Thin Film Growth Effects on Electrical Conductivity in Entropy Stabilized Oxides

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Abstract

Entropy stabilization has garnered significant attention as a new approach to designing novel materials. Much of the work in this area has focused on bulk ceramic processing, leaving entropy-stabilized thin films relatively underexplored. Following an extensive multi-variable investigation of polycrystalline (Mg\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}Zn\textsubscript{0.2})O thin films deposited via pulsed laser deposition (PLD), it is shown here that substrate temperature and deposition pressure have strong and repeatable effects on film texture and lattice parameter. Further analysis shows that films deposited at lower temperatures and under lower oxygen chamber pressure are \textasciitilde 40x more electrically conductive than otherwise identical films grown at higher temperature and pressure. This electronic conductivity is hypothesized to be the result of polaron hopping mediated by transition metal valence changes which compensate for oxygen off-stoichiometry.

Keywords: Entropy Stabilized, Resistivity, Lattice, SEM, TEM, Morphology

1 Introduction

High entropy alloys are a well established field of work with applications in metallic property optimization.\textsuperscript{[13]} In 2015, entropy stabilization was first applied to ceramic oxides\textsuperscript{[2]} and a five cation material system, (Mg\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}Zn\textsubscript{0.2})O, was found to crystallize reversibly into a uniform rock salt structure when heated to a sufficiently high temperature (\textasciitilde 875°C for the equimolar composition); when quenched to room temperature, the material system retains the rock salt structure. Cation distribution within the entropy stabilized rock salt structure has been shown to be truly random and homogeneous over long range, with some local distortions in the oxygen anion sublattice in order to accommodate the different cation sizes\textsuperscript{[3]} (Fig. 1). This entropy stabilized oxide has since been the focus of many studies, and versions of it have been reported to work well as an Li-ion conductor\textsuperscript{[4, 5]} and anode for Li-ion batteries\textsuperscript{[6]}, and redox material for thermochemical water splitting\textsuperscript{[7]}. Extremely high dielectric constants have also been reported\textsuperscript{[8, 9]}. The majority of these studies have been carried out on samples processed as bulk ceramics\textsuperscript{[10, 11]}, thin film studies are less common. The seminal work on these oxides\textsuperscript{[12]} showed an inverse relationship between both pO\textsubscript{2} and substrate temperature on out-of-plane tetragonal lattice parameter in epitaxial thin films of (Mg\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}Zn\textsubscript{0.2})O. Another thin film study used pulsed laser deposition (PLD) to show that entropy stabilized thin films of (Mg\textsubscript{x}Co\textsubscript{y}Ni\textsubscript{z}Cu\textsubscript{w}Zn\textsubscript{v})O can be tailored to engineer long range magnetic order and shows promise for enhancing exchange coupling\textsuperscript{[13]}. PLD has also been used to explore structural stabil-
energy of 200mJ were selected as standard for continued study. Both Zn and Cu from the (Mg$_{0.2}$Co$_{0.2}$Ni$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$)O target ablated in slightly lower concentrations than the other cations in the target, so separate CuO and ZnO targets were used to supplement depositions and grow stoichiometrical films, with ZnO requiring approximately 1.2% more laser pulses and CuO requiring approximately 3.5% more. Substrate temperature and chamber (oxygen) pressure combinations of 200°C, 300°C, or 450°C and 50 mT or 100 mT were explored. The rest of this report focuses on samples deposited with a substrate temperature of 200°C or 450°C and oxygen pressure set to 50mT or 100mT; trends reported here are consistent across the rest of the deposition space. Substrates used in this study were Borosilicate (Eagle2000) glass (EXG) and Pilkington NSG TEC 15 Glass with approximately 340nm of fluorinated tin oxide coating (FTO, 13-15 Ω/sq).

2.3 Sample Characterization

Samples were characterized using a variety of methods to validate their structure and composition before analyzing properties. Each thin film was measured in 44 different locations in order to confirm consistency of the film across the 2" x 2" substrate.

Crystal structure and phase purity of PLD Targets were confirmed using a PANalytical PW3040 X-ray Diffractometer (XRD) and Cu-κ radiation. XRD data for films were collected at the Stanford Linear Accelerator on Beamline 1-5 (measurements calibrated with a LaB$_6$ standard, however BL 1-5 does not correct for tilt of sample. Data presented here is measured to be approximately 0.08 Q low) and with a Bruker D8 Discover with Cu-κ radiation. Composition was confirmed using a Fischer XUV x-ray fluorescence tool (XRF) in addition to energy dispersive spectroscopy (EDS) data collected using a FEI Talos F200X transmission electron microscope (TEM), which was also used for bright field and high angle annular dark field imaging. Top electrical contacts were deposited through a shadow mask using a Temescal FC2000 e-beam tool, with 10nm of Ti and 50nm of Pt. Current density measurements were taken with a Keithley 2400 source meter. Microstructure of the top down was taken with an FEI Nova 630 SEM, while the cross sections were imaged using a Hitachi 4800 SEM in order to manage sample charging. The opensource COMB1gor package for commercial Igor Pro was used for data analysis and visualization.

3 Results and Discussion

3.1 Crystal structure

Arrays of XRF measurements (Table 1) confirm that cations are homogeneously distributed in these thin films, at least on a mesoscopic scale. On average, samples are all slightly lower in Cu than other measurable cations; Mg could not be measured using XRF because its atomic mass is too low for the instrument to identify. The slightly lower amounts of Cu do not alter the structure and are consistent across all depositions, so it does not appear to be the cause for the property trends reported here.

XRD confirms that the rock salt structure of the films matches that of the desired rock salt ESO (Mg$_{0.2}$Co$_{0.2}$Ni$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$)O (Fig. 3), similar to the target (Fig. 2), and suggests that all
constituent cations are most likely randomly and homogeneously dispersed throughout the cation FCC sublattice. Films grown on EXG at 200°C under 50mT pO$_2$ exhibit moderate levels of texturing in the (111) growth direction (Fig. 3) where the correct cubic lattice constant \( a \) is 4.22 Å. It is interesting to note the difference in the thin film lattice constant with that of the (Mg$_2$Co$_2$Ni$_2$Cu$_2$Zn$_2$O) target (4.3 Å), indicating that the thin film growth on an amorphous substrate exhibits some lattice compression over that of the target material in all directions. Figure 4 shows changes in film texture with substrate temperature and chamber pressure of oxygen. Note that all of the lattice constants for samples shown here are smaller than that of the bulk ESO target lattice constant (4.3 Å, Fig. 2). The samples in this study do not show the specific out of plane lattice compression identified in earlier work on this material system because the films here are not epitaxially constrained by the substrates; rather they show a cubic compression where both the \( a \) and \( c \) lattice constants are slightly compressed relative to the bulk ceramic.

Figure 5 illustrates different types of growth observed in this study, and their respective definitions. Three distinct growth types have been identified based on texture and lattice constant and will be the focus for the remainder of this paper. Each of these three types of films is grown on FTO substrates and will be referred to as “HTHP” (Higher Temperature, Higher Pressure), “LTLP” (Lower Temperature, Lower Pressure), and “HTLP” (Higher Temperature, Lower Pressure) and are defined as follows: HTHP and HTLP both have a lattice constant of 4.22 Å while LTLP samples have a lattice constant of 4.19 Å. The Lattice Compression Factor is used here to quantify the degree of crystallographic texturing; LF = 0 is purely random, LF = 100% is perfectly textured. All LF values in this paper were calculated from an integration across 4 degrees of Chi from 2d detectors. Films designated as “HTHP” show a (111) texture with an LF = 31% and are grown at 100mT pO$_2$ and 450°C; “LTLP” films show (111) texturing as well, but have an LF = 41% and are grown at 50mT pO$_2$ and 200°C; “HTLP” films show (002) texture with an LF = 36% and are grown at 50mT pO$_2$ and 450°C. This information is summarized in Table 2.

![Chi Integrated Counts](MgCoNiCuZnO (111) Polycrystalline Rock Salt)

Table 1: Average cation concentration from 44 points across each sample per XRF.

| Sample Type | Co (at%) | Ni (at%) | Cu (at%) | Zn (at%) | Mg (at%) |
|-------------|----------|----------|----------|----------|----------|
| HTHP        | 26 ± 0.4 | 25 ± 0.4 | 23 ± 0.4 | 25 ± 0.4 | –        |
| HTLP        | 26 ± 0.5 | 24 ± 0.5 | 23 ± 0.5 | 26 ± 0.5 | –        |
| LTLP        | 25 ± 0.4 | 25 ± 0.5 | 23 ± 0.5 | 26 ± 0.4 | –        |

Fig. 3 Top: High resolution XRD data collected at SLAC on BL 1-5 show the (111)-textured polycrystalline growth of a cubic rock salt with moderate (111) crystallographic texture on a borosilicate glass substrate. Bottom: Integrated counts across approximately 4 degrees through the center of the measured Chi emphasize the (111) texture of the sample.

3.2 Microstructure

SEM images revealed notably different microstructures among these three growth types. The HTLP textured samples, grown at 450°C and 50mT O$_2$, have almost circular grains growing in a largely columnar fashion, as seen in Fig. 6c,d. HTHP samples, grown at 450°C and 100mT O$_2$, also show columnar grains, however these grains exhibit a triangular shape at the surface consistent with the cube corners of a (111)-textured rock salt, shown in Fig. 6e,f. LTLP samples, grown at 200°C and 50mT O$_2$, do not exhibit columnar growth, and grains show no consistent morphology, seen in Fig. 6g,1. It is not unusual for films grown at higher temperatures to exhibit more regular columnar growth as the higher substrate temperature provides additional mobility for atoms to settle into a somewhat lower energy configuration before being fully “quenched”. The HTHP films are grown under usual XRD scans using the 2θ positions of the center of at least two peaks from different crystal plane families. This lattice compression for LTLP samples indicates some fundamental difference in these samples from the HTHP and HTLP samples. All LTLP samples grown on FTO have an isotropic compression greater than 2.7%, while HTLP and HTHP samples have an isotropic compression no greater than 2.1%.
Crystallographic texturing was found to change as a result of deposition temperature and partial pressure of oxygen. Overall, samples grown at 450°C have a tendency to grow with an (002) texture when grown on either EXG or FTO substrates and at both 50 mT and 100 mT pO₂. Samples grown at 300°C show (111) texturing at both 50 mT and 100 mT and on either EXG or FTO substrates. Samples grown at 200°C with 50 mT or 100 mT all show (111) texturing along with peaks at higher 2θ, indicating a shorter lattice constant for these films. Samples grown on EXG glass versus FTO-coated glass are designated by “EXG” and “FTO”.

Uniformity of the cation distributions is shown with an EDS map across a HAADF image in Fig. 7. The microstructures and z-contrast seen in Fig. 7 are consistent throughout the thickness of each film, suggesting that any variation in electrical response between these three types of samples arises from something other than cation segregation. A TEM and atom probe tomography study on bulk samples of the same composition showed that annealing could lead to Cu segregation, but no evidence of such segregation is observed here.

It has been established that phase decomposition of bulk samples begins in an annealing process around 600°C, which may suggest some likelihood of phase segregation for film samples grown at higher temperatures. Such segregation is accompanied by XRD peak broadening. Films in this study exhibit consistent full width half maximum values for XRD peaks across all deposition temperatures (Fig. 8). Thus, neither XRD nor TEM (imaging and EDS) show any evidence of cation segregation in these films.

3.3 Electrical Properties
Films of approximately 1 µm thickness were grown on FTO coated borosilicate glass in order to enable through-thickness current density measurements. Measuring the conductivity of these films as a function of applied voltage reveals different electrical behavior for the LTLP samples from the other two types of films. Measurements collected on HTLP samples reveal a nonlinear re-
The hopping distance is shorter for polarons in the compressed lattice, making the hop more likely to occur and increasing electrical conductivity. There is also a clear correlation between higher electrical conductivity (Fig. 9) and non-columnar microstructure (Fig. 9), but the exact origin of this correlation is not clear.

The results presented here are consistent with previously published data as represented by Table 2. One publication has reported electrical conductivity in bulk samples to be 5 MΩcm, which is consistent with the resistive measurements in the present study. Presumably, the bulk samples from this previous publication also have a random microstructure similar to that of the LTLP samples, but the improved density of a thin film over a bulk processed sample would increase electrical conductivity and explain the lower resistance values measured in our thin film samples. Other publications do not present resistivity data, however they do show a consistent lattice constant across non-epitaxial samples. The epitaxial samples grown on MgO (001) substrates are reported to have a much smaller lattice constant (4.15 Å). Nanopowder samples show some tetragonal distortion not seen in other bulk studies.

4 Conclusions

Single phase rock salt (Mg0.2Co0.2Ni0.2Cu0.2Zn0.2)O samples can be deposited efficiently using PLD, and temperature and partial pressure of oxygen can be used to control crystallographic texturing. Thin film samples grown on FTO with a lattice constant of 4.22 Å and either (111) or (002) texturing (HTHP or HTLP, respectively) demonstrate a nonlinear electrical resistance between 1 and 3 MΩcm, while (111) textured films with a lattice constant of 4.19 Å (LTLP) are significantly more conductive, with resistivity values on the order of 50 kΩcm. The primary difference in microstructure for resistive versus conductive films is that the conductive films have a more random grain structure with nucleation occurring throughout the films, and the resistive films show...
columnar grains with nucleation occurring primarily at the substrate. It is unclear whether this is correlation or causation. The smaller lattice constant also indicates a shorter hopping distance for any induced charge in the material system. This, coupled with a likely oxygen off-stoichiometry during growth, makes polaron hopping a likely candidate for the conduction mechanism. Ultimately, this work indicates that thin film samples grown on FTO at 50mT P2O5 and a substrate temperature of 200°C are more electrically conductive than samples grown at higher substrate temperatures with a more organized microstructure by approximately 40x. The data presented here are consistent with previous reports on this material, but also shows that manipulating microstructure and crystal lattice can have dramatic effects on electrical conductivity.

Conflicts of interest
There are no conflicts to declare.

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Table 2 Summary of growth conditions and characteristics for all samples grown on FTO substrates and compared to previous works. *Note: LF and microstructure information for previous works have been approximated based on data provided in articles.

| Sample Type       | Pressure (mT P<sub>O</sub>)<sup>2</sup> | Temperature (°C) | Crystal Texture  | Lattice Constant (Å) | Lotgering Factor | Average Lattice Compression(%) | Microstructure | Resistance (kΩcm) |
|-------------------|---------------------------------------|------------------|-------------------|----------------------|------------------|-------------------------------|----------------|------------------|
| HTLP              | 100                                   | 450              | (002)             | 4.22                 | 30%              | 1.81 ± 0.24                  | Columnar       | 3400 ± 175       |
| HTHP              | 50                                    | 450              | (111)             | 4.22                 | 31%              | 1.59 ± 0.13                  | Columnar       | 1200 ± 50        |
| LTLP              | 50                                    | 200              | (111)             | 4.19                 | 41%              | 2.75 ± 0.06                  | Random         | 51 ± 0.65        |
| Bulk Polyxtal<sup>9</sup> | 20%                                   | 1000             | N/A               | 4.22                 | 0%               | 1.86                         | Random         | 5000             |
| Nanoparticles<sup>7</sup> | 20%                                   | 1000             | N/A               | a=4.17; c=4.2       | 0%               | 2.33                         | Random         | –                |
| MgO(001) <sup>13</sup> | 50                                    | 300              | (002)             | 4.15                 | 100%             | 3.49                         | Epitaxial       | –                |
| TF on Al<sub>2</sub>O<sub>3</sub> <sup>12</sup> | 50                                    | 500              | N/A               | 4.25                 | 0%               | 1.16                         | Random         | –                |