

Scalable Fabrication of Flexible Two-Dimensional Indium Tin Oxide via Continuous Liquid Metal Printing

Md Saifur Rahman¹, Anand P. Tiwari¹ and William J. Scheideler¹, Senior Member, IEEE

¹Dartmouth College, Hanover NH 03755

william.j.scheideler@dartmouth.edu

ORCID: 0000-0003-1626-1443

Abstract— In this study, we present continuous liquid metal printing (CLMP) to produce flexible and transparent indium tin oxide (ITO) layers compatible with plastic substrates with low glass transition temperatures. By leveraging the low melting point of an indium-tin (In-Sn) alloy, we achieve spontaneous two-dimensional (2D) oxide growth at low temperatures, following Cabrera-Mott (CM) oxidation kinetics. A robotically controlled roller deforms the molten alloys, depositing a thin native oxide (ITO) via van der Waals adhesion across large areas (approximately 1200 cm²) in mere seconds. The printed 2D ITO is highly crystalline with large plate-like grains with an average size of 55 nm. They demonstrate low resistivity (approximately 714 $\mu\Omega\text{-cm}$) and transparency (>92% in visible light) with an optical bandgap of 3.71 eV. Mechanical testing reveals superior adhesion, 2X greater bendability, and 3X better scratch resistance of flexible 2D ITO. Finally, we demonstrate an application towards flexible transparent electrocardiogram electrodes based on flexible 2D ITO.

Keywords—Liquid metal, TCO, Flexible electronics, Wearable devices, Bioelectrodes

I. INTRODUCTION

The demand for lightweight, bendable, and high-performance devices in flexible electronics is rising, particularly for applications like virtual and augmented reality systems. [1], [2] These systems require the development of transparent conductors capable of maintaining high performance while accommodating the mechanical stresses of flexible device's operation. In rigid systems, this need is well satisfied by Indium Tin Oxide (ITO), which has traditionally met this need, finding use in touch screens, solar cells, and smart windows[3]. However, when produced via vacuum deposition methods like sputtering, ITO's performance and stability under mechanical stresses are often limited by factors such as thermal budget, cost, and crystallinity of the film [4]. There is a pressing need for innovative large-area processing techniques that can reduce costs for large-scale applications and address the limitations of ITO's material properties, such as crystallinity, to enhance the performance of flexible electronics. Traditional fabrication techniques, such as sputtering, involve high production costs, limiting scalability and adoption of low-cost, flexible electronics [5]. In addition to vacuum deposition, solution-processable methods such as spin and dip coating are also used for ITO production. Although these methods might require a low deposition

temperature, they often exhibit a poor-quality film at a low post-processing temperature, which is necessary for using a flexible substrate[6].

Addressing these challenges, our research introduces a novel methodology based on Continuous Liquid Metal Printing (CLMP) [7] for the scalable, cost-effective deposition of high-performance, transparent 2D ITO layers directly onto polymer substrates (PEN and Polyimide). By leveraging an In-Sn alloy mixture's low melting point (<150 °C), we exploit the unique physics of liquid metal surface oxides to achieve spontaneous oxide growth at remarkably low temperatures, following the Cabrera Mott growth kinetics. Previous studies have established the foundation for depositing liquid metal-synthesized ITO film over a small area (< 1cm²) via a squeeze transfer from a donor substrate containing the molten alloy to a target substrate [8], [9]. However, comprehensive work on controlling and optimizing film metrics to enhance electrical conductivity and mechanical properties remains largely unexplored. In this study, we manipulate the electrical and optical characteristics of liquid metal printed ITO films across large areas by controlling the oxidation process, leveraging classic oxidation kinetic models. Our roller-based printing system offers scalability and high throughput, providing significant advantages for widespread adoption. This novel approach enables the production of 2D ITO films with enhanced electrical conductivity, flexibility, and optical transparency while allowing precise adjustment of key properties like thickness and conductivity through control of the oxidation kinetics. Through comprehensive surface characterization and mechanical evaluation, we highlight the exceptional capabilities of our ITO electrodes and demonstrate their utility in practical applications like next-generation bioelectrodes for ECG monitoring.

II. RESULT AND DISCUSSION

Our roller-based CLMP technique enables the fabrication of large-scale indium tin oxide (ITO) films at lower temperatures. This method leverages the unique property of binary mixtures of the In-Sn alloy. As the proportion of Sn in the alloy increases, its melting temperature decreases towards a eutectic point substantially lower than that of indium and tin[10]. This process facilitates the growth of a thin oxide film around

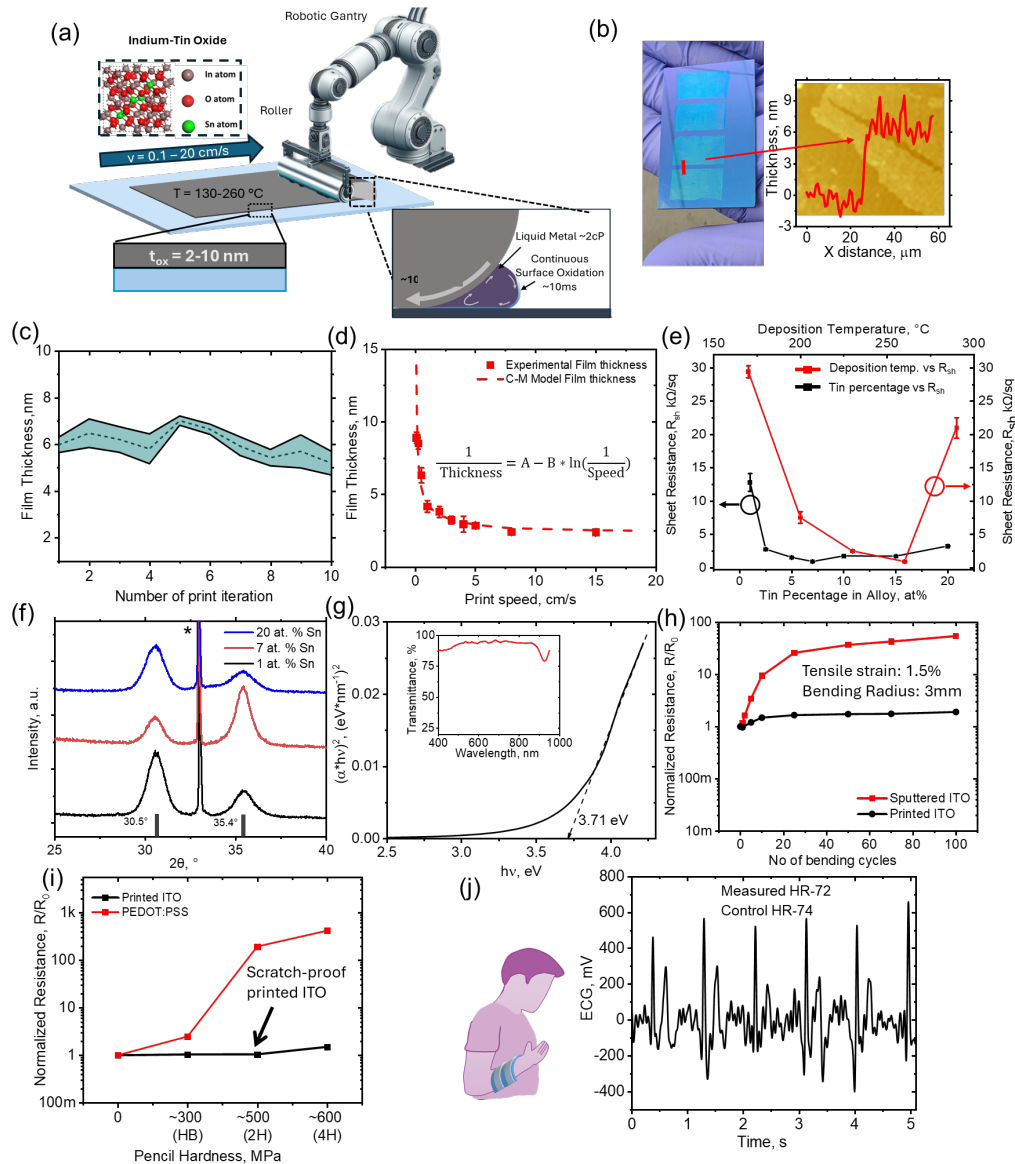


Fig. 1 (a) Schematic of continuous liquid metal printing of ITO (b) Optical microscope and AFM scan of large-scale ITO film (c) Print-to-print variability in the thickness of printed ITO films (d) Cabrera-Mott (C-M) model of the thickness of 2D ITO films (e) ITO sheet resistance vs. Sn percentage and temperature of deposition (f) XRD spectra of ITO for different Sn ratio, * denotes Si substrate peak (g) Tauc Plot fitting for 7 at. % Sn-doped ITO films, processed at 260 °C. The inset shows the transmittance vs wavelength for the same film. (h) Normalized resistance after 100 bending cycle test for printed and sputtered ITO (i) ASTM standardized scratch test for ITO and PEDOT: PSS (j) ECG signal and hear rate measurement with transparent ITO bioelectrodes. The graphic shows the location of the hand where the ECG is measured.

the molten alloy at a lower temperature. Moreover, we can vary the oxide composition by varying the tin amount in the alloy due to the high solubility of tin ions within indium oxide [11]. This thermodynamically favored formation of ITO over pure In_2O_3 and SnO_2 makes it particularly suitable for our fabrication process [11].

The substrate is heated to a temperature ranging from 140 °C to 290 °C, and the tin concentration within the alloy was 1 – 30 % Sn. A robotic gantry precisely controls the roller, which is then pressed onto the substrate surface and rolled, displacing the molten alloy along the roller direction. This process deposits and regenerates nanometer-thick oxide layers on the substrate, as depicted in Figure 1a. Depending on the roller's speed, the thickness of the ITO films can be finely adjusted across a broad range, from 2.4 to 10 nm, addressing diverse applications. Film thickness is measured using AFM, as illustrated in

Figure 1b (single-layer print at 5 mm/s, 260 °C). Additionally, figure 1c illustrates the remarkable consistency in film thickness across multiple prints under identical parameters, confirming the precision of the fabrication process. Specifically, ten different single-layer films with a 7% Sn percentage, printed at 260 °C with a roller speed of 5 mm/s, exhibit a variability of only 5.5 Å. Furthermore, we demonstrate how the growth kinetics of the 2D ITO film align with the logarithmic relationship between print speed and film thickness, consistent with the Cabrera-Mott model as depicted in Figure 1d. This modeling approach provides a controlling knob in the fabrication processes for optimizing thickness and print speed to achieve desired film properties.

We investigated and optimized the sheet resistance by varying the In-Sn source alloy's deposition temperature and tin percentage. Sheet resistance, measured via a four-

point probe, initially decreased with rising tin content, then increased beyond 7 at% (black data, Figure 1e). A similar trend occurred with deposition temperature (red data). Under optimized 7 at% Sn and 260 °C conditions, the sheet resistance reached an impressive 950 Ω /sq – much lower than previously reported squeezed printing of liquid metal ITO films [8]. This is notable since no post-processing, such as drying or annealing, is involved, emphasizing the rapid nature of our fabrication process. X-ray diffraction (XRD) analysis was conducted on CLMP ITO films deposited on Si wafers with a 300 nm thermally grown SiO₂ layer. Figure 1f illustrates the XRD spectra for ITO films as a function of Sn at. % percentage in ITO. The films exhibited characteristic (222) and (400) peaks of cubic In₂O₃, similar to pure In₂O₃ films [12]. Figure 1g presents the Tauc plot of a single-layer ITO film, revealing an indirect bandgap of 3.71 eV. The inset highlights its high optical transparency (>92%) in the visible range.

Our study demonstrates the potential of printed indium tin oxide (ITO) electrodes on plastic substrates for wearable sensor applications. They exhibit a 25 \times lower resistance increase than sputtered ITO after 100 bending cycles at 1.5% strain (Figure 1h). We also compared ultrathin ITO hardness to PEDOT:PSS using the ASTM pencil hardness test [13]. As shown in Figure 1i, the ultrathin ITO films exhibit a hardness three times greater than that of PEDOT:PSS. This enhanced scratch resistance is crucial for mitigating degradation and wear. These findings, highlighting both superior flexibility and improved hardness, suggest that printed ITO electrodes are promising candidates for wearable bioelectrodes. We integrated our highly conductive ITO bioelectrodes into Electrocardiogram (ECG) leads. Unlike traditional leads, our electrodes are transparent and flexible. As illustrated in Figure 1j, we captured ECG signals with a signal-to-noise ratio (SNR) of 21 dB, followed by heart rate (HR) extraction through peak detection of the QRS complex. Our electrodes recorded an HR of 72 bpm, closely matching the control electrodes, such as gel electrodes.

III. CONCLUSIONS

In summary, we introduce a novel, scalable, high-speed roller-based liquid metal printing method for depositing 2D ITO onto thermally constrained plastic substrates. Leveraging the Cabrera-Mott (CM) kinetics, we achieve rapid and reliable deposition of thin ITO layers from molten In-Sn alloy, eliminating the need for vacuum and post-processing steps. This process enables precise parametric tuning of highly crystalline 2D films spanning large areas with sheet resistance below 1000 Ω /sq. The film properties, including thickness, are modeled using CM kinetics, offering a systematic approach to optimize film properties. These ultrathin and flexible films exhibit minimal resistance change after 100 bending cycles. Additionally, bioelectrodes fabricated from these scratch-resistant ITO films exhibit solid performance for ECG measurements while offering high transparency. Overall, our results show the potential of liquid metal printing to enhance the electronic properties of ITO.

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