Characterization of Inkjet-Printed Stacked MIM Thin-film Solid-State Flexible Super-Capacitor

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***Abstract*—Electrical energy storage need has evolved to lightweight and portable devices such as electric vehicle, drones, robotics, wearables, etc. Current technology of batteries such as Li-Ion or Li-Poly are not able to meet the requirement for future. We have been developing a new type of supercapacitor for this technological barrier. Our supercapacitors are fabricated with inkjet-printing (IJP) technique that uses very precise MEMS based cartridge to print thin-films on planar substrates. We have previously demonstrated metal-insulator-metal (MIM) capacitor fabrication and simulation, as well as stacked MIM supercapacitor fabrication. In this paper, we present electrical characterization (such as charging-discharging cycles) and scanning electron microscopy image for IJP stacked MIM supercapacitor. The electrical characterization validates the charge storage capability of the supercapacitor. We have tested the samples for up to 20 V charging voltage. The corresponding stored charge can be as high as 40 nC, and the charge density is 17.4 C/m^3. These solid-state IJP stacked MIM supercapacitors are flexible with high energy-density and safe for prolonged use which can be applicable in electric vehicles, wearables, implantable, drones, and other energy storage applications.**

Keywords-Energy storage, Flexible Electronics, Inkjet-printing, Solid-state, Super-Capacitor.

I. Introduction

Ever increasing lightweight and portable electric energy storage demand in many technologies, such as electric vehicles (EV), drones, robotics, smart devices, wearables, and internet-of-things (IoT), urges to impelled extensive research in the development of new eco-friendly, high-energy density, lightweight, solid-state rechargeable energy storage technologies [1]. Currently, high energy density rechargeable batteries are based on electrochemical process that contains rare materials and toxic chemicals. For instance, Lithium Ion (Li-Ion or LiI) batteries are most popular rechargeable batteries with high energy density, large current capacity, and lightweight, while Lithium-iodide polymer batteries (Li-poly or LiPo) are commonly used in many commercial drones, wearables, and smart devices. However, these rechargeable batteries use toxic and flammable chemical, unsafe, and degrades over time and charging cycles. Solid-state technologies can resolve most of these issues such as, recharged rapidly which can drastically change consumer appeals of EV and drones. Solid-state batteries (SSB) and supercapacitors are safer, can store higher energy density, do not degrade over charging cycles, and can be even lighter to the best LiPo battery technology. Current technologies of SSB can be categorized in three types: Polymer/composites, Ceramic (oxide), and Glassy (sulfide) [2]. SSB uses solid electrolyte sandwiched between anode and cathode terminals. Electrolyte is the most challenging aspect of SSB, as they can be very expensive, very hard or heavy, and low energy density.

On the other hand, supercapacitors do not use electrolyte. It can be fabricated with dielectric material sandwiched between two metal plates. Electric double-layer supercapacitors can deliver quick charging and discharging rates, within seconds, and sustain millions of charge and discharge cycles, as opposed to batteries which can only endure thousands of cycles [3-5]. Current technologies for supercapacitor types can be categorized in three types: electrochemical double layer capacitor (EDLC), pseudocapacitor, and a hybrid of these two [6,7]. EDLC can be fabricated with carbon aerogels, activated carbons, carbon fibers, or carbon nanotubes. Pseudocapacitors can be fabricated with metal oxides and conducting polymers. Hybrid supercapacitors are developed with combinations of carbon materials with conducting polymers and metal oxides [7]. Most of these are fabricated with electrochemical deposition, chemical vapor deposition (CVD), sputter-coating, solgel, chemical precipitation, etc. Some of the solid-state supercapacitor fabrication processes includes Micro-Electro-Mechanical Systems (MEMS) or sputter-coating of interdigitated electrode (IDE) based capacitors results low capacitance per unit area. These produces 2D capacitors and they cannot be stacked (layer a capacitor on top of another capacitor) using monolithic fabrication process, as well as volume and weight per unit capacitance are high [8,9]. Current supercapacitors suffer from low-energy density, unstable materials, or high cost. We are attempting to fabricate a new type of supercapacitor using Inkjet-Printing (IJP) additive manufacturing technology [10-15].

Inkjet printing is a solution-based printing and patterning technology that is highly efficient, low-cost, and offers high-quality and high-throughput benefits. It is suitable for large-scale fabrication of flexible electronics. Our research group aims to develop IJP as a monolithic fabrication technique for low-cost and customizable flexible electronics [11,12,16-22]. IJP fabricated a body-worn flexible temperature sensor that was capable of monitoring body temperature for our recent smart and connected community research project.

We have been studying metal-insulator-metal (MIM) type IJP capacitor fabrication. We use Silver (Ag) nanoparticle-based ink for metal layer fabrication and Poly-4-vinylphenol (PVP) for dielectric layer fabrication. Silver and PVP are inexpensive and easily available materials that can be used for the fabrication of supercapacitors. In our previous study, we have successfully demonstrated IJP fabricated parallel plate MIM capacitors on flexible polyimide substrate using silver conductive ink and PVP dielectric ink [20]. We found that to avoid short-circuiting of subsequent metal layers, multiple coatings (4 or more) of PVP is required as the dielectric layer. We compared our fabricated capacitor's performance with a finite element simulation and obtained a similar capacitance of ~9 pF/mm^2 for 6 coatings of PVP as the dielectric layer [21].

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MIM capacitors stack can provide higher capacitance and higher energy density per unit volume and can be considered as supercapacitors when sufficiently large number of layers are stacked.

II. Theory of Operation

A. MIM capacitor

The ideal value of capacitance for MIM capacitors can be expressed as [23]:

$$C = \varepsilon_0 \varepsilon_r A_e / d$$

where A_e is the geometric surface area of the electrodes, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the dielectric material, and d is the distance between the two opposite biased electrodes. In this ideal case, fringe capacitance and resistive effect of the metal traces are ignored.

B. *Stacked* MIM capacitor

Stacked MIM capacitor are alterative formation of metal layers (*n+1*) and dielectric layers (*n*) as shown in Fig. 1. Each alternate metal layers are connected to either positive terminal or negative terminals. This stacked MIM configuration can achieve *n*C* capacitance due to parallel arrangement of *n* capacitors. Here C is the capacitance of each MIM capacitor. This will result in high capacitance per unit footprint with capacity for a small volume leading to high energy density.

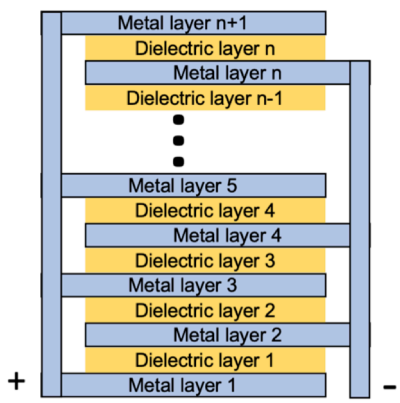

Fig. 1: Concept of stacked MIM supercapacitor where subsequent (*n+1*) metal layers are isolated by (*n*) dielectric layers forming *n*C* capacitance where C is capacitance of each MIM capacitor.

The total capacitance (ideal) can be expressed as,

$$C_{stack} = nC = n(\frac{\varepsilon_0 \varepsilon_r A_e}{d})$$

where C is the capacitance for a single MIM capacitor. Thus, capacitance per unit area can be calculated as,

$$C_{per\ area} = C_{stack}/A_e = n(\frac{\varepsilon_0 \varepsilon_r}{d})$$

Assuming the thickness of metal and dielectric layers are m and d, and the thickness of substrate is s, the total thickness of n stacked capacitor is,

$$(n+1)m + nd + s$$

Thus, the volume of this supercapacitor is,

$$\big((n+1)m + nd + s\big) * A_e$$

Then the capacitance per unit volume can be expressed as,

$$C_{per\ vol} = \frac{C_{stack}}{((n+1)m + nd + s) * A_e}$$

The stored charge per unit volume or charge density of this capacitor can be expressed as,

$$Q_{per\ vol} = C_{per\ vol} V = \frac{C_{stack} V}{((n+1)m + nd + s) * A_e}$$

III. Fabrication

A. IJP printer

We have used a PC-controlled Dimatix Materials Printer (DMP-2850, FujiFilm Inc., USA) to fabricate the IJP supercapacitors on 25 µm thin polyimide substrates. The printer uses a silicon micro-electro-mechanical system (Si-MEMS) based printhead (samba cartridge). This cartridge has 12 printing nozzles which are arranged linearly at 338.67 µm gaps. The number of printing nozzles can be selected based on printing requirements. For this work, we used all 12 nozzles with the cartridge head angle setting at 2.5°, which results in 15 µm drop spacing at 1693 dpi printing resolution. In the IJP process, the ink is ejected from the cartridge nozzle drop-by-drop from left-to-right printing direction. In the inkjet printing process, the volume and speed of ink droplets are related to the piezoelectric actuation, which is controlled by pulsating voltages, waveforms, jetting frequencies, jetting height, meniscus setpoint, and the size of the nozzle.

B. IJP Inks

A commercial silver nanoparticle ink Metalon® JS-A191 (Novacentrix Inc., TX, USA) was used for conductive metal layer fabrication. Silver A191 ink contains 40% silver nanoparticle by weight, where the silver concentration is 25-50% with 10-15% ethylene glycol and 0.2 – 1% polyethylene glycol 4-(tert-octylphenyl) ether. At 25° C the viscosity of this ink is 8 to 12 cP and the surface tension is 28 to 32 dyne/cm. With a specific gravity of 1.6, the Z-avg particle size of JS-A191 ink is 30-50 nm.

For a dielectric layer, a customized ink made of Poly(4-vinylphenol) (PVP) was formulated. This ink was created by combining 5% wt of PVP powder (Sigma Aldrich 436216) and 0.77% wt of Poly(melamine-co-formaldehyde) (Sigma Aldrich 418560) and dissolving the mixture in hexanol (Sigma Aldrich 471402). The PVP was then dispersed by subjecting the mixture to a bath-type sonicator for approximately 20 minutes until the solution turned transparent. The ink could then be used for printing, with a minimum curing temperature of 118° C.

C. IJP supercapacitor fabrication process

In the first step polyimide (PI) substrate was cleaned with Isopropyl alcohol to remove dust particles from it. In the next step Ag nanoparticle ink was printed into the substrate to fabricate one of the metal layer (M1). After printing the first silver layer, we proceeded to cure it in an oven for thermal curing process. We have used a Thermo Scientific Heratherm (Thermo Fisher Scientific Inc., MA, USA) for this purpose. The Ag layer was cured at 180°C for 30 minutes. After that 2 coatings of the PVP were printed and cured at 180°C for 25 minutes. We repeat this PVP coating printing (2 coatings at a time) once or twice to obtain 4 coatings or 6 coatings of PVP for the dielectric layer (D1). Then we print the other Ag layer (M2). For stacked MIM supercapacitor, this process is repeated (printing of Metal layer followed by printing of dielectric layer) as many times as needed. The IJP stacked MIM supercapacitor fabrication process is depicted in Fig. 2.

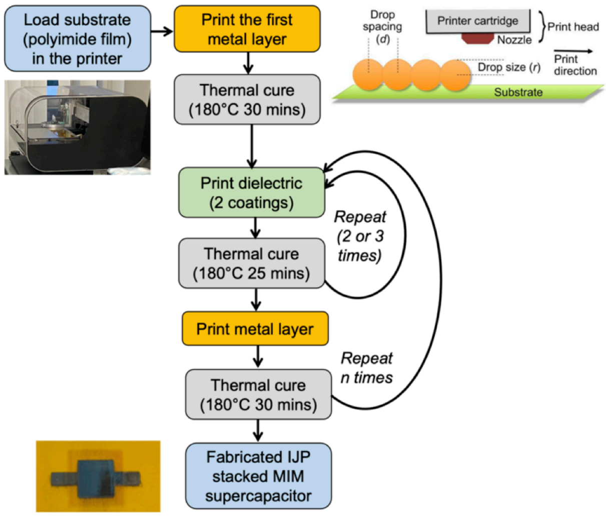

Fig. 2: IJP stacked MIM supercapacitor fabrication process.

IV. Results

A. Printed supercapacitor

We have printed IJP supercapacitors in various configurations [23]. Fig. 3 shows a IJP supercapacitor with 3 metal layers and 2 dielectric layers. Each dielectric layer was composed of 6 coatings of PVP. The footprint of the metal layers was *w*=10 mm by *w*=10 mm, and the area of PVP was *w+4*=14 mm by *w+4*=14 mm (2 mm overlap on all sides). The connector traces on both sides (connecting to positive metal layers and negative metal layers) were 3 mm by 8 mm.

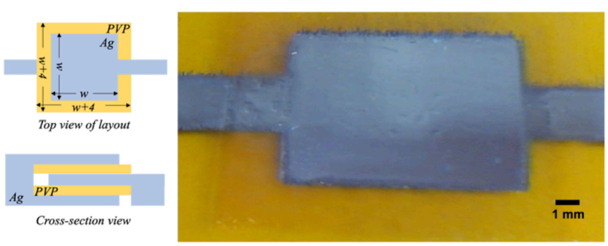

Fig. 3: A photograph of an IJP stacked MIM supercapacitor.

B. Electrical characterization

We have demonstrated the ability of the IJP supercapacitors to store charge. Fig. 4 and Fig. 5 show three samples of supercapacitors that were charged and discharged at different charging-discharging frequencies (100 Hz and 200 Hz, respectively). We have connected a 1 MΩ series resistance to charge the supercapacitors (top waveform) and observed the voltage across the supercapacitors (bottom waveform) using an oscilloscope (Model: KT-DSOX1204G, Keysight Technologies, Santa Rosa, CA). For these testing, we have used 100 Hz square wave from a signal generator (Model: KT-DSOX1204G, Keysight Technologies, Santa Rosa, CA).

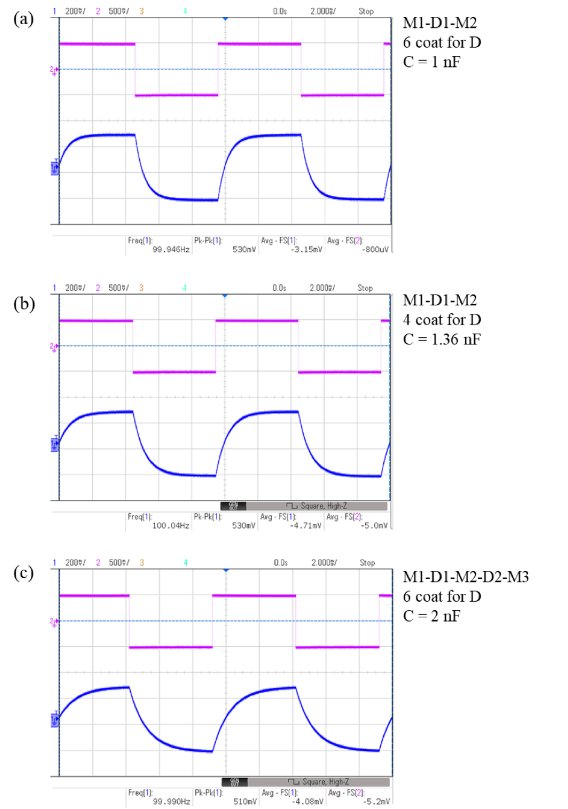

Fig. 4: Charging and discharging cycles of 3 samples of IJP stacked MIM supercapacitor with 100 Hz frequency.

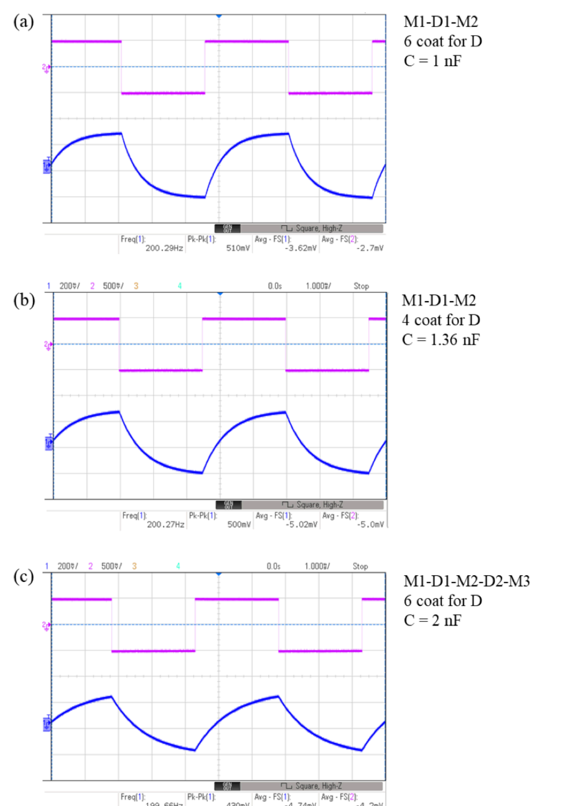

Fig. 5: Charging and discharging cycles of 3 samples of IJP stacked MIM supercapacitor with 200 Hz frequency.

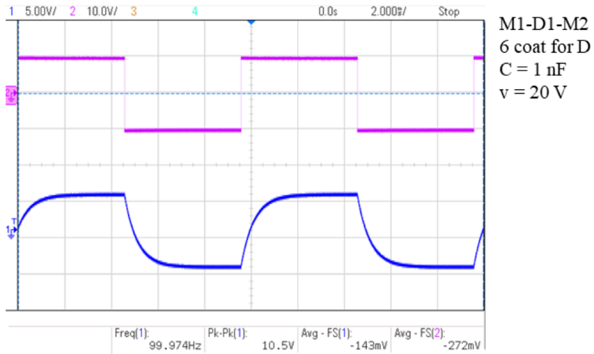

Fig. 6: Charging and discharging cycles with a high voltage of 20 V for an IJP stacked MIM supercapacitor.

We have also tested the IJP stacked MIM supercapacitor for charging at various voltage levels. Fig. 6 shows charging and discharging with 20 V across the capacitor. The capacitor did not get damaged and continued to operate rending this voltage to be safe. For 2 nF supercapacitor, the stored charge is 40 nC. As the volume of this capacitor is $23\text{x}10^{-10}$ m^3 (ignoring the substrate), thus the charge density for this capacitor is 17.4 C/m^3. If we consider the substrate, charge density becomes 8.3 C/m^3. By stacking more layers, such as n of 100, the change density can be very high towards a thousand C/m^3.

C. Scanning electron microscopy characterization

We have observed the cross section of an IJP stacked MIM supercapacitor under scanning electron microscopy (SEM). Fig. 7 shows the cross-sectional image that depicts multiple layers of metals and dielectric printed with IJP technique.

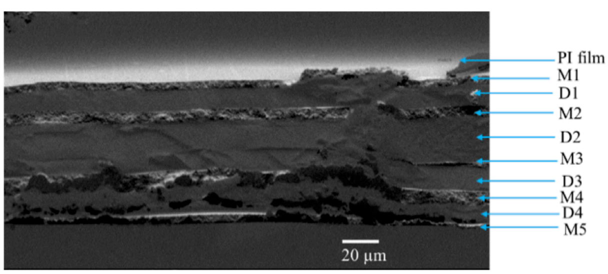

Fig. 7: Cross-sectional view of an IJP stacked MIM supercapacitor using SEM equipment.

V. Conclusions

We have demonstrated fabrication of IJP stacked MIM capacitor toward supercapacitor development. Ag nanoparticle ink was used for metal layers and PVP was used for dielectric layer. These solid-state supercapacitors are flexible and can store charge. The samples were tested for up to 20 V without any damage or degradation. Higher levels of voltage testing will be conducted in future work. The fabricated supercapacitors had a footprint of 1 cm^2 and stacked 3 metal layers for two capacitors in parallel. Each Ag layer was 7 µm thin and dielectric layer was 1 µm thin. The total thickness of the IJP capacitor was 23 µm and the substrate PI film was 25 µm thin, resulting to a total thickness of 48 µm which was flexible. The samples did not peel off or crack with a bending fixture of 10 mm radius for over a thousand repeat cycles. The sheet resistances of the metal layers were about 35 mΩ/sq. The capacitance per cm^2 was 1 nF for 2 metal layers and 2 nF for 3 metal layers. The capacitance per unit volume for three metal layer supercapacitors was 412.5 pF/mm^3. These IJP stacked MIM supercapacitors shows promising results that stacking multiple dielectric-metal layers can increase the capacitance linearly. There can be many applications for this type of high energy, low volume, lightweight, flexible supercapacitors such as EV, drones, wearables, robotics, and other energy storage solutions.

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