

Additive Manufacturing of Hybrid Circuits

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Abstract

There is a rising interest in developing functional electronics using additively manufactured (AM) components (1, 2). Considerations in materials selection and pathways to forming hybrid circuits and devices must demonstrate useful electronic function, enable integration and complement the complex-shaped, low cost, high volume, and high functionality of structural but generally electronically passive AM components. This paper reviews several emerging technologies being used in industry and research/development to provide integration advantages of fabricating multilayer hybrid circuits or devices. First, we review a maskless, non-contact, Direct Write (DW) technology that excels in the depositions of metallic colloid inks for electrical interconnects. Second, we review a complementary technology, Aerosol Deposition (AD), which excels in depositing metallic and ceramic powder as consolidated, thick conformal coatings, and is additionally patternable through masking. Finally, we show examples of hybrid circuits/devices integrated beyond 2-D planes, using combinations of DW or AD processes with conventional, established processes.

Keywords

Additive Manufacturing, Direct Write, Aerosol Deposition, Embedded Sensors, Hybrid Circuits

1. INTRODUCTION TO ADDITIVE MANUFACTURING OF HYBRID CIRCUITS

Advances in deposition technologies and the understanding of processing-microstructure-property relationships play a critical role in enabling circuits and electronics manufacturing. The precise control over chemistry, crystallographic orientation, and building of metallic, ceramic, and polymeric materials structures from nano- to macro- length scales, has led to significant advances in the performance of electronic devices. Traditional masking and deposition technologies (e.g. CVD, PVD, ALD, etc.) along with printing technologies are among the first examples of mass production of electronic materials for information storage and transfer. Screen printing and gravure methods have been historically used in 2-D and flexible electronics printing applications. When utilizing lithography processes to mask and define gravure cells, feature definition to 1 μm has been reported; however, 19–50 μm is more practically achievable (3-7). While screen printing and gravure methods offer the ability to mass produce standardized electronic components, significant tooling investments and a constraint of intimate contact between the substrate and printing hardware limit the ability to prototype and fabricate advanced hybrid circuits.

The integration of disparate polymeric, metallic, and ceramic materials for functional purposes in the fabrication of advanced hybrid circuits is driven by the development of additively manufactured components. In additive manufacturing (AM), complex 3-D model designs are transformed into objects by joining materials layer-by-layer, using integration of innovative technologies (8). Additive manufacturing processes are generally associated with 3-D printing of polymers and metals for the prototyping and production of complex hardware. However, computer controlled materials deposition with chemical reactivity or functionality resulting from post-processing has been accomplished in an array of materials, including natural materials,

elastomers and polymers, composites, structural and electronic ceramics, metals, and alloys (9). Although AM processes currently produce components at lower resolution than conventional methods, AM processes offer advantages—conformal deposition and integration of multi-material components in non-planar configurations (9). AM can produce high value products due to efficient integration of discrete materials during fabrication. Thus, there is a rising interest in novel processing to form functional circuits, electronics, and energized devices. (1, 2). These components require the integration of discrete materials to form conductors, resistors, capacitors, inductors, batteries, sensors, and displays. When selecting materials and considering alternative pathways to fabricate hybrid circuits and electronic devices, advantages and limitations of the technologies must be understood to enable multi-material integration and complement the complex shaped, low cost, high volume, and high functionality of the AM components.

The key materials and process developments needed to promote the formation of hybrid circuits and devices with requisite mechanical and electronic properties hinge on the ability to generate and integrate densified conductors, ceramics, and polymers, using either low or very rapid thermal profiles. Metals, ceramics, and polymers are physically consolidated at varying temperatures by conventional thermal means. Additionally, these materials must be integrated with acceptable precision and accuracy by the AM deposition process. Espalin *et al.* (2) reported the integration of multiple deposition techniques to form integrated components by their multi3D system, which formed a space exploration satellite called the CubeSat Trailblazer in 2013. Materials research in AM has emphasized the lowering of thermal processing ranges for metals and ceramics to accommodate the degradation or structural sensitivity of polymer components (10). Direct write (DW) and aerosol deposition (AD), coupled with rapid thermal processing technologies, including selective laser sintering or flash lamp annealing, have been used to

integrate materials for hybrid circuit fabrication at low temperatures using metallic and ceramic nanoparticles.

This review paper addresses several non-traditional, high throughput, both established and emerging technologies that are being used in industry and in research/development to provide agility and integration advantages for fabricating multilayer hybrid circuits or devices. All of the processes that will be discussed utilize metallic and/or ceramic particles that are suspended in media (binder) or are dry and free-flowing (**Error! Reference source not found.**).

First, a family of maskless, non-contact, printing technologies commonly referred to as Direct Write (DW) will be discussed. Direct Write processes including Ink Jet (IJ), Aerosol Jet (AJ), and Extrusion Casting (EC) offer high definition and conformal writing on complex surfaces, and excel in the deposition of metal inks for electrical interconnect formation. DW processes involve dispensing particles through a deposition nozzle that is precisely positioned over a target substrate utilizing a Computer Aided Design and Manufacturing (CAD/CAM) platform. (**Error! Reference source not found.a,b**). They enable the application of printed electronic networks and expand the design space beyond that of a 2-D plane on the substrates (**Error! Reference source not found.c,d**). During deposition, substrate handling and waste generation is highly minimized. Post-deposition thermal processing for particle sintering as well as binder burn-off is performed, leaving densified patterns on the target substrates. The particles and media are specifically selected to provide properties appropriate for the required pattern uniformity/resolution, materials usage, and thermal tolerance of the underlying structures and devices.

Thermal spray processes provide a complementary deposition technology that can deposit ceramics and has the potential to be integrated with DW technologies for AM of hybrid circuits and devices. Thermal spray commonly involves propelling dry particles suspended in carrier gas through a deposition nozzle towards a target substrate. The particles can be deposited in droplets in the case of Plasma Spray (PS) or they can be deposited in solid-state in the case of Aerosol Deposition (AD), a focus of this review. These spray processes offer rapid conformal deposition on large surface areas but feature definition is highly dependent on masking used to define the component geometry. Ceramic layers deposited by thermal spray are mechanically robust in the as-deposited state, but may require post-process thermal treatment to achieve the desired properties. In this paper, examples of hybrid circuits fabricated using combinations of established conventional processes, DW processes, and spray processes are reviewed and discussed.

2. DIRECT WRITE (DW) TECHNOLOGY

Direct Write (DW) technology encompasses a family of maskless, non-contact, printing processes and involves dispensing particles through a deposition nozzle. Originally established as a solid, free-form ceramic AM process, DW processes also excel in the deposition of metal inks for electrical interconnect fabrication. This section focuses on recent developments in colloidal inks, and post-process thermal treatment techniques for the IJ, AJ, and EC DW techniques relevant to AM of hybrid circuits and devices.

2.1 Direct Write Additive Manufacturing

Ink Jet, Aerosol Jet, and Extrusion Casting deposition processes raise challenges and opportunities for achieving the necessary end-state performance criterion of a functional device. As DW processes mature, practitioners must consider not only compatibility with the deposition

technique, but also compatibility with the post-processing employed during component fabrication. The ability to employ a collection of deposition processes using specially designed materials allow researchers and production engineers to address a myriad of electronics printing applications.

2.1.1 Ink Jet (IJ)

The droplet-on-demand technique utilizing thermal or piezoelectric actuation is widely used in dispensing inks onto substrates. Shearing forces generated at a nozzle create and eject discrete liquid droplets, which are subsequently propelled from the nozzle (19). When coupled with a CAD/CAM platform, discrete patterns can be printed without the use of masking. The IJ process uses inks with viscosities < 20 mPas (19). Thus, IJ deposition is used to print a variety of inks producing features with specific structural, optical, electrical, and biological functions. In today's manufacturing arena, IJ processes are widely used for printing Cu and Ag conductive elements for flexible electronics applications (20). The continuously dispensed discrete droplets, with diameters ranging between $18\mu\text{m}$ – $635\mu\text{m}$, form conductive traces with reported $0.1\mu\text{m}$ thickness and $20\ \mu\text{m}$ – $50\ \mu\text{m}$ lateral resolution, at $\sim 0.01\ \text{m}^2/\text{sec}$ throughput (19). After post deposition thermal treatment at temperatures between 80°C – 230°C , the nanoparticles in the traces densify and provide electrical continuity (3, 19).

The IJ process offers flexibility in handling low viscosity fluids and generates minimal waste; however, direct contact between the ink and the nozzle as well as the single droplet deposition feature are notable disadvantages. The ink must be engineered and preserved to a tight viscosity tolerance as the nozzles have a tendency to clog. Control over dispensing similar sized droplets in a timely manner must be rigorous as the device performance is highly dependent on

the uniformity, continuity, and definition of the IJ printed traces. Although the feasibility of using IJ printing for photovoltaic cell constructions has been shown (21), the IJ printing method is not well suited for integrating circuits and devices directly onto rough, unfinished surfaces of 3-D printed AM components. IJ yields relatively low throughput, which can be overcome by adding more nozzles and synchronizing them for parallel processing to scale up manufacturing. Adding and synchronizing thousands of jets were reported for manufacturing of graphics (19).

2.1.2 Aerosol Jet (AJ)

The Aerosol Jet (AJ) process is similar to the IJ process, but the jet is comprised of numerous droplets instead of a single droplet (22). Ink solution is ultrasonically atomized and suspended in inert gas. The atomized droplets are transported to and focused through an orifice ranging in diameter from 25 μm –350 μm . A coaxial polydispersed aerosol droplet stream (0.5 μm – 3 μm) in N_2 carrier gas is surrounded by an annular sheath gas envelope as the aerosol stream is introduced into an aerodynamic lens system. The sheath gas serves to limit droplet impact on the first lens and assists in the collimation process. This also helps to reduce nozzle clogging. Multiple aerodynamic lenses are used to collimate different sized droplets in the stream. The ability to focus the droplet stream coupled with a CAD/CAM platform provides superior line definition over challenging surface topographies. Deposited ink for electrical traces with 10 μm minimum feature width and line thickness of ~ 1 μm was reported (19). The AJ process has been used to print seed layers with a specific metallic ink for subsequent electroplating when formulation is not available for direct deposition (23, 24).

The current AJ technology uses only one aerodynamic lens. Using only one lens has proved difficult to achieve monodispersed aerosol droplets in the range of 0.5 μm – 5 μm for

AD. Recent developments in AJ technology employ multiple aerodynamic lenses in order to fully collimate a polydispersed aerosol droplet distribution. Computational fluid dynamics (CFD) modeling results for a two-lens aerodynamic lens system is shown in **Error! Reference source not found..** Using 0.5 μm , 1.0 μm , and 3.0 μm diameter droplets as inputs to the CFD model, visualization of different sized droplet behavior as the particles propagate through the lens system is possible. The addition of a sheath gas used to surround the aerosol stream prior to passing through the first aerodynamic lens is also depicted in this CFD model. This sheath enhances the droplets' ability to pass through the first lens without impacting on the lens surface, effectively eliminating clogging and increasing mean time between failures. In this simulation, the polydispersed droplets are focused to the center axis of the lens system as the droplets approach the first lens. Subsequently, the droplets pass through the first lens (orifice) and propagate through the first expansion chamber, with some divergence from the center axis. Since the Stokes numbers for the 1 μm and the 0.5 μm droplets were sufficiently different from unity, the divergence of the focused stream from the center axis limited collimation of these droplets. The modeling results show that the 3 μm droplets are highly collimated after passing through the first lens and remain collimated as they propagate through the first expansion chamber. As the polydispersed droplet stream approaches the second aerodynamic lens, the 1.0 μm and 0.5 μm particles are collimated and remain collimated as they exit the second aerodynamic lens. Detailed examination shows that some of the smallest droplets are collimated less tightly than the two larger droplet sizes. The use of multiple aerosol lens focusing technology shows positive development at Sandia National Laboratory, with appreciable impact on line resolution and definition in the AJ technology.

2.1.3 Extrusion Casting (EC)

Extrusion Casting, including Micro Extrusion (ME) or Robocasting, processes are capable of dispensing low, medium, and high viscosity inks pastes and slurries for 2-D as well as 3-D printing applications (25). The materials, particle size, and solution chemistry used to formulate printing fluids for these syringe based writing applications greatly impact rheological properties, and consequently the minimum feature definition achievable. A broad range of materials are compatible with these deposition techniques and include ceramics, polymers, and metals. As a result, EC techniques are ideally suited for the integration of multiple materials during additive manufacturing processes. Robocasting is currently being used to evaluate thick-film screen printing replacement techniques as CAD/CAM interfaces eliminate the need to fabricate tooling typically required for component metallization. Robocasting has been integrated with other AM processes, and offers other potential applications including RF and DC sensing/interconnects.

2.2 Colloid and Post Deposition Thermal Annealing Development

In order to ensure feature materials compatibility with DW process technologies, the development of colloid solutions and inks for DW has been the subject of significant research and development. The ink is comprised of metallic or ceramic particles suspended in solvents. Subsequently, the ink solution is dispensed as droplets and deposited conformally onto the target substrate. Post deposition thermal annealing is then performed to burn off the solvent and sinter the particles.

2.2.1 Particle Size and Materials Selection

A fundamental understanding of structure and chemistry of metals and ceramics is required to form reliable devices. Electronic conductors are often fabricated using silver (Ag),

copper (Cu), or other metals. While the semiconductor industry utilizes masking and physical vapor deposition or electrochemistry, AM processes utilize the reactive properties of metallic nanoparticles, metal filled composites, conductive metal oxides, and metal organic decomposition inks to form conductor materials (26-29).

Metallic nanoparticles are utilized to form conductors due to the effects of their high curvature, surface energy, and surface to volume ratio on thermal consolidation of printed elements. The Lindemann criterion may be applied to define the solid-liquid melting point in crystalline and amorphous materials, in which a material melts at the temperature where the amplitude of thermal vibrations exceeds a critical fraction of the interatomic distance (30). The high surface to volume ratio of nanoparticles and the low cohesive energy of surface atoms cause the melting point to vary based on particle size, shape, or other parameters, thus modifying the energetic state of the particles. Material specific properties including but not limited to atomic mass, density, surface energy, and enthalpy of melting directly affect the melting point depression of nanomaterials (31, 32). This is observed in particles with diameters less than 10 nm. The impact of nanostructured materials can be substantial. For example, whereas bulk Ag melts at 962°C, Ag nanoparticles are predicted to linearly lower their melting point to 527°C at 6 nm, and to 127°C at 1 nm diameters (33). Moreover, this linear decrease in melting point with decreasing nanoparticle size is quantifiable from the optical properties. Such changes are revealed in the nanoparticle characteristic phonon spectra when the particle surface becomes irregular due to the onset of surface melting (34). Consequently, Ag nanoparticles are reported to show liquid-like pseudoplasticity (i.e. deformation flow by non-Coble mechanisms) under applied pressure, and restore their equilibrium shape when the pressure is removed (35). Thus, melting point suppression enables metal nanoparticles to be thermally processed at relatively low

temperatures. This characteristic allows DW fabrication of traces without affecting the integrity of the underlying layers.

The formation of conductive traces can also be achieved by chemical reaction or coalescence of nanoparticles. Coalescence is a process that exhibits both endothermal melting and exothermal solidification reactions in the metallic films. Liquid-like sintering of nanoparticle clusters has been noted for several elements including Ag, Cu, Pb, Sn, and Ni (33, 36, 37). When the exposed temperature is just below the melting point, coalescence occurs by the conversion of surface energy to an internal temperature rise of 100–200 K, resulting in densification and recrystallization. Practically, this means that reactive nanomaterials can be sintered at low temperatures if recrystallization is avoided or minimized. Rapid crystallization prevents further densification due to the increase in grain size and the stabilization of grain boundaries. This behavior is also affected by the environment, such as the interaction with the substrate. A nanoparticle on a substrate can have altered melting characteristics based on the bonding with that substrate: low contact angles lead to lower melting point and high contact angle leads to higher melting points than would be estimated by the free nanoparticle melting point (38).

2.2.2 Metallic Ink Development

In practice, the manipulation of metal nanoparticles for deposition is performed using nanoparticles in fluids as stabilized ink formulations. Nanoparticle inks are used for conductor printing by EJ (39), IJ (40), and AJ (41) processes. There is a vast literature on the formation of metallic nanoparticles using chemical synthesis based on a metal precursor or salt, a reducing agent, and a nanoparticle stabilizing ligand specific to the solvent system. From a materials perspective, what must be appreciated is the paradox that the activity of nanoparticles is related

to their high surface energy, but the method to create a stable nanoparticle colloidal suspension quite often necessitates the use of specifically adsorbing molecules, which lowers the surface energy. Common stabilizers include thiol, sulphides, thiosulfate, xanthate, amine, selenide and isocyanide, sugar-derivatives and carboxylate surface groups with stabilizing antecedents having good solubility in the solvent system (42). In the Ag system, there are several synthesis routes leading to nanoparticle inks for IJ printing (26, 43-45). Likewise, Cu nanoinks have similar themes, with the complication of Cu oxidation to Cu_2O or CuO degrading properties in the conductive line (46-51). The formation of a superior printed conductor must therefore consider the removal of organic species at the interface by thermal or other means such as resistive heating (52) and microwave sintering (53), to enable the low temperature formation of grain boundaries between a tightly packed bed of nanomaterials.

Solutions with particles that are dispensed and deposited on the substrate undergo inertial, wetting, and drying forces. These forces directly affect printed feature size, definition, uniformity, and ultimately, electrical or RF performance of the deposited materials. The inertial behavior of a droplet during impact exhibits (i) contact (ii) radius expansion, and (iii) oscillation damping and drying (54). Both the inertial forces and contact angle in the wetting behavior affect the final size of the printed droplet. Stringer and Derby considered the line definition for printed lines and the lower limits of deposited material (55). As droplets become smaller, surface energy factors dominate. Wetting angle also can affect the migration of particles within the ink, known as the coffee ring phenomenon (56). If the curvature at the droplet-substrate interface is high, there will be a vapor pressure gradient creating the relatively flat center of the droplet and causing rapid evaporation at the contact line and flow induced migration of solids to the interface. This creates the stick-slip profile of a drying droplet and can concentrate particles so

strongly that near bulk conductivity is obtained in Ag nanoparticles (28). Methods to mitigate or prevent inhomogeneous films are derived by counter-flows in the liquid, and include heating the substrate to create thermal Marangoni flows. Marangoni flow arises based on surface tension differences, viscosity, and the length scale of the drop. It is also common to use solvent mixtures, where a high boiling point solvent with low receding contact angle creates mixing by Marangoni flow to redistribute solids (56-60). Marangoni flow increases with drying, leading to a counterbalancing effect of particle migration flow.

2.2.3 Particle Sintering Through Post Deposition Thermal Treatment

While specialty ink systems have been developed, which allow for room temperature (RT) curing of Ag nanoparticle films on selected substrates, new materials are required to meet the needs of the printed electronics community (22, 61.) While the thick film inks and pastes used for the screen printing applications require elevated thermal processing to impart functionality, nanomaterials inks are generally post-processed to useful states, using bulk thermal heat treatments at temperatures at or below 250°C (23, 62). Research of selective laser processing and flash lamp annealing of printed nanoparticle films has provided alternative sintering solutions to conventional bulk thermal routes (63-66). Such methods are well suited to functional electronic networks on thermally sensitive substrates and can be readily integrated into manufacturing processes (67-69).

Conventional thermal processing often used in printed electronics manufacturing can be restrictive when the substrate on which a device is built cannot support optimal annealing temperatures and cure schedules of the materials used in fabrication. To overcome this constraint, *photonic curing* (flash lamp assisted sintering) has been implemented for the rapid

densification and annealing of thin films on thermally sensitive substrates (70-73). Schroder describes photonic curing as a transient, milli-second time scale heating process achieved through energy transfer to a thin film from a flash lamp (74). Substrate thermal conductivity and material properties of deposited layers greatly influence the effectiveness of photonic curing. Current research has shown enabling electronics materials and structures have resulted from application of the technique. A number of studies demonstrate the effectiveness of photonic curing in printed Ag, Cu, and Ni interconnects on thermally sensitive substrates (65, 66, 75). Photonic curing has also been applied to form hafnium oxide layers on silicon (Si), which exhibit dielectric properties similar to what would be derived from atomic layer deposition techniques (67). As flash curing exploits transient heating phenomenon, it is thought possible to expand the photo processing technique to support ceramic film formation on substrates such as polyimide or polyethylene terephthalate (PET). Also enabled by photonic curing, the formation of free standing, 5 μm – 10 μm thick polycrystalline Si sheets from nanoparticle solutions has demonstrated an ability to not only process materials on existing substrates, but to create entirely new scaffolds for circuit fabrication (76).

It should be noted that thermal sintering of metallic nanoparticle ink traces may not always provide fully dense metallic components. Moreover, processing under non-atmospheric environments may be necessary to prevent material degradation or to promote reduction of metallic species. Inherent porosity in sintered traces causes higher electrical resistivity and lower mechanical properties in comparison to those conventionally processed bulk materials (wire drawing, pressed and sintered, etc.) (65, 66). The presence of surface defects such as voids may also be potential crack initiation locations, leading to conductor failure should the traces be subjected to mechanical or thermal strain from temperature cycling (61).

3. THERMAL SPRAY TECHNOLOGY

Thermal spray technology is comprised of a family of well proven line-of-sight droplet and solid-state deposition processes used to prepare metal, ceramic, polymer, and composite coatings. Conventionally, thermal spray technology is used to apply “passive materials” (i.e. no other functions besides protection), providing a conformal barrier coating to prevent degradation of the underlying substrate due to extreme erosive, corrosive, thermal, or electromagnetic environment (77). Traditional thermal spray processes use arc plasmas, oxy-fuel flames, and electric arcs to melt and propel powder feedstock material towards a substrate where the molten droplets melt and solidify to form a coating (78). Droplet size ($<100\ \mu\text{m}$) results in rapid solidification, minimizing in-process alloying and enabling dissimilar materials to be co-deposited. Droplet deposition processes include High Velocity Oxygen Fuel (HVOF), plasma spray (PS), powder flame spray, wire flame spray, wire arc spray, etc. The high throughput and ability to work high melting point materials allow the use of traditional thermal spray processes, especially PS, for depositing metallic and ceramic functional coatings.

Much research and development has been focusing on the potential of thermal spray technology for bridging the $10\ \mu\text{m}$ to mm scale in fabricating mesoscale electronic devices and sensor materials (77, 79-82). A recent disruptive development in “Direct Write Thermal Spray”

(DWTS)¹ on a CAD platform showed the ability to fabricate and integrate thick film materials, sensors, and electronics on non-planar surfaces while keeping the underlying structure temperature below 200°C (83). A few examples include DWTS of multilayer inductor circuits (83), thermocouples (84, 85), antennas (83), humidity sensors (86), and magnetoresistive sensors (87). A combination of thermal spray and laser micromachining has been used to achieve metallic sensor traces with ~50µm line definition. This technology moves beyond laboratory settings. MesoScribe Technologies has developed a plasma spray “printing technology” to manufacture functioning patterned coatings as high performance antennas, heaters, and sensors integrated conformally onto structures (88).

In this paper, we only review the solid-state deposition process, enabling ceramic deposition, which has the potential to be integrated with the previously discussed DW technologies for hybrid circuits and devices. Aerosol Deposition (AD), a RT, solid-state deposition process that can consolidate metallic, ceramic, and composite materials in vacuum for electronics packaging has been gaining momentum since the early 2000’s. Aerosol deposition uses dry submicron sized metallic or ceramic particles suspended in carrier gas. Particles are accelerated by carrier gas via a pressure differential between the aerosol generation chamber and the vacuum chamber, where they impact and consolidate as coatings on the substrates. The ability to utilize AD to deposit ceramics without melting/solidification or without the addition of glassy phase/organic binder is unique and significant. Post deposition thermal annealing must be performed to achieve optimal properties beyond mechanical properties. This section focuses on

¹ DWTS was developed under the Defense Advanced Research Projects Agency (DARPA)’s Mesoscale Integrated Conformal Electronics (MICE) program by Stony Brook University and their program partner.

enabling masking techniques, tooling platform, as well as recent developments in AD techniques relevant to AM of hybrid circuits and devices.

3.1 Masking Techniques and Tooling Platform

The ability to pattern and control definition and resolution of the deposited coatings are essential to mesoscale circuit and device fabrication. Contact and photolithography masks have been used for patterning fine features in AD coatings. In addition, improvements in nozzle design for particle collimation and tooling may be able to advance the AD process towards being a true DW deposition process.

The most convenient masking technique for spray processes are stationary contact shadow masks. Openings in the registered shadow masks allow particles to deposit onto the substrates in the desired locations. Machined or laser cut metallic or ceramic sheets are registered to features on the target substrates as single-use, disposable masks. Low cost laser cut Kapton masking was recently demonstrated for patterning plasma sprayed molybdenum coatings to resolve $\sim 200 \mu\text{m}$ features (89). Oversprayed, loose particles follow the carrier gas flow and often undercut the shadow masks, preventing sharp feature definition. Moreover, high aspect ratio masking limits patterned feature definition and vertical side wall coating is virtually impossible (**Error! Reference source not found.**).

Dynamic, non-contact shadow mask using small openings/slits placed between the particle stream and the substrates can also be used to define features. The dynamic, configurable mask may move in synchronization with the stream, blocking the majority of the particles that do not pass through the openings, enabling a deposition process similar to “direct writing” in which the particles in a reduced size spray plume stream arrive at desired locations on the substrates.

However, the feature definition and resolution for stationary and dynamic shadow masking techniques are still limited to the few hundred micron range.

Feature definition and resolution of patterned AD coatings ranging between 5 μm –60 μm can be achieved by traditional photolithography processes as shown in **Error! Reference source not found.** Intimate contact between the photoresist and the underlying structures prevent mask undercutting from the carrier gas and removal of the oversprayed particles in the unwanted areas. Post-processing using chemical dissolution of the photoresist mask is used to complete the processing of the defined component.

The traditional tooling platform for thermal spray technology usually involves a robot holding the spray nozzle, traversing over the relatively planar substrates in a stationary fixture or simply curved surfaces in a rotating spindle. For AD, standoff distance and traverse speed are important process parameters. Standoff distance between the spray nozzle and the substrate should remain constant in order to ensure uniform coating microstructures and properties. Either moving the substrate or the nozzle or both mitigates high erosion rates of the substrate and facilitates deposition. Appropriate traverse speed must be selected to balance the erosion rate with the deposition rate by solid particle impaction.

As DW and thermal spray deposition technologies converge, complementary coating techniques may benefit from integration onto a common platform. First, an improved AD nozzle design and/or dynamic shadow masking approach are needed to collimate the particle stream. Second, outfitting AD systems with a CAD/CAM type platform similar to those used in DW processes enable spray stream and/or substrate manipulation for better conformal deposition, definition, resolution, and appropriate coverage. The use of multiple nozzles may also aid scale

up and promote design for manufacturing. As DW processes are capable of depositing conventional photoresist materials, it is conceivable that hybrid DW printed masks could be used to replace traditional lithography approaches used in defining AD and other thermal spray deposited patterns. Nevertheless, there are several microstructural problems remaining to be solved with thermal spray processing. Typically, microstructures are not optimized in comparison to conventional thermal sintering technology, and performance can be limited. Novel research and routes to improved structures are a key need, but coupling thermal spray and DW processes still have the potential to fabricate components and properties unobtainable via other means.

3.2 Aerosol Deposition (AD) Process

As AM processes evolve, integration of functional devices containing ceramics without degrading underlying structures must mature. The maturation of such devices requires consideration of the deposition technique and also the post processing mechanism required for optimal functional properties—optical, piezoelectric, dielectric, magnetic, etc.—of the devices.

3.2.1 Process and Mechanisms

Room Temperature (RT) deposition of metallic, ceramic, and composite materials in vacuum for electronic devices has been gaining momentum. A nominal RT deposition process known as Kinetic Vacuum Spray (KVS), Room Temperature Spray in Vacuum (RTSV), Room Temperature Impact Consolidation (RTIC), Aerosol Type Nanoparticle Deposition (AT-NPD), or Aerosol Deposition (AD) can be used to fabricate coatings in a solid-state. AD relies on submicron sized metal and ceramic particles to plastically deform and consolidate into coatings. Growth rates of 10–30 $\mu\text{m}/\text{min}$ are possible over a 1 cm^2 area, and film thicknesses of up to 80

μm with bulk ceramic properties have been reported (91, 92). Successful deposition of structural ceramics (Al_2O_3 , TiO_2 , AlN) (90, 93-96), dielectric BaTiO_3 (97, 98), piezoelectric (PZT, PNN, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$) (99), magnetic (Sm-Fe-N, Bi:YIG, YIG) (100-102), and battery cathodes (LiMn_2O_4 , LiCoO_2) (92) have been demonstrated. Moreover, patterned features $<5 \mu\text{m}$ size achieved by photolithography has been demonstrated (90). Greater understanding of the effects of particle treatment and deformation mechanisms during impact is needed to mature AD technology.

Particle size effects on AD coating consolidation was first reported by Akedo and Ogiso (93). Akedo and Ogiso showed $5.0 \mu\text{m}$ alumina particles fractured in compression and did not lead to consolidation in AD process, whereas $0.5 \mu\text{m}$ alumina particles demonstrated plastic deformation in compression and led to coating consolidation in AD process. Thus, submicron particles capable of plastic deformation are used in AD. These submicron particles travel at the speed of the carrier gas as the gas stream exits the nozzle and expands into the vacuum. As the carrier gas hits the substrate, it rebounds and creates a barrier gas layer above the substrate, known as the bow shock effect. The bow shock effect is reduced in vacuum, allowing particles with momentum to penetrate through the shock layer, reaching and impacting on the substrates. Finite element modeling has been used to understand particle deformation and bonding (90, 103, 104). It was found that $0.3 \mu\text{m}$ alumina particles undergo high pressure (2.5 GPa) and temperature rise (500°C) at the particle/substrate interface during impact, which were not high enough to cause sintering (90). During impact, the submicron particles deform, fracture, and break up into small crystallites (20–75 nm) that bind together. Dislocations, stacking faults, and amorphous phase formation from pressure induced amorphization phenomenon were observed within the AD consolidated coatings (104). Molecular dynamics simulations by Imakana *et al.* showed that amorphous layers hold the key to particle-particle bonding and facilitate ZnO

coating consolidation (105). Imakana *et al.* believe that the small fragments (2 nm) in the tail of the particle distribution are those that provide thin amorphous layers. The fragments impact on the substrate or the previously deposited particles and become amorphized. As larger particles arrive and impact on the amorphized layers, they adhere and build up the coating layer-by-layer. Imakana *et al.* also showed that without the amorphized layer, arriving crystalline ZnO particles rebounded off the surface. These studies of a nominally RT deposition process revealed insights into ceramic particle-particle bonding and consolidation that are still not well characterized or understood.

3.2.2 Particle Selection and Treatment

As previously discussed, submicron particles capable of deformation are used in AD processes and their fragments/fines that become amorphized upon impact may facilitate coating consolidation. Moreover, deposition efficiency in the AD process is optimized through particle treatments. Many research studies in literature showed that vigorous ball-milling, powder annealing, and/or calcination must be performed to increase the deposition efficiency (106). Optimized parameters for particle treatment have been empirically achieved. For example, Akedo and Lebedev found ball milling PZT particles for 5 hours increased the deposition rate by 30 times to 73 $\mu\text{m}/\text{min}$ over a 5 mm^2 area (106). However, further ball milling for 30 hours resulted in a reduced deposition rate to $\sim 30 \mu\text{m}/\text{min}$. They also found that ball milling for 5 hours and subsequently heat treating PZT particles at 800°C for 4 hours in air before deposition only resulted in a deposition rate of $\sim 25 \mu\text{m}/\text{min}$. It appeared that ball milling facilitated both particle deformation and particle-particle bonding in the AD coatings. It is assumed that ball milling changes the particle surface properties—surface activation, defects, and gas absorption. Sarobol *et al.* observed, through *in situ* TEM and molecular dynamics simulation, dislocation nucleation

and glide during alumina particle deformation in compression (107). They hypothesized that ball milling would introduce mobile dislocations in the particle interior, responsible for facilitating particle plastic deformation during impact. Less energy is required to move existing mobile dislocations in contrast to nucleating new dislocations before moving them. This means ball milled particles that are full of mobile dislocations will be able to deform more easily and likely at lower particle velocity during impact. Annealing ball milled particles to high temperatures would encourage defect combination and dislocation annihilation, possibly lowering the particle ability to deform and resulting in lower deposition rate. Moreover, based on atomistic simulation results by Imakana *et al.* (105), ball milling provides many small fragments that become amorphized as they impact on the substrate and facilitate particle-particle bonding for consolidation.

3.2.3 Carrier Gas Selection

Particle carrier gas type has been shown to influence residual stress and properties of the AD ceramic coatings; however, the fundamental mechanisms behind this are not very well understood. For the same flow rate, carrier gas type influences particle velocity, particle impact behavior, consolidation, and subsequent coating properties. For gas consumption rate of ~15 l/min, both alumina and PZT particle velocities were 350 m/s and 500 m/s in air and He carrier gas, respectively (note that a critical velocity to achieve alumina deposition over erosion was reported to be ~150 m/s) (95). Schubert *et al.* showed that the oxygen carrier gas produced a slightly oxygen enriched environment and provided stoichiometric, white Al_2O_3 coatings, whereas, the nitrogen or helium rich carrier gas produced a reducing environment and provided non-stoichiometric gray $\text{Al}_2\text{O}_{3-\delta}$ coatings with oxygen vacancies (108). Another example where carrier gas and gas flow directly affect electrical discharge upon particle impact during AD and

resulting AD coating optical properties was shown by Akedo (90). PZT particles suspended in helium carrier gas showed plasma discharging during impact and resulted in dark gray colored film. Plasma discharging introduced defects in the consolidated PZT films which in turn decreased the film transmittance. On the other hand, PZT particles suspended in nitrogen gas showed no plasma discharging during impact and resulted in yellow colored, transparent film. Non-stoichiometry, crystallography, grain size, defects, and residual stress in the coatings from the AD process can be altered with post deposition annealing treatment.

3.2.4 Post Deposition Thermal Annealing Treatment

The as-deposited coatings have very small grain size (20–75 nm or less). Whereas the small grain size may be beneficial for structural ceramics, larger grain size is needed for desirable properties beyond mechanical properties. Thus, post deposition annealing treatment must be performed to achieve grain growth for stress relaxation and better optical, electrical, magnetic, and piezoelectric properties; although this inadvertently diminishes the realization of RT multi-material integration processes. Schubert *et al.* produced 9 μm AD Al_2O_3 coatings on Al_2O_3 substrates using nitrogen carrier gas, performed heat treatment, and examined coating residual stress (108). The as deposited coating showed highly compressive residual stress at 2.1 GPa. The coating residual stress decreased with increased annealing temperature and completed relaxation after 300°C. Higher annealing temperatures have been used to achieve grain growth and alter coating properties. For example, Inoue *et al.* (109) showed annealing $\text{Bi}_{0.5}\text{Y}_{2.5}\text{Fe}_5\text{O}_{12}$ (Bi:YIG) AD coatings in air at 800°C for 10 minutes grew the grain size from 15 nm to 28 nm and increased the saturation magnetization ($4\pi M_s$) from 0.25 kG to 1.1 kG. Another example by Furuta *et al.* (110) showed a dense BaTiO_3 thick film fabricated by the AD method was crystallized then detached from the substrate by an annealing treatment at 600°C. Subsequently,

annealing treatments at various temperatures were performed, resulting in freestanding BaTiO₃ thick films with grain sizes from 24 nm to 170 nm. Polarization-electric field (P-E) measurement revealed that BaTiO₃ ceramics with grain sizes of more than 58 nm showed ferroelectricity, whereas BaTiO₃ ceramics with an average grain size of 24 nm showed paraelectricity at RT. Dielectric measurement indicated that the permittivity decreased with decreasing grain size in the range of 170 nm to 24 nm. Future work is required to explore integrated in-process annealing treatments to achieve grain growth in the AD layers while minimizing heat transfer to the underlying structures/parts.

4. ADDITIVE MANUFACTURING OF HYBRID CIRCUITS USING DW AND AD TECHNOLOGY

Based on current state-of-the-art of DW and AD technologies, we can exploit their strengths and couple them with established subtractive processes, ceramic sintering processes, and/or metallic deposition processes for AM of hybrid circuits and devices. Combining and exploiting strengths of different processes can reduce costs, speed up delivery of prototypes and production, and pave a path forward beyond planar integration constraints on high value AM parts. /This section will discuss three examples of how DW and AD technologies can be integrated with established subtractive technologies and materials processing technologies such as low temperature co-fired ceramic processing, plasma spraying, sputtering, and electroplating.

4.1 LTCC and DW Thick Film Electronics

Low Temperature Co-fired Ceramic (LTCC) technology is widely used to fabricate metalized circuits using ceramic-glass composite substrates. Standard processes often involve punching vias in unfired ceramic tape, fabricating stencils, screen printing masks to define circuit

geometry, and then screen printing thick film conductive inks and dielectrics onto unfired ceramic substrates. The process is repeated for multi-layer devices as layers are aligned, collated, and laminated together before firing at temperatures below $\sim 1,000^{\circ}\text{C}$. By adapting DW processes to deposit thick film and nanoparticle inks as well as by utilizing established LTCC materials and densification procedures, it is possible to reduce development cycle time, materials waste, and expand the design space for LTCC component fabrication. Eastman and Cook used EC/AJ printing to demonstrate circuit metallization and printed wire bond replacement on a custom CAD/CAM platform for LTCC component fabrication (111). The design and fabricated interior and exterior circuits on the demonstration part are shown in **Error! Reference source not found.**

4.2 Embedded DW Sensors in Plasma Sprayed Dielectrics

An emerging capability useful in embedding electrically conductive elements in ceramic materials employs spray technologies. Using stainless steel plates with Air Plasma Sprayed (APS) metallic underlying bond coat and alumina top coat, DW printed thick film and nanoparticle inks of both Ag and Au have been deposited atop the dielectric coating. Following deposition of subsequent APS alumina coatings, multi-material AM parts, having embedded electrical traces, have been generated. Electrical traces were deposited via an EC DW process and thermally processed at $\sim 100^{\circ}\text{C}$ to densify the ink. During the APS process, the stainless steel substrate temperature reached $\sim 200^{\circ}\text{C}$. This could be reduced by increasing the APS torch traverse speed over the substrate. The APS alumina coatings are extremely dense and possess a mean dielectric constant of 9.0 ± 1.3 , comparable to that of bulk alumina of 9.1 at 1 MHz. Resistance of the Ag traces increased after being embedded in the coating. Detailed characterization of the trace embedded in the coatings was performed. The Ag nanoink traces

followed the contour of the rough alumina coating surface well. All traces appeared continuous. The Ag traces were not oxidized. In the future, CAD/CAM tooling platforms can be used to enable conformal deposition on curvilinear surfaces. Moreover, APS graded materials can be used to mitigate abrupt changes in coefficient of thermal expansion between the metallic substrates and the alumina coatings. This approach should allow the coating assembly to stay intact during future thermal cycles and heat treatments.

4.3 Aerosol Deposited, Electroplated, and Sputtered Electronics

Finally, Imakana *et al.* have demonstrated fabrication at room temperature of mesoscale circuits and devices on Cu foils via a combination of established electroplating and sputtering processes with the AD process (**Error! Reference source not found.**) (105). Imakana *et al.* fabricated multilayered devices such as those shown in Figure 7 layer-by-layer by employing AD to deposit ceramic films, including high permittivity BaTiO₃ dielectric and low permittivity Al₂O₃ dielectric; photolithography for patterning and dry chemical (HF/HNO₃) etching to selectively remove materials; and electroplating or sputtering to deposit internal conductors such as Cu. Dielectric properties of BaTiO₃ films are highly dependent on grain size as well as measurement temperatures and frequencies. The as-deposited AD films showed grain sizes ranging from 5nm - 40nm. As a final step to complete the integrated structures, a post process annealing treatment was performed at 900°C–1000°C in N₂ inert atmosphere. The annealed AD BaTiO₃ films underwent solid-state sintering via grain boundary controlled lattice diffusion during annealing. The film final grain size ranged from 60nm–150nm. The annealed AD BaTiO₃ film physical and dielectric properties were similar to bulk pressed and sintered (1,400°C) BaTiO₃ as summarized in **Error! Reference source not found.**. It should be noted that the integration of ceramics onto conductors demonstrated here would not have been possible via

conventional fabrication methods because the bulk sintering of (pressed) Al_2O_3 and BaTiO_3 is usually performed at $1,600^\circ\text{C}$ and $1,400^\circ\text{C}$ respectively, well above the Cu melting point of $1,083^\circ\text{C}$. Imakana *et al.* have established a path forward to embed such structures in a resin-based electronics packaging. Moreover, they stated that similar approach can be used to deposit multilayered solid-state lithium ion batteries directly onto polymer substrates or FPC (105).

5. SUMMARY

Direct write (DW) and aerosol deposition (AD) processes reviewed here are emerging technologies enabling materials integration and are suitable for AM of hybrid circuits and devices. Both DW and AD can deposit materials at room temperature and rely on colloid/dry particle development for successful deposition. Maskless DW processes outfitted with a CAD/CAM tooling platform excel at metallic and conductor trace deposition beyond planar, 2-D patterning. With appropriate masking, AD achieves both ceramic and metallic conformal coating. The AD process generates low heat input, and post deposition annealing can be employed for optimal functional properties of the devices. With further development in outfitting AD with the CAD/CAM type tooling platform and nozzle design for carrier gas/particle stream collimation, AD may be used as a true DW technology. Considerable research and development is underway for post process annealing treatments to densify the DW traces and to optimize materials properties in AD coatings. Based on current state-of-the-art of DW and AD technologies, we can exploit their strengths and couple them with established subtractive processes and conventional materials deposition processes for AM of hybrid circuits and devices. Combining and exploiting strengths of the different processes pave a path forward beyond planar

integration constraints on high value AM parts. DW in combination of LTCC helps reduce cost and waste, reduces prototyping turnaround, and extends integration beyond planar LTCC constraints. DW traces and high dielectric air plasma sprayed conformal coatings have been demonstrated for robust embedded sensors. AM of multilayered electronic devices on Cu foil has been demonstrated by employing AD to deposit ceramic films, applying photolithography for patterning and dry chemical etching to selectively remove materials, and then electroplating or sputtering to deposit internal conductors. Current advancement in feedstock/ink materials, DW technology, AD technology, and post processing heat treatment has already provided a path forward to formation of hybrid circuits and devices. We believe combining DW and AD on the CAD/CAM tooling platform, along with employing an in-process thermal treatment, has the potential for widespread AM of hybrid functional circuits, electronics, and energized devices built into complex shaped low cost/high volume components.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that may be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

This work is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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