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Thermoelectric Properties and Microstructure of Cu−In−O Thin Films

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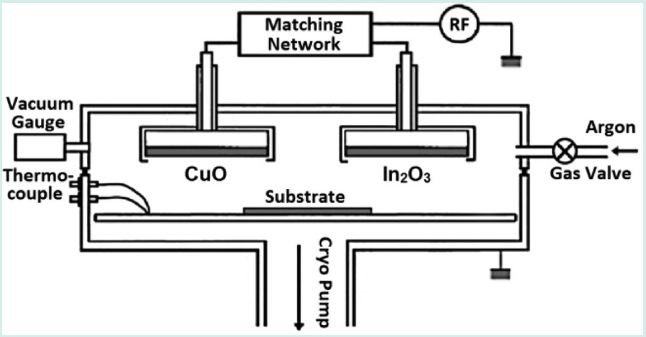
ABSTRACT: Combinatorial chemistry techniques were used to study the thermoelectric properties of sputtered thin films in the system copper oxide (CuO) and indium oxide (In_2O_3). Seven hundred seventy thin film thermocouples or combinatorial library elements were simultaneously deposited, each with a unique spatially dependent chemistry, based on the relative position of the thermocouples to each sputtering target. The resulting thermoelectric properties of each element were determined along with electrical resistivity as a function of composition. Energy dispersive spectroscopy was used to identify the composition of each thermo-element, and electron and X-ray diffraction were used to determine the degree of crystallinity and phases present. Transmission electron microscopy was used to characterize the microstructure of selected thermo-elements. A change in sign of the thermoelectric voltage was observed in the thermo-element containing 40.0 atomic percent indium, which suggests a change in the dominant carrier type occurred, from p-type to n-type. Based on this finding, the fabrication of thermoelectric p-n junctions using the same base Cu−In−O semiconductor appears feasible.



KEYWORDS: *thermoelectric, combinatorial chemistry, r.f. sputtering, copper indium oxide*

INTRODUCTION

Transparent conducting oxides (TCO) based on the material system Cu−In−O have been considered for applications such as flat panel displays, solar cells, and thin film transistors.[1,2] However, there have been relatively few studies of the thermoelectric properties of such materials to date.[3] Recently, considerable efforts have focused on the thermoelectric properties of oxides for applications such as energy harvesting, and power generation.[4−7] Compared with more conventional thermoelectric materials, oxides offer dramatically improved chemical stability in air, inherently higher carrier concentrations, and can be used at significantly higher temperatures. Both, indium oxide (In_2O_3), an n-type semiconductor, and In_2O_3 doped with +4 cations have shown promise as a thermoelectric material.[3,4] Copper oxide (CuO), a p-type semiconductor, has been considered for thermoelectric applications but has a relatively small band gap (1.2 eV) compared to In_2O_3,[8] which limits its use in high temperature thermoelectric applications. Furthermore, CuO changes oxidation state as a function of temperature.[9,10] However, alloys composed of CuO and In_2O_3 typically exhibit larger band gaps (on the order of 3 eV) than the stand-alone materials, making them more suitable for thermoelectric applications.

The delafossite ($Cu^{1+}In^{3+}O_2$) phase in the Cu−In−O system has received considerable attention for TCO applications.[11−13] This material can be "tuned" in such a way that either p-type or n-type carriers can dominate; for example, by substituting Sn^{4+} for indium or Ca^{2+} for copper.[12,14] The formation of this phase, or this phase with the inclusion of dopants, requires careful processing routes. These routes have been demonstrated successfully in previous studies.[14,15] However, few if any studies have focused on tuning the composition of the Cu−In−O compounds to achieve p-type or n-type dominant carriers in the base compound without the need for doping.

In this study, combinatorial chemistry techniques were used to fabricate thin film thermo-elements based on Cu−In−O prepared by sputtering from CuO and In_2O_3 targets. Combinatorial chemistry provides an efficient means to study an entire material system to rapidly narrow down the composition ranges of interest, depending on the material properties of interest. The combinatorial chemistry techniques were only used for screening purposes to narrow down the composition range between CuO and In_2O_3 where high magnitude thermoelectric voltages and low resistivities were observed. By combining a p-type semiconductor (CuO) with an n-type semiconductor (In_2O_3), thin film thermo-elements with either p-type or n-type character could be produced without relying on synthesizing the p-type or n-type autodoped $CuInO_2$ phase. The library thermo-elements were largely amorphous, and each was catalogued according to the atomic percentage of indium in the film. The relation between the library element composition and the dominant carrier type was characterized using the hot probe method. A transition from p-type to n-type conduction in the Cu−In−O system was observed at a film composition of 40.0 atom % indium. Energy dispersive spectroscopy (EDS) was used to determine the

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composition of each thermo-element, and the microstructures of both as-deposited and annealed thermo-elements were characterized using transmission electron microscopy (TEM). Electron diffraction in conjunction with TEM and X-ray diffraction (XRD) were used to determine the extent of crystallinity and the distribution of phases in select library thermo-elements.

RESULTS AND DISCUSSION

I. Thermoelectric Properties. The thermoelectric voltages of the Cu−In−O combinatorial library thermo-elements are summarized in Figure 1, which shows a map of thermoelectric voltage as a function of position. This map was a useful representation of the thermoelectric data in that the ranges containing the most promising n-type and p-type observed thermoelectric properties were identified prior to compositional analysis. By comparing the thermoelectric voltage and spatial distribution of the chemical composition, maps of thermoelectric voltage and resistivity as a function of composition were generated (Figure 2). Figure 2a shows a continuous transition from n- to p- conduction occurring at a film composition of 40.0 atom % indium. The CuO-In_2O_3 phase regions were superimposed over the data in Figure 2a. It indicates that the n- to p- transition occurs in an indium rich film, which falls within a two phase region of $Cu_2In_2O_5$ and In_2O_3. Since the films studied are largely amorphous, we suggest that a doping effect from the copper was responsible for the observed p-type behavior rather than from the formation of different phases in the material. Figure 2b indicates that little variation in the electrical resistivity was observed for thermo-elements containing 25.0−45.0 atom % indium. However, the thermoelectric response changed by nearly 3 mV over the same range. This phenomenon was likely due to the increased copper oxide content in the films as the indium content was varied from 45.0 atom % to 25.0 atom %. Also apparent in Figures 2a and b are horizontal "flat" regions (<15.0 atom % and >75.0 atom % indium) over which reliable thermoelectric measurements could not be obtained because of the high electrical resistivity of the thermo-elements in these composition ranges. Peak thermoelectric voltages for the library thermo-elements exhibiting p-type behavior and n-type behavior occurred between 20.0 and 25.0 atom % indium and 50.0−60.0 atom % indium, respectively. Plots of resistivity as a function of composition (Figure 2b) clearly show two minima at 25.0−30.0 atom % indium and 55.0−60.0 atom % indium, which are the same compositional ranges as the p-type and n-type materials with the largest thermoelectric responses. It is important to note here that the thermo-elements were not heated in air and thus the use of Cu−In−O thermoelectric materials in oxidizing ambient may be limited because copper undergoes an oxidation state change from +1 to +2 between 200 and 350 °C, which may alter the thin film properties.[9]

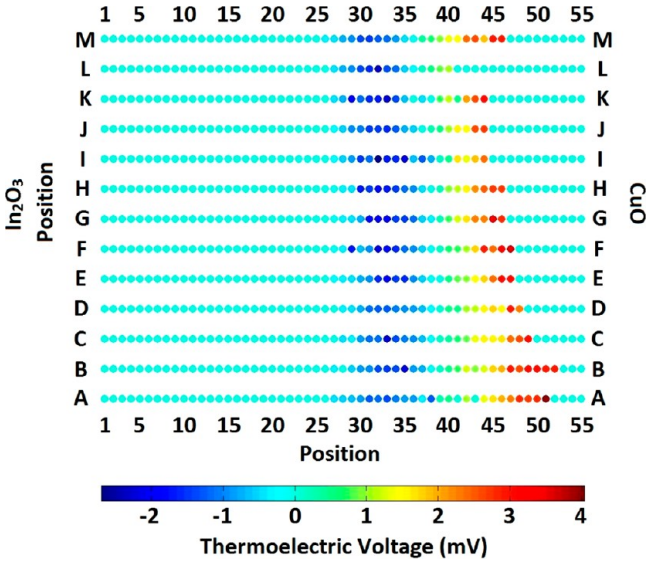

Figure 1. Map of the thermoelectric voltage as a function of position for nitrogen annealed combinatorial library (a temperature gradient of $T \sim 7.7$ K was applied across individual thermocouples).

II. Crystallography and Phases. XRD patterns of four nitrogen annealed Cu−In−O thermo-elements grown on sapphire substrates are shown in Figure 3. The two copper rich films (35.0 atom % In and 28.5 atom % In) exhibited a low intensity CuO {111} peak, and no other peaks were observed. As the indium oxide content in the thermo-elements increased (61.0 atom % In, 45.5 atom % In), the degree of crystallinity increased as determined by peaks corresponding to $Cu_2In_2O_5$

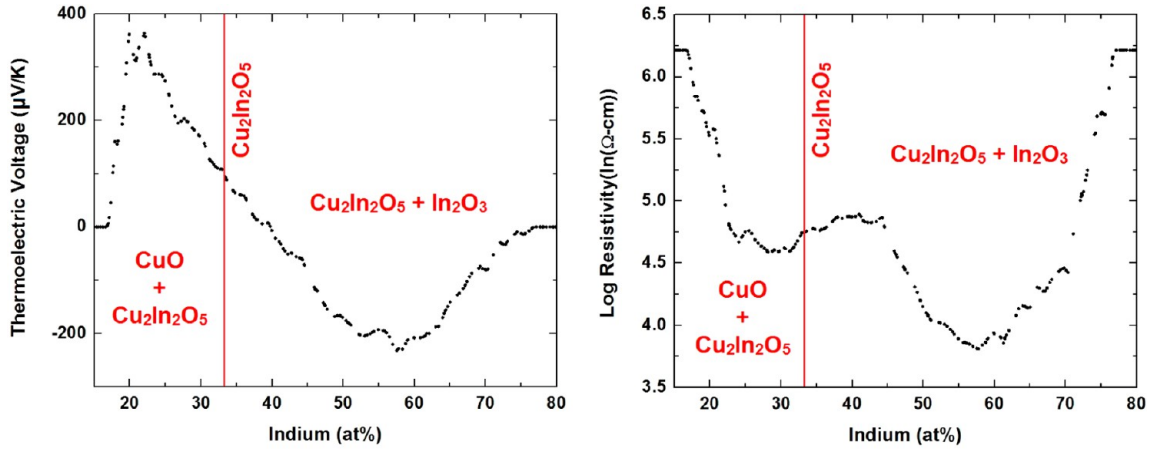

Figure 2. Plots of (a) thermoelectric voltage and (b) electrical resistivity of Cu−In−O films as a function of composition (atom % indium) and phase region. Red line represents the single phase composition $Cu_2In_2O_5$. The CuO and $Cu_2In_2O_5$ phase region is to the left of the red line, and the $Cu_2In_2O_5$ and In_2O_3 phase region is to the right of the red line.[10]

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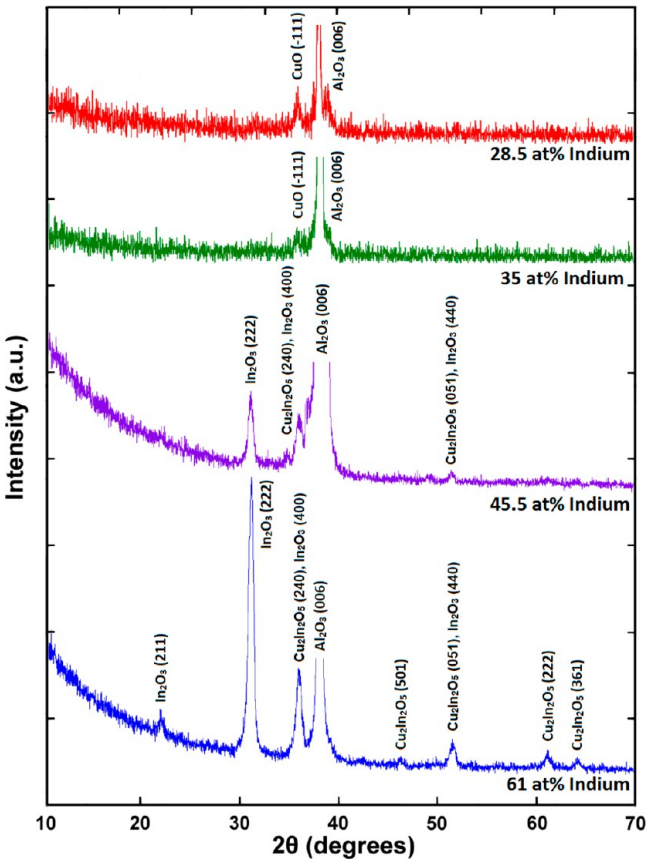

Figure 3. XRD patterns of four Cu−In−O films; three copper oxide rich at 28.5 atom % In and 35.0 atom % In and 45.5 atom % In and one indium-rich at 61.0 atom % In.

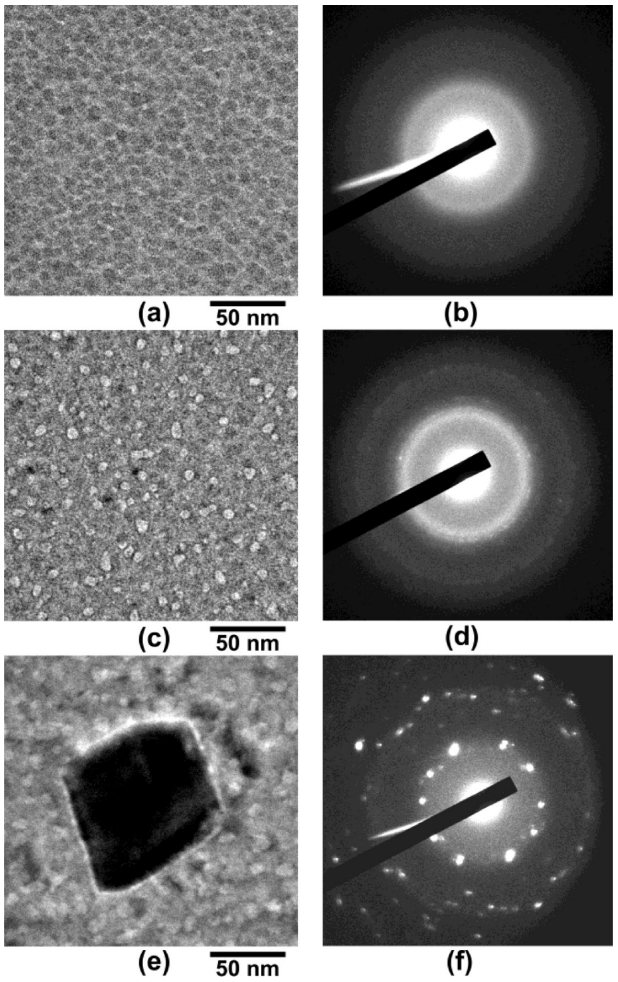

Figure 4. TEM micrographs and electron diffraction patterns for (a, b) typical as deposited films showing totally amorphous and uniform structure, (c, d) at onset of crystallinity, and (e, f) after phase separation of the film into large copper-rich particles.

and In_2O_3 phases. Typically, films in the Cu−In−O system grown at or near room temperature are largely amorphous or have significant amorphous regions,[11] which was clearly evident in the copper rich films. However, the indium oxide rich thermo-elements had well-defined crystalline phases, although many of the additional peaks were low in intensity. The presence of CuO, $Cu_2In_2O_5$, and In_2O_3 phases as a function of composition was in close agreement with the phase diagram for the CuO-In_2O_3 system.[10] The investigators established the phase diagram by combining CuO and In_2O_3 in various ratios, sintering them in air, and determining the resulting phase distribution by XRD. The thermo-elements fabricated in the present study were annealed in nitrogen and remained consistent with the phase diagram for this system up to high temperatures in an inert environment such as argon or nitrogen.[10]

III. Microstructure. TEM was used to follow microstructural changes of selected elements from the combinatorial library as a function of heat treatment. The TEM images of various Cu−In−O elements are shown in Figures 4 and 5. The electron diffraction patterns of the as-deposited films indicated they were amorphous with little or no fine structure (Figure 4a). Annealing of the indium oxide rich films (>40.0 atom % In) resulted in the formation of small crystallites in an amorphous matrix. As the copper oxide content was systematically increased (<40.0 atom % In), relatively large, faceted particles were observed (Figures 4e and 5a). EDS analysis of those dispersed particles indicated that they have increased oxygen and copper content relative to the surrounding matrix. At lower magnification, Figure 5a shows phase separation of highly crystalline, copper oxide particles (dark) against a distinct lighter background matrix. The lighter phase was further magnified to disclose a copper oxide rich phase (light) and indium oxide rich phase (dark) as shown in Figures 5b and 5d, respectively, with corresponding electron diffraction patterns in Figures 5c and 5e. Preferred orientation of the matrix tends to increase as the amount of copper in the thermo-element was increased (Figures 4f and 5c). This contrasts with the XRD spectra from above because these same copper rich thermo-elements were amorphous. This was due to the relative size scale at which these measurements were taken. The TEM images corresponded to a much smaller area of the thermo-elements than that examined using XRD. Therefore, variations in the thermo-element crystallinity are prevalent.

CONCLUSION

The Cu−In−O thermo-elements with the largest p-type and n-type response are promising candidates for further consideration as thermoelectric materials. Cu−In−O p-n junctions can be fabricated for thermoelectric applications such as thermoelectric generators by sputtering thermo-elements from targets of the same compositions as the best performing p-type and n-type materials to form thermocouples. Addition-

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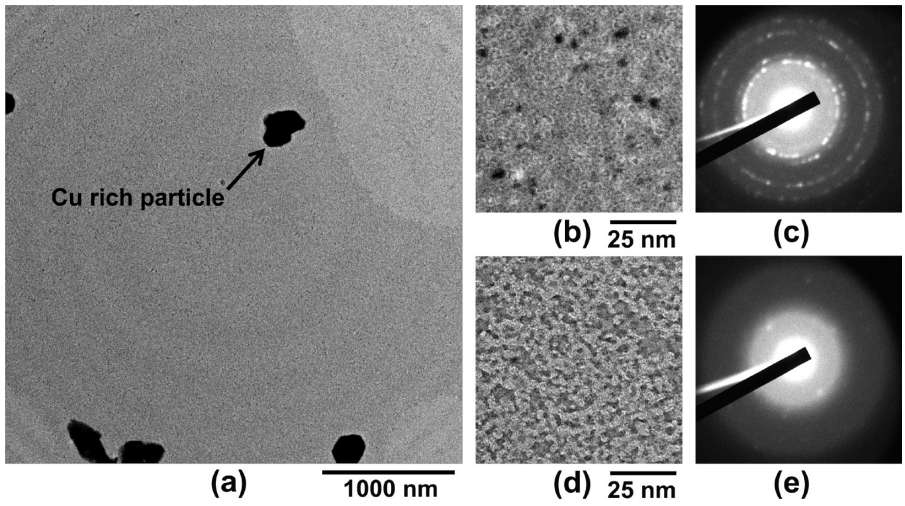

Figure 5. TEM micrographs and electron diffraction patterns showing phase separation in a Cu−In−O film (50.0 atom % In): (a) low magnification image indicating copper-rich precipitates in an amorphous background, (b) high resolution image of copper-rich region with (c) corresponding electron diffraction pattern, and (d) high resolution image of (nearly) amorphous background with (e) corresponding electron diffraction pattern.

ally, the p-type and n-type thermo-elements will be compatible in terms of thermal expansion during thermal cycling since they are from the same materials system.

EXPERIMENTAL PROCEDURES

Cu−In−O films were deposited onto high purity alumina substrate and oxidized silicon wafer by cosputtering from CuO and In_2O_3 targets to form a combinatorial library containing thermo-elements in the Cu−In−O system. Prior to deposition, reference electrodes (complementary thermocouple leg to Cu−In−O thermo-element) were fabricated using photolithography in conjunction with lift-off. Platinum, sputtered in ultra high purity (UHP) argon at 9 mT, was deposited as the reference electrode material. A photolithographic step was used to create 770 (55 × 14 array) Cu−In−O thermo-elements with each thermo-element at different position relative to the two sputtering targets. The sputtering targets were 15.2 cm in diameter and were spaced 27.3 cm apart. A radio frequency power of 200 W was fed continuously to each sputtering target during deposition. In this way, a chemical composition gradient was established in the thermo-elements along the axis between the targets, and a thickness gradient was established in the orthogonal direction. The resulting thermocouples formed an array suitable for rapid thermoelectric property screening, as shown in Figure 6.

All thermocouples were subsequently annealed in nitrogen at 400 °C for 5 h to release trapped argon and densify the thermo-elements. Final film thicknesses ranged from 1 to 2 μm. Thermoelectric data were obtained from the library thermocouples deposited on an alumina substrate, after a temperature difference was established between the hot and cold junctions. Each thermo-element was typed p- or n- based on the voltage sign relative to the platinum reference electrode. Voltages were recorded using an IOTech USB data acquisition system and *Personal Daq View Plus* software. Thin film type-K thermocouples were deposited, by sputtering from alumel and chromel targets in 9 mT Ar, at the hot and cold junction of a thermocouple with the same geometry as the library thermocouples to calibrate the temperature difference across the junction. Electrical resistivity was measured on films deposited on the oxidized surface of a silicon wafer after the

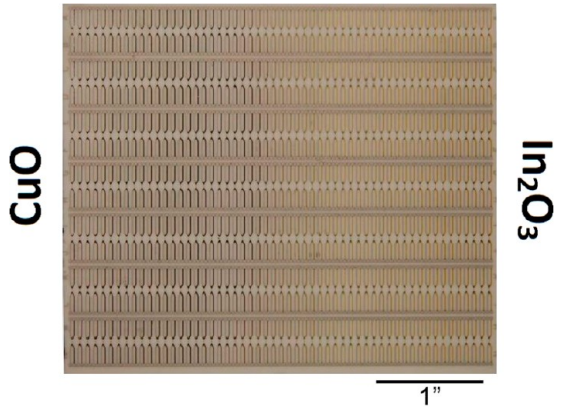

Figure 6. Combinatorial library of 770 Cu−In−O thermo-elements deposited using radio frequency sputtering. Each thermo-element was arranged for rapid property screening and had a spatially dependent composition based on its position relative to each sputtering target.

thermocouples were nitrogen annealing. The composition of each thermo-element in the library array was determined with EDS measurements on a JEOL-5900 scanning electron microscope (SEM). The microstructures of select library thermo-elements were examined in a JEOL JEM-2100 TEM by depositing films directly onto silicon nitride grids. The thin films were examined as-deposited, after a 400 °C, 5 h nitrogen anneal, and after repeating the nitrogen anneal another 5 h at 400 °C. A Rigaku Ultima-IV XRD system was used to determine the degree of crystallinity and distribution of phases present in selected thermo-elements.

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Author Contributions

†The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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Notes

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■ ABBREVIATIONS

CuO, copper oxide; In_2O_3, indium oxide; TCO, transparent conducting oxide; EDS, energy dispersive spectroscopy; TEM, transmission electron microscopy; XRD, X-ray diffraction; UHP, ultra high purity; SEM, scanning electron microscopy

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