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Selective Electroplating for 3D-Printed Electronics

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Creating 3D-printed parts with embedded circuitry is the next frontier in additive manufacturing, but printing of conductors with performance comparable to bulk metals such as copper is a difficult challenge. A hybrid process based on 3D printing followed by electroplating on highly conductive thermoplastic filament is used to manufacture 3D circuit boards and electronic packaging. Dual extruder heads on a standard fused filament fabrication printer are used to selectively define regions for electroplating, allowing distinct traces and multiple materials to be patterned in the same 3D-printed parts. Using this approach, a 3D-printed surface-mount package and a 555 timer oscillator circuit are demonstrated, including soldering of components onto the electroplated copper surface.

Building up parts layer by layer, a process known as additive manufacturing or 3D printing, has become a mainstream manufacturing technology allowing customization to the end user, reduced waste, and rapid turnaround.[1] While long used for creating structural components, there have recently been numerous efforts to add functionality through the addition of sensors and other electronics into a 3D printed part.[2] Metal conductors are nearly universal in electronic packaging and circuit boards due to their superior electrical conductivity, but the high cost of metal 3D printing relative to polymer alternatives[3] has limited the use of bulk metals in 3D printed electronics. The 3D printing community has therefore investigated a variety of alternative conductors such as room temperature liquid metals,[4] thermoplastic composites,[5] and silver pastes.[6] The current state of the art in 3D printed conductors is reactive silver inks able to reach bulk or near bulk conductivity after sintering at moderate temperatures.[7] Conductors based on reactive inks are however highly porous and experience current crowding and early device failure due to high pore density.[8] The resulting systems are not yet truly competitive with traditional conductors such as metallic copper.

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In this paper, we demonstrate electroplating copper and nickel selectively onto traces printed in a highly conductive thermoplastic composite filament and use of the resulting bulk metal conductors for 3D printed electronics packaging. Electroless plating has long been used for metallization of polymer 3D printed parts[9,10] to obtain superior mechanical and electrical properties, but results in blanket deposition of metal over the entire part. Since most 3D printable plastics are difficult to directly electrolessly plate, metallization through this technique is typically a multistep process requiring roughening[11] and surface activation[12] for proper plating. Creating separate electrodes using electroless plating requires additional steps to define the conductors, for instance through laser ablation,[13] variable swelling,[14] or mechanical polishing.[15] In 2017, researchers demonstrated that conductive polymer composites can be used as a conductive seed layer for electroplating.[16] Based on this finding, we demonstrated selective electroplating of a 3D printed fused filament fabrication (FFF) part, combining conductive composite filament to define plated regions with a nonconductive plastic as a mechanical support.[17] Fused filament fabrication, the extrusion of melted thermoplastics to build a part, is a cheap and widely available 3D printing technology.[18] While successful, the composite we used was resistive relative to traditional electroplating seed layers, requiring electrical contact near the region being plated and therefore strongly limiting the complexity of the resulting parts and preventing use for electronics packaging. Building on our work, a group at Southeast University in China subsequently demonstrated the use of a similar dual filament FFF 3D printing process to define regions for selective electroless plating through selective adhesion onto two different printable polymers and showed its use for 3D printed electronic packaging.[19] Electroless plating is however significantly slower than electroplating,[20] limiting possible deposition thickness, and also unlike electroplating lacks the ability to selectively plate different thicknesses or materials on the same part. A more detailed survey of past work on electro- and electroless plating of 3D printed parts was also given in ref. [17].

Here, we use a very low resistivity filament to plate centimeters from the contact point and demonstrate the ability to selectively plate complex 3D parts such as electronic packages and 3D printed circuit boards (PCBs). A very low resistivity copper-based FFF filament developed at Duke University and commercialized under the name Electrifi[21] was recently demonstrated as a seed layer for electroplating of copper on simple 3D printed parts such as a single electrical trace.[22] Due to its low resistivity, Electrifi can be plated far from the plating contact, allowing complex electrical structures to be created. Here we demonstrate that this technique allows the creation of complex electrical circuits with bulk metal copper on FFF printed parts, an important advance for additive manufacturing of electronics. We characterize the plating rate and improvement in resistivity of traces before and after plating with copper, followed by selective deposition of multiple materials (copper and nickel) on the same 3D printed part. The technique is then used to selectively define low resistivity copper traces for electronics integration and packaging, including a 3D printed package for an eight-pin surface mount chip and a complete 555 timer 3D printed circuit board. The electroplated copper is also demonstrated to be sufficiently robust to survive soldering of through hole components for circuit board assembly, allowing use of traditional printed circuit board assembly techniques.

Our approach relies on the use of a dual extrusion FFF 3D printer, a 3D printer with two extruder heads. In fused filament fabrication, rolls of thermoplastic filament are fed into a heated extruder that deposits layers of melted polymer to build the part. A single extruder head is limited to putting down only a single material at a time unless the build is paused to switch out the filament passing through the extruder. By incorporating a second extruder head, FFF printers become able to print multiple filaments simultaneously, allowing more complicated builds. Many commercially available FFF printers use multiple extruder heads to deposit different materials during a single print, for instance to add different colors or to incorporate a dissolvable support material to allow overhangs. Here, this multimaterial extrusion ability is instead used to define plated and nonplated regions. One extruder head is used to deposit a nonconductive thermoplastic, acrylonitrile butadiene styrene (ABS), to serve as a mechanical support while a second extruder head deposits Electrifi to define electrically conductive regions for electroplating (**Figure 1**a).

Figure 1b shows the process here for selective metallization of 3D printed electronic systems. The parts are first printed using a low cost consumer FFF printer (Makerbot Replicator 2X), using Electrifi as the conductive seed layer and ABS filament as the nonconductive mechanical layer. After printing, electrical contact for electroplating is made to the Electrifi using conductive paste, along with mounting of surface mount components. The sample is then electroplated with copper using a copper sulfate electroplating bath; an example part during plating is shown in Figure S1 in the Supporting Information. Electroplating, applying a current through an electrolyte solution to deposit metallic species onto a negatively charged electrode (cathode),[23] is a widespread commercial technology for applying surface finishes to conductive parts. In our process, the 3D printed part is suspended in the plating solution a fixed distance from a copper foil using a custom plating fixture, and a current applied to the desired features for plating. Selective electroplating is possible since only regions with an applied voltage are electroplated during the plating process. When it is desirable to plate all the conductive regions, as in the printed surface mount package shown in Figure 1b, an electrical contact region can be snapped off to leave distinct conductors in the final part as shown. While this process does require exposure to an acidic chemistry, no damage or discoloration was observed for the materials here, including common 3D printed thermoplastics (ABS and Electrifi as well as polylactic acid (PLA) in our prior work in ref. [17]), and surface mount packages/electrodes, and conductive epoxy.

One of the advantages of electroplating over electroless plating is the faster deposition rate, making the technique more suitable for thicker deposits useful for minimizing electrical resistance. The plating rate on the Electrifi was first characterized using a simple test structure, a 3D printed 20 mm by 20 mm square Electrifi region (**Figure 2**a). Four samples were plated for different times at 50 mA plating current (Figure 2b), a plating current density of 0.125 mA mm^{-2}. The deposit thickness was then measured by encasing the parts in epoxy

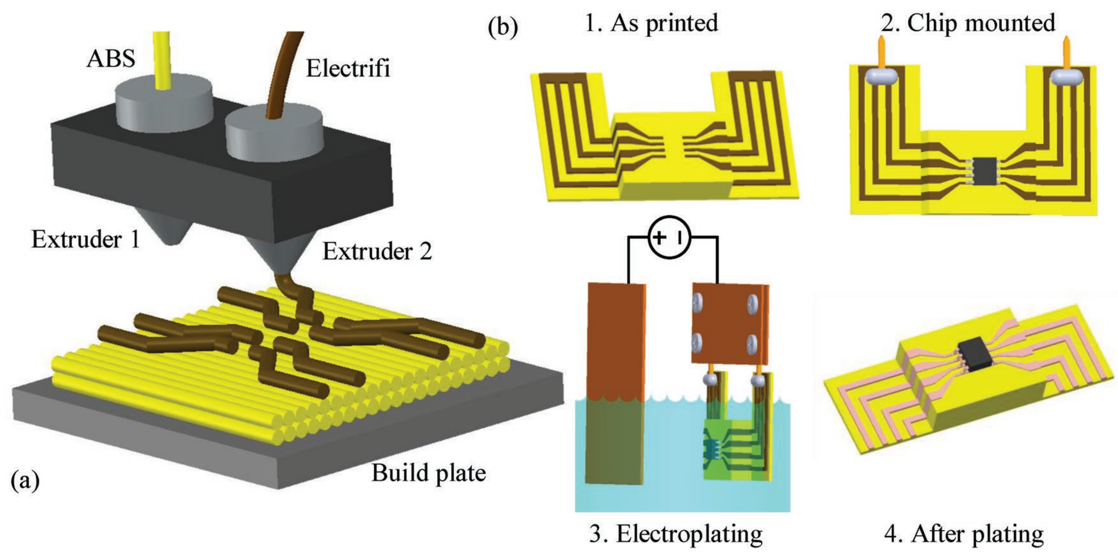

Figure 1. a) Dual extrusion fused filament fabrication and b) electroplating process.

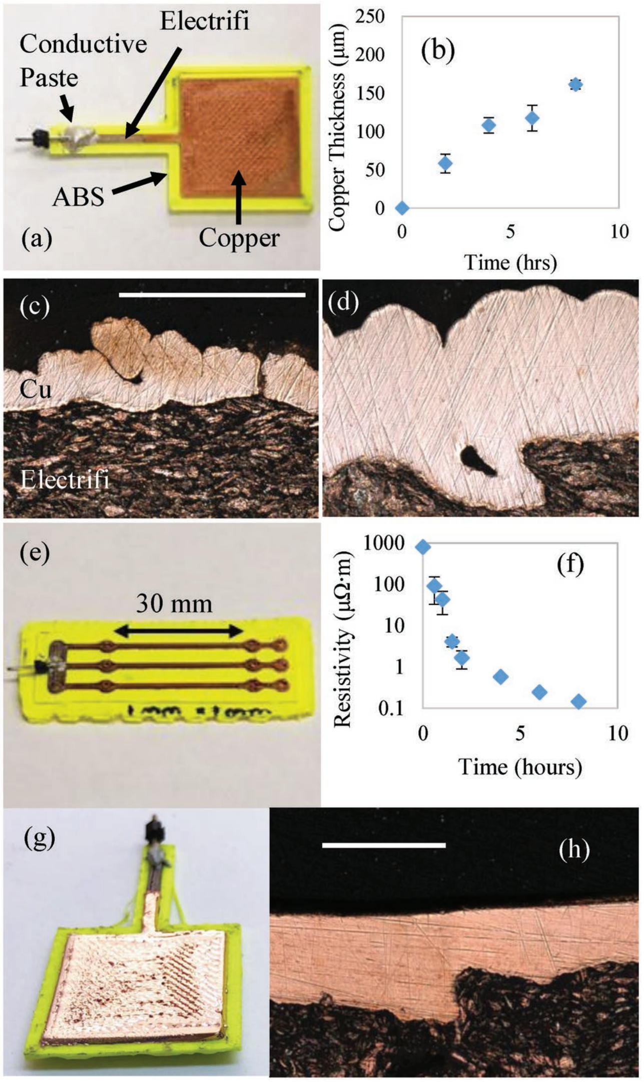

Figure 2. a) 20 mm by 20 mm square plating test sample (plated for 6 h at 50 mA), b) plating rate characterization and plating characterization samples after c) 2 and d) 8 h (scale identical for both images, white scale bar 200 µm), e) four point testing sample plated for 90 min, f) resistance of a 30 mm long, 1 mm by 1 mm cross-section line for different copper electroplating times, g) plating demonstration with copper leveler at 8 h, 50 mA, and h) cross-section of leveler sample (white scale bar 200 µm).

and polishing to allow optical measurement of the cross-section (Figure 2c,d). The measured plating rate was found to be 19 µm h^{-1} of plating. As shown in the cross-sections, the resulting copper is a solid deposit in close contact with the Electrifi layer. The topology of the final plating is dominated by the roughness and surface structure of the original 3D printed part, rather than the plating process. Due to the ability to apply a voltage selectively, it is possible to plate different regions to varying thickness or different materials; for instance, Figure S2a in the Supporting Information shows the characterization of nickel plating at the same plating current density and Figure S2b in the Supporting Information selective plating of regions of copper and nickel in close proximity on the same test part. A more complex 3D shape, a one-turn, four arm hemispherical helix,[24] was also printed in ABS/Electrifi and copper plated to show the process is not limited to 2D or near 2D geometries (Figure S3, Supporting Information).

Since copper has several orders of magnitude lower resistance than the original Electrifi, plating results in a sizeable drop in resistance. This behavior was characterized by measuring the resistance of a printed trace 1 mm by 1 mm in cross-section, plated at approximately the same current density as in the plating test. A test piece with three printed traces (Figure 2e) was used for each time point, with the average and standard deviation shown in Figure 2f. The measured trace length was 30 mm, and the resistance was measured using a four point measurement using a Keithley 2100 multimeter. Unplated, the average resistance was 23.8 Ω; after 8 h of plating, corresponding to roughly 170 µm of copper, the resistance had dropped to 4.3 mΩ, a reduction of four orders of magnitude. Due to the plating, the average resistivity of the printed trace has correspondingly dropped from 0.8 mΩ m to 0.14 µΩ m.

In 3D printing, objects are built by putting down lines of melted thermoplastic, and the result tends to be a relatively rough surface. This same roughness results in a highly irregular surface with voids once electroplated with copper, as is clearly evident in the cross-sections in Figure 2c,d. It is however possible to achieve a smoothing effect during electroplating by incorporating chemical additives known as levelers that act to reduce the current at high plating density sites and obtain a more level deposit.[25] In our prior work with Electrifi on PLA substrates,[22] it was demonstrated that adding organic additives had a pronounced effect on reducing the resulting surface roughness. A plating test sample was printed on the Makerbot with Electrifi on ABS, similar to the ones used for the plating characterization of the original bath (Figure 2g) and plated using a bath with the addition of Cl^-–PEG (polyethylene glycol)–MPSA (sodium 3-mercapto-1-propanesulfonate)–JGB (Janus Green B). After plating for 8 h, the plating resulted in a shiny and far more polished looking appearance. When the cross-section was taken (Figure 2h), the roughness was also obviously smoother than the original samples. The plating deposit thickness for the bath with the levelers was characterized and was found to have a similar plating rate (138 ± 42 µm, with the large uncertainty due to the variation in thickness of deposit resulting from the leveling effect). Since smoother metal films can be obtained by filling concave gaps between the thermoplastic lines, additives used for Cu metallization in semiconductor and PCB processes can further improve the surface morphology of the electroplated films.[26–28] Furthermore, while not specifically demonstrated here, levelers can also be used in other plating baths such as nickel.[28]

The electroplating process here is suitable for integration with electronics. A 3D printed mount for a surface mount package, SOIC8, was printed in Electrifi and ABS (**Figure 3**a). SOIC8 packages are commonly used on PCBs, and were chosen as an aggressive example of what is possible in the process. The chip here has eight landing pads with pitch 1.27 mm (0.5 mm pad, 0.77 mm spacing), near the resolution limits of the Makerbot, and the printed package also requires each trace to go over two 90° corners. A representative chip, a 555 timer integrated circuit (NE555, Texas Instruments) was then mounted using conductive paste. For ease of plating, the part was designed with a breakaway region, a region for making

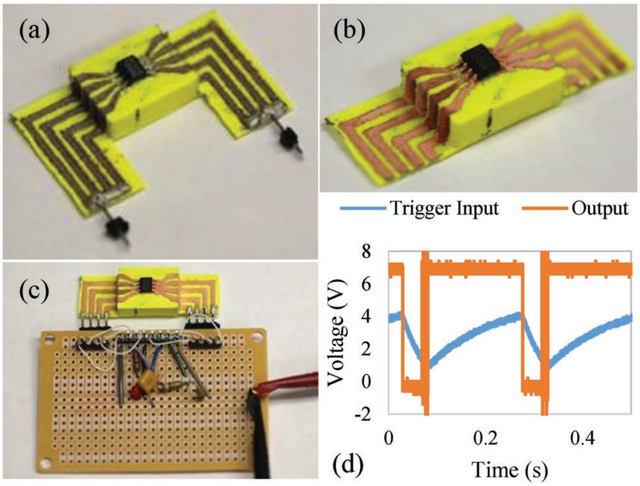

Figure 3. a) 3D printed SOIC8 mount with 555 timer chip, b) SOIC8 mount after plating and removal of breakaway region, c) astable 555 oscillator circuit, and d) circuit output.

electrical contact during the electroplating that could be folded and broken away, leaving only the designed surface mount package after plating (Figure 3b). All traces remained isolated after plating, and both the horizontal and vertical portions of the trace were visibly plated with copper.

For verification, the 555 timer was connected to a standard 555 astable oscillator circuit (Figure 3c and Figure S4, Supporting Information[29]). 555 timer oscillators based on an resistor-capacitor exponential decay to switch between two threshold voltages, are a widely used timing circuit, and are often chosen for demonstration of 3D printed electronic systems, as in ref. [19]. The oscillator is a convenient choice since the blinking of an light emitting diode (LED) can be used to demonstrate functionality of the circuit. After connection to the oscillator circuit, the oscillator behaved correctly, blinking an LED as expected and as seen in the measured electrical outputs (Figure 3d).

Electrifi and other similar conductive filaments are intended to melt at moderate temperatures for the purposes of printing, making soldering directly to the composite impractical. Close proximity to a heated soldering iron results in melting or burning of the polymer. In ref. [22], we demonstrated that a wire could however be soldered to a piece of Electrifi that has been plated with copper. The plated copper is robust enough to survive contact with the soldering iron, and solder wets copper sufficiently for electrical contact. It should therefore be possible to solder ICs and other discrete components onto a 3D printed circuit board, much as printed circuit boards are soldered. A representative circuit, again a 555 astable oscillator circuit as in the prior section, was designed and printed on the Makerbot in Electrifi filament (**Figure** 4a). The 3D printed circuit board is 35 mm on a side and is designed to take an eight-pin dual in-line package and five through-hole discrete components. The circuit board was plated resulting in uniform copper deposits on the printed traces (Figure 4b). While soldering requires appropriate care to avoid excessive heating in the neighboring ABS polymer, the board was successfully populated and each component soldered into place (Figure 4c). After soldering, the circuit was tested electrically and again the LED blinked as expected, and functionality of the resulting oscillator was demonstrated electrically (Figure 4d).

As an additional demonstration of the 3D nature of the process, a simple hemispherical structure designed to interface with several LEDs was designed, printed, and plated using the selective plating process (Figure 4e). In this demonstration, the LEDs were attached using conductive epoxy before electroplating. Figure 4f shows the LEDs after a voltage is applied.

3D printing of electronics competitive with more traditional printed circuit boards has long been an important dream in additive manufacturing. In this work, a powerful new technique for incorporating high performance electrical traces into polymer 3D printed parts was demonstrated, an important milestone toward 3D printed circuit boards. By using electroplating to selectively deposit copper and other metal layers onto FFF printed conductive composites, it becomes possible to create very low resistivity electrical traces in low cost 3D printed parts. Here, we demonstrate complex circuit boards made through integration of bulk metallic copper onto a common and low cost 3D printing technology, resulting in a reduction in trace resistance by four orders of magnitude. Unlike alternatives such as silver paste, the plating process occurs at room temperature, requiring no additional high temperature sintering to obtain low resistivity. The technique is ideal for 3D printed electronics, and integration with ICs, including surface mount components with narrow lead spacing, is an important

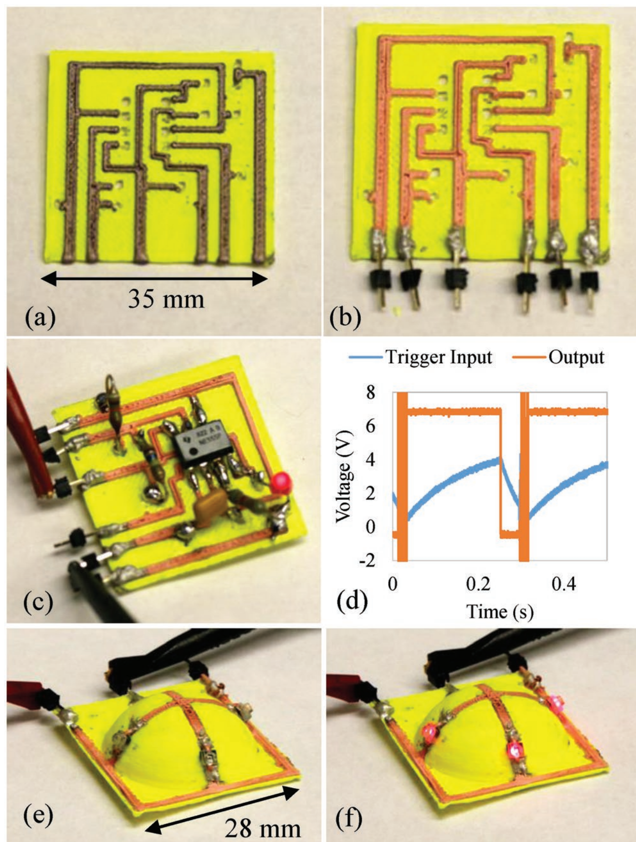

Figure 4. 3D printed astable 555 timer circuit a) as printed, b) after plating, c) tested after soldering, and d) circuit output, and plated traces connecting to LEDs on a hemisphere e) before and f) after LEDs turned on.

advance. Our demonstration of soldering chips onto 3D printed circuit boards is another important advantage in allowing direct use in PCB applications, as we have demonstrated with our representative 3D printed circuit, a 555-timer-based oscillator. The demonstration here was done at relatively low resolution using a consumer grade printer, but the technique could also be performed with a higher resolution FFF printer such as the nScrypt, which is capable of printing resolutions on the order of tens of micrometers using FFF technology.[30]

Experimental Section

3D Printing: All electroplated parts here were printed on a Makerbot Replicator 2X, with Electrifi filament (Multi3D LLC) as the conductor and True Yellow ABS Filament (Makerbot.com) for mechanical support. The extruder temperatures were 130 and 185 °C for the Electrifi and ABS respectively, with a build plate temperature of 100 °C on a thin Kapton tape build surface. For ease of removal and adhesion, the parts were built on an ABS raft using Makerbot's predefined raft settings.

Copper Electroplating: The parts here were electroplated using a standard copper sulfate bath consisting of 160 mL of water, 40 mL of 96% by weight sulfuric acid, and 20 g of copper sulfate. Using a 3D printed fixture, the part is mounted roughly 35 mm from a copper foil anode, and a plating power supply is used to apply a current for electroplating. For the leveler plated test sample, 1×10^{-3} M NaCl (Fisher Scientific), 100×10^{-6} M PEG (average molecular weight 3350, Sigma-Aldrich), 20×10^{-6} M MPSA (TCI), and 50×10^{-6} M JGB (Alfa Aesar) were added to the standard copper sulfate bath prior to plating. While electroplating with the organic additives, the electrolyte was stirred with a magnetic stir bar to maximize the leveling effect.

Nickel Electroplating: For nickel deposition, a commercial nickel sulfamate bath (5910 RTU solution, Technic) was instead used, with a similar fixture and plating setup to the copper plating testing. A nickel foil was used as the sacrificial anode.

Conductive Epoxy: Electrical contact to unplated Electrifi was made using a two part conductive epoxy, MG Chemicals 8331. The two parts were mixed in equal volume, then deposited using an applicator on the Electrifi, followed by attachment of the pin or surface mount component. The epoxy was then allowed to cure at room temperature for 5 h before testing.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

One of the co-authors, Dr. Wiley of Duke University, developed the Electrifi filament used here and commercialized the filament through the company Multi3D.

Keywords

3D printing, composite filament, electroplating, fused filament fabrication

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