Nanoscale

Cite this: *Nanoscale*, 2011, **3**, 2700

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COMMUNICATION

Transparent conductive grids *via* direct writing of silver nanoparticle inks

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Received 14th January 2011, Accepted 16th March 2011
DOI: 10.1039/c1nr10048c

Transparent conductive grids are patterned by direct writing of concentrated silver nanoparticle inks. This maskless, etch-free patterning approach is used to produce well-defined, two-dimensional periodic arrays composed of conductive features with center-to-center separation distances of up to 400 μm and an optical transmittance as high as 94.1%.

Transparent conducting electrodes are playing an increasingly important role in large-area electronic and optoelectronic devices, including radiofrequency identification (RFID) tags,[1] displays,[2] sensor arrays,[3] and photovoltaics.[4] To date, indium tin oxide, a transparent conductive oxide (TCO), is the most widely used material.[5] In these applications, TCOs are usually deposited as a uniform thin film across the entire device surface, requiring significant consumption of scarce materials like indium. As displays move to increasingly larger area (*i.e.*, Gen 10; 100 ft^2 with pixel sizes as large as 1 mm^2) and the implementation of photovoltaics grows exponentially, new low-cost patterning approaches and alternate materials are needed that meet the demanding requirements for both high optical transparency and electrical conductivity.[6]

Recent efforts have focused on printing and other solution routes for patterning conductive features from metallic[7–10] and carbon-based building blocks.[11,12] For example, Magdassi and co-workers have produced transparent conductive arrays by inkjet printing of dilute silver nanoparticle inks to form overlapping rings.[7] In another example, Cui *et al.* formed transparent coatings of sparse, random networks of silver nanowires on plastic substrates using a Meyer rod.[8] Importantly, even though the patterned metallic features are opaque, a high degree of optical transparency results due to their low areal coverage. However, neither approach allows for precise control over building block placement.

More recently, dip-pen nanolithography (DPN)[9,13] and e-jet printing[10,14] have been used to pattern conductive features. Pearton and co-workers used DPN to deposit a commercially available, silver nanoparticle ink at write speeds of up to 1600 μm s^{-1} and line widths of ~0.5 μm. However, reproducible patterns over large areas using these inks have yet to be demonstrated.[9] Silver nanoparticle inks have also been deposited by e-jet printing to form conductive traces with line widths of ~1.5 μm; in this example, the printing speed was not reported. However, like inkjet printing, this approach may suffer from satellite drop formation and non-uniform drop drying resulting in less homogeneous printed features.[10]

Here, we demonstrate the patterning of transparent conductive grids *via* direct writing of metallic nanoparticle inks on glass and plastic substrates. In this filamentary printing approach, 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).[15] The printed feature dimensions are determined by the ink rheology and printing parameters. Using this approach, microscale features (~1 μm) in one-dimensional (1D) to three-dimensional (3D) motifs can be patterned.[16,17] In the present work, we focus our efforts on two-dimensional (2D) grid-like motifs to produce transparent conducting arrays for large-area electronics and optoelectronic devices.

We begin by synthesizing a highly concentrated silver nanoparticle ink. In this procedure, silver nanoparticles are grown in an aqueous solution containing silver nitrate ($AgNO_3$) as the metallic source, poly (acrylic acid) (PAA) as a capping agent, and diethanolamine (DEA) as a reducing agent.[16] The transmission electron microscopy (TEM) image shows that silver nanoparticles with a mean particle size of 20 ± 5 nm, and a particle size distribution between 5 and 50 nm are obtained (Fig. 1B). To produce the desired concentrated ink (78 wt% solids), the silver nanoparticles are coagulated by adding ethanol,

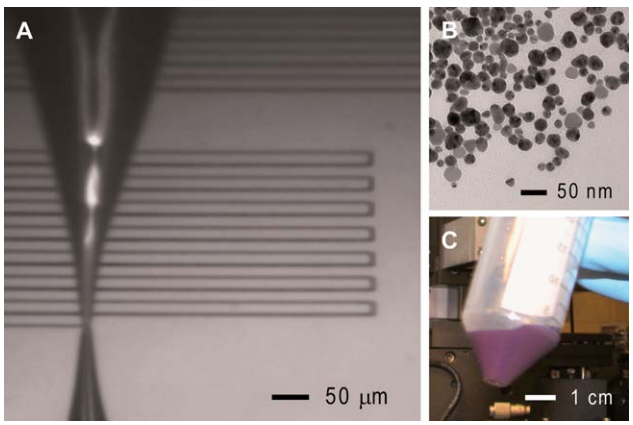

Fig. 1 (A) Optical image of direct writing of silver nanoparticle ink on a silicon wafer using a 5 μm nozzle. (B) TEM image of the synthesized silver nanoparticles. (C) Optical image of the concentrated silver nanoparticle ink (78 wt% solids).

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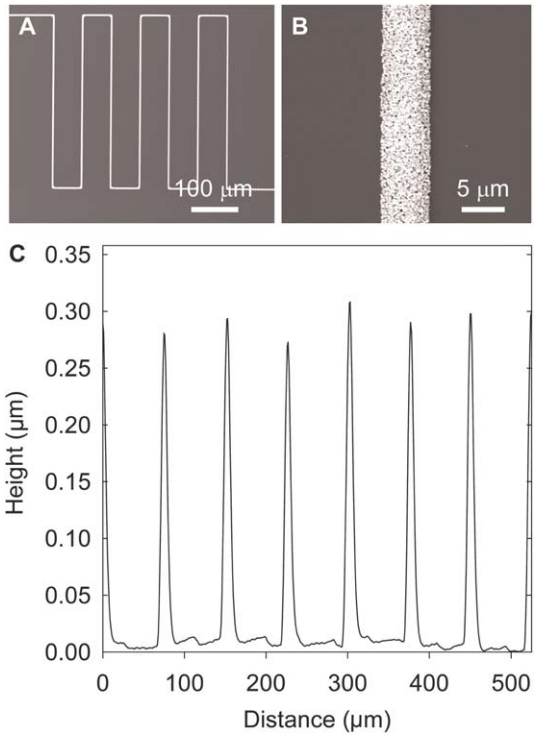

Fig. 2 (A) SEM image of 1D serpentine pattern printed onto a silicon wafer with a center-to-center spacing between patterned features of 125 μm. (B) Higher magnification SEM image of a conductive feature, and (C) height profile taken across the 1D array of patterned features.

a poor solvent, followed by centrifuging at 9000 rpm for 20 min (Fig. 1C).[18] This ink flows readily through deposition nozzles as small as 1 μm in diameter. In addition, the ink can be easily re-dispersed in water or ethylene glycol to form a low viscosity solution. The required deposition pressure depends upon the ink rheology, nozzle diameter, geometry, and printing speed, but typically ranges from 10–500 psi at 0.05–2.0 mm s^{-1}.

We first demonstrate this patterning technique by printing a 1D serpentine pattern on a silicon wafer using the concentrated silver nanoparticle ink (71 wt% solids, 1 : 1 water : glycerol by weight), which is deposited through a 2 μm nozzle (pressure = 5 psi, speed = 100 μm s^{-1}). This architecture is produced by continuously printing a 1D array of conductive features with a center-to-center spacing between adjacent features of 125 μm (Fig. 2A). After printing, this structure is annealed on a hotplate at 200 °C for 2 h. The higher magnification SEM image reveals that the annealed silver features are approximately 5.7 μm wide (w) (Fig. 2B) with a nearly uniform height (h) of 280 ± 30 nm, as measured by profilometry (Fig. 2C). The size of printed features depends upon the nozzle diameter, ink solids loading, applied pressure, and printing speed.[16,19] To date, conductive traces have been patterned using a 1 μm nozzle at modest speeds (<2 mm s^{-1}). By tailoring the ink composition and nozzle geometry, maximum printing speeds in excess of 10 cm s^{-1} are possible.

The electrical resistivity measured for thin films produced from this silver nanoparticle ink ranges from 1.22×10^{-4} Ω cm to 3.64×10^{-5} Ω cm, when annealed at 200 °C to 350 °C for 2 h, respectively, which is one to two orders of magnitude below that reported for TCO films.[5] Importantly, TCO films also require much higher processing temperatures of ≥400 °C.[5]

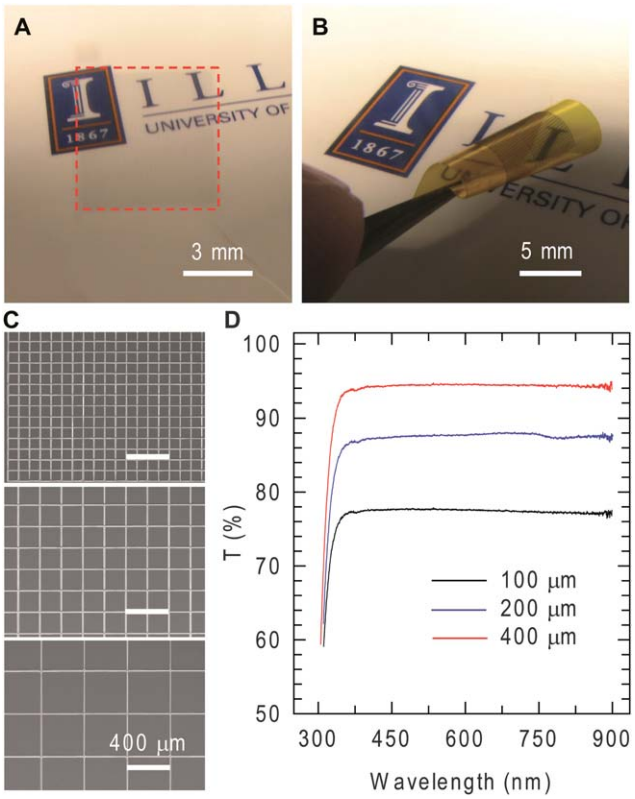

Fig. 3 Optical images of the transparent conductive grids with center-to-center line spacing of 200 μm, printed on (A) glass and (B) polyimide substrates. (C) SEM micrographs of the conductive grids, printed with center-to-center spacing of 100 μm (top), 200 μm (middle), and 400 μm, respectively. (D) Transmittance of the conductive grids of varying center-to-center spacing patterned on glass substrates.

To demonstrate patterning of transparent conductive grids, we printed 2D periodic arrays on glass and flexible polyimide substrates by depositing the silver nanoparticle ink (78 wt% solids) through a 5 μm nozzle (pressure = 50 psi, speed = 250 μm s^{-1}), followed by annealing at 200 °C for 2 h. The grids have overall dimensions of 6 mm × 6 mm and a center-to-center spacing of 200 μm, and exhibit a high degree of transparency on both substrates (Fig. 3A and B). The logos and text underneath are clearly visible through the printed grids. To quantify their optical transmittance, we patterned arrays (6 mm × 6 mm) composed of orthogonal silver features (w = 9 μm, h = 3 μm) with center-to-center spacing between 100 and 400 μm (Fig. 3C). Because the patterned features are intrinsically opaque to visible light, their optical transmittance (T) depends solely upon the unpatterned (open) area within each array (Fig. 3D). We find that the transmittance of conductive grids with 100 μm spacing (*i.e.*, 82.8% open area) is 77.4% from visible to near infrared region, and increases up to 94.1% as the spacing increases to 400 μm (*i.e.*, 95.5% open area).[20] Notably, these values are comparable, or even superior to TCO films.[5]

In conclusion, we have demonstrated the fabrication of transparent conductive grids on glass and flexible plastic substrates by direct writing of concentrated silver nanoparticle inks. Given that these metallic grids provide high transmittance over 94% with low resistivity at modest annealing temperatures, our printing approach may find a widespread application in large-area electronics, photovoltaics and optoelectronics.

This work was supported by the DOE Energy Frontier Research Center on Light-Material Interactions in Energy Conversion under grant DE-SC0001293. The silver inks were developed through funding provided by the U.S. Department of Energy, Materials Sciences and Engineering Division under award no. DEFG-02-07ER46471. We gratefully acknowledge the use of facilities at the Frederick Seitz MRL Center for Microanalysis of Materials at the University of Illinois at Urbana-Champaign.

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15 Direct ink writing is carried out by first loading the ink into a syringe barrel (3 ml barrel, EFD Inc., East Providence, RI). After attaching a deposition nozzle (diameter = 1–5 μm produced using a P-2000 micropipette puller, Sutter Instrument Co., Novato, CA), the ink-loaded syringe barrel is mounted onto the 3-axis printing stage (ABL 900010, Aerotech Inc., Pittsburgh, PA), whose motion is controlled by computer-aided design software (RoboCAD, 3D Inks, Stillwater, OK). Next, the nozzle height is adjusted with the aid of telescope lens with a 10× zoom. After applying pressure using an air-powered fluid dispensing system (800 ultra dispensing system, EFD Inc.), the ink is deposited onto the substrate with a controlled flow rate. Printing is performed in air under ambient conditions.
16 B. Y. Ahn, E. B. Duoss, M. J. Motala, X. Guo, S.-I. Park, Y. Xiong, J. Yoon, R. G. Nuzzo, J. A. Rogers and J. A. Lewis, *Science*, 2009, **323**, 1590.
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18 A concentrated silver nanoparticle ink (78.1 wt% solids) is prepared by first dissolving 1.99 g poly(acrylic acid) (PAA) (molecular weight = 5000 g mol^{-1}, 50 wt% aqueous solution), 1.00 g PAA (molecular weight = 50000 g mol^{-1}, 25 wt% aqueous solution), and 40 g diethanolamine (DEA) in 50 ml of water. A silver nitrate solution (20 g $AgNO_3$ in 20 ml water) is then added to this solution, stirred for 24 h at room temperature, followed by sonicating at 65 ± 5 °C for 2 h. The resulting nanoparticles are then coagulated by adding ethanol, followed by centrifuging at 9000 rpm for 20 min. After evaporating the remaining solvent, a highly concentrated silver nanoparticle ink is obtained.
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20 The open area, A_{open} (%) = $[1 - (A_{electrode}/A_{total})] \times 100\%$, where the electrode area $A_{electrode} = 2wL - w^2$, the total area $A_{total} = L^2$, w = electrode width, and L = center-to-center spacing.

