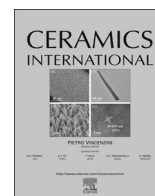




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# Inkjet-printed thin film radio-frequency capacitors based on sol-gel derived alumina dielectric ink

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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. Al<sub>2</sub>O<sub>3</sub> is one of the best and widely implemented dielectrics for RF passive electronics. The ability to spatially pattern high quality Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> films ~120 nm thick, with roughness of < 2 nm. Metal-insulator-metal capacitors, show high capacitance density > 450 pF/mm<sup>2</sup>, and quality factors of ~200. The devices have high break down voltages, > 25 V, with extremely low leakage currents, < 2×10<sup>-9</sup> A/cm<sup>2</sup> at 1 MV/cm. The capacitors compare well with similar Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub>) 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> is considered the model process and was first developed in the 1980's [6]. There are several reports of high quality RF Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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

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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  $\text{Al}_2\text{O}_3$  MIM capacitors (MHz Frequency), but to-date non-particle based printing or thin-film printing of  $\text{Al}_2\text{O}_3$  has not, to the authors best knowledge been reported. Furthermore, RF MIM capacitors using printed  $\text{Al}_2\text{O}_3$  have not been demonstrated for GHz operation.

## 2. Experimental section

### 2.1. Chemicals and ink formulation

Aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  FLUKA-06275), Poly-4-vinylphenol (MW =11000, Sigma-Aldrich 436216), poly (melamine-co-formaldehyde) (Sigma-Aldrich 418560), 1-Hexanol ( $\text{C}_6\text{H}_{14}\text{O}$  Sigma-Aldrich 436216), 2-Methoxyethanol ( $\text{C}_3\text{H}_8\text{O}_2$  Sigma-Aldrich 185469), Ethanol ( $\text{C}_2\text{H}_6\text{O}$ , 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 5 ml of ethanol with 5 ml of 2-ME in a 20 ml vial. Then 3.0 g of aluminum nitrate is added to the vial and vortex mixed for 30 min 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.

### 2.2. Inkjet-printing

The as formulated ink was used with a drop-on-demand piezo-electric 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 11 m/s drop velocity ( $\sim 23$  V). 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  $\mu\text{m}$  drop spacing.

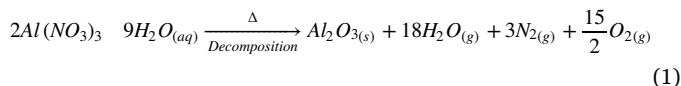
### 2.3. Fabrication and measurement of capacitors

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 s and baked at 200 °C for 10 min. A 150 s UV Ozone treatment is given to promote wetting. The ink is then printed in square patterns and annealed at 70 °C for 5 min, then 90 °C for 5 min, and finally ramped at 10 °C/min to 400 °C for 10 min. 3 printed layers are used with a final 2 h 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 (15–250 nm) is deposited by RF sputtering and a 3.5  $\mu\text{m}$  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  $\text{XeF}_2$  gas at room temperature for  $\sim 90$  min. Capacitors were measured with an Agilent 4980 A LCR meter and high frequency measurements were taken in a two port configuration using 500  $\mu\text{m}$  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 processed 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. $\text{Al}_2\text{O}_3$ 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  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{Ta}_2\text{O}_5$  [17]. Of these sol-gel dielectrics,  $\text{ZrO}_2$  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  $\text{ZrO}_2$ , and serves as a stepping stone for this field.  $\text{ZrO}_2$  has relatively poor RF performance due to its loss tangent of 0.05–0.1 [19], making it unsuitable for RF capacitors. Recipes for solution based  $\text{Al}_2\text{O}_3$ , have been based on aluminum chloride as well as aluminum nitrate precursors [20,21]. In our investigations it was found that quality  $\text{Al}_2\text{O}_3$ , 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 Fig. 1. Fig. 1a shows the continuous weight loss, which starts at room-temperature and ends at  $\sim 150$  °C. A zoomed in view of the TGA is shown in Fig. 1b where it is evident that there is considerable mass loss from  $\sim 150$  °C to  $\sim 350$  °C, after 350 °C the rate of loss slows considerably. The DSC curve in Fig. 1c endothermic peaks maximum at  $\sim 71$  °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  $\sim 165$  °C which may be due to hydrolysis of the metal precursors [22]. s endothermic peak followed by a broad exothermic peaks ranges from 230 to 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 Eq. (1) [23].



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 Fig. 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  $\text{Al}_2\text{O}_3$ . The single aluminum peak  $\sim 74.2$  eV confirms the formation of  $\text{Al}_2\text{O}_3$ , Fig. 1e. The oxygen peak at  $\sim 531.0$  eV is recognized as  $\text{O}^{2-}$  in  $\text{Al}_2\text{O}_3$ , which is attributed to 74% of the oxygen bonding, Fig. 1f. The smaller oxygen peak at  $\sim 532.3$  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  $\text{Al}_2\text{O}_3$ , ink

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