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Title: Inkjet-Printed Thin Film Radio-Frequency Capacitors Based on Sol-gel Derived Alumina Dielectric Ink

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ABSTRACT

There has been significant interest in printing radio frequency passives, however the dissipation factor of printed dielectric materials has limited the quality factor achievable. Al₂O₃ is one of the best and widely implemented dielectrics for RF passive electronics. The ability to spatially pattern high quality Al₂O₃ thin films using, for example, inkjet printing would tremendously simplify the incumbent fabrication processes – significantly reducing cost and allowing for the development of large area electronics. To-date, particle based Al₂O₃ inks have been explored as dielectrics, although several drawbacks including nozzle clogging and grain boundary formation in the films hinder progress. In this work, a particle free Al₂O₃ ink is developed and demonstrated in RF capacitors. Fluid and jetting properties are explored, along with control of ink spreading and coffee ring suppression. The liquid ink is heated to 400 °C decomposing to smooth Al₂O₃ films ~120 nm thick, with roughness of < 2 nm. Metal-insulator-metal capacitors, show high capacitance density > 450 pF/mm², and quality factors of ~200. The devices have high break down voltages, > 25V, with extremely low leakage currents, < 2x10⁻⁹ A/cm² at 1 MV/cm. The capacitors compare well with similar Al₂O₃ devices fabricated by atomic layer deposition.

1. Introduction

The metal-insulator-metal (MIM) capacitor is a fundamental radio frequency (RF) passive device and is often made of high quality ceramic materials. Alumina (Al_2O_3) is one of the most commonly used ceramics for RF passives since it is abundant, has a relatively high dielectric constant (~ 9), decent dielectric temperature coefficient, good chemical stability, and a high bandgap of 8.7 eV.^{1,2} Al_2O_3 in its pure form, is the dielectric material with the lowest known dielectric loss, which is important for RF electronics often sensitive to loss.³ Early reports of Al_2O_3 MIM's in the 1970's were prepared by evaporation of aluminum in an oxygen rich environment.^{4,5} Today atomic layer deposition (ALD) of Al_2O_3 is considered the model process and was first developed in the 1980's.⁶ There are several reports of high quality RF Al_2O_3 MIM's fabricated using ALD.^{7,8,9} However, ALD has downfalls since it requires an additional patterning step compared to inkjet, it does not lend itself to large area fabrication which RF passives often need, and it requires stringent thermal and environmental conditions to ensure ALD occurs. RF passives have a size proportional to the frequency of operation and typically large RF passives need to be individually bonded to a separate circuit board as opposed to being placed "on chip". A large area printing process capable of producing a high quality dielectric is an important step in simplifying the fabrication process. Previous reports on inkjet printed RF capacitors show poor quality factors (< 20 , even at low frequency).^{10,11,12} A major reason for the poor QF in these reports is the high dielectric loss of the printed insulator. Inkjet printed Al_2O_3 is an ideal candidate for tackling the loss issue. There are two reports of micro-meter sized particle based inks aimed at RF passives.^{13,14} While MIM capacitors printed with this ink have QFs > 100 , the micrometer sized particles are not capable of forming high density capacitors and large particles are known to aggregate which clogs inkjet nozzles. Another approach is to use an ink composed of Al_2O_3 nanoparticles, which has been investigated by Mogalicherla *et al.* (although MIM devices

were not fabricated).¹⁵ Nanoparticle inks are more robust against nozzle clogging and aggregation but not immune to it, they have complex synthesis protocol, and higher cost. It appears problematic to create thin uniform films with these aqueous nanoparticle solutions. It is likely that thin nanoparticle films would be inferior to the particle free solution approach due to porosity and the presence of grain boundaries. Overall, there have been two demonstrations of inkjet Al₂O₃ MIM capacitors (MHz Frequency), but to-date non-particle based printing or thin-film printing of Al₂O₃ has not, to the authors best knowledge been reported. Furthermore, RF MIM capacitors using printed Al₂O₃ have not been demonstrated for GHz operation.

2. Experimental Section

Chemicals and Ink formulation: Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O FLUKA-06275), Poly-4-vinylphenol (MW = 11000, Sigma-Aldrich 436216), poly (melamine-co-formaldehyde) (Sigma-Aldrich 418560), 1-Hexanol (C₆H₁₄O Sigma-Aldrich 436216), 2-Methoxyethanol (C₃H₈O₂ Sigma-Aldrich 185469), Ethanol (C₂H₆O, Sigma-Aldrich 32221) were used as they were received, without further purification. In an illustrative example 0.8 M solution of ink is made by mixing 5ml of ethanol with 5ml of 2-ME in a 20ml vial. Then 3.0 g of aluminum nitrate is added to the vial and vortex mixed for 30 mins and left to sit for one hour prior to using the ink. The ink is made and used in ambient environment. The cartridge is refrigerated when not in use to avoid drying out and clogging the nozzles. The cartridge can be used for several months.

Inkjet-printing: The as formulated ink was used with a drop-on-demand piezoelectric inkjet print head (Dimatix 16010) and a 2831 Dimatix printer. A waveform was utilized as shown in the **Supporting Information S1** and the voltage was varied for each nozzle to obtain 11m/s drop velocity (~23V). Average drop mass was measured by weighing the total mass of 5

million drops of ink. Ink is printed with a cartridge and substrate temperature of 30°C and 40°C respectively, at a 5 KHz frequency and a 55 μm drop spacing.

Fabrication and Measurement of Capacitors: Starting with Borofloat wafers that were freshly cleaned in Piranha solution. The bottom electrodes Ti-Au (15 nm - 500 nm) are deposited by RF sputtering and patterned with a lift off technique. A 0.5% wt. Poly-4-vinylphenol with 0.077% wt. poly (melamine-co-formaldehyde) solution in 1-Hexanol is then spun over the surface at 5000 RPM for 45 seconds and baked at 200°C for 10 minutes. A 150 second UV Ozone treatment is given to promote wetting. The ink is then printed in square patterns and annealed at 70°C for 5 minutes, then 90°C for 5 minutes, and finally ramped at 10°C/min to 400°C for 10 minutes. 3 printed layers are used with a final 2 hour 400°C anneal in air. A UV ozone treatment is necessary before printing each additional layer. A two micro-meter amorphous silicon sacrificial layer is deposited by plasma enhanced chemical vapor deposition at the low processing temperature of 50°C to avoid hard baking the photoresist. The amorphous silicon is then patterned using a standard lift off procedure. Note that AZ developer is used from Microchem to avoid damaging the alumina film which is sensitive to other developers. Finally a seed layer of Ti-Au (15 nm - 250 nm) is deposited by RF sputtering and a 3.5 μm copper layer is electroplated. The seed layer is etched with reactive ion etching with argon gas for three minutes. The amorphous silicon is etched with exposure to XeF_2 gas at room temperature for ~90 minutes. Capacitors were measured with an Agilent 4980A LCR meter and high frequency measurements were taken in a two port configuration using 500 μm pitch Z-probes and a cascade probe station with a Agilent E8361A network analyzer. Leakage current was measured with (Keithley 4200-SCS). The structural properties were examined using scanning electron microscopy (FEI NovaNano FEG-SEM 630). The thickness and uniformity of printed features on substrates were performed using a surface profiler (Veeco Dektak 150) and 3D interferometry (Zygo, Newview 7300). Surface tension

and viscosity of the inks were measured using a KRUSS DSA100 and Brookfield Rheometer (DV3T). Thermogravimetric analysis was performed using a TG 209 F1 analyzer (Netzsch), with a heating rate of 10 °C/min in air flow.

3. Al₂O₃ Ink Development:

Since the first report of high mobility amorphous oxide semiconductors in 2004, solution-processed sol-gel based oxides have quickly gained momentum.¹⁶ The drive has been towards thin film transistors (TFTs) for displays. The main dielectric contenders for these devices have been SiO₂, ZrO₂, HfO₂, Al₂O₃, TiO₂, Y₂O₃, and Ta₂O₅.¹⁷ Of these sol-gel dielectrics, ZrO₂ has been inkjet printed in a fully inkjet-printed TFT by Jang *et al.*¹⁸ This innovative work relies on a sacrificial polymer layer to modify the surface energy before printing ZrO₂, and serves as a stepping stone for this field. ZrO₂ has relatively poor RF performance due to its loss tangent of 0.05-0.1¹⁹, making it unsuitable for RF capacitors. Recipes for solution based Al₂O₃, have been based on aluminum chloride as well as aluminum nitrate precursors.²⁰⁻²¹ In our investigations it was found that quality Al₂O₃ films could be made with both aluminum chloride hexahydrate and aluminum nitrate nonahydrate. However aluminum nitrate was much more stable in ambient environment making it easier to process. In this work aluminum nitrate is used with the common solvent 2-methoxyethanol (2-ME) and ethanol. The co-solvent system of 2-ME and ethanol was necessary for inkjet film formation and is further discussed in the next section. The Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) of the ink was carried out, as shown in **Figure 1**. **Figure 1a** shows the continuous weight loss, which starts at room-temperature and ends at ~150 °C. A zoomed in view of the TGA is shown in **Figure 1b** where it is evident that there is considerable mass loss from ~150°C to ~350 °C, after 350°C the rate of loss slows considerably. The DSC curve in **Figure 1c** endothermic peaks maximum at ~71 °C and 105 °C, corresponding to the solvent evaporation of the ink, mainly due to ethanol and 2-

methoxyethanol. There is another endothermic peak followed by sharp decrease and centered at ~165 °C which may be due to hydrolysis of the metal precursors.²² Second endothermic peak followed by a broad exothermic peaks ranges from 230-310 °C and 310-400 °C was observed, which was attributed to the final decomposition to aluminum oxide. It is believed that most of the aluminum nitrate in solvent is decomposed below 400 °C, thus, annealing temperature was set at 400 °C for thin-film formation. The decomposition reaction is described by **Equation (1)**.²³

Figure 1. TGA of aluminum nitrate 0.8M in 50% by volume 2-Methoxyethanol and Ethanol (b) Zoomed in view of the TGA (c) Corresponding DSC (d) XPS survey of $Al(NO_3)_3 \cdot 9H_2O$ in 2-ME after heating to 400°C. (e) XPS aluminum peak (f) XPS oxygen peak.

X-ray Photoelectron Spectroscopy (XPS) analysis of the aluminum nitrate and 2-ME solutions confirmed that alumina was formed after the 400 °C thermal annealing step. From XPS analysis **Figure 1d**, there is an undetectable amount of nitrogen left in the films, which indicates that the nitrate precursor has decomposed. From analysis of the XPS survey it was found that there is 61% oxygen to 39% aluminum, nearly stoichiometric Al_2O_3 . The single

aluminum peak ~ 74.2 eV confirms the formation of Al_2O_3 , **Figure 1e**. The oxygen peak at ~ 531.0 eV is recognized as O^{2-} in Al_2O_3 , which is attributed to 74% of the oxygen bonding, **Figure 1f**. The smaller oxygen peak at ~ 532.3 eV is mostly associated with aluminum hydroxide $\sim 26\%$. A similar hydroxide component is also shown in alumina sol-gel films annealed at 500°C by Nayak *et al* ²⁴. XPS is a surface analysis technique and this hydroxide component may be due to moisture adsorption on the surface of the film after final annealing. X-ray diffraction measurements confirm that these films are amorphous at 400°C and it was found Prasanna *et al.* that alumina films were still amorphous after a 750°C heat treatment by.²⁵

The most challenging problem with inkjet printing the Al_2O_3 ink was obtaining a smooth and uniform printed thin film, which is absolutely necessary to fabricate consistent and non-shortened capacitors. In the current work we utilize a Dimatix 2831 inkjet printer with a 10 pL cartridge. Devices were fabricated on borosilicate glass as the mechanical support with a thin titanium bonding layer and a 500 nm thick gold electrode sputtered on the surface. It proved difficult and inconsistent to inkjet print on the gold surface directly. A thin layer of poly-4-vinylphenol was spun on top of the gold (~ 5 nm). An optimized ultra-violet ozone (UVO) treatment was then applied for 150 seconds. The PVP provided a measured surface energy of 61 dyne/cm and ink completely wets on this surface. It was found that using only the 2-ME solvent for the solution had significant capillary-driven spreading and high coffee ring staining.

Figure 2. (a) White light interferometer profile of droplets with different volume ratios of ethanol solvent to 2-ME (b) White light interferometer image of a droplet with 50% by volume ethanol and 2-ME solvents .

Different solvents were attempted to alleviate the uniform printing issue including ethanol, 2-propanol, 1-butanol, and 2-butanol. In the end, ethanol gave the best results as its higher volatility limited the capillary-driven spreading, which in turn reduced the coffee ring effect. To investigate the coffee ring effect droplets were printed and images were taken with a Zygo interferometer **Figure 2**, similar to the work done by Soltman *et al.* and Jang *et al.* on printing uniform patterns.^{26,18} It can be seen from **Figure 2a** that the droplet size and coffee ring at the edges is reduced with the addition of ethanol in the films. It was found experimentally that 50% v/v ethanol provided the most uniform films, and a single droplet can be seen in **Figure 2b**. The ink with 50% v/v ethanol was capable of producing uniform square films (**Supporting Information S2**) a single printed layer is ~30 nm thick.

The sputtered gold used for the electrodes is extremely smooth, with an RMS roughness of 2.8 nm. The Al₂O₃ films printed on top of the gold show only 0.4 nm of RMS roughness (**Supporting Information S3**). The profilometer scan in **Figure 3a** shows a typical printed square with three layers and a thicker area around the edge is still evident but the central region

Figure 3 (a) Profilometer scan over a printed square with three printed layers of alumina ink after 400 °C thermal treatments. (b) Viscosity of 50% by volume 2-ME/ethanol solvent with different molar concentrations of aluminum nitrate precursor.

is fairly flat. This central region is used to make the capacitors. Three layers were necessary in order to avoid cracking which occurred with a single thick layer. Multiple layers also aid in creating a denser film.

The final ink used a 50% v/v ethanol to 2-ME ratio with a 0.8 M concentration of aluminum nitrate. While these low viscosity solvents alone had a viscosity of 1.3 centipoise, the addition of the precursor raised the viscosity into a much better range of 7.0 centipoise for the 0.8 M concentration, as shown in **Figure 3b**. This viscosity is in a good range for inkjet printing, and there was no evidence of shear thickening or thinning behavior from **Figure 3b**. The characteristics of the ink are highlighted in **Table 1**. This ink has near ideal fluid properties for jettability.²⁷ The inkjet waveform is provided in the **Supporting Information S1**

Table 1. Characteristics of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 0.8M concentration ink with 50 % v/v ethanol and 2-ME solvent at 25 °C, using the 10 pL cartridge with 21 um diameter orifice at 11 m/s velocity.

Viscosity (cP)	Surface T. Dyne/cm	Density (g/cc)	Drop Mass (ng)	Ohnesorge (Oh)	Reynolds (Re)	Weber (We)	Capillary (Ca)
7.0	28.3	1.04	6.8	0.28	34	93	2.7

cP = centipoise, Surface T. = surface tension

4. MIM Fabrication

To create MIM capacitors the Al_2O_3 ink is used to print the dielectric and a conventional fabrication process utilizing photolithography is employed to create the electrodes. Due to the leakage current that develops at the edges of the bottom metal, an airbridge is commonly used for RF capacitors.^{28,9} An airbridge is especially important when using an inkjet-printed film where de-wetting at the edge of the bottom metal is observed. The ink de-wetting not only causes leakage but completely shorts the devices. A depiction of the fabrication process including cross section cartoons and microscope images can be seen in Figure 4a-d.

Figure 4. Fabrication of MIM Capacitors (a) Bi-layer photoresist after development (b) Bottom metal- titanium/gold 500 nm and dielectric-inkjet printed aluminum oxide ~120 nm thick (c) Sacrificial layer for air bridge amorphous silicon ~2 μm thick (d) Top metal titanium/gold seed layer and electroplated copper 4 μm thick.

Finding the appropriate sacrificial layer and etching process to remove the layer from under the airbridge proved to be rather challenging. This is because many etchants and even photo-developers etch aluminum and also damage the thin Al_2O_3 film, which causes excessive leakage current in devices. Photoresists were first attempted as sacrificial layers, but in the end a sacrificial layer of amorphous silicon (α -Si) worked best. A lift-off process with α -Si was used by depositing it at the unusually low temperature (50 °C) using Plasma Enhanced

Chemical Vapor Deposition (PECVD). This was necessary so that the photoresist would not be hard-baked to the wafer and the resist could easily be removed with acetone. The α -Si has the added advantage that it can be selectively etched away with XeF_2 gas without damaging any of the other materials. A micrograph of the α -Si during the fabrication process can be seen in **Figure 4c**. An SEM image of the airbridge with a 1.8 μm gap is shown in **Figure 5a**. From the cross-sectional focused ion beam (FIB) SEM image at high magnification, there are few details about the Al_2O_3 structure, although a ~ 120 nm thickness of the layer is shown. The thin ~ 15 nm titanium layer can be vaguely seen below the top seed layer of gold.

Figure 5. (a) SEM image of the airbridge. (b) FIB-SEM image of alumina film.

5. Capacitor Characterization

Using the inkjet printed films and fabrication process described in the previous section the capacitors proved to have high quality factors ~ 200 . The leakage current of the capacitors is excellent, better than 2×10^{-9} at 1MV/cm, **Figure 6a**. These results are comparable to high vacuum ALD grade films. The breakdown fields for the capacitors is not ideal with no predictable breakdown voltage, **Figure 6ab**. However, most of the capacitors break above

25V, which is useful for many applications. A major concern for printed devices is the variability in capacitance values caused by the fluctuations in the film thickness. This is seen from the variation in capacitance values of 50 devices in **Figure 6c**. The capacitance values for the 0.173 mm² area devices have a standard deviation of 5.1 pF (7%), while the 0.045 mm² caps show a 1.2 pF deviation (6%). However, this is a new process and it is expected that with further improvement to the ink formulation and optimization of a uniform surface treatment, more uniform layers could be printed and the capacitance variation reduced. The dielectric constant is estimated at ~6.2 based on measurements of different capacitor sizes. The estimated Dielectric Constant (Dk) of 6.2 for the inkjet alumina is low (~70%)³; however, it is similar to spin-coated sol-gel results (**Supporting Information S4**) and other reports in the literature^{20,24}. Hu et al.²¹ used aluminum nitrate precursors aimed at making dense spin-coated films and investigated 550 °C annealing, yet reported a similarly low dielectric constant. The lower dielectric constant has been attributed to a lower density of the film in comparison to ALD, which is expected based on the previous reports. Capacitance and bias were tested against measurement temperature in **Figure 7**.

Figure 6. (a) Typical leakage current through the capacitors until breakdown. (b) Breakdown voltage plot of 50 capacitors. (c) Variation in capacitance values of 50 sample devices.

There is a significant drop in the quality factor with temperature. While there is also a change in the ALD film, this change was less significant (ALD grade capacitor results are in the **Supporting Information S5**). The reason for this could have to do with the hydroxide component in the sol-gel films, although the understanding of this phenomenon would require

further investigation. Nonetheless, QFs in the range of 200 are excellent for an inkjet-printed film. There is some frequency-dispersion as well as a change due to temperature. The Temperature Coefficient of Capacitance (TCC) at 100 KHz is calculated to be ~ 330 ppm/ $^{\circ}\text{C}$, which is comparable to sputtered films²⁹ and ALD films (**Supporting Information S6**). The bias has been measured as a function of temperature as well; see **Figure 7c**.

Figure 7. (a) Low frequency capacitance testing. (b) Quality factor. (c) Bias testing. (d) Normalized capacitance versus bias.

While these measurements look flat, there is a small change as shown in the zoomed in and normalized plot in **Figure 7d**. This change in capacitance can be used to find the voltage characteristics given from Equation 2.³⁰

$$\frac{C(V)}{C_o} = \alpha V^2 + \beta V + 1 \quad (2)$$

From the normalized plot in **Figure 7d** we find that α is calculated as 10.2 ppm/V² and β as 3.1 ppm/V. This shows slightly better voltage characteristics in comparison to ALD capacitors in ⁹; however, it is important to bear in mind that the parameters are influenced by capacitance density, which is higher in the ALD films. RF measurements are obtained by taking the measured S-parameters from the two-port network analyzer and then converting these to Y-parameters and extracting the capacitance with Equation 3 and 4 ¹²:

$$C = -\frac{1}{im\left(\frac{4}{Y_{11} + Y_{22} - Y_{12} - Y_{21}}\right) 2\pi f} \quad (3)$$

$$Q = -\left(\frac{im(Y_{11} + Y_{22} - Y_{12} - Y_{21})}{re(Y_{11} + Y_{22} - Y_{12} - Y_{21})}\right) \quad (4)$$

An electromagnetic simulation that was developed in Ansoft High Frequency Structure Simulator compares well with the measured results, as shown in Figure 8. The simulation was run with 500 nm of sputtered gold and 3 um of copper top metal. With a 120 nm dielectric, Dk of 6.2 and a loss tangent of 0.005 (which was extracted by taking the inverse of the low frequency quality factor.³¹ The simulation results and measurements have consistent self-resonance frequencies, capacitance, and quality factors.

Figure 8. (a) RF testing capacitance measurement and simulation. (b) RF quality factor. (c) Self resonant frequency versus capacitance size (d) Quality Factor versus capacitance size and frequency. Note that the input pads are 250 μm in this case which has an effect on self-resonance frequency.

The simulated capacitance value is 23 pF and measurement is 21.5 pF, and the difference can easily be attributed to thickness variations in the printed films. The higher capacitance in simulation is also the reason for the slightly lower self-resonant frequency (1.5 GHz versus 1.9 GHz). The high frequency quality factor follows the same trend as the low frequency quality factors approaching 200, which is consistent with low frequency measurements in **Figure 7b**. The quality factor of the 20 pF capacitor approaches 20 at 500 MHz. Design curves have been created from the capacitor measurements and simulations to aid the designer in choosing which capacitors to use with this process. The results in **Figure 8c** show the trend of self-resonant frequency on a log-log axis as expected. The quality factors are plotted in **Figure 8d** and also a clear trend, all capacitors peak off at a quality factor of 200 as was shown with the low frequency measurements.

6. Conclusions

A sol-gel dielectric has been developed and successfully deposited using inkjet printing. Inkjet printed MIM capacitors with QFs ~ 200 have been fabricated using a photolithography process developed in-house, which includes a 2 μm airbridge. The Al_2O_3 layers are ~ 120 nm thick, with ~ 0.5 nm RMS surface roughness after the 400 $^\circ\text{C}$ annealing step. Coffee ring staining has been studied and suppressed by utilizing an ethanol and 2-ME solvent system. The printed alumina exhibits an estimated dielectric constant of 6.2 and temperature coefficient of capacitance of 330 ppm/ $^\circ\text{C}$. The leakage current through the films is excellent at 2×10^{-9} A/ cm^2 at 1MV/cm. Dielectric breakdown occurs above 20V. RF capacitors are shown with self-resonant frequencies in the GHz regime and a 20 pF capacitor has a low frequency quality factor of 200 dropping as expected to ~ 20 at 500 MHz. Likely the biggest concern is that the variation in capacitor value of these printed devices is $\sim 7\%$ standard deviation. It is expected that with further development of the ink and surface treatment to optimize wetting, this variation could be further reduced. Another concern is the high temperature (400 $^\circ\text{C}$) processing required. It may be possible to reduce this high temperature requirement with alternative decomposition methods such as UV curing or by adjusting solution PH and precursor choice. Nonetheless, these are promising results that demonstrate that high quality alumina thin films can be made by inkjet.

Supporting Information

Supporting Information is available online or from the author.

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Supporting Information

Title: Inkjet Printed Alumina Thin-Films for Radio Frequency Metal-Insulator-Metal Capacitors

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Supporting Information

Figure S1. Inkjet printing waveform used with the alumina ink.

Figure S2. (a) Microscope images of printed alumina squares after 400 °C annealing, the worst case situation is where the ink solely uses 2-ME solvent and a higher substrate temperature of 60 °C promoting the coffee ring effect. The ink is too thick around the edges of the printed square (>100 nm in a single print) causing cracks after the 400 °C heating step. (b) Microscope image of printed uniform alumina square utilizing 50/50 2-ME solvent and ethanol.

Figure S3. (a) AFM scan showing 2.8 nm RMS surface roughness on the bottom sputtered gold electrode (b) AFM scan of 0.4 nm RMS of surface roughness on the printed alumina on top the gold.

Figure S4. Capacitance versus capacitor area measured at 100 KHz with a 1V signal and an Agilent 4980A LCR meter. The sol-gel capacitors are formed with three layer spin coated and

a 400 °C anneal between each layer. ALD capacitors were formed with a standard 300 °C plasma recipe.

The reason for the lower dielectric constant in the printed capacitors does not have to do with the fact they are inkjet printed and the spin coated devices show similarly low density. From Figure S4. using slope of the lines and knowing the thickness of the films the dielectric constant of the films was estimated to be ~6.2 for the sol-gel alumina spin coated (similar to the inkjet printed capacitors) and ~9.2 for the ALD. A dielectric constant around 9 is expected from a dense film. Both spin coating and inkjet printing the sol-gel solutions produced a less dense film. Hu et al. (reference below) also demonstrated this lower density with sol-gel spin coated devices with annealing temperatures of 550 °C. Producing a denser film with higher dielectric constant may require even higher processing temperatures which is impractical for most substrates.

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Figure S5. (a) Capacitance versus frequency of MIM capacitor made using standard recipe Plasma ALD at 300 °C (b) Quality factor of the same ALD MIM capacitor (c) Capacitance versus frequency of MIM capacitor made using sol-gel inkjet printed capacitor annealed at 400 °C (d) Quality factor of the same inkjet printed MIM capacitor.

Figure S6. (a) Normalized capacitance versus bias voltage of inkjet printed sol-gel dielectric ~120 nm thick. (b) Normalized capacitance versus bias voltage of standard 300 °C plasma ALD capacitor.