the film thickness at the center of the wafer ~350 nm. After deposition, the film was annealed for 1 h at 773 K in 0.1 MPa (1 atm) O_2.

2.2. Thickness, composition, and XRD mapping

Film thickness data for the depositions was determined experimentally as a function of wafer position. First, a pattern (2 mm × 5 mm rectangles with 1 mm borders on all sides) was etched into the film using photolithography. The $Ca_3Fe_xCo_{4-x}O_9$ film was etched using a solution of 5 wt.% citric acid, 1 wt.% phosphoric acid, and 0.25 wt.% H_2O_2 (balance water). Then, the step height was measured at various locations using an Alphastep D-120 profilometer. Composition data was collected via EDS on a FEI Quanta SEM capable of x–y mapping 100 mm wafers and equipped with an Octane Silicon Drift Detector. X-ray diffraction was performed on the combinatorial wafer using a Bruker D8 Discover (Cu radiation; $K\alpha_1\lambda = 0.1540598$ nm) equipped with a Lynxeye 1D detector. Theta–two theta (θ–2θ) data was collected from $5° < 2\theta < 100°$ at various x–y locations on the wafer.

3. Combinatorial method and model development

3.1. Thickness and composition model

UV excimer lasers, similar to the one used in our experiments, have a rectangular beam profile with a cross section on the order of a few square millimeters. This rectangular beam profile leads to anisotropy in the spatial distribution of the material flux which can be described as the product of two 1D power law angular distributions, as shown in Eqs. (2) and (3) [31]. This equation can also be used to model a thermal