Fully 3D-Printed, Ultrathin Capacitors via Multi-Material Microsputtering

Yosef S. Kornbluth, Lalitha Parameswaran, Richard Mathews, Livia M. Racz, and Luis F. Velásquez-García*

This study reports the first fully additively manufactured capacitors as a proof-of-concept demonstration of direct-write, ultrathin-film electronic components made via multi-material microplasma sputtering. This is also the first demonstration of a cleanroom-quality, multi-material electrical device produced entirely through additive manufacturing. Ultrathin metal and dielectric films are deposited at <80 °C and atmospheric pressure conditions on a substrate using a novel, continuously fed, dual target microsputtering printhead. The conductive films are created by sputtering gold in an air atmosphere and shown to attain near-bulk electrical resistivity. The dielectric films are created by sputtering aluminum in a gas blend of argon and air; the aluminum oxidizes in the high-energy, high-collisionality plasma, forming alumina nanoparticles that are deposited on the substrate. Ultra-thin (35 nm) alumina films showed extremely high resistivity (100 GΩ-m) and dielectric strength (6.2 GV m⁻¹). Also, the frequency response of the capacitor is satisfactorily described by the universal dielectric response typically found in heterogenous dielectrics. It is hypothesized that the dielectric response is the result of the presence of condensed water in the pores of the alumina film.

1. Introduction

Integrated circuit (IC) chips, that is, monolithic networks of up to millions of electronic components, are manufactured in large, multibillion dollar foundries while involving extreme processing conditions, for example, high temperature and high vacuum. Consequently, to attain low per-chip and per-component cost, thousands to millions of identical IC chips are batch processed.[8] Lower volume electronics, that is, tens to hundreds of relatively less complex circuits, are manufactured at a low cost using printed circuit boards (PCBs), where premade components are soldered onto a dielectric plate with an arrangement of thin film conductive traces and a set of drilled vias.[2] PCB components see relatively high temperatures during circuit manufacturing (soldering temperature is typically 180–190 °C).[3] also, in many cases the components attached to the PCB are packaged chips made in a foundry. However, currently, there is no cost-effective approach to make one or a few integrated electronic devices, conduct chip-to-chip customization, or rework IC chips—particularly if the devices involve temperature-sensitive materials.

This problem also existed in mechanical manufacturing until the start of this century. A variety of manufacturing methods existed, each suited for a different set of materials and a different volume of production. For example, injection molding is most economical at a large-volume production of identical parts, while CNC machining or thermoforming are a better fit to efficiently manufacture smaller runs.[4] However, there was no affordable technique for extremely low volume manufacturing such as a personalized prosthetic or a prototype.

In the last two decades, additive manufacturing, that is, the process of joining materials to make parts, usually layer by layer,[5] has fulfilled the need for extremely low volume mechanical manufacturing. In its most popular embodiment, called fused filament fabrication (FFF), a thermoplastic filament is heated to the point of softening. The filament is extruded through a nozzle that raster layer by layer a volume defined by a computer-aided design (CAD) file; each layer of extruded material cools and hardens, bonding to the already-deposited feedstock, until a solid object resembling that described by the CAD file is created.[6] Because the shape of the printed part is determined solely by the movement of the nozzle without the need for the separate production of a physical template, new shapes can be manufactured at a very low fixed cost. This is ideal for extremely low volume manufacturing.
Another mainstream additive manufacturing method is vat polymerization, based on selective solidification of resin using light while following a CAD file. The original implementation of this technique is called stereolithography (SLA). A SLA system has a vat full of UV-reactive resin, a build platform with vertical movement, a UV laser diode above the vat, and an optical system that steers the laser beam: the object is created, layer by layer, by the rastering of the laser beam near the surface of the vat to cure specific voxels of each layer as the platform moves downwards after each layer is formed. An improved version of the vat polymerization technique is called digital light processing (DLP). In a digital light processing (DLP) system, the light source is a 2D projector at the bottom of the vat that cures each layer at the same time, greatly reducing the build times, eliminating the need for the vat to fully contain the object and attaining higher resolution. Besides sharing with FFF the issue of an extremely low volume manufacturing capability, even though progress has been made in the chemistry of the printable materials and the mechanical design of the printer, vat polymerization does not allow the monolithic creation of freeform, finely structured, and multi-material objects at the scales required for IC manufacturing.

Powder bed fusion (PBF) encompasses a group of mainstream additive manufacturing methods for creating objects following a CAD file, which uses a bed of powder as feedstock. In PBF, a high-energy electron beam (PBF-EB) or laser beam (PBF-L) rasters a bed of fine powder, often metallic or ceramic, fusing it on its path; the powder bed is incrementally moved downward, while a fresh layer of powder is applied on top of the existing printed object using a blade or roller. The process continues, integrating a new layer of fused material to the previously printed layers, until the object is completed. PBF-L is widely referred to in the literature as direct metal laser sintering (DMLS), selective laser melting (SLM), or selective laser sintering (SLS). These techniques differ in the amount of melting that takes place. PFB-EB is also known as electron beam melting (EBM). Like vat polymerization, PBF is compatible with very low volume manufacturing and is, in practice, geared for the production of single-material objects. Nonetheless, unlike vat polymerization, the powder bed provides some mechanical support to the printed object, making it often unnecessary to print dummy structures when creating unsupported objects. However, the removal of loose powder from the internal cavities of a PBF-printed object is challenging if there is no direct access to such material or the cavities are intricate. Although the build speed, dimensional accuracy, printed mass density, and surface finish of PBF systems have greatly improved in the last decade, PBF-printed parts have a complex thermal history due to the sequential consolidation of feedstock in small segments, leading to significant accumulation of residual stresses. Furthermore, PBF-fabricated objects usually exhibit mechanical anisotropy due to the directional microstructure generated during cooling, with the out-of-layer direction generally being the weakest, and the attainable surface finish and resolution are too coarse for producing finely featured objects.

Binding material jetting (BMJ) is an additive manufacturing method with powder bed feedstock and binder as integrating agent. BMJ decouples the definition of the object from its sintering/solidification, eliminating stress build-up and attaining faster printing speed and better precision compared to PBF. The manufacture of a BMJ-printed object starts by injecting at room temperature with an inkjet head a slurry of water and polymer into the regions of the powder layer described by a CAD file; the slurry dries, leaving the polymer that amalgamates the powder particles. The printed object immersed in loose powder is heated up to increase its mechanical strength, and is then extracted from the unprocessed powder and heated up in a furnace to completely burn out the binder and sinter the printed object. A variation of BMJ for polymers is called Multijet fusion (MJF) and uses an infrared lamp to heat the binding liquid, fusing regions of the powder together; this is repeated for each layer of the manufactured object. BMJ and Multijet fusion have similar issues of single-material printing, surface coarseness, and low resolution of PBF, and show as well mechanical anisotropy in nominally isotropic prints.

Material jetting (MJ) is an additive manufacturing method that selectively cures liquid photopolymer to create solid objects following a CAD file. In MJ, a series of nozzles eject droplets to deposit a thin layer of liquid that was previously heated; UV light is shined onto the layer, curing the liquid. After that, the platform is lowered and a new layer is poured and solidified, eventually completing the object. MJ can monolithically fabricate multi-material objects and can create parts with internal voids (filled in with a support material that can be removed after printing), but the available materials are polymers that differ in optical transparency and mechanical properties, for example, stiffness, yield stress, and maximum elongation. MJ has been used to demonstrate polymer electronics, but the electrical properties and film thickness (at least 16 µm) of the materials are not on par with IC manufacturing.

As is evident from the above summary, a multi-material additive manufacturing platform for monolithic fabrication of electronics is yet to be satisfactorily developed. Although mature additive manufacturing methods for metals exist, they involve temperatures well above those that a polymer can withstand and typically produce highly stressed parts. Moreover, there are reports of conductive and piezoresistive devices made via FFF using undoped thermoplastics for the dielectric layers and thermoplastics highly doped with micro and nanoparticles for the electrically conductive layers. However, the electrical resistivity of the doped material is orders of magnitude higher than that of bulk metal and the minimum height of the layering of the printable feedstock is on the order of tens of micrometers, greatly limiting the performance of the electrical components printed, for example, causing large voltage drops across interconnects, limiting the capacitance per unit of area that can be attained.

Several other techniques for the direct-write manufacturing of electronic components have been developed, particularly for interconnects. For example, imprints formed by drying and annealing (>200 °C) a suspension of silver nanoparticles deposited on a substrate via inkjet printing, extrusion, or spraying have been shown to attain high electrical conductivity. Other additive manufacturing techniques such as electrophoretic deposition, laser-assisted electrophoretic deposition, laser-induced forward transfer, local electroplating methods, laser-induced photoemission, and focused electron/ion beam
induced deposition have been shown to create structured metallization with feature sizes between 100 nm and 10 μm; however, these techniques are still in a prototype stage and have issues such as the use of high temperature to attain high electrical conductivity, the limited number printable materials available, and limited substrate compatibility.

Dielectric films have also been produced via additive manufacturing. Alumina films have been printed using inks processed via extrusion and high-temperature annealing. In addition, Young et al. used a laser to transfer a BaTiO₃ film from a ribbon to a substrate, also conducting high-temperature annealing to remove the binder from the deposited film; the resultant film is porous and with a relative electrical permittivity of ≈30. Zhang et al. used the same laser direct-write technology to produce an RF filter, however, they noted that the ribbon preparation is difficult to scale to industrial settings. In addition, focused ion beam deposition (in which an ion beam dissociates a precursor gas, leaving behind an imprint) has also been used to produce high-quality dielectric films, although this method requires significant postprocessing.

Other researchers have used nanoparticle-infused pastes that are extruded, dried (≈120 °C), debinded (≈450 °C), and sintered (≈950 °C) to produce dielectric films. However, besides the high temperatures involved, these techniques result in thick layers (≈1 mm)—out of scale of the thickness needed for thin-film electronics.

There are also reports on integrating various additive manufacturing methods to create multi-material electrical components, but no single method has been developed for the integrated deposition of thin-film dielectrics and conductive components at low temperature (<80 °C). For example, Kadanova and colleagues used an inkjet printhead to deposit a solution containing barium, strontium, and titanium; after annealing the imprints in an oxygen atmosphere to force the metals to react and the precursors to evaporate, barium strontium titanate (a material with high dielectric constant) was formed. Silver traces were then sprayed on top of the dielectric film and interdigitated capacitors were produced. Although this work demonstrates the ability to fully print a capacitor, its approach requires significant postprocessing.

Other methods used colloidal inks to produce both dielectric (BaTiO₃) films and conductive films. However, although this method requires significant postprocessing, it has also been used to produce high-quality dielectric films.

2. Dual Target Microsputtering Printhead

Microsputtering employs a plasma generated at atmospheric pressure using an arrangement of electrodes separated a small distance (>1 mm or less). The plasma dislodges atoms from solid surfaces using energetic ions; the sputtered material is agglomerated into a thin film, coating a substrate, taking advantage of the energy and directionality of the sputtered particulates. The behavior of a plasma is largely governed by the product of the interelectrode distance and the pressure; therefore, microsputtering is similar to traditional sputtering, which takes place in a vacuum (<1 Pa) using a larger interelectrode distance (>10 cm). Given the small length scale of microsputtering reactors, microsputtering is suited for use as a direct-write technology. The microsputterer can be moved around the surface of a substrate using motorized stages, tracing out a pattern, causing sputtered material land on the substrate area right below, hence creating a patterned thin film. Furthermore, the energy used by a microsputterer is small (≈2 W) and is greatly dissipated before the plasma reaches the substrate; therefore, it is feasible to microplasma print thin films on temperature-sensitive substrates.

The dual target microsputtering printhead used in this study is an improved version of previously reported single target hardware that uses a DC plasma fed by a coaxial gas flow to create gold imprints. To the best of our knowledge, the new apparatus is the first multi-target microsputterer reported in the literature. At a high level, the printer is a microplasma printhead moved by two motorized stages (Thorlabs NRT100) across a flat surface, that is, bed (the gap between the printhead and the bed is set manually using a micrometer). The printhead (Figure 1a,b) has two grounded wire targets, two gas flow feeds, a system to feed the wire targets to the microplasma region, and a set of anode electrodes to strike and sustain a plasma. The gas flows are fed to a coaxial tube using mass flow controllers (MFCs); one gas flow feeds a quartz inner tube (700 μm inner diameter, 1.1 mm outer diameter) and the other gas flow feeds a borosilicate glass outer tube (3 mm inner diameter, 5 mm outer diameter) concentric and coplanar with the quartz tube. The gas flows feed the plasma formed at the exit of the coaxial tube, setting velocity fields that control gas transport and hydrodynamic focusing. The Darcy–Weisbach equation predicts that the average flow velocity (v) in a tube is equal to:

\[ v = \sqrt{\frac{2D_0 \Delta P}{LDp}} \]  

(1)
where $D_H$ is the hydraulic diameter of the tube (equal to the inner diameter for the inner flow and to the difference between the inner diameter of the outer tube and the outer diameter of the inner tube for the outer flow), $\Delta P$ is the pressure drop across the tube, $L$ is the length of the tube, $\rho$ is the density of the gas, and $F$ is the Darcy friction factor. In this apparatus the flow is laminar or in transition and can be considered incompressible. The plasma is sustained by a voltage, controlled by a Keithley 2657A power supply to maintain a plasma current of 2.7 mA. The sputtered material is deposited on silicon wafers coated with 200 nm of thermal silicon dioxide, which are biased at $-300$ V with a HP 6516A power supply.

The dual target printhead uses two thin wires as sputtering targets: a 100 $\mu$m diameter gold wire (99.95% purity, Alfa Aesar) to create the conductive films, and a 127 $\mu$m diameter aluminum wire (99.999% purity, Alfa Aesar) to create the dielectric films. The two target wires are fed through an innovative dual wire feed system that consists of two grounded side rollers actuated by stepper motors and a central roller (Figure 1c–e). Each wire is fed between one of the side rollers and the central roller, into the inner quartz tube, down towards the stainless-steel anode of the microplasma reactor, which is positioned 2 mm horizontally from the exit of the inner tube (Figure 2a).

A wire selector knob moves the side rollers, so that only one of them is in contact with its wire at any given time. The central roller is rotated manually (by means of a knob) to retract or push down the tube a given wire. To sputter a wire, the wire is pushed down to $\approx 1$ mm before the exit of the inner quartz tube, effectively immersing the wire in the microplasma, while the other wire is retracted away of the microplasma. To switch wires: i) the plasma is extinguished; ii) the active wire is retracted; iii) the wire selector knob is turned; iv) the new wire is pushed down; and v) the plasma is reignited between the anode and the new wire. This procedure can be done in less than a minute and without moving the microplasma reactor, allowing for the sequential sputtering of the two targets without the risk of cross-contamination or the need to move the plasma reactor and realign it.

A nozzle with a 1 mm × 5 mm tapered aperture is attached at the end of the dual target printhead with a set of screws and
and the electric field by the product of the ion mobility, $vE$.

Instead, the method developed uses a tailored blend of gases. Solution, as the high current can melt the thin target wire. Increasing the ion energy by increasing the power fed to the plasma is not a viable option to sustain a large electric field without ionization avalanche; and ii) it will provide an adequate flux of energetic ions for sputtering the target wire. When an electron with an energy of $\approx 2-4 \text{ eV}$ impacts a diatomic nitrogen molecule, it has a large chance of colliding with a gas atom before it reaches the anode. Thus, no electric field will cause runaway ionization provided the pressure is low enough (product of pressure and interelectrode distance $<50 \text{ Pa-cm}$).

Instead, for a plasma operating at atmospheric pressure, using a blend of argon (minority species) and diatomic nitrogen (majority species) can accomplish two goals, that is: i) it will sustain a large electric field without ionization avalanche; and ii) it will provide an adequate flux of energetic ions for sputtering the target wire. When an electron with an energy of $\approx 2-4 \text{ eV}$ impacts a diatomic nitrogen molecule, it has a large chance (cross-section) of exciting one of the rotational modes of the molecule, losing much of its kinetic energy in that inelastic collision (Figure 3). Given that collisions happen so frequently in dense plasmas, the process of exciting the rotational modes of the diatomic nitrogen molecule is very common, limiting the number of electrons exceeding $\approx 4 \text{ eV}$ of energy. As a result, very few electrons can ionize the nitrogen atoms, as an electron would need $13 \text{ eV}$ to do so. To counteract the energy-robbing rotational mode, a nitrogen plasma requires a much higher electric field (and thus a much faster transfer of energy to electrons) than a monatomic plasma in which there is no rotational excitation, and the only non-elastic collisions are ionization and

\[ v = \mu E \]  

The ion mobility is a function of the gas pressure, and to a minor extent, of the gas species. Thus, in traditional sputtering, the velocity (and thus kinetic energy) of the plasma ions can easily be controlled by increasing the electric field. However, in atmospheric plasmas, increasing the electric field to increase the ion energy causes an undesirable runaway ionization effect. A higher electric field increases the electron energy; the more energetic the electrons, the greater the chance that their collision with an atom will ionize that atom, which in turn will produce a second free electron that will be accelerated by the electric field and ionize yet another atom, causing an avalanche, that is, a rapid, exponential growth in the ionization rate and the plasma current, eventually heating and melting the thin target wire. As a result, the power supply used to set the plasma delivers a constant current of $2.7 \text{ mA}$, which, from empirical characterization, allows the target wire to avoid melting.

In traditional vacuum sputtering, increasing the power fed to the plasma increases the ion energy without causing an avalanche because in a vacuum, an electron, no matter how energetic, has a low chance of colliding with a gas atom before it reaches the anode. Thus, no electric field will cause runaway ionization provided the pressure is low enough (product of pressure and interelectrode distance $<50 \text{ Pa-cm}$).

Therefore, a method to create dielectric films from DC sputtered aluminum shaped into a wire was developed. Previous microsputtering studies have used compressed dry air or argon as the sputtering gas,[43–48] while these are sufficient to sputter materials such as gold and copper, they cannot sputter aluminum, as aluminum needs more energetic ions to strip the aluminum atoms from the target wire. Increasing the ion energy by increasing the power fed to the plasma is not a viable solution, as the high current can melt the thin wire. Instead, the method developed uses a tailored blend of gases.

The mean velocity of the ions in the plasma $v$ is determined by the product of the ion mobility $\mu$ and the electric field $E$.

\[ v = \mu E \]  

Figure 2. Photograph of the microplasma sputterer in operation (a). The stainless-steel anode is $\approx 2 \text{ mm}$ to the left of the exit of the inner tube. The plasma can be seen as a thick glow inside the end of the inner tube and as a thinner glow once it exits the inner tube and is carried by the fast jet flow. The reflective substrate receiving the deposit can be seen. Photograph of the microsputtering printhead with the nozzle installed and wrapped in copper tape (b) and close-up cutaway schematic of the nozzle (c). The tab and screws keep the nozzle in position above the substrate, the view hole allows for visible inspection of the plasma, and the tapered aperture maximizes the deposition rate inside the desired region.
electron excitation. Thus, the diatomic gas plays the role of a dielectric gas, that is, a gas that can sustain a relatively high electric field without triggering significant ionization. Consequently, by using a diatomic plasma, such as nitrogen, a higher electric field can be maintained without triggering runaway ionization, and thus higher ion energy is possible.

However, diatomic molecules are not ideal for sputtering: before the diatomic ion collides with the target, stripping an atom from the target, the diatomic ion will break apart into two constituent atoms, each with half the energy of the molecule.[52] A gas mixture, majority nitrogen and minority argon, will provide the necessary qualities for effective sputtering: the diatomic nitrogen will maintain a high electric field and low ionization rate by robbing electrons of their energy in low-energy inelastic collisions, while the monoatomic argon, when ionized, will sputter the wire target effectively as it cannot break apart while traveling to the target wire.

The difference between nitrogen and argon is evident while examining the Townsend coefficients of the gases. The breakdown voltage $V_{BK}$ (i.e., the bias voltage necessary to spark a plasma) is a function of the product of the pressure $P$ and the interelectrode distance $d$, following the formula:

$$V_{BK} = \frac{B_T P d}{\ln(A_T P d) - \ln\left(\ln\left(1 + \frac{1}{\gamma_0}\right)\right)} \quad (3)$$

where $\gamma_0$ is the secondary electron emission coefficient (which can be neglected for large $P d$, as in this case), and $A_T$ and $B_T$ are constants of the gas, known as the Townsend coefficients.

It has been shown that the higher the inelastic cross-sections, the higher $B_T$, and the higher the electric field needed to accelerate the electrons before they lose energy to inelastic collisions.[53] Nitrogen has a very high breakdown voltage compared to argon,[51] further supporting the claim that nitrogen, overall, has higher inelastic cross-sections.

The difference between monatomic and diatomic gases can also be seen by examining the ionization rate coefficient (a measure of the rate of ionization for a given electron and neutral atom density) for a given reduced electric field. For argon, the ionization rate coefficient becomes meaningful ($>10^{-19}$ m$^{-3}$ s$^{-1}$) at 30 Td (800 kV m$^{-1}$ at atmospheric pressure), while for nitrogen, a reduced electric field of 120 Td (3.2 MV m$^{-1}$ at atmospheric pressure) is necessary.[53]

The idea of using a mix of a diatomic gas and a monoatomic gas to improve sputtering yield without affecting the target wire was tested using a gold target, where the plasma is sustained with a 2.7 mA constant current and the film thickness of the deposited film is measured after 10 min of deposition (Figure 4). Compressed dry air (instead of nitrogen) is used as the majority ingredient, while a small amount of argon is added. The experimental results show that decreasing the diatomic fraction of the atmosphere decreases the plasma voltage. The maximum sputtering rate is not at either extreme of pure air or pure argon, but instead at 5% argon, 95% air (the 5% value does not include the argon naturally present in air). At this point, the diatomic content (nitrogen and oxygen) is high enough to sustain a large plasma voltage and low ionization rate, but the monoatomic content is high enough to sputter effectively. The gas mixture doubles the sputtering rate compared to that of pure air.

Using a blend of nitrogen and argon is crucial for the sputtering of aluminum. Aluminum needs more energy to sputter than gold; as such, in pure air, aluminum sputters extremely slowly ($<10$ pm s$^{-1}$) in the microsputter. However, in a 5%
argon and 95% air gas blend, it sputters at $\approx 1$ Å s$^{-1}$. In the high-energy, high-collisionality environment of the plasma, the sputtered Al atoms cluster into nanoparticles$^{[40]}$ that react with the oxygen in the air gas flow to form alumina. The alumina nanoparticles are carried to the substrate by the gas flow, where they form a porous, thin film (Figure 5). EDX confirms that the film is alumina (Figure 6); by comparing the EDX results of a silicon dioxide-coated silicon wafer and a similar wafer with the microsputtered alumina coating, the stoichiometry of the microsputtered film is found to be AlO$_{1.05}$, as opposed to pure alumina, which is Al$_2$O$_3$. Oxygen-rich alumina has also been seen in other porous, thin films with a stoichiometry of AlO$_{1.95}$. In both cases, the excess surface area leads to extra oxygen atoms in the crystal structure.

4. Fully Microsputtered, Ultrathin Capacitors

Fully additively manufactured capacitors were created and characterized as a proof-of-concept demonstration of direct-write, ultrathin-film electronic components made via room-temperature, atmospheric pressure, multi-material microplasma sputtering. The capacitor consists of a 7 mm-long microsputtered gold line, a 3 mm by 3 mm microsputtered alumina square printed over the center of the bottom gold line, and a second 7 mm-long gold line microsputtered perpendicular to the first line, over the alumina square (Figure 7). The centers of all three patterned films lay on top of each other. Conductive epoxy is placed on the four exposed ends of the two gold lines. Electrical measurements show that each gold line is electrically conductive with an electrical conductivity near bulk metal,$^{[40]}$ but the alumina square prevents current from passing between the gold lines. Infrared measurements of the substrate suggest a maximum substrate temperature of 80 °C during printing. The maximum temperature is reached when the printhead moves slowly (so heat cannot dissipate), with a large gas flow (so plasma heat reaches the substrate), and with a high plasma voltage (leading to higher energy).

The development of the process for microplasma sputtering of gold is reported elsewhere.$^{[40,45,46]}$ The gold traces are made of grains composed of larger nanoparticles separated by chasms that are filled in with smaller nanoparticles,$^{[40]}$ with
electrical behavior that resembles a resistor network (an infinite square mesh of resistors $R_1$ equal to the average resistance of a gold grain and the inter-grain resistance). In microsputtered films, this is slightly higher than the bulk resistance of gold, due to the imperfect filling of the chasms by gold nanoparticles. Specifically, we estimate $R_1 = 9.1 \ \mu\Omega \cdot \text{cm}$. The electrical conductivity of such a network follows the scaling law:[54]

$$\sigma = \sigma_1 (C - C^*)^p$$

where $\sigma$ and $\sigma_1$ are the reciprocals of the total resistance per unit length and $R_1$, respectively, $C$ is the probability of a chasm to be filled in, and $C^*$ is the critical probability, that is, the minimum fraction of resistors that must have $R_1$ resistance for the network to have finite resistance between two parts an arbitrary distance away. This critical probability is equal to 0.25 (i.e., if every grain is, on average, connected to its neighbors, the film will be electrically conductive) and $p$ is found to be 1. Therefore, the resistivity $R_R$ between two points a distance $N$ away in the trace will be:

$$R_R = \frac{N \cdot R_1}{C - 0.5}$$

$C$ can be estimated if it is assumed that the film is made of square grains with an average size $A$, separated by a chasm with width $B$. Thus, the total coverage $T$ of the film will be equal to the fraction of covered area (grains and filled-in chasms) divided by the total area (grains and chasms), that is:

$$T = \frac{A^2 + 2C \cdot A \cdot B}{A^2 + 2A \cdot B}$$

or

$$C = T \left(1 + \frac{A}{2B}\right) \frac{A}{2B}$$

By inspection of SEM micrographs of the gold films, $A = 0.4B$, and thus $C = 1.2T - 0.2$. Substituting into Equation (5) yields:

$$R_R = \frac{N \cdot R_1}{1.2T - 0.7}$$

The prediction of Equation (8) compares well to the experimental data, (Figure 8). The model also predicts that at least 90% of the chasms are filled in with nanoparticles, resulting in $\approx 1.2 \times$ bulk electrical resistivity.[40]

5. Electrical Characterization of Ultrathin, Microsputtered Alumina Films

5.1. AC Response

AC measurements for frequencies between 1 kHz and 1 MHz were taken between pairs of electrodes. Based on the AC measurements, the electrical behavior of the ultrathin aluminum film can be described by a complex impedance formed by a resistance $R$ and a reactance $X$ connected in parallel, where the current can either flow without a phase change with respect to the driving voltage (i.e., through the resistor) or with a phase change (i.e., through the capacitor). $R$ and $X$ follow a power law dependence on the frequency (Figure 9a), where both the real and imaginary components have a similar exponent (about $-0.84$) and the resistance is approximately the triple of the reactance. From these measurements, the real and imaginary components of the electrical permittivity are extracted (Figure 9b). This permittivity describes the ultrathin alumina film as a lossy dielectric with a loss tangent of $\approx 0.29$.

The impedance decreases as the frequency increases, albeit at a slower rate than that caused by a dielectric with constant permittivity. This behavior is indicative of the universal dielectric response, a phenomenon often found in heterogeneous dielectrics.[56] If a dielectric has both dielectric and conductive components, it will exhibit the same properties: a real and imaginary permittivity, a similar power-law dependence for each permittivity, and an exponent for that power-law between $-1$ and 0. It is hypothesized that the universal dielectric response shown in the microsputtered alumina film is due to the current’s changing path as the frequency changes. At low frequencies, very little current can flow across the dielectric (acting as a capacitor); as a result, the current is all funneled through the conductive regions. Because the path that only travels through conductive regions is circuitous, the current is low, leading to a high imaginary permittivity. As the frequency increases, more current flows through the dielectric components, increasing the total current and decreasing the imaginary permittivity. Similarly, at high frequencies, given that current can flow across the dielectric regions, the polarization of the material is lower, leading to a lower real permittivity.[57] The universal dielectric response has been seen in other agglomerations of nanoparticles[58] and in porous alumina;[59] in the latter case, it is hypothesized that water vapor in the air may condense to fill the pores and act as the conductive element.

Figure 8. Electrical conductivity versus film coverage. In the figure the units of conductivity are $1.1 \times 10^8 \ \Omega^{-1}\cdot \text{m}^{-1}$, representing an estimate of $\sigma_1$ of Equation (4). This yields a least-squares fit equation $\frac{\sigma}{\sigma_1} = 1.076T - 0.756$, very similar to Equation (8).
where \( \omega \) is the angular velocity of the signal (equal to \( 2\pi f \), where \( f \) is the frequency of the signal), \( \alpha \) is the fraction of the heterogeneous dielectric that is comprised of dielectric regions, \( \varepsilon \) is the relative permittivity of the dielectric regions, \( \varepsilon_0 \) is the permittivity of vacuum, and \( \sigma \) is the electrical conductivity of the conductive regions.\(^{[57]}\) Based on Figure 9a, \( \alpha = 0.84 \); in other words, the alumina is \( \approx 84\% \) by volume of the dielectric film. The volume not filled with alumina nanoparticles is approximately half the void volume expected from the random packing of equal-sized spheres.\(^{[60]}\) This suggests that, as previously found, a variety of nanoparticle sizes fills space more efficiently.\(^{[40]}\) However, this effect is insufficient to explain such a high packing density; \(^{[60]}\) thus, it seems that the nanoparticles are energetic enough to arrange themselves into a denser structure upon impinging the existing film.\(^{[46]}\) This packing volume is comparable to the film coverage shown earlier, in Section 4.

Using \( \varepsilon = 10 \) (bulk alumina)\(^{[57]}\) and \( \varepsilon_0 = 8.84 \times 10^{-12} \text{ F} \cdot \text{m}^{-1} \)

Equations (9) and (10) become, respectively:

\[
R = (\omega \varepsilon \varepsilon_0)^\alpha \sigma^\alpha \cos \left( \frac{\alpha \pi}{2} \right) \tag{9}
\]

\[
X = (\omega \varepsilon \varepsilon_0)^\alpha \sigma^\alpha \sin \left( \frac{\alpha \pi}{2} \right) \tag{10}
\]

with the prefactors of the right side of Equations (11) and (12) found by calculating a best-fit line of the bulk resistance and reactance as proportional to \( \omega^{0.85} \). It is found that \( \sigma^{0.15} = 5.6 \pm 0.6 \text{ S} \cdot \text{m}^{-1} \), that is, \( \sigma = 20.6 \mu\text{S} \cdot \text{m}^{-1} \). This value is typical for a liquid with total dissolved solids of \( \approx 100 \mu\text{g} \cdot \text{L}^{-1} \), which matches the solubility of aluminum hydroxide in distilled water.\(^{[61]}\) This result suggests that the pores of the porous alumina are filled-in with condensed water from the air, in which aluminum is dissolved.\(^{[57,61]}\)

Furthermore, the imaginary electrical permittivity of the heterogeneous dielectric is most dependent on the frequency between 5 and 200 kHz (Figure 9b). This range is centered on the characteristic frequency \( f_c = \frac{\sigma}{2 \varepsilon \varepsilon_0} = 33.7 \text{ kHz} \) at which the impedance of the alumina regions and water regions are equal. Far above and below this frequency, the imaginary permittivity is not a linear function of the frequency—even as the frequency increases, no additional current flows through the conductive region. Below this frequency, almost all the current flows (for part of its journey) through the conductive region; above this frequency, almost all the current flows through the capacitive region. This phenomenon has been seen in other heterogeneous dielectrics.\(^{[57]}\) Nonetheless, regardless of the universal dielectric response, the capacitor shows cleanroom-quality behavior. The capacitor is extremely thin (\( \approx 150 \text{ nm} \) thickness, Figure 7b) and exhibits a high permittivity, particularly at low frequencies. The universal dielectric response is a byproduct of the porosity of the film, which is due to the lack of annealing.

5.2. DC Response

The DC response of fully microplasma-printed capacitors was also characterized (Figure 10). The capacitor was found to have a resistance of \( 4.05 \text{ G}\Omega \) and a resistivity of \( 1.0 \times 10^{11} \text{\Omega} \cdot \text{m} \). This is \( \approx 10\% \) of the bulk resistivity of thin-film alumina, but ten times the resistivity of other nanoporous alumina deposits reported.\(^{[61,62]}\) It is possible that this is because of the high-quality of the alumina nanoparticles in the microplasma-printed plasma reactor. Although the nanoparticles are connected in an amorphous structure, they are formed in a high-energy plasma and are thus assumed to be of high quality.

The breakdown voltage of the dielectric film is 220 V, for a dielectric strength of \( 6.2 \text{ GV} \cdot \text{m}^{-1} \). This is twice the strength of the best reported results from any alumina.\(^{[63]}\) The aggregation of nanoparticles seems uniquely suited to avoid the propagation of electrical current; more study into the mechanism is needed. Thus, the microsputtered alumina film serves as an
excellent dielectric barrier between two electrically conductive traces; for example, a bias voltage below 50 V across two conductive traces separated by the dielectric film will have minimal (nanoamperes level or less) leakage current and will not cause dielectric breakdown.

6. Conclusion

This study reported the first fully additively manufactured capacitors as a proof-of-concept demonstration of direct-write ultrathin-film electronic components made via multi-material microplasma sputtering. Ultrathin metal and dielectric films were deposited at <80 °C and atmospheric pressure conditions on a substrate using a novel, continuously fed, dual target microsputtering printhead. The conductive films were created by sputtering gold in an air atmosphere; the dielectric films were created by sputtering aluminum in a gas blend of 5% argon and 95% air. The gas mixture to deposit dielectrics was optimized to increase the ion energy and the sputtering rate compared to what either pure argon or pure nitrogen could achieve without casing runaway ionization. The study demonstrated cleanroom-quality dielectric films. Characterization of the microsputtered dielectric films shows the film is porous alumina with a 15% per volume content of small pores filled-in with water with excellent DC and AC electrical properties. To the best of our knowledge, this the first demonstration of a cleanroom-quality, multi-material electrical device produced entirely through additive manufacturing and serves as an important demonstration of the potential of microplasma sputtering.

7. Experimental Section

Effect of Argon Content in Plasma Voltage, Deposition Rate: Gold wire (100 µm diameter, 99.95% purity, Alfa Aesar) was sputtered using the microsputter reactor described in Section 2 with an inner gas flow of 4.5 slm through the inner quartz tube. The gas flow was dry compressed air with additions of argon at varying concentrations (99.997% purity, Airgas), measured with a mass flow controller MKS MFC-1. An additional gas flow of air (0.5 slm) flowed through a concentric, outer borosilicate tube. The gold target wire was retracted 1 mm from the mouth of the inner quartz tube, and the anode was laterally displaced 2 mm from the center of the inner tube. A plasma was struck with the plasma voltage controlled by a Keithley 2657A power supply so that the plasma current was constant and equal to 2.7 mA; the plasma voltage ranged from 600 to 900 V. Films were deposited for 5 min with the plasma reactor held stationary 3 mm above oxidized silicon samples (200 nm thermal oxide). The silicon was biased at ~300 V. Film thickness measurements were taken with a Dektak XT profilometer.

Capacitor Fabrication: Gold (100 µm diameter, 99.95% purity, Alfa Aesar) and aluminum (99.999% purity, Alfa Aesar) wires were sputtered using a 5% argon, 95% compressed air mixture for the inner quartz tube with the other parameters as specified at the beginning of Section 7. The plasma voltage ranged between 800 and 1100 V. The gold lines, 7 mm in length, were printed by moving the printhead 50 µm s⁻¹ for 20 passes (10 in each direction). The alumina cap was produced by rastering the printhead over a 3 mm by 3 mm area for 120 min. Conductive epoxy (MG Chemicals 8331D) was deposited on the exposed ends of the gold traces, and 36 AWG copper wire was attached to the epoxy, before it was allowed to cure at room temperature, to facilitate the electrical measurements.

Characterization of the Capacitors: To measure the AC response of the sputtered alumina films, a Digilent Analog Discovery 2 impedance analyzer was used to measure the impedance between pairs of leads. The electrical path between two leads involves two gold traces, which stretch from the periphery of the capacitor to the center (see Figure 7a). These gold traces either connect to each other directly or are separated by the dielectric layer of the capacitor. Thus, the dielectric layer’s frequency response can be calculated by summing the two paths that pass through the dielectric and subtracting the two paths that do not. Using the numbering of Figure 7a, the frequency response of paths 1 and 2, less those of 3 and 4 (i.e., Path 1 + Path 2 – Path 3 – Path 4) is twice the frequency response of the dielectric layer without the effects of the gold traces.

The DC response of the capacitors was measured with a Keithley 2657A power source. The capacitor was held at a bias voltage, starting at 100 mV, and held for 5 s. A current limit of 100 µA was implemented, to protect the power supply at the point of capacitor breakdown. The current was recorded, and the voltage was increased (10 mV until 1 V, 100 mV until 5 V, 500 mV until 10 V, etc., until 100 V, at which point steps of 10 V were used). This continued until the current surpassed 100 µA and the current limit was reached, representing the capacitor’s breakdown voltage.

EDX measurements were taken using a JEOL JSM-6010LA of two identical silicon wafer pieces with 200 nm of silicon dioxide coating. One piece had a layer of microsputtered alumina; by comparing the ratio of added alumina to added oxygen, the chemical composition of the alumina was determined.

The capacitor was cleaved, and cross-sections were taken by a Zeiss 1525 SEM.

The conductivity of the gold films was measured using a 4-point probe (Jandel RM3). The film thickness was measured with a Dektak XT profilometer and film coverage was measured with an SEM, and the imaged processed using Wolfram Mathematica.

Statistical Analysis: Best-fit lines and R² values were found using a standard least-squares formula. Data outliers, identified by being greater than 5 standard deviations from the fit line and no more than 1% of total data, are excluded from the calculations. No probability values are presented in this paper.

Acknowledgements

This research was supported by the Kansas City National Security Center. The help of Hyeonseok Kim of Massachusetts Institute of Technology...
(MIT) in the manufacture of the nozzles, Tayo Akinwande of MIT for helpful suggestions, and the MIT Institute for Soldier Nanotechnologies for their facilities were instrumental in this work.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
3D printing of electronics, alumina, heterogeneous dielectrics, microplasma sputtering, ultrathin films

Received: January 17, 2022
Revised: February 27, 2022
Published online: April 3, 2022

[1] S. A. Campbell, Fabrication Engineering and the Micro- and Nanoscale, Oxford University Press, New York, NY 2013.
[2] R. Khandpur, Printed Circuit Boards: Design, Fabrication, and Assembly, McGraw-Hill, New York, NY 2006.
[3] F. Oberg, F. D. Jones, H. L. Horton, H. H. Ryffel, Machinery’s Handbook, 23rd edition, Industrial Press Inc, South Norwalk, CT 1988.
[4] M. P. Groover, Introduction to Manufacturing Processes, John Wiley & Sons, Hoboken, NJ 2013.
[5] I. Gibson, D. Rosen, B. Stucker, Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing, 2nd edition, Springer, New York, NY 2015.
[6] E. Gkartzou, E. P. Koumoulos, C. A. Charitidis, Manuf. Rev. 2017, 4, 1.
[7] Y. Bar-Cohen, (Ed.), Advances in Manufacturing and Processing of Materials and Structures, CRC Press, Boca Raton, FL 2018.
[8] J. Huang, Q. Qin, J. Wang, Processes 2020, 8, 1138.
[9] K. L. Sampson, B. Deore, A. Go, M. A. Nayak, A. Orth, M. Gallerneault, P. R. L. Malenfant, C. Paquet, ACS Appl. Polym. Mater. 2021, 3, 4304.
[10] L. F. Velásquez-García, Y. Kornbluth, Annu. Rev. Biomed. Eng. 2021, 23, 307.
[11] J. L. Hirt, A. Reiser, R. Spolenak, T. Zambelli, Annu. Rev. Biomed. Eng. 2021, 24, 1138.
[12] W. E. Frazier, J. Mater. Eng. Perform. 2014, 23, 1917.
[13] X. Shen, H. E. Naguib, Addit. Manuf. 2019, 29, 100820.
[14] W. J. Sames, F. A. List, S. Pannala, R. R. Dehoff, S. S. Babu, Int. Mater. Rev. 2016, 61, 315.
[15] A. P. Singh, S. Pervaiz, ASME Int. Mech. Eng. Congr. Expo. 2021, 2A, V02AT02A023.
[16] F. Sillani, R. G. Kleijnjen, M. Vetterli, M. Schmid, K. Wegener, Addit. Manuf. 2019, 27, 32.
[17] M. Leary, Design for Additive Manufacturing, Elsevier Publishing, Amsterdam, The Netherlands 2020.
[18] O. Gülcen, K. Gündaydin, A. Tamer, Polymers 2021, 13, 2829.
[55] B. G. Segda, M. Jacquet, J. P. Besse, Vacuum. 2001, 62, 27.
[56] A. K. Jonscher, Nature 1977, 267, 673.
[57] C. R. Bowen, D. P. Almond, Mater. Sci. Technol. 2006, 22, 719.
[58] K. N. Rathod, Z. Joshi, D. Dhruv, K. Gadani, H. Boricha, A. D. Joshi, P. S. Solanki, N. A. Shah, Mater. Res. Express 2018, 5, 035040.
[59] M. Tahir, M. Mehmood, M. Nadeem, A. Waheed, M. T. Tanvir, Phys. B: Condens. Matter 2013, 425, 48.
[60] D. He, N. N. Eke, L. Cai, Phys Rev. E 1999, 60, 7098.
[61] A. F. Rusydi, IOP Conf. Ser.: Earth Environ. Sci. 2018, 118, 012019.
[62] Q. Li, Y. H. Yu, C. S. Bhatia, L. D. Marks, S. C. Lee, Y. W. Chung, J. Vac. Sci. Technol., A 2000, 18, 2333.
[63] H. C. Lin, P. D. Ye, G. D. Wilk, Appl. Phys. Lett. 2005, 87, 182904.