Aerosol Jet Printed Functional Nanoinks with High Reliability and Reconfigurability

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ABSTRACT

Printed electronic components have long been desired in the aerospace industry to enable prototyping, design verification, and concept validation of electronics at a much more rapid pace than photolithography or manual wire bonding processes. For satellites that are subjected to extreme thermal environments, highly reliable materials and processes are used. Aerosol jet printing has recently become more prevalent in commercial electronic manufacturing processes due to its consistency and fine feature size (<10 µm) when compared to other ink-based printing methods. Traditional conductive Ag and Cu inks produce printed materials that react under modest conditions, which degrades their electrical and RF properties leading to unreliable materials. Here we present a tailored Au nanoink that is aerosol jet printed to produce robust interconnects directly on GaAs microwave monolithic integrated circuit (MMIC) chips. The chips were subsequently subjected to reliability testing that included thermal shock, thermal cycling, and current stress testing. At the conclusion of the reliability tests, no DC performance degradation was found indicating that aerosol jet printed Au nanoinks are an effective method for adding highly reliable on-chip circuit functionalities and features.

Additionally, we present a new functional phase change nanoink based on GeTe to enable direct printing of radio frequency (RF) reconfigurable switches and control circuitry into flexible antenna apertures, which eliminates the need for costly and time consuming wafer preparation, dicing, and assembly. The nanoink formulation, printed GeTe material characterization, and electrical measurement results will be discussed including the phase change from amorphous state to crystalline state.

Keywords: Aerosol Jet, Direct Write, Nanoink, Phase Change Materials, Printed RF Electronics

1 INTRODUCTION

The aerospace industry has been an early adopter of addtive manufacturing based techniques, such as polymer and laser sintered metal processing, due to the niche engineering requirements to rapidly iterate and optimally design complex parts that are typically needed in very small quantities. These one-off printed parts may even be spot examined and individually qualified for usage, which is extremely attractive for aerospace because most manufacturing occurs outside of the company that does the final integration and acceptance testing, therefore these techniques have the potential for a paradigm shift. The lack of understanding in the structure-property relationships, which ultimately determine print quality has precluded widespread adoption of additive techniques across the industry as a whole to date.

More recently, aerosol jet printing has emerged as a viable method to extend beyond more traditional laser sintered metal and polymer additive techniques to include semiconductors, dielectrics, and metals delivered in a finely controlled mist to give both high quality and small feature size into the 10 µm regime. While this technique is promising, there is a limited toolbox of inks to choose from commercially, and some of the formulations are short-lived as the aerosol ink industry continues to mature. As the internet of things (IoT) increasingly drives the need for current ink-based printing technologies, affordability and low power printed electronic devices are the most well understood from a fundamental research perspective. For aerospace, our focus is on performance and reliability, which have not been well documented in the literature to date. We have found that the most well studied Ag-based inks are not suitable for aerospace environments as they are susceptible to ambient conditions and rapidly degrade over time. Thus, we have developed our own Au ink and print parameters to provide a reliable Au interconnect to an existing GaAs chip that does not degrade under extreme environmental testing. To our knowledge our work is the only reported study to date. Additionally, a more exotic GeTe ink has been developed for the first time for potential use as a non-volatile RF switch to enable reconfigurable electronics. The ink preparations, print parameters, and testing are discussed herein.

2 METHODS

2.1 Ink Preparation

Initially a Au ink was purchased commercially, however, due to the short shelf life, propensity to deteriorate upon exposure to air, and limited print flexibily we quickly decided to develop our own Au ink. Aqueous and organic solvent based Au inks were aerosol jet printed and their properties compared.

Aqueous Au inks hold several advantages over organic solvent-based including easier handling and longer storage life, but organic solvent based inks show less overspray on printed lines due to their higher volatility. Optimization of both ink preparation and aerosol jet printing parameters are

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necessary to obtain high quality, reliable metal interconnect using this type of processing.

Organic solvent (Xylene and Toluene)-based gold nanoparticle inks are commercially available, however a major drawback of the commercially available product its short shelf life. With this motivation in mind, we decided to develop our Au ink. We decided to attempt an aqueous version to try to improve colloid stability and shelf life.

Aqueous gold nanospheres were prepared via the seed-mediated method [1]. Aqueous solutions of $HAuCl_4.3H_2O$ are mixed with CTAB and $NaBH_4$ to form the seed solution consisting of <5 nm Au nanospheres. In parallel a growth solution is prepared by mixing $HAuCl_4.3H_2O$, $AgNO_3$, CTAB, H_2SO_4, and ascorbic acid. The ratio of the $AgNO_3$ to the $HAuCl_4$ determines the Au nanoparticle shape and aspect ratio. It is possible to synthesize well controlled shapes, sizes and corresponding extinction spectra of Au nanoparticles [2]. After centrifugation, the resulting nanoparticles are coated with polyethylene glycol or polystyrene sulfonate and redispersed in methanol/IPA/ water mixtures in order to control the volatility of the aerosol jet printed ink. Care is taken to adjust surfactant level so that the colloidal solution does not aggregate after centrifugation. The ratio of the methanol and water is an experimental parameter that determines ink viability and will be systematically studied. Another important factor that needs to be studied is the effect of the shape and the size of the Au nanoparticles on sintering temperature. We hypothesize that smaller particles with assymetric shape will exhibit the lowest temperature.

Addtionally, we prepared a solution of amorphous GeTe nanoparticles by stoichiometrically reacting GeI_2 and Te-TOP via the hot injection method according to Wong et. al. [3]. After repeated washing with chlorofom and hexane to isolate the nanoparticles, they were suspended in a toluene/chloroform solution prior to printing.

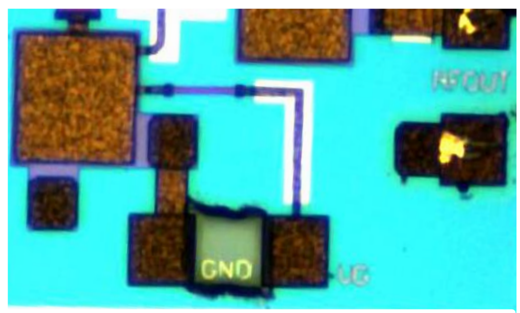
2.2 Ink Characterization

Characterization of Au ink nanoparticles was performed using transmission electron microscopy (TEM) to determine the sphere morphology along with the crystallinity and size window with preference for sintering going to nanoparticles <5 nm in diameter Additionally, UV/VIS spectroscopy was used to determine the particle size and morphology via the plasmon resonance peak.

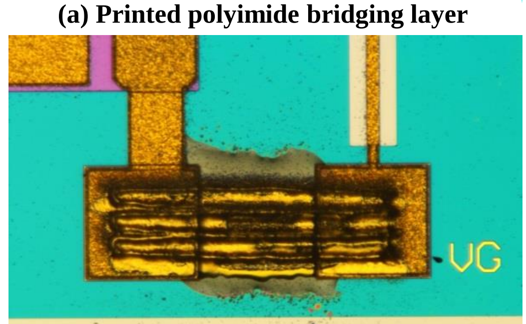
The resultant ink containing GeTe nanoparticles was characterized by x-ray diffraction (XRD), TEM, and energy dispersive spectroscopy (EDS). The XRD patterns as-synthesized did not contain any distinct peaks, however after heating above the crystalline transition temperature to 350ºC the distinct rhombahedral pattern emerged. The TEM data highlighted the particle sizes, which ranged from 30-60 nm in diameter, with the majority of the particles analyzed being ~50 nm in diameter. Finally, the EDS data confirmed the atomic percentage ratios of Ge:Te to be 1:1 as expected.

2.3 Print Process Parameters

We have iteratively printed both Au and GeTe inks to reach satisfactory microstructural and overall electrical properties [4,5]. We selected an existing GaAs low noise distributed amplifer MMIC chip to demonstrate the Au ink printing and its capability for chip reconfiguration. As an example, the printed Au wirebond example was performed between the gate bias pad (Vg) and the ground pad on chip. By protecting against shorting the connection a standard polyimide ink obtained from Sigma Aldrich was printed between the gap connecting the Vg to ground, and then the Au ink was printed over top connected the Au pads. The chip's gate bias voltage is readily set to 0 V if the wirebond provides a low resistance routing as expected. This is a simple way to verify the function and performance of the Au printed wirebond. In real chip applications, many of these wirebonds will be required inside a DC resistor ladder network to provide a large range of selectable voltage to the gate transistor of the chip. The printing of the wirebond can be broken down into two steps. First, a polyimide layer is printed and cured between the gate and ground pads. Next, printed Au metallization occurs on top of the polyimide pattern, as shown in Fig. 1. The printing control parameters were optimized for our Optomec Aerosol Jet AJ-300 printer during these processes and are given below.



(a) Printed polyimide bridging layer



(b) Au printed on top of Polyimide

Figure 1. For gold interconnects a polyimide layer is first printed to bridge the Au pads and then a Au layer is printed over top to form the interconnects.

After the completion of printing and sintering procedures (see Table 1), the chip was measured for DC resistance, RF return losses, gain, and noise figure. The chip was then put into reliability testing and post-reliability testing, the chips were re-tested to see determine any change in electrical and mechanical performance. The detailed summary of the related sintering and reliability tests are given in Section 2.4, 3, and 4 below, respectively.

Au Printing Parameters	Values	Comments
Substrate	GaAs wafer	Wafer passivated with Ni
Ink type	Water based Au	Suitable for on-wafer printing
Au particle size	~5 nm	For Aerosol Jet printing
Over-spray control	Terpineol added (10% in volume)	Lowers vapor pressure for overspray control
Nozzle size	200 um	Optimized for printed structure size
Sheath gas flow rate	80 ml/min	Optimized for reducing overspray
Atomizer gas flow rate	15 ml/min	Optimized for reducing overspray

Table 1. Printing parameters for Au ink.

Separately we developed a procedure to print GeTe with the main parameters identified in Table 2. A thermally actuated amorphous-to-crystalline phase change material (PCM) on a GaAs wafer using our newly developed GeTe ink. We adopted a coplanar waveguide (CPW) test structure for easy characterizaton of the material. There is a 20 µm gap at the center of the CPW area, where GeTe material is deposited.

GeTe Printing Parameters	Values	Comments
Substrate	GaAs wafer	25-mil thickness Wafer
Ink type	Toluene/Chloroform based GeTe	Suitable for on-wafer printing
GeTe particle size	~50 nm	Fit to Aerosol Jet printing
Nozzle size	300 um	Optimized for printed structure size
Sheath gas flow rate	40 ml/min	Optimized for reducing overspray
Atomizer gas flow rate	20 ml/min	Optimized for reducing overspray

Table 2. Printing parameters for GeTe ink.

2.4 Au Sintering and Phase Change Process

The Au inks that were prepared purposefully contained nanoparticles that were <5 nm in size, because above that diameter, Au nanoparticles sinter at near bulk temperatures >850ºC. The Au ink print on GaAs wafer were sintered using the following steps. First, we heat the ink at lower temperature, ~100ºC, to evaporate solvent. If the Au ink printed structure is heated at higher temperature at the beginning, an overcoat forms on the top of the printed line. This coating inhibits evaporation of solvent which results in incomplete sintering. After the initial evaporation step for 1 hour, we then increased the temperature to 250ºC for 3 hours. The degree of sintering is measured by the electrical conductivity of the printed lines.

The GeTe structure was heated up to 350ºC in the oven and changed from amorphous state into crystallized state over localized area. This area is responsible for the conductivity of the switching structure. Multiple device sites were tested which shows variation in resistance from the variations of printed GeTe thickness. Overall the resistance is reduced down to tens of ohms indicated the phase change has ocurred. In one site, a 9 ohm resistance is measured (see Fig. 2), which indicates this material has great potential for future agile RF switching applications.

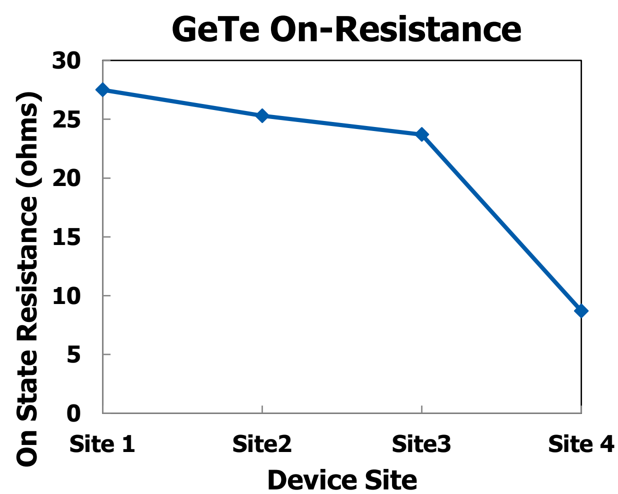


Figure 2. Measured GeTe switch after being thermally activated into crystallized "on" state.

3 ELECTRICAL PERFORMANCE

Comprehensive tests were done to characterize the Au printed wirebond and the amplifier chip where the wirebond was characterized before and after thermal shock and thermal cycle tests. There is no noticeable change in both DC and RF performances across full chip operation band as shown in Table 3. The detailed performances are reported in Section 4.

For the GeTe printed CPW test cells, measured resistance is summarized below across different sites which shows a relative low resistance. The off resistance is over mega ohms. The estimated off resistance over on resistance is in the range of ~10^5 to 10^6 range. This means this switch has an excellent on/off ratio, comparable to or better than many existing semiconductor switch devices for high isolation performance.

Performance	Pre-Reliability Testing	Post-Reliability Testing
DC resistance of printed Au (Ω)	0.1	0.1
Gain of chip	12.1	12.1
Input return loss of chip	17.0	17.1
Noise figure (dB)	1.66	1.65

Table 3. Pre/Post reliability test results of a distributed amplifier with Au ink printed wirebond, all results at 10 GHz, except DC resistances.

4 RELIABILITY TESTING

We have run extensive reliability testing on the Au printed wirebond on the GaAs MMIC chips and also printed test transmission line structures on wafer with various aspect ratios (length/width). Aerospace standard flight thermal reliability test procedures were applied.

Two thermal reliability test guidelines that we performed are from MIL-STD-883, m1010 (thermal cycling) and m1011 (thermal shock). A total of 200 thermal cycles ranging from -65ºC to 150ºC were performed in a closed chamber and 10 thermal shock cycles from -65ºC to 150ºC were performed in dual hot/cold chambers. The temperature cycling equipment consists of one chamber where the temperature is ramped between hot and cold at a rate of about 14ºC per minute, plus a 15 minute dwell at the temperature extremes. For the thermal shock test, the transition time between temperature extremes is very short to induce an extreme thermal stress compared to that of thermal cycling test. The samples were automatically transferred within 15 seconds between dual hot/cold chambers held at the temperature extremes.

The stress due to CTE mismatch of the gold ribbon interconnect is distributed over the surface area. The maximum stress is typically along the diagonal dimension of the area. A set test of interconnects with different aspect ratios, ranging from 3 to 15, were tested through thermal cycling and thermal shock. After going through these tests, all sites survived the thermal reliability tests without any peeling or damage. We plan to run similar reliability tests for the GeTe based printed structures in the future.

5 SUMMARY AND CONCLUSIONS

We have prepared new inks that may finally enable aerospace-grade printed electronics including Au and GeTe. We have demonstrated an on-wafer Au printing technique that will replace manual bias bonding with 3D printed bias bonding. Bias bonding is a manual process which correctly biases MMICs to the optimal operating point. Current process requires a large amount of documentation and is prone to low yields in practice. We propose a new approach in which bias bonding is done using an automated 3D printer such that MMICs are delivered from the foundry with the bias bonding (unique to each chip) already applied. This research has successfully demonstrated a 3D printing technology to print bias bonds onto MMICs, which has many benefits including reduced cost and schedule impact. Quality is improved through reduced mistakes and by reducing documentation load, improving configuration management and reduced handling. Assurance of an accurate bias provides both reliability and performance. The technology enables designs where manual bias bonding is cumbersome.

Additionally we have demonstrated a printable GeTe phase change material that will enable agile and reconfigurable electronics at affordable cost and fast turnaround time. Most current systems are for a fixed mission and do not have reconfigurable functionalities, such as operating frequencies, bandwidth, polarization, and radiation patterns. We believe these results demonstrate the potential impact to printed and flexible RF electronics that challenge the existing ways of designing, fabricating, and packaging electronics components and systems.

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