Direct-write assembly of microperiodic planar and spanning ITO microelectrodes†

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Printed Sn-doped In2O3 (ITO) microelectrodes are fabricated by direct-write assembly of sol–gel inks with varying concentration. This maskless, non-lithographic approach provides a facile route to patterning transparent conductive features in planar arrays and spanning architectures.

Printed electronic devices are finding widespread application in thin film transistors,1 solar cells,2 batteries,3 displays,4 and radio frequency identification (RFID) tags.5 Common printing techniques, such as ink jet, roll-to-roll, and screen printing, allow only supported, planar structures to be produced. Recently, Ahn et al. reported omnidirectional printing of flexible, stretchable, and spanning silver microelectrodes.6 Here, we demonstrate direct-write assembly of transparent microelectrodes composed of Sn-doped indium oxide (ITO), a widely used conductor in optoelectronic devices.

Direct-write assembly is a maskless, non-lithographic route for patterning planar and three-dimensional (3D) structures.7–9 In this printing method, a concentrated ink is extruded through a tapered cylindrical nozzle that is translated using a three-axis (x–y–z), robotic motion stage (Fig. 1a). To date, myriad materials, including metallic,6 polymer,8 and ceramic9 inks, have been patterned by this filamentary printing approach. Concentrated inks are typically desired to avoid significant spreading10 and inhomogeneous drying effects11 that occur in droplet-based approaches, such as ink-jet printing.

To pattern planar and spanning transparent microelectrodes with fine features (≤5 μm), we developed concentrated sol–gel inks of varying solids loadings. Each ink is produced by first dissolving indium acetate and tin bis(acetylacetonate) dichloride in acetylacetone solvent at 90 °C on a hot plate. The In and Sn precursors are not soluble in alcohol or water, thus acetylacetone is used to both promote their solubility and chelation. Next, an aqueous solution (25 wt%) of tetramethylammonium hydroxide is added drop-wise to each solution, followed by concentrating it to a high solids loading (up to 30 wt%) via solvent evaporation at 120 °C. During this step, an aqueous solution (35 wt%) of hydrogen peroxide with a molar ratio of H2O2/In > 5 is added in a dropwise manner to accelerate oxidation and suppress recrystallization. Upon cooling to room temperature, a viscous, reddish yellow, transparent ink is obtained (Fig. 1b), which is stable for several months without a noticeable change in printing behavior. More details are given in the ESI.†

To demonstrate direct writing of planar arrays, we printed a sol–gel ink (25 wt% solids) on a Si wafer using either a 1 μm or 4 μm nozzle, respectively. The insets show cross-section images of the printed and annealed features. (e) SEM micrograph of spanning ITO microelectrodes printed on Si ribbons. (f) SEM micrograph of an as-patterned 3D structure (8 layers).

Fig. 1 (a) Schematic illustration of direct-write assembly. (b) Optical image of a representative sol–gel ink. (c) and (d) SEM micrographs of 1D planar array of ITO microelectrodes patterned on a Si wafer using either a 1 μm or 4 μm nozzle, respectively. The insets show cross-section images of the printed and annealed features. (e) SEM micrograph of spanning ITO microelectrodes printed on Si ribbons. (f) SEM micrograph of an as-patterned 3D structure (8 layers).

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The apparent viscosity of a 5 wt% solids ink is ~0.01 Pa s. However, the ink viscosity increases by four orders of magnitude at a solids loading of 28 wt% (Fig. 2a). Importantly, a modest increase in ink solids loading from 25% to 28% results in nearly a two-order of magnitude increase in apparent viscosity (Fig. 2a), which translates to an order of magnitude difference between the aspect ratios of their respective patterned and annealed features (Fig. 1c and e). During printing, the ink begins to dry immediately as it exits the nozzle, which leads to a concomitant rise in its elastic ($G'$) modulus (Fig. 2b). Unlike the data shown, the printed microelectrodes are expected to undergo solidification ($G'$ > $G''$) on a much faster timescale (~10 ms) due to their vastly higher surface area-to-volume ratio.

To further quantify the relationship between ink rheology and printed feature morphology, we measured the printed rod width ($w$) and height ($h$) for inks of varying solids loading deposited through a 1 μm nozzle at different applied pressures (Fig. 2c and d). At a constant printing speed of 500 μm s⁻¹, the printed feature width and height increase as the applied pressure increases from 5 to 90 psi. As expected, the minimum pressure required for ink flow increases with increasing solids loading. For example, inks with 20 wt% solids flow through a 1 μm nozzle at applied pressures as low as 5 psi, yielding printed features of $w = 10 \mu m$, $h = 1.2 \mu m$. Upon increasing the applied pressure to 30 psi, printed features of $w = 33.2 \mu m$, $h = 2.5 \mu m$ are obtained as a result of over pumping. Due to the lower viscosity of this ink, lateral spreading gives rise to features with a low aspect ratio ($h/w$) ~ 0.08, which would decrease further upon annealing. Similarly, the widths of features printed from inks with solids loading of 22–28% increase as the applied pressure increases. However, lateral spreading is significantly reduced due to their increased viscosity and shear elastic modulus. For example, inks with 28 wt% solids require a minimum deposition pressure as high as 50 psi to initiate flow, and yield printed features of $w = 1.10 \mu m$, $h = 1.05 \mu m$ at this pressure, with aspect ratio ~0.95. Rapid solidification of these highly concentrated inks enables printing of fine spanning features with nearly cylindrical morphologies.

During thermal annealing of a representative ink (25 wt% solids) in air, significant weight loss occurs followed by crystallization (Fig. 3a and b). First, solvent evaporation occurs at temperatures below ~150 °C, followed by organic decomposition at higher temperatures yielding the desired metal oxide. Thermogravimetric analysis (TGA) indicates that approximately 63 wt% mass loss occurs by 350 °C (Fig. 3a), while X-ray diffraction (XRD) reveals that the onset crystallization occurs by 350 °C (Fig. 3b). All peaks are assigned to In$_2$O$_3$, and their intensities increase with increasing temperature. Fig. 3c shows the resistivity ($\rho$) of ITO thin films (thickness = 150 nm), spin coated from inks containing various tin concentrations and annealed at 570 °C in air, followed by reductive post-annealing in flowing N$_2$. Reductive post-annealing results in a one order of magnitude decrease in resistivity. Resistivity of these films decreases with increasing tin concentration, attaining a minimum value of 2.4 × 10⁻³ Ω cm at Sn/In = 0.06. The resistivity increase at excess tin concentration is likely due to the deposition of SnO$_2$ in the
grain boundaries of In$_2$O$_3$.\textsuperscript{17} Although this minimum resistivity value is in good accord with those reported for other solution-based ITO films,\textsuperscript{18} it is about an order of magnitude higher than the lowest reported values in the literature.\textsuperscript{19} Further optimization of the ink formulation and annealing conditions is now underway to improve electrical performance. Fig. 3d shows the optical transmittance of 1D arrays of ITO microelectrodes ($w = 2$ $\mu$m, $h = 200$ nm) as a function of their center-to-center spacing. Transmittance ($T$) of patterned microelectrode arrays with 20 $\mu$m spacing is as high as 94% in the visible to near infrared region, and increases to 98% as the spacing between ITO microelectrodes increases to 80 $\mu$m.

In conclusion, we have demonstrated that planar and spanning ITO microelectrodes can be patterned in both 1D and 3D arrays by direct-write assembly of a concentrated sol–gel ink. Our approach may open new avenues for fabricating printed electronic and optoelectronic devices in unusual layouts.

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Notes and references