Enhancing Electrostatic Control of High-Speed Liquid-Metal-Printed In_2O_3 TFTs via Ga Doping

Simon A. Agnew[1] and William J. Scheideler[1]
[1]*Thayer School of Engineering, Dartmouth College, 15 Thayer Dr, Hanover, NH 03755, USA*
Email: william.j.scheideler@dartmouth.edu

Introduction: We present a strategy to reduce the high free electron concentrations in continuous liquid metal printed (CLMP) indium oxide (InO_x) thin films by doping with Ga to achieve improved off-state behavior at a low, flexible substrate-compatible processing temperature of 180 °C. By trace doping of the precursor metal alloy with Ga, we produce CLMP indium gallium oxide (IGO) with varying Ga concentrations to achieve IGO TFTs with near-zero V_{on} and ~5X improved subthreshold slope (SS) compared to pure InO_x devices. IGO devices also exhibit enhanced bias stress stability, highlighting their potential application in next-generation flexible display technologies.

Results and Discussion: Our CLMP process is scalable to large, flexible substrates for roll-to-roll processes with deposition speeds beyond 10 m/min, with many advantages over traditional vacuum technologies. As seen in Fig. 1a, liquid metal on a heated substrate spontaneously generates an oxide skin which is exfoliated to a target substrate via a roller. Van der Waals forces ensure the film adheres to the substrate, with resulting metal oxide films exhibiting plate-like grain morphologies and thicknesses of ~3 nm [1,2]. CLMP InO_x TFTs printed at low temperatures exhibit a high free electron concentration, resulting in depletion-mode operation with extremely negative turn-on voltages ($V_{on} < -50$ V). It has been shown that Ga doping to form ternary IGO can improve off-state behavior and lead to near 0 V_{on} [3]. Recent studies observed that surface oxides of liquid metal alloys are dominated by the metal with the lowest redox potential [4,5]. We have characterized the tendency for gallium oxide (GaO_x) to dominate the resultant CLMP film when printing with Ga:In alloys as determined by x-ray photoelectron spectroscopy (XPS) in Fig. 1b. Even at 0.1 wt.% Ga in the the alloy, the resulting film is composed of majority GaO_x, which was amorphous and inactive. With a 0.001 wt.% Ga alloy, we fabricated $In_{0.91}Ga_{0.09}O_x$ films. The presence of (222) and (400) cubic bixbyite In_2O_3 peaks in x-ray diffraction (XRD) scans of this IGO film (Fig. 2a) indicate a comparable crystal structure to pure CLMP InO_x films, with grain sizes of ~6 nm for both. No Ga_2O_3 peaks were detected, indicating doping of Ga into the InO_x.

Substrate-gated (100 nm SiO_2) top-contact (Au) TFTs were fabricated using CLMP deposited InO_x and IGO films printed at 180 °C in less than 2 s. To achieve a conductive channel for high-performance TFTs, two layers of IGO were printed to form a ~6 nm thick channel. Representative transfer characteristics (Fig. 2b) show a large improvement in V_{on} (+20 V) and a 5X improvement in SS for IGO devices over pure InO_x. The lower conductivity of IGO films (187 S/cm) vs InO_x (215 S/cm) as measured by a four-point probe suggest the lowering of the free carrier concentration as a result of Ga-doping, explaining the push towards enhancement-mode operation. Reduction of the free carrier concentration improves the off state and I_{on}/I_{off} up to 10^6. Representative output curves of IGO TFTs (Fig. 2c) show better current saturation than previously reported for InO_x printed at low temperatures [6]. The incremental linear and saturation mobility vs. V_{GS} was extracted for IGO devices (Fig. 3a), reaching a peak at a moderate gate bias. For applications in flat panel displays and back-end-of-line (BEOL) circuits, bias stress stability is crucial. Negative bias illumination stress (NBIS) was applied to IGO and InO_x TFTs with a $V_{GS} = -40$ V for 3 h (Fig. 3b). After 3 h, the threshold voltage (V_{th}) of the InO_x TFT had shifted -15 V, whereas the IGO TFT shifted slightly negative but returned to around the original V_{th}. With enhanced bias stress stability, our 2D IGO channels would outperform pure InO_x in flexible displays. Post-annealing of IGO TFTs further improves the SS to 570 mV/dec and increases V_{on} even closer to enhancement-mode operation. Fig. 3c shows a comparison between an IGO device as-deposited at 180 °C, with no post-annealing, vs after annealing for 4 h at 250 °C. While the off-state current is slightly improved, the I_{on}/I_{off} ratio is not significantly affected, highlighting the ability to fabricate high-performance IGO channels without requiring a post-annealing step. Due to the low processing temperature of 180 °C, these CLMP IGO TFTs can be fabricated on a variety of flexible polymer substrates, such as polyimide or PET. Fig. 4 illustrates the compatibility of the CLMP process with the maximum working temperatures of common flexible substrates. The low thermal budget and high processing speed of IGO TFTs demonstrated in this work make them ideal for high-throughput roll-to-roll fabrication of flexible thin film circuits.

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References:

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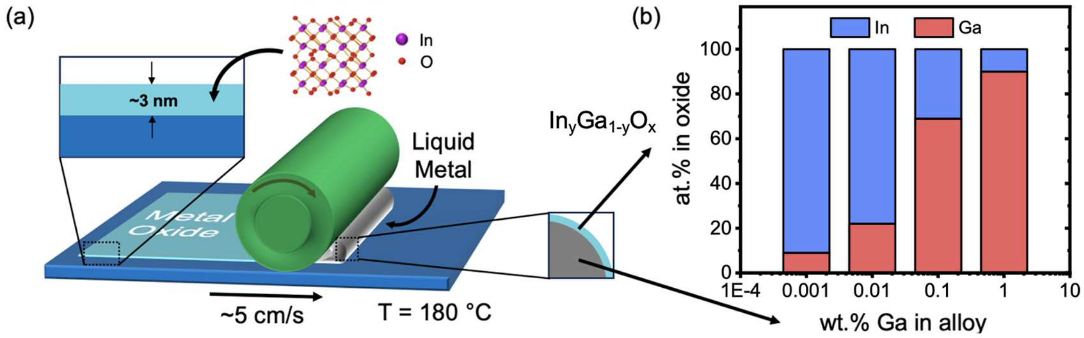

Fig. 1 (a) Continuous liquid metal printing (CLMP) process for rapidly depositing 2D semiconducting metal oxides. (b) Metal oxide film composition vs alloy composition as determined by XPS for various concentrations of Ga.

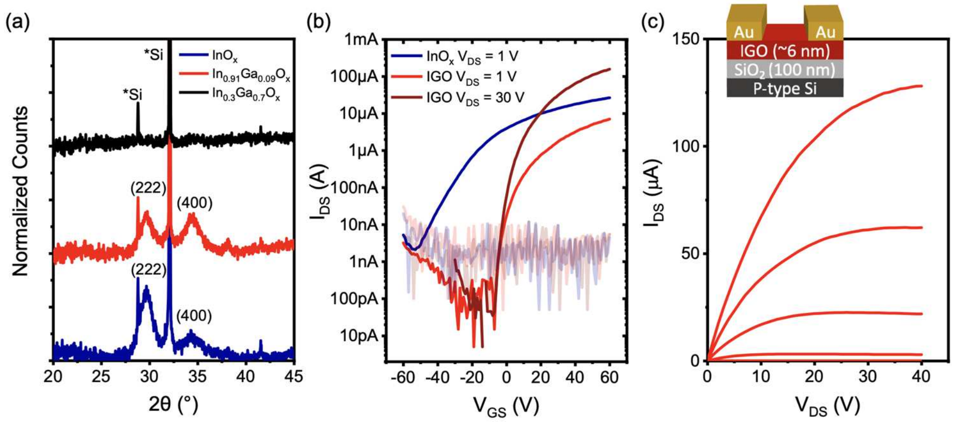

Fig. 2 (a) XRD spectra of InO_x and IGO films fabricated at 180 °C, peaks matching cubic In_2O_3 reference. b) Transfer characteristic comparison between InO_x and IGO thin film transistors fabricated via CLMP at 180 °C. (c) Output characteristic of IGO TFT with V_{GS} stepped from -20 to 60 V in 16 V increments, inset of device architecture.

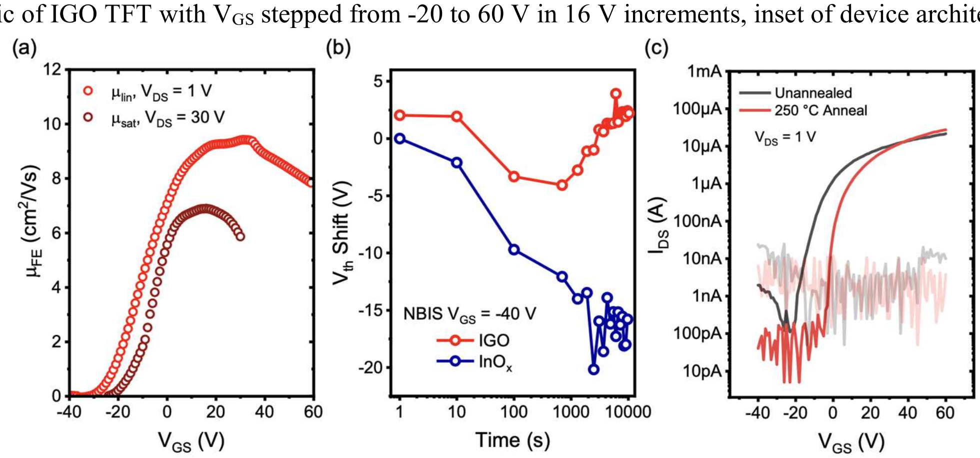

Fig. 3 (a) μ_{lin} and μ_{sat} vs V_{GS} for a representative IGO TFT. (b) NBIS shift in threshold voltage. (c) Transfer curve comparison between as-deposited, unannealed IGO fabricated at 180 °C versus after annealing 4 h at 250 °C in air.

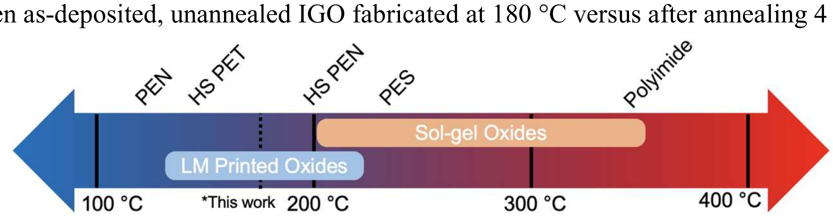

Fig. 4 Maximum process temperatures of flexible polymer substrates versus the temperature ranges of liquid metal printing and sol-gel processes for fabricating metal oxides (HS denotes heat-stabilized).