Printed Components (from Nanoparticles) and Large Area Capacitors

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ADEPT Metacapacitors

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ADEPT Program (Agile Delivery of Efficient Power Technology)

and City University of New York Energy Institute (CUNY Energy Institute), New York State Energy Research and Development Authority (NYSERDA), Con Edison (Con Ed)
Team Overview: CUNY Energy Institute

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Alex Couzis, Prof., Chem E

Limin Huang, Sr Research Scientist, Materials
Team Overview: Columbia and UC Berkeley

Peter Kinget is an associate professor of Electrical Engineering at Columbia University, with integrated circuit and system integration expertise and keen understanding of analog and RF integrated circuits and signal processing.

Ioannis Kymissis is an assistant professor of Electrical Engineering at Columbia University, Columbia Laboratory for Unconventional Electronics, and a member of the DOE EFRC at Columbia University.

Seth Sanders is a professor of Electrical Engineering and the University of California, Berkeley. His research interests are in high frequency power conversion circuits and components, in design and control of electric machine systems, and in nonlinear circuit and system theory as related to the power electronics field. - novel designs of switch capacitors topologies.
Nanoparticles (O’Brien)
Chemical Approaches to Nanomaterials

Making Materials Chemistry a Technology
Atomic or molecular units, with well known subatomic structure in isolation, offer the ultimate building blocks for a bottom-up manufacturing synthesis with applications in many industries.
- Can chemistry provide us with a means to produce technologically useful monolayers, thin films and ultimately more complex devices?
Synthesis of nanocrystals – preparation of nanoscale building blocks

Start with a molecular precursor (e.g., CVD or MBE precursors work well)

Solvent, surfactant (ligand), e.g. \( \text{CH}_3(\text{CH}_2)_7\text{CH=CH(} \text{CH}_2)_7\text{COOH} \)

Obrien Nanoparticle Film Strategy: Increasing Complexity: towards enhancing properties –
collective properties

$M^I_x X_y$, $Doping$, integrated synthesis, add $M^{II}$

$X = O, e.g. M^{II}(CH_3CO)_2$

$X = O, S, Se$

e.g. Semiconductor-Metal, Metal Oxide-Metal or Semiconductor-Semiconductor

Nanoparticle Film
Formation of Binary Nanoparticle Superlattices (BNSLs)  

Evaporation Driven Assembly.

Prepare by co-evaporation

1. solvent: thiol + toluene
2. solvent: thiol
3. solvent: thiol
4. dried

Temperature, T
Volume fraction, φ

F
F + C
C

Structural Characterization
Structural diversity in binary nanoparticle superlattices

Made from Pairs of Nanoparticles of Ag, Pd, Au, PbSe, Fe₂O₃.

e.g. (a) 13.4 nm Fe₂O₃ and 5nm Au

Scaling Barium Titanate (BaTiO$_3$) and the Ferroelectric Phase Transition


Remnant polarization = $P_r$(OD)

Electric field, $E$ (kV/mm)

OA = normal dielectric

Polarization, $P$ (mC/cm$^2$)

FRAM: Non-Volatile Memory

“Superparaelectric” Capacitors?

Complex Oxide Nanocrystal Synthesis with Applications in Flexible/Printable Thin Film Technologies

- BaTi alkoxide
  - Ba(3aO) + Ti(IPr)
  - Ba/Ti citrathesano-isoproxide
  - Ba(Pr) + Ti(Pr)

- Alcohol
  - Ethanol, ethanol with controlled amount of water (5-20 wt%)
  - Isopropanol
  - Ethanol + Isopropanol

Solvolothermal: 200-220°C, 14 days

Individual BaTiO₃ nanocrystals → stable suspension
Hydrophilic surface: ethanol, DMF as solvents
Hydrophobic surface (oleic acid coating): hexane, toluene as solvents
Adding polymer (optional) → low T processing (spin-coating)

Thin film of BaTiO₃ nanocrystals or polymer/BaTiO₃ nanocomposites

Solvothermal process: BaTi alkoxide + alcohol/water
Ethanol suspension of BaTiO₃ nanocrystals
Toluene suspension of polymer/nanocrystal nanocomposites

Capacitor structure
Pentacene transistors

Low temperature processing: Individual, well crystallized Nanocrystals as building blocks
Free Standing Films
a) SEM images of a BaTiO$_3$ nanocrystal thin film (8nm), top view. (inset) a photo image of a homogeneous ethanol suspension of BaTiO$_3$ nanocrystals (~20 mg/ml); (b) cross-sectional view of the film; (c) SEM image of poly(alpha-methylstyrene)/BaTiO$_3$ nanocomposite thin film, top view. (inset) a photo image of a transparent poly(a-methyl styrene)/BaTiO$_3$ nanocomposite solution (~ 20 mg/ml, 8 nm, weight ratio of polymer/BaTiO$_3$ = 1), and a TEM image of the uniform polymer/BaTiO$_3$ nanocomposite; (d) SEM image of poly(alpha-methylstyrene)/BaTiO$_3$ nanocomposite thin film, top view. (inset) a cross-section view of the uniform polymer/BaTiO$_3$ nanocomposite thin film and a photo image of a semitransparent BaTiO$_3$ nanocrystal solution (~ 20 mg/ml, 25 nm).
**BT and BST Thin Film Capacitors**

<table>
<thead>
<tr>
<th>Thin film sample</th>
<th>Crystal size (nm)</th>
<th>Dielectric constant (measured at 100kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>8-12</td>
<td>22-25</td>
</tr>
<tr>
<td>BaTiO$_3$/parylene</td>
<td>25-30</td>
<td>34</td>
</tr>
<tr>
<td>Ba$<em>{0.7}$Sr$</em>{0.3}$TiO$_3$</td>
<td>8-12</td>
<td>10</td>
</tr>
<tr>
<td>Ba$<em>{0.7}$Sr$</em>{0.3}$TiO$_3$/parylene</td>
<td>25-30</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>8-12</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>25-30</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>8-12</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>25-30</td>
<td>16</td>
</tr>
</tbody>
</table>

Ferroelectric measurements of assembled nanocrystal thin films of BT and BST in Sawyer Tower configuration under conditions of (a) demoisturized films with an evaporated film of parylene, dried at 60 °C (b) RT and immersed in liquid N$_2$ for the BT/parylene thin film.

Concept: Metacapacitors™

Goals:
- In-structure integrated circuits can make programmable switched capacitor arrays
- Processing can be scaled using roll-to-roll coating techniques
- Long lifetime, high power, high energy density, flexible energy storage, conversion, and conditioning
Magnetic-based power converters are currently the common solution for higher power applications (1W and above). The use of switched-capacitor (SC) DC/DC conversion circuits (a.k.a. charge pumps) has been limited to very low power levels. For practical switching frequencies, the power levels of SC designs can only be increased by using larger capacitors. SC designs have a number of important advantages as long as cheap and dense capacitors are available and they can outperform magnetic-based converters for medium to high conversion ratios.

Project to make switched-capacitor DC/DC converter amenable to address a wide range of new applications in power conversion.
The circuit architectures to be exploited in the Metacapacitor program rely on switched capacitor dc-dc and multi-level inverter conversion topologies. Switched capacitor dc-dc converter topologies have been the poor step-sister technology to the industry dominating magnetic-based power conversion topologies due to many factors. Some of these pertain to sunken investments and mature design strategies built on standardized designs for key components: switch technologies (eg. Si MOSFET and IGBTs); ferrite, powdered-metal, and laminated metal magnetic cores; and CMOS based analog and digital PWM controllers.

However, the all capacitor approach is especially effective due to the higher energy density of many capacitor technologies in comparison to compact magnetic devices. Given the exceptional energy densities of the capacitors being developed in this Metacapacitor program, the advantage of the all capacitor topologies is further accentuated.

Application example: PV inverter topology - single PV panel (eg. ~30 Vdc @ 200 W) with a local stabilizing Metacapacitor (20-100 mF for 120 Hz ripple filtering) and a power MOSFET H-bridge to form a single submodule.
Printed/Spin Coated Thin Film Capacitors

The key requirement in the formation of the BST nanoparticle based capacitors is the consolidation of the nanoparticles into dense interconnected structures upon deposition onto a flexible conductively coated substrate. Requirements emerge from this approach:

(i) that the particle form dense monolayer clusters;
(ii) that multilayers can be deposited with appropriate registry
(iii) that the coating approach provides appropriate lateral position control
(iv) the process must be scalable, materials agnostic, and economically viable. Gravure and rotogravure printing of nano-colloid inks is a process that satisfies these requirements and provides a direct path to process scalability and lost cost.
(v) Preparation of Multilayer Capacitors is possible
Collaboration and Acknowledgements

**Project Faculty**
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(Columbia)  
Lev Sviridov  
(Energy Institute)
2. LED Driver Topology (ADEPT)
A Metacapacitor solid-state LED driver topology is illustrated in Figure 8. Possible target applications are single-unit screw-in Edison replacement lamp devices rated at about 15 W, as well as higher power commercial lighting fixtures.

A bulk storage capacitor in the range of 25-100 uF, rated for 200 Vdc, is convenient for the dc bus to handle 120 Hz ripple. The controls and switches can be implemented on a single CMOS IC with devices rated for handling voltages indicated, and junction isolation to provide for the overall voltage stand-offs to the substrate.

*The switched capacitor approach enables graceful low power operation by simply reducing clock rate, thus enabling a wide range of dimming without sacrificing efficiency.*
1. PV Inverter (Not Part of ADEPT Scope)
PV inverter topology is conceptually illustrated merges a single PV panel (eg. ~30 Vdc @ 200 W) with a local stabilizing Metacapacitor (20-100 mF for 120 Hz ripple filtering) and a power MOSFET H-bridge to form a single submodule. The diagram of only four submodules which enable nine-level modulation at the inverter output, a representative rooftop installation rated for 3 kW might be comprised of 15 submodules. An array of 15 such submodules would allow a peak output voltage capability of roughly 450 Vdc, making an interface with a 220 Vrms line quite convenient.

This proposed architecture provides all the best features required for a highly reliable distributed PV line interface. These include peak power tracking on a panel by panel basis (i.e. “micro-inverter” functionality), no use of electrolytic capacitors, no substantial use of magnetic devices, highest possible panel efficiency, very low electromagnetic interference (EMI), fault tolerance and high safety potential.
Gate Dielectric: Thin Film TFTs on Flexible Substrates Using Nanocrystal Films of BT/BST (Collaborator Ioannis (John) Kymissis)

Transport characteristics of OFETs on flexible PEN substrate, with 200 nm BST and 53 nm parylene C as the gate dielectric (effective dielectric constant is 11.3). (a) is the drain IV curves under different gate biases. The device has an on/off ratio $10^4$ and mobility 0.25 cm$^2$/Vs in the saturation region fitted using the data from (b). Leakage characteristics: (9–12 nA/cm$^2$, measured at 5Vdc for a 1mm$^2$ area.
High k materials - capacitors
Innovation in Core Technologies for Power Conversion and Energy Storage

Metacapacitors
Currently there exists a fundamental tradeoff between chemical storage and charge separation:

- Chemical bonds store energy, but kinetically limit power.
- Charge separation quickly releases power, but cannot store temporally or spatially chemical bonds.

**PROPOSED GOAL(S):**

Through the combination of a proven, low-T materials synthesis and a novel approach to device fabrication, we will make large capacitors with compelling energy density and power density.

<table>
<thead>
<tr>
<th></th>
<th>Batteries</th>
<th>Ultracapacitors</th>
<th>Metacapacitors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Programmable</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Energy Density Range (Wh/kg)</td>
<td>10-500</td>
<td>1-10</td>
<td>1-100</td>
</tr>
<tr>
<td>Power Density Range (W/kg)</td>
<td>10-500</td>
<td>1000-8000</td>
<td>1000-20000</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>500-3000</td>
<td>&gt;1,000,000</td>
<td>&gt;1,000,000</td>
</tr>
<tr>
<td>Whr/kg over life</td>
<td>50,000 to 900,000</td>
<td>1,000,000 – 10,000,000</td>
<td>1,000,000 – 100,000,000</td>
</tr>
<tr>
<td>Market Saturation?</td>
<td>Mature</td>
<td>Moderate</td>
<td>Nascent</td>
</tr>
</tbody>
</table>

**ASSUMPTIONS AND LIMITATIONS:**

- We assume we can create a system with an effective dielectric constant of 50.
- We assume we can manufacturing such capacitors in a large scale roll-to-roll process.

**NEW INSIGHTS:**

- Barium Titanate Nanoparticles exhibit excellent dielectric properties.
- Through low temperature processing, such particles can be assembled into devices with exceptional energy density and power density.

**END-OF-PHASE GOAL:**

Demonstration of long term charge retention at or above EDLC capacity, with the power density of a capacitor.
Metacapacitors™: Background

- We have a new process for making high $k$ dielectric films at room temperature based on solution control processing.
- We have demonstrated high value/low hysteresis capacitors with high voltage tolerance.
- The substrate and device design allows full integrated device manufacture.
- The principal of $E = CV^2$: The energy stored scales with the square of the voltage. We propose a “metacapacitor” – the energy density of a battery or ultracapacitor but the discharge and lifetime of a ceramic capacitor.

Homogeneous solvent suspensions of BaTiO3 nanocrystals (inks) are deposited as thin films through evaporative driven self assembly. Alternatively facile incorporation into a range of high k/low k polymers can generate a series of nanocomposites.