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Note: A Simple Thermal Gradient Annealing Unit for the Treatment of Thin Films

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Note: A simple thermal gradient annealing unit for the treatment of thin films

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A gradient annealing cell has been developed for the high-throughput study of thermal annealing effects on thin-film libraries in different environments. The inexpensive gradient annealing unit permits temperature gradients as large as 28 °C/mm and can accommodate samples ranging in length from 13 mm to 51 mm. The system was validated by investigating the effects of annealing temperature on the crystallinity, resistivity, and transparency of tin-doped indium oxide deposited on a glass substrate by magnetron sputtering. The unit developed in this work will permit the rapid optimization of materials properties such as crystallinity, homogeneity, and conductivity across a variety of applications.
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Thermal processing is essential for producing materials with well-developed crystallinity, compositional homogeneity, reduced-residual stresses, and optimized electronic properties.[1–3] As materials with increasing compositional and microstructural complexity are developed, a systematic approach toward probing processing-composition phase space is required.[4,5] For these systems, high-throughput methodologies[6–12] can be used to efficiently investigate large phase spaces. In this approach, a library of samples is formed by varying one or more variables on a single substrate. The library is then screened for its figures of merit using parallel or sequential measurement techniques. The use of high-throughput methods for temperature dependence studies has been demonstrated previously by other groups; however, these systems have been complicated, specialized, and expensive.[13–17]

Here, we present a gradient annealing unit (GAU) that can be used to thermally anneal thin film samples deposited on thermally insulating substrates of lengths varying from 13 mm to 51 mm. This system is simple, inexpensive, and versatile while creating relatively large temperature gradients. We demonstrate the capability of the GAU to maintain temperature gradients at atmospheric pressures of air and validate its use on an indium tin oxide (ITO) thin film. Evidence of the ITO glass transition temperature is observed via measurements of resistivity, optical transmission, and crystallinity.

The GAU was designed based on thermal gradient models developed in Comsol Multiphysics 4.2a. These models only accounted for the thermal conduction of the substrate. All models were calculated using an L × 25.5 mm × 0.5 mm rectangular parallelepiped; where L is the length of the substrate, with a thermal conductivity matching that of Corning 1737. The models did not account for thermal loss due to convection, which can be a dominating mechanism for heat loss near atmospheric pressures. The initial system was modeled with an L = 13 mm blank substrate at 0.1 MPa in different gas environments (e.g., air, nitrogen, hydrogen, etc.). Of particular interest was the predicted feasibility of the GAU to maintain a 20 °C to 340 °C thermal gradient across a 13 mm glass substrate under different conditions.

The GAU is schematically shown in Figure 1(a) and pictured in Figure 1(b). The hot stage is composed of a machined copper block with an overhang where a thin film sample on a substrate is mechanically clamped. A 200 watt cartridge heater (Omega Engineering, Inc.) is inserted into a hole in the clamp and powered by a 210 watt Staco Energy Variac. The stage is mounted on a threaded rod, which allows the height to be adjusted by ±25 mm. The cold stage is composed of a copper clamp similar to the hot stage with a through-hole for a 6 mm stainless steel cooling line.

Both copper stages are 64 mm across and are wide enough to ensure that a 25 mm wide substrate is uniformly heated in the direction orthogonal to the temperature gradient. In the current design, the water cooling lines extended too far radially to permit mounting the cooling stage in a standard 6″ CF tee; however, it was determined that testing the cell in air would be sufficient as a proof-of-concept.

The temperature profile of the GAU was measured at atmospheric pressure across substrates of various lengths along the temperature gradient using a thermocouple probe. This temperature profile was taken before each run to ensure that drift in the system would not affect the results. Thermal gradients for 13 mm, 25 mm, 38 mm, and 51 mm substrates were characterized by cutting Corning 1737 substrates to the appropriate length and clamping them between the hot and cold stage. The temperature curves were taken by mechanically fixing the thermocouple probe to the glass substrate for each measured point. Each point was marked by a small scribed line to ensure the thermocouple was consistently and accurately located on the substrate. To quantify error in the temperature readings, multiple measurements were taken over time for each point. The thermocouple was allowed to equilibrate

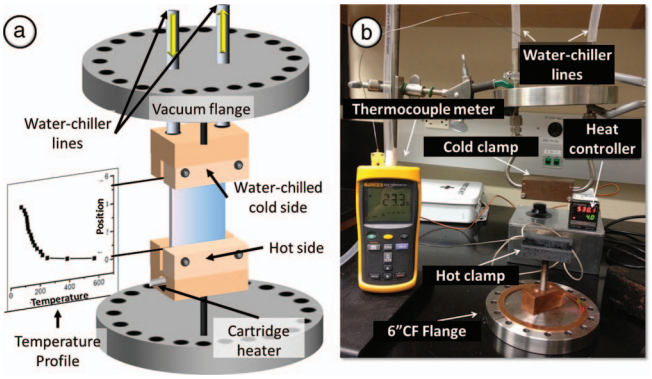

FIG. 1. (a) A schematic of the GAU system with the main components labeled. (b) A photograph of the system.

for 1 min before temperature data were taken. After the initial 1 min, temperature data were taken every 0.5 min for 2 min. After each data point, the thermocouple probe was removed and allowed to cool. The thermocouple was then placed back on the substrate to ensure the reproducibility of the measurement. No deviation outside of the error was observed in subsequent temperature measurements.

In the case of the 13 mm substrate, a nearly linear temperature gradient was observed across the entire length, spanning from 108 °C to 342 °C. For substrates longer than 13 mm, the temperature gradient became less linear with a sharp increase in the gradient within 10 mm of the hot stage.

Post-characterization models of the 13 mm and 51 mm glass substrate were re-run using the highest experimentally observed temperature as the initial hot-side temperature and compared to the experimental data. From Figure 2(a), the model and the experimental data follow roughly the same trend, although the experimentally observed temperature of the cold side is 130 °C higher than that predicted by the model. This is attributed to the insufficient cooling of the cold stage, and could be mitigated in the future by either increasing the water flow rate or improving the thermal contact between

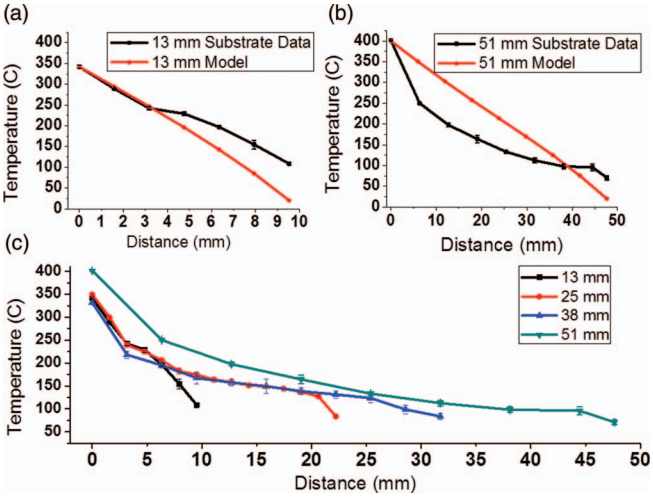

FIG. 2. Temperature results for (a) a 13 mm substrate with the model results, (b) a 51 mm substrate with the model results, and (c) a comparison of temperature curves for 4 sample sizes in air.

the stainless steel pipe and the copper block. In the case of the 51 mm substrate, the experimental data and the model show significant deviation from one another. This difference is ascribed to convective cooling dominating near the hot-stage.

An ITO thin film was used to validate the GAU. The ITO film was deposited from a 99.99% purity 90 wt. % In_2O_3:10 wt. % SnO_2 target onto a 50.8 mm × 25.5 mm × 0.5 mm Corning 1737 glass substrate using RF magnetron sputtering. The base pressure of the sputtering system was 4×10^{-6} Pa and the samples were deposited at room temperature. The film was deposited under 0.1 Pa of Ar at a working power of 200 watt to produce a ∼200 nm thick film, measured using a Tencor Alpha-step 200 surface profiler. The gun tilt, substrate distance, and substrate rotation rate were optimized to produce a uniform film.

Approximately 5.0 mm of the sample was clamped in each stage to secure it to the GAU. The sample was oriented so that the temperature gradient was aligned with the long axis (schematically shown in Figure 1(a)). The sample was then heated and allowed to equilibrate for 30 min, followed by a 2 h anneal. During the thermal anneal, temperatures were measured at discrete points with a thermocouple. The temperature curve produced from these measurements is provided in the supplementary material.[23] The 0 mm position was defined as the edge of the hot side copper clamp where the sample was exposed directly to atmosphere. After the heat treatment, the sample was air cooled with the cooling water running continuously.

Once annealed, crystal structure and crystallinity were characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV X-ray diffractometer. Resistivity measurements were also performed using a four-point probe method in linear contact geometry using a Cascade Microtech probe station (Micromanipulator 6000). Finally, optical transmittance measurements were taken with a Shimadzu UV-2101PC for wavelengths between 300–800 nm.

ITO has a glass transition temperature around 150 °C to 280 °C depending on thickness, deposition temperature, tin concentration, deposition method, atmosphere, and a variety of other factors.[18–21] The films treated in the GAU were of sufficient thickness to form a poorly crystalline phase during deposition, as observed in the diffraction pattern for the as-deposited sample.

After annealing, the sample showed a visible transition in opacity in the region between 130 °C and 160 °C. XRD, resistivity, and transmission measurements all provide evidence of a crystallization transition at ∼140 °C, as shown in Figure 3. In this region, the film became more transparent, the resistivity decreased, and the FWHM of the (222) diffraction peak sharply decreased. Resistivity data exhibited a broader transition, consistent with the competition between grain boundaries and charge carriers reported by the literature.[22] After the transition, both the resistivity and the FWHM of the (222) diffraction peak steadily increased while the transmission stayed relatively constant. This increase in resistivity is likely due to an increase in oxygen concentration resulting from the anneal in air,[21] which reduces the oxygen vacancies that act as donor levels in ITO. The increase in FWHM is likely related to an increase in stress between

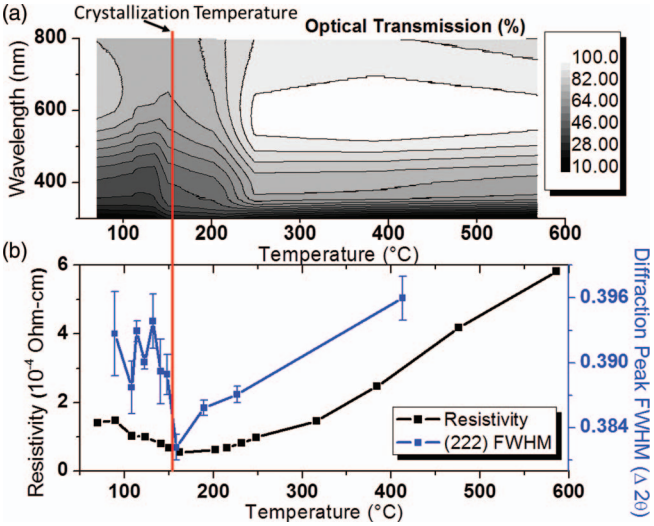

FIG. 3. The observed crystallization transition in (a) optical transmission measurements, (b) resistivity measurements, and the full width half maximum for the (222) ITO diffraction peak. The error on the full width half maximum is calculated from the average of three runs on the same diffraction peak.

the film and the substrate as the temperature increased, due to differences in thermal expansion coefficients.

The temperature gradient annealing unit in this work is unique in that it is designed to produce relatively large and tunable temperature gradients across samples varying in size from 13 mm to 51 mm under different annealing atmospheres. The temperature gradient was characterized in air for 4 different substrate sizes. A 200 nm thickness ITO thin film sample was used to validate the experimental procedure. Evidence for the crystallization temperature was observed by XRD, optical transmittance, and resistivity.

Future work will use the CF flange to allow for thermal annealing in different atmospheres, including vacuum. Six thermocouples will be connected by electrical feed-throughs and attached to the substrate with thin specially designed clips.

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[23]See supplementary material at http://dx.doi.org/10.1063/1.4795831 for a plot of the temperature data used for the ITO measurements.