Supercapacitors: Enabling the Next Generation of Energy Storage Devices

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Abstract – We present a brief overview of the supercapacitor technology with its unique advantages over other energy storage technologies. Supercapacitors combine the high energy storage capability of batteries with the high power delivery capability of capacitors. Supercapacitors have the potential to revolutionize SensArray's SensorWafers, which are used to monitor the effects of process environment on production wafers, and dramatically increase their reliability, robustness, and usability. Furthermore, supercapacitors can be screen printed and integrated on the SensorWafer as an electrical component. We have presented our experimental results and supercapacitor material selection criterion that is based on the optimization of both energy density and power density, with desirable form factor and reliability. We successfully fabricated a supercapacitor in 7-finger interdigitated configuration with a capacitance of 14μF at 4V. Using our experimental learning, we discuss the next steps that will bring us closer to our vision of integrating supercapacitors on SensorWafers.

I. Introduction

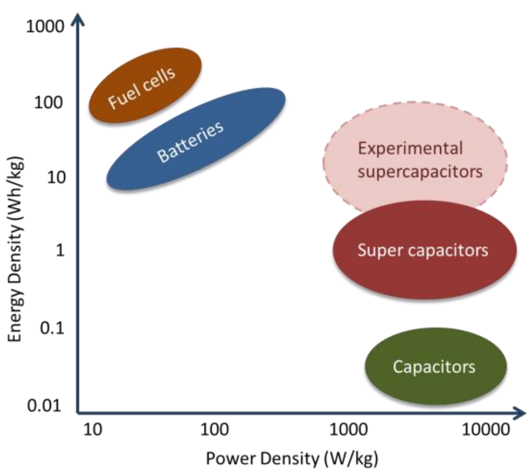

Fig. 1 Comparison of different energy storage devices (Adapted from [1])

The dramatic proliferation of portable electronic devices has increased the demand for energy storage device that is adequately compact and can potentially be integrated on a flexible chip with other electronic components. Conventional charge storage devices, such as batteries, have drawbacks such as short cycle life and relatively slow charging/discharging rates. Supercapacitors have attracted significant attention because of their higher power density, longer cycle life, and higher charge/discharge rates as compared to batteries [1].

A. SensorWafer introduction

KLA-Tencor's SensArray SensorWafers provide a unique way to monitor the effect of the process environment on production wafers. Spatial and temporal measurements of temperature and RF voltage are used by both chipmakers and wafer process equipment manufacturers to visualize, diagnose, and control their processes and process tools such as plasma etch chambers. Plasma etch chambers have harsh environments consisting of high power RF fields (2-15kW), high magnetic fields, high temperatures (>100C) and reactive chemistries [2].

SensorWafers' batteries are among the components most sensitive to harsh processing environments. Supercapacitors, as an alternative to batteries, provide a unique advantage to enhance the capability of SensArray's products in terms of reliability, form factor and robustness, and to open the doors to new high power and high temperature wafer processing markets.

B. Supercapacitor types

The three main categories of supercapacitors are shown in **Fig. 2**; In this paper, we will explore the world of Electric double layer capacitor (EDLC).

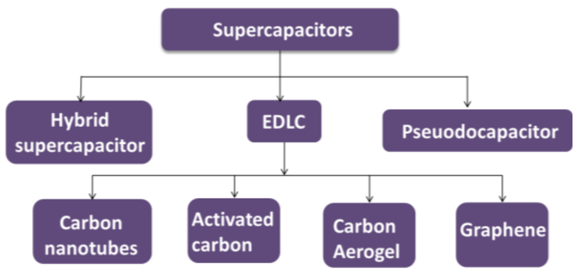

Fig. 2 Types of Supercapacitors

C. EDLC construction and working

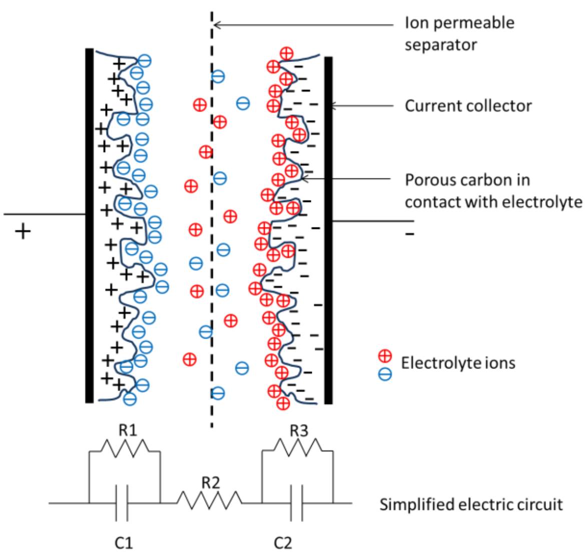

Fig. 3 EDLC Arrangement (Adapted from [4])

EDLCs are constructed from high specific surface area carbon electrodes that are cast onto a metallic current collector. These two electrodes are impregnated with an electrolyte and separated by an ion permeable membrane that prevents the two electrodes from short circuiting. **Fig. 3** shows the typical arrangement of an EDLC [4].

When an external electric field is applied to the device, a double layer of charge is formed at each electrode. The use of high specific surface area (SSA) porous electrode and nanometer-scale charge separation leads to devices with significantly higher effective capacitance than typical dielectric capacitors [4].

II. Supercapacitor material selection

Our selection criterion is to optimize EDLCs for following critical parameters: energy density and power density, with good form factor and reliability.

When a supercapacitor is charged, a voltage (V) builds up across the two electrodes. Maximum energy (E_{max}) is determined by **Eq. 1** and Maximum Power (P_{max}) is determined by **Eq. 2** ([5])

$$E_{max} = (1/2)CV^2=QV/2 \qquad \textbf{(Eq. 1)}$$

$$P_{max} = V^2/4R \qquad \textbf{(Eq. 2)}$$

where C is capacitance, V is cell voltage, Q is the total charge stored and R is total equivalent series resistance (ESR) of the capacitor.

The square dependence of energy on voltage indicates that substantial improvement to device can be made if the EDLC is operated at higher voltage.

A. Electrode selection

Conductive carbonaceous materials are good conductors, have high surface areas, and are chemically stable, making them the preferred materials for EDLCs. The most basic high surface area carbon material is activated carbon (AC). Graphene is a new advanced carbonaceous material that has unique morphology and that is able to reach the high theoretical surface area of 2630 m^2/g of its parent graphite, with low internal resistance [6].

In this paper, we will focus on graphene and activated carbon (AC). Their high surface area and high density lead to high specific capacitance. Comparison of different carbon materials is shown in **Table 1**. **Fig. 5** shows the high surface area nature of AC in a scanning electron microscopy (SEM) image.

Materials	Specific surface area(m^2/g)	Density (g/cm^3)	Specific capacitance* (F/g)
Activated carbon	1000-3500	0.4-0.7	150-200
Graphene	2675	1-2	100-205
Carbon nanotubes	120-500	0.6	50-100
Carbon aerogels	400-1000	0.5-0.7	100-125

*values for aqueous electrolyte

Table 1. Comparison of different carbon materials (adapted from [5])

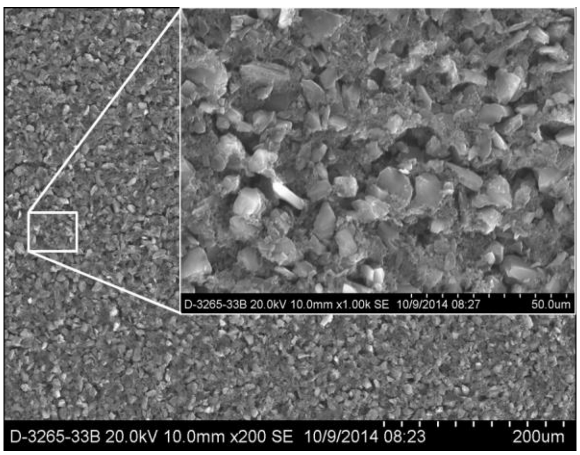

Fig. 5 Activated carbon SEM picture

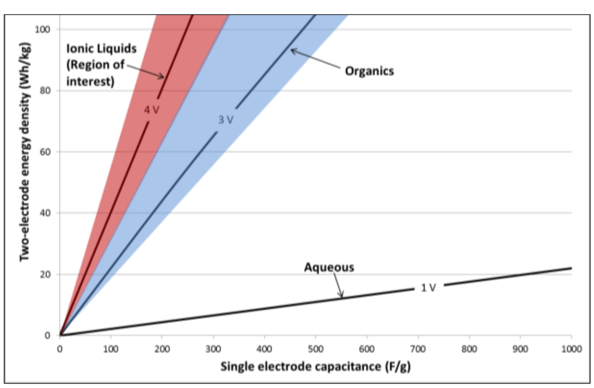

Fig. 6 Comparison of different electrolytes (Adapted from [4])

B. *Electrolyte selection*

Different electrolyte types, primarily aqueous, organic, and ionic electrolytes, can alter operating voltage. **Fig. 6** shows the relationship between capacitance, operating voltage and device energy density for these electrolytes.

Our main strategy is to improve the capacitance of EDLCs in a way that is compatible with electrolytes capable of stable high voltage operation. For serving this purpose, we selected ionic electrolytes. Some of the advantages of ionic electrolytes include wide working temperature range (-90 to 400C, thermal stabilities approaching 300C with no measurable vapor pressure) and higher voltage stability [7]. **Table 2** shows the properties of different ionic electrolytes selected for our experiments.

Electrolyte	Stability temp (C)	Charge Voltage(Volt)
1-Butyl-1methylpyrrolidinium bis (trifluoromethylsulfonyl)imide	>220	5.3
1-Propyl-1-methylpiperidinium bis(trifluoromethulsulfonyl)imide	>220	5.9
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	>200	4.6

Table 2. Ionic electrolytes properties (Courtesy: Iolitec, Ionic liquid technologies)

III. Experimental results

A. *Sandwiched coupon based method*

Early work of constructing supercapacitor cells focused on the use of mono-layer graphene on copper foil or 25 μm thick graphene sheet as electrodes. Ionic liquid (BMImCl or 1-butyl-3-methylimidazolium chloride) mixed with polyvinyl alcohol polymer formed a solid electrolyte. The electrodes and electrolyte were placed in a parallel plate configuration. Results and details of constructed cells are shown in summary **Table 3**.

Cell#	Electrode	Capacitance(uF)
1	25µm graphene sheet	15
2	Monolayer graphene	90
3	25µm graphene sheet	17
4	25µm graphene sheet with Al foil current collector	11

Table 3. Results for sandwiched coupon cells

Learnings

Monolayer graphene was found to have the highest capacitance. We theorized the reason was monolayer graphene having higher effective exposed surface area than 25µm graphene sheet.

We learned that the leakage current for this type of construction was generally high because the two sandwiched electrodes were not isolated properly from each other, and the supercapacitor would self-discharge relatively fast.

B. Supercapacitor on silicon wafer

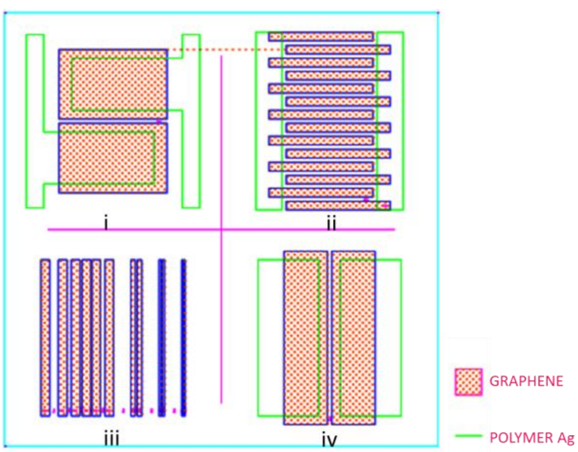

Fig. 7 Fabricated pattern on Silicon (i) Interdigitated 1 finger (ii) Interdigitated 7 fingers (iii) Printing resolution check (iv) Block pattern

The first effort to produce a supercapacitor on silicon wafer was the printing of Vorbeck graphene conductive inks onto oxidized silicon coupons. These inks contain disassociated graphene layers with high specific surface area. The printing properties of these inks, such as adhesion, resolution and thickness per print layer were studied. The pattern as shown in **Fig 7** was fabricated on silicon substrates.

1. Experimental setup

Silicon wafers with 2.5 µm of thermal oxide were cut into 2"x2" substrates for supercapacitor fabrication. Screen print masks of the pattern in **Fig. 7** were made with 325 stainless steel mesh and 0.5 mil emulsion. Out of the 3 inks selected only one ink (S701) passed the screen printing process in terms of resolution, adhesion and cohesion. The S701 sample had graphene thickness of 5µm and silver thickness of 13-17µm. It printed with lower than expected resolution as shown in **Fig. 8**. Masterbond EP21 epoxy was used to form a dam around the electrodes to contain the ionic liquid electrolyte.

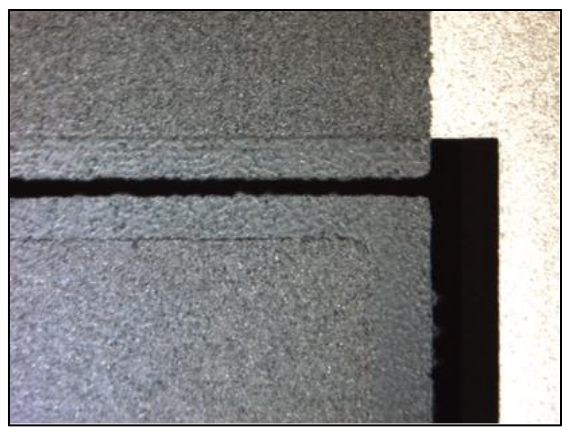

Fig. 8 Low printing resolution for Sample S701

Learnings

The interdigitated configuration is more robust against shorting/leakage in comparison to sandwiched coupon configuration as the fingers are physically isolated from each other. Interdigitated configuration also helps to maximize the exposed surface area to form a supercapacitor. We found that going from a one-finger interdigitated configuration to a 7-finger configuration increased the capacitance from 10nF to 14µF. This is most likely because having more fingers increases the effective exposed surface area that can be used to store more charge. We have created a supercapacitor as the capacitance measured for S701 sample with 7 interdigitated fingers is 14μF at 4V charging voltage. This is unusually high capacitance compared to a same sized (form factor) conventional capacitor.

IV. Current status and next steps

After encouraging results from using commercially available inks, custom formulation was then considered to improve printability on silicon. Electro Science Laboratory (ESL), a thick film paste provider, has been engaged to create custom formulations of screen printable ink with activated carbon(AC). Cost and availability are the primary reasons to use AC over graphene.

The initial round of printing test has showed improved resolution, adhesion, and cohesion. **Fig. 9** shows the improved printing resolution for AC on silicon wafers. Sample printing in the form of interdigitated electrodes have been made, and electrical testing will take place in near future.

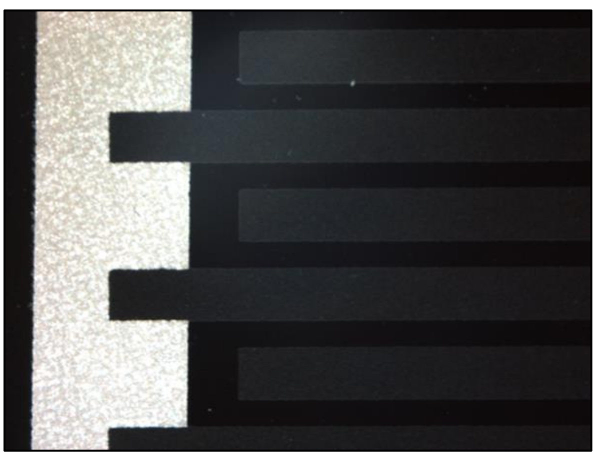

Fig. 9 Improved screen printing resolution using custom formulation of activated carbon

Other future works include forming solid state electrolyte by integrating ionic liquid into polymer and filler matrix to enhance temperature durability and to make electrolyte containment easier. Printing functional supercapacitors onto full size wafer will be another milestone before reaching the eventual goal of powering a SensorWafer.

V. Conclusion

We have chosen to investigate supercapacitor as the energy storage device for SensorWafers because of its higher power density, longer cycle life, higher reliability and higher temperature stability as compared to lithium-ion batteries. After initial studies of sandwiched coupon test vehicles, we have successfully built supercapacitors in a 7-finger interdigitated configuration using screen printing. We achieved a capacitance of 14μF at 4V, which is an unusually high value when compared to a conventional capacitor of the same size. We are working with ESL to formulate a custom carbon ink, and we plan to produce more sample supercapacitors for further investigation.

VI. Bibliography

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