Electronic Supplementary Information

Direct-write assembly of microperiodic planar and spanning ITO microelectrodes

Bok Yeop Ahn,[a] David J. Lorang,[a] Eric B. Duoss[a] and Jennifer A. Lewis*[a,b]

[a] Department of Materials Science and Engineering and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA. Fax: 217 333-2736; Tel: 217 244-4973; E-mail: jalewis@illinois.edu

[b] Department of Chemistry and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA.

Ink synthesis

Indium acetate (99.99%, Aldrich), tin bis(acetylacetonate) dichloride (98%, Aldrich), acetylacetone (99%, Aldrich), tetramethylammonium hydroxide (25 wt% in H_2O), Aldrich), hydrogen peroxide (35 wt% in H_2O, Fisher) are used as-received. Concentrated ITO inks are prepared by first dissolving 0.09 g tin bis(acetylacetonate) dichloride into 5.0 g acetylacetone at 90°C for 30 min on a hot plate. Next, 1.11 g indium acetate is added into the solution to yield a Sn/In ratio of 0.06. A transparent light yellowish solution results after stirring for 1 h. 1.0 g hydrogen peroxide is then added drop-wise to the solution, followed by stirring for 30 min. Subsequently, 0.6 g tetramethylammonium hydroxide is added drop-wise into the solution. After stirring for 1 h, hydrogen peroxide is added drop-wise in three aliquots (each 1 g, total 3 g) at 30 min intervals. Hydrogen peroxide plays a critical role in stabilizing the solution, preventing phase separation due to recrystallization from occurring after cooling to room temperature. The resultant solution is further concentrated by solvent evaporation on a hot plate 120^{o}C to yield ~ 28 wt% solids as ITO. This viscous, reddish yellow, transparent ink is stable for several months under ambient conditions.

Direct-write assembly

A 3-axis micropositioning stage (ABL 9000 *x-y-z* motion, Aerotech Inc., Pittsburgh, PA) is used to create patterned ITO structures, whose motion is controlled by computer-aided design software (RoboCAD, 3D Inks, Stillwater, OK). Concentrated sol-gel inks are housed in a syringe (3 mL barrel, EFD Inc., East Providence, RI) attached by a luer-

lok to a tapered borosilicate nozzle (1-4 μm in diameter, *d*). An air-powered fluid dispenser (800 ultra dispensing system, EFD Inc.) is used to pressurize the barrel and control the ink flow rate. The applied pressure required depends upon ink rheology, nozzle diameter, and printing speed, but typical values range from 10 – 100 psi at 0.05 – 1 mm s^{-1}.

Planar arrays of ITO microelectrodes are patterned on corning 7059 glass or silicon wafer substrates using a concentrated sol-gel ink (~ 25 wt% solids), which is deposited through a 1 μm nozzle (pressure = 25 psi, speed = 500 μm s^{-1}, center-to-center rod spacing = 8 μm). Next, spanning ITO microelectrodes are deposited using a more concentrated, sol-gel ink (~ 28 wt% solids) through a 2 μm nozzle (pressure = 50 psi, speed = 200 μm s^{-1}, center-to-center rod spacing = 12 μm) on a substrate composed of parallel rectangular silicon microribbons (width = 45 μm, height = 26 μm, center-to-center spacing = 70 μm). The Si microribbon array is prepared by lithography and etching process; the detailed procedure appears elsewhere.[1-3] Planar and spanning ITO microelectrodes are printed onto substrates, with a nozzle height (*z*) of 0.80 ~ 0.95*d* to ensure moderate adhesion to the substrates. 3D periodic arrays of ITO microelectrodes are patterned onto silicon wafers that are pre-coated with a sacrificial layer (Crystalbond™ 509, Structure Probe, Inc., West Chester, PA, T_m = 121°C).[4] A representative 8-layer structure is printed from a sol-gel ink (28 wt% solids) using a 1 μm nozzle (pressure = 95 psi, speed = 400 μm s^{-1}, center-to-center rod spacing = 4 μm). All structures are printed in air at room temperature. The as-printed structures are annealed at 570°C in air for 1 h, followed by reductive annealing at 570°C in flowing N_2 for 1 h.

Ink and Printed Feature Characterization

The ink rheology is measured using a controlled-stress rheometer (C-VOR, Malvern Instruments, Malvern, UK) equipped with a cup and bob (C8, 8 mm bob diameter, 0.4 mm gap) geometry at 25°C in the presence of solvent trap to prevent evaporation. The elastic (G') and viscous (G'') moduli are measured as a function of drying time using an oscillatory mode at a frequency of 1 Hz in the absence of the solvent trap.

Images of 1D and 3D arrays are obtained using a scanning electron microscopy (SEM, JOEL 6060LV, JEOL Ltd.) after sputtering with Au/Pd for 30 s (Emitech K575 Sputter Coater, Emitech Ltd.). The width (*w*) and height (*h*) of the printed features are evaluated from the top- and cross-sectional images.

XRD diffraction (D-Max, Rigaku International Corp., Tokyo, Japan) is carried out on after annealing the ITO inks at different temperatures (250-550^{o}C), followed by grinding to produce powder specimens. Thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA851, Columbus, OH) is performed by heating the ITO ink to 700°C at 10 °C min^{-1} in air.

Electrical resistivity (ρ) is measured by a four-point probe method on ITO thin films (thickness ~ 150 nm) produced by spin coating (3000 rpm, 60 s) a dilute ITO ink (5 wt% solids) on a corning 7059 glass substrate. The as-coated sample is dried at 120^{o}C for 5 min and then annealed at 570^{o}C for 5 min by directly inserting the sample into a tube furnace. The coating and annealing cycle is repeated seven times to achieve the desired film thickness, while avoiding crack formation.[5,6] For the last cycle, the samples are annealed at 570^{o}C for 1 h, followed by annealing under reductive conditions (flowing N_2) at 570°C for 1 h. Transmittance (T) of the planar arrays of periodic (center-to-center spacing = 20-80 μm) ITO microelectrodes are measured using a UV-VIS spectrometer.

References

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