Air stable high resolution organic transistors by selective laser sintering of ink-jet printed metal nanoparticles

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A high resolution organic field effect transistor (OFET) fabrication process has been developed based on the selective laser sintering of ink-jet printed nanoparticle inks and the recent development of an air stable carboxylate-functionalized polythiophene semiconducting polymer. The entire fabrication and device characterization are performed at room temperature, ambient pressure, and air environment without using complex lithographic methods. This low temperature OFET fabrication process based on nanoparticle laser sintering has great potential for realizing inexpensive, large area flexible electronics on heat sensitive polymer substrates. © 2007 American Institute of Physics. [DOI: 10.1063/1.2719162]

The development of direct printing of functional materials has gained significant interest as an alternative to conventional integrated circuit processing, especially in the area of low cost or large area electronics on flexible substrates. Ink-jet direct writing has emerged as an attractive direct patterning technique because the fully data driven and maskless nature of drop-on-demand processing allows more versatility than other direct printing methods. Despite considerable advantages, the resolution is typically limited to the order of 50–100 μm. Hybrid ink-jet printing methods using water-based conductive polymers and surface energy patterning have been developed for resolution improvement. However, they still need several photolithography steps and are therefore neither readily amenable to the fabrication of low cost, flexible, and large area electronics nor desirable for large area or high speed electronics due to high resistivity.

The current research aims at overcoming the above difficulties in functional material ink-jet printing by relying on the combination of advanced laser processing, direct ink-jet printing, and utilization of the metal component in the form of nanoparticles.

Nanomaterials exhibit remarkable specific properties due to their large surface to volume ratio, large surface energy, and spatial confinement that cannot be observed in bulk materials. Metal nanoparticles are known to exhibit large melting temperature depression due to the thermodynamic size effect. In this regard, 2 nm sized nanoparticles start to melt at around 130–140 °C, a range that is compatible with plastic substrates. Nanoparticle ink sintering can be done in a furnace or by applying a heat source such as a continuous laser. Gold nanoparticles show a resonance light absorption peak around the 520 nm wavelength due to surface plasmon oscillation modes, suggesting strong visible laser light coupling. Local laser heating is advantageous due to the reduced heat affected zone and more efficient energy deposition. This is in turn very important for applications on polymer substrates with low transition/melting temperatures that are sensitive to heating in a furnace or on a heater. Our laser sintered gold lines show much greater uniformity and higher resolution (down to 1–2 μm) than lines that are ink-jet printed and sintered using a conventional heater (∼100 μm). Note that this high resolution is nontrivial, even via conventional photolithography or ultrafast lasers.

Enhanced resolution can be explained by the combined effects of melting temperature depression, lower conductive heat transfer, and strong absorption of the incident laser beam during laser irradiation. The sintered feature size and quality can be controlled by varying the applied laser power, beam size, and scanning speed. Using this approach, we could produce low resistivity (5.41 μΩ cm) metal interconnectors (Fig. 1).

Gold nanoparticles (1–3 nm diameter, Fig. 1 inset) encapsulated by hexanethiol self-assembled monolayer (SAM) 

![FIG. 1. Resistivity change of an ink-jet printed nanoparticle line on polyimide substrate at various laser powers [Ar ion laser, 514.5 nm wavelength, 27 μm beam waist (1/e²)]. Solid line is the resistivity of bulk gold (2.65 μΩ cm). Inset is a transmission electron microscopy picture of nanoparticles.](image-url)
were synthesized using a two-phase reduction method. The SAM is critical because it controls the size of the nanoparticles in addition to enhancing the long term stability and achieving favorable optical properties through Au-thiol chemistry.

The organic field effect transistors (OFETs) fabricated in this study have a typical bottom gate/bottom contact coplanar transistor configuration. Figure 2 shows the OFET fabrication process which consists of metal nanoparticle ink-jet printing and subsequent selective laser sintering of the nanoparticle film to form a high resolution channel and metal electrodes. The fabrication processes were carried out in ambient pressure and room temperature unless specified otherwise. Poly-4-vinylphenol (PVP) dielectric layer dissolved in hexanol with a small amount of the cross-linking agent [poly(melamine-co-formaldehyde)] was spin coated (3000 rpm, 2 min) to form a 380 nm thick film on top of the highly doped p-type silicon wafer. This dielectric layer was then cross-linked at 150 °C for 5 min [Fig. 2(ii)]. The source and drain electrodes for the OFETs were made by ink-jetting, selective laser sintering of the metal nanoparticle ink, and washing out the unsintered and loose particles. The metal nanoparticle suspension, consisting of hexanethiol-encapsulated gold nanoparticles diluted in an alpha terpineol carrier solvent (10 wt %) was ink-jet printed on top of the PVP layer by piezoelectrically driven microcapillary tube (MicroFab, 50 μm nozzle diameter) to produce a 100 μm wide nanoparticle ink line [Fig. 2(ii)]. After the gold nanoparticle ink was printed on the dielectric layer, a focused Ar ion laser beam [λ=514 nm, beam diameter (1/e²)~3.5 μm] was irradiated and scanned along an ink-jet printed line twice to write two parallel high resolution electrodes by selective laser sintering [Fig. 2(iii)]. After selective laser sintering, the remaining unsintered nanoparticle ink was washed away in a toluene solution exposing the two laser sintered parallel lines [Fig. 2(iv)]. These lines form the source and drain electrodes. The channel was defined by the separation distance between those electrodes. The final step consisted of spin coating an air stable carboxylate-functionalized polythiophene semiconducting polymer[16] at 1500 rpm for 30 s [Fig. 2(v)]. The semiconducting polymers were dissolved in warm (>45 °C) 1,2-dichlorobenzene (o-DCB) solvent (3 mg/ml). The remaining solvent was removed and annealed in air for 5 min on a hot plate at 150 °C.

A micrograph [(a) and (b)] and cross sectional schematics (c) of an OFET test structure are shown in Fig. 3. A single ink-jet line (~100 μm wide) is originally printed, as indicated by the blue dotted lines and the arrow. The two bright parallel lines depict the source and drain electrodes, and the gap between the two lines is the transistor channel (~4.5 μm). Note how the selective laser sintering can reduce the feature size to yield a very short channel. The channel gap size is determined by the scanning laser beam separation distance and could be as small as 1 μm. This minimum channel size is effectively limited by the lateral thermal diffusion length. The dark background is the cross-linked PVP dielectric layer on top of the P+ silicon wafer. The inset shows the chemical structure of the polythiophene derivative containing electron-withdrawing substituents. The use of a solution-dispersed organic semiconducting polymer is a key element for realizing low cost, large area electronics via direct writing. However, most commonly used organic semiconducting polymers are sensitive to air. This shortcoming may offset advantages of the current direct writing process because it would require a special oxygen-free environment during the device fabrication. To minimize air exposure effects, carboxylated polythiophene with increased air stability was used as semiconducting polymer.

![Micrograph of OFET test structure](image)

![Cross sectional schematic of OFET](image)
The OFET output and transfer characteristics were measured in air using an HP4155A semiconductor parameter analyzer and a probe station with micropositioning manipulators in a dark Faraday cage. Figure 4 shows the output and transfer characteristics of OFETs with a relatively long channel [Figs. 4(a) and 4(b)] and with a short channel [Figs. 4(c) and 4(d)]. The OFET with relatively longer channel [Figs. 4(a) and 4(b)] shows typical output and transfer characteristics with operation in p-type accumulation mode. The $I_{on}/I_{off}$ ratio ranged from $10^4$ to $10^5$ and threshold voltage ($V_t$) was around $-10$ V, while the OFET with relatively shorter channel [Figs. 4(c) and 4(d)] exhibited output characteristics with less pronounced saturation and similar $I_{on}/I_{off}$ ratio due to the contact effect. The measured value of carrier mobility was as high as 0.01 cm$^2$/V s in the saturation and linear regimes.

For verification of the current process, a standard OFET sample was fabricated using lithographic techniques on SiO$_2$ (115 nm)/P+ silicon wafer with evaporated gold electrodes. The semiconducting polymer was deposited under the same conditions as on the laser sintered samples. The overall performance of the lithographically processed OFET with a SiO$_2$ dielectric layer exhibited similar performance as the laser-fabricated OFETs. This test proves that the direct writing process presented in this work offers an inexpensive fabrication method that nevertheless yields devices performing as well as those produced by conventional lithography processes.

The performance of the OFETs can be enhanced by applying a more complex transistor design such as a top contact configuration with a patterned gate and a semiconducting polymer. Further performance enhancement can be achieved by using an alternative metal nanoparticle system (such as silver nanoparticles) and semiconducting polymer combination to reduce the work function mismatch. As noted previously, the transistor channel length is limited by the spatial diffusion in the current laser sintering method. Shrinking of the feature size can be achieved by selective nanoparticle ablation. This work is currently being performed in our group.

In conclusion, laser-enabled OFET fabrication was demonstrated, benefiting from the recent development of an air stable carboxylate-functionalized polythiophene$^{16}$ that avoids unintentional doping during processing. All processing steps consist of ink-jet printing of functional materials and application of laser irradiation. Furthermore, the entire fabrication and device characterization are performed at room temperature, ambient pressure, and air environment without any lithographic methods. OFET fabrication based on nanoparticle laser sintering shows great potential for implementing a manufacturing sequence realizing inexpensive, large area flexible electronics on heat sensitive polymer substrates.

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