Nanoparticle Technology for Power Integration With Flexible Substrates

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Abstract. The nanoparticle technologies consisting of multiple layers of mixtures of activated carbon and ruthenium (IV) oxide for super capacitors are reported. The mono-particulate layer process described here is a modified Langmuir-Blodgett trough. We report the processes for a spray-coated zinc nanopowder electrode used as a counter-electrode forming a galvanic cell of extremely high charge storage capacity (>40A-hr/cm^2). Hydrated ruthenium oxide as a nanopowder (10-100nm) with a surface area that approaches tens of square meters per gram is layered with nano-powder activated carbon. Thin separating insulating layers are interposed between the $RuO_2 \cdot xH_2O$ and the counter-electrode. As the counter-electrode, thin films of zinc and aluminum, and powders of zinc for surface area enhancement have been applied. These cells are processed on flexible substrates in order to form a totally self -powered multi-pixel flexible display. Current-Voltage characteristics of thin film transistors biased by the nanoparticle flexible batteries show fast power-on characteristics.

Introduction

The emerging field of flexible electronics is growing on many fronts and holds great promise for applications within electronic systems. Various display needs require harsh environment, reliability, light weight as well are ideal for integration with a flexible power source or battery. Flexible displays are made possible by electro-optic devices integrated with an active matrix backplane which must have its own power system. Powered thin film transistors in each display pixel must switch and power an electro-optic device. Other applications include integrated analog organic electronics, reconfigurable flexible antennas, as well as flexible pollutant detection for environmental applications. Micro autonomous sensor systems must also have the power system integrated with lightweight flexible electronics.

The present paper reports the performance of an integrated power distribution system for flexible electronics in general and specifically for flexible displays. Our results are based on two substrates:

[1] Polyethylene naphthalate PEN from Dupont Teijin Films
[2] Stainless steel (Type 304 hard tension annealed)

Both substrates have a coefficient of linear expansion of approximately 18ppm/C – but each presents different mechanical stress issues in manufacturing. Stainless steel has layer adhesion and leakage problems while PEN appears to be stretching under stress from the thin films being deposited.

Amorphous Si:H thin film transistors have been integrated via the source electrode with a thin film $RuO_x/Zn/Pb$ power cell. The present approach is to create a hydrated ruthenium oxide/ metal galvanic redox cell. In such a system, the electrolyte is charged by redox processes occurring at the RuO_2/xH_2O electrode.

The fabrication procedures for such flexible electronics is reported as well as an analysis of the amorphous silicon thin film transistors. The electrical assessment of the integrated transistor-flexible battery is reported in the final section of the present paper. Finally, the mechanical stress limitations of power sources and thin film electronics on flexible substrates is reported, since solution of such mechanical limitations is critical for future advances of a totally integrated, self powered technology.

Experimental Aproach

Fabrication Procedure. The present approach consists of fabricating the thin film transistors directly onto the kapton or thin stainless steel flexible substrate and then connecting the power input interconnects to the flexible substrate using reflow soldering in order to provide bias to the source and drain of the MOSFETs. The fabrication of the integrated structure consisted of a flexible wafer with a pixel array and an area for test circuitry.

Figure 1 is a diagram of an individual pixel. The display allows each pixel to be addressed in the matrix by row and column drivers. The schematic diagram of an individual pixel circuit shows that is composed of a thin film transistor, a capacitor connected between the transistor's drain contact and ground, and the connection of the bottom electrode of pixel connected to the drain contact as well. Electro-optic material is then deposited on the bottom electrode, either electrophoretic or organic, and then a top transparent electrode is then deposited to complete the pixel[1-3].

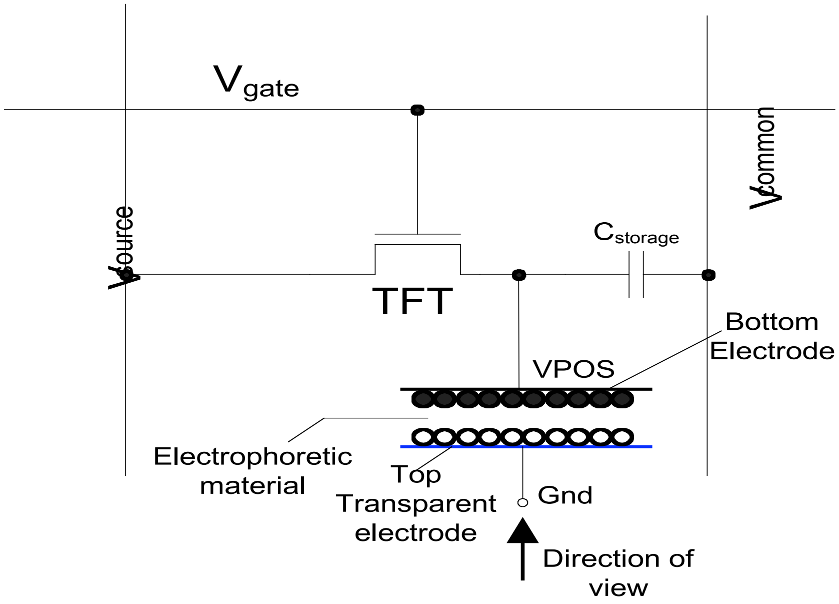


Fig.1. A schematic of an individual pixel circuit, showing the thin film transistor and the capacitor, as well as the required connections.

Signature of amorphous Silicon. Fourier Transform Infrared (FTIR) Spectroscopy was used for determining the impurity concentration of the amorphous silicon being used. This will provide a signature of the material and give insight into the bending modes and bond vibrational modes. Figure 2 shows the spectra of a sample using polarized attenuated total reflection (ATR) measurements together with (FTIR) to investigate the vibrational spectra of $a\text{-}SiH_x/Si$ films 0.5-1.0 microns in thickness, showing characteristic bending modes at 2000 cm^{-1} as well as the vibrational spectra in the range of 600 cm^{-1}. This signature shows the lack of hydride formation indicating typical FTIR characteristics for transistor active layers. Such signature analysis was used prior to fabrication in order to optimize transistor performance.

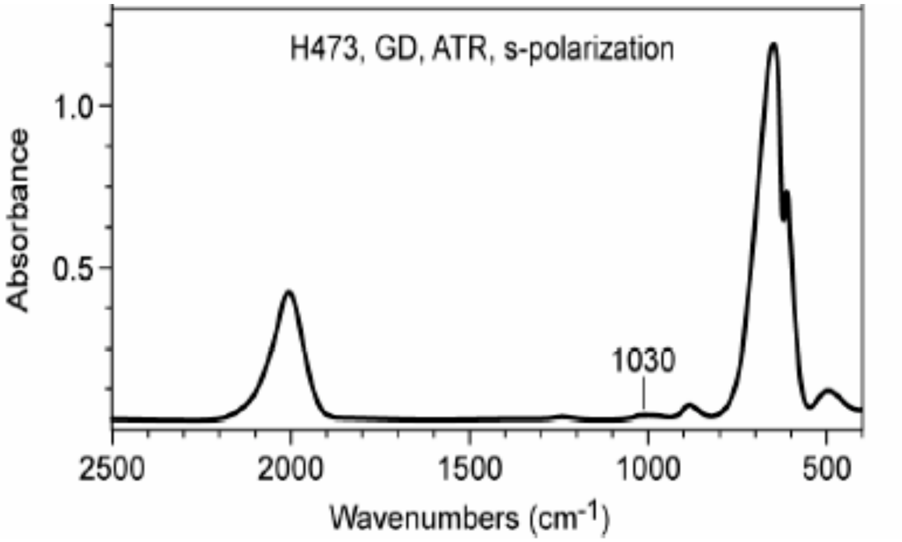


Fig. 2. Polarized FTIR-ATR spectra of a-SiH_x/Si sample (Webb, 1999), [15].

Nano-Particle Based Battery. Electrochemical cells that can conform to a variety of electronic system packages, surface geometries as well as cells that can be embedded in flexible electronic systems are of tremendous technological importance[4]. Previous work has demonstrated that it is possible to make flexible cells with near-theoretical volumetric storage capacities. We present a flexible galvanic cell that can be optimized for volume manufacture and capable of integration with flexible electronic components. In addition, we describe a flexible cell whose attributes favor radio-frequency charging, as they are able to utilize low recharging voltages. Using the approach described in this paper, one can create "hybrids" of redox-cells and super-capacitors. These cells are based on chemicals with low toxicity and are thus environmentally benign. We show that the cells can achieve a specific capacity of over 2mA h/cm^2.

The approach of the present work is to create a hydrated ruthenium oxide ($RuO_2 \cdot xH_2O$) /metal galvanic redox cell (a battery). Previous investigations have reported that $RuO_2{\cdot}xH_2O$ has been used as a super-capacitor material due to its ability to generate high pseudo-capacitance. Tthe electrolyte is charged by redox processes occurring at the $RuO_2{\cdot}xH_2O$ electrode. A dipole layer is formed by charge injection across the $RuO_2 \cdot xH_2O$/electrode interface and the amount of charge transported is proportional to the change in electrode bias. The constant of proportionality is the pseudo-capacitance. This process, has been previously reported[5-8].

Nanoparticles provide a large surface-to-volume ratios and nano-particulate films can be made with exceptionally high surface area and the requisite porosity needed to form the electrolyte/electrode interface. The necessary nanoparticle coating technologies that can create "stackable" layers of nanostructures a single layer thick (100 nm) must be adopted to the present structure. Nano-particulate "hetero-structures" can thus be formed with well-controlled material proportions, just based on mean particulate diameter and size distributions. Hydrated ruthenium oxide as a nano-powder (10-100nm) was measured to have a surface area range of 10-20 square meters per gram. The Ruthenium oxide combined with activated carbon (AC), resulted in a decrease in surface resistance which was achieved at ten weight percent Ruthenium. The resulting compound was patterned using standard silk-screening techniques, which is not part of the present investigation. Thin separating insulating layers (0.5 micron thickness) was interposed between the $RuO_2 \cdot xH_2O$ and the counter-electrode. As the counter-electrode, we report the use of thin films of zinc and aluminum, and powders of zinc for surface area enhancement.

This process is distinct from that of the electrochemical double-layer cell. In the present investigation the electrode bias charge forms an image in the electrolyte and no mobile charge crosses the boundary. The performance of the super-capacitor is an indirect demonstration that the reduction of the $RuO_2 \cdot xH_2O$ material was achieved. As such, a redox couple was formed with a metal which can be oxidized (such as the zinc or aluminum anode) and a battery structure was achieved.

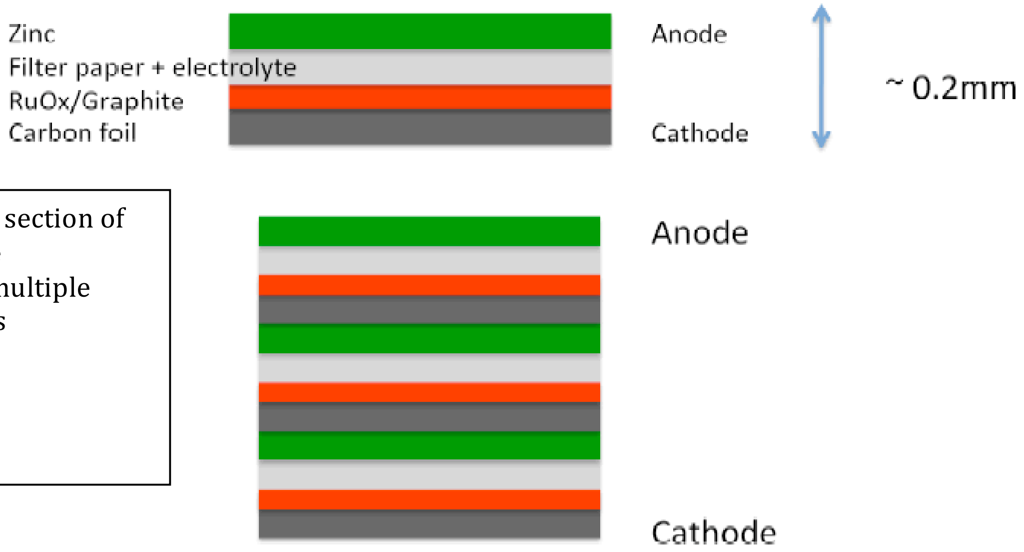
As such, this investigation is the first reported on the use of this material system as a redox cell. The relatively high internal resistance limits its application in large cell capacity systems, but is ideal for macroelectronic applications. For low power electronics, however, small amounts of current must be supplied over long periods of time. This offsets the internal dissipation of the cell. In addition, as we shall show, $RuO_2 \cdot xH_2O$ redox systems initially exhibit low internal resistance, enabling large amounts of "burst" power. In any event, it is clear that hybrid combinations of $RuO_2 \cdot xH_2O$//metal and $RuO_2 \cdot xH_2O$//$RuO_2 \cdot xH_2O$ electrode combinations can be made in which the first combination serves as a battery and the second as a super-capacitor, as described above.

There are a number of other potential advantages of the $RuO_2 \cdot xH_2O$ cell. Hydrated ruthenium oxide exists in a multiplicity of oxidation states and as the $RuO_2 \cdot xH_2O$/metal cell discharges, all of these oxidation states may be activated, leading to a "graceful" rather than a discontinuous drop in source potential. In the past, such a graceful discharge was viewed as undesirable for a battery. With the advent of ultralow-power, low-volume integrated circuit voltage regulators, this is no longer the case. All of these approaches yield viable electrochemical cells.

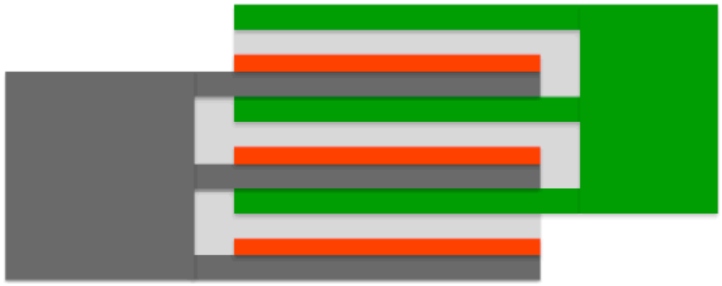
The implemented cells consist of an electrolyte composed of a weak acid and ethylene glycol that is close to neutral pH to prevent rapid dissolution of the electrode materials or package sealing materials while favoring the needed redox reactions. In fact, the actual working pH is 5, which enables the reaction chemistry to proceed as close to equilibrium as possible to allow electrically driven reversibility (re-charging). The system of materials and the packaging approach used are targeted to yield a cell with small weight, small volume and high mechanical flexibility. Integration with thin film transistors on a flexible polymer substrate has been achieved by attaching the battery via Van der Waals forces onto the common substrate.

Displayed in Figure 3 is the physical cross-section of the fabricated flexible battery which was used to power the amorphous silicon thin film transistors on a flexible substrate. In the schematic, the zinc layer is the anode, while the carbon based foil is the cathode. These alternating layers may be stacked forming a multilayer integrated cell. Interconnects may be interdigitated resulting in a single contact point for either the anode or the cathode.

Again it must be emphasized that both galvanic cells and super-capacitors can be fabricated in the same process flow. A hetero-structure of two compounded ruthenium oxide electrodes (or a non-oxidizing electrode) forms a capacitor. Compounded ruthenium oxide electrodes on the surface of an oxidizing metal anode will form a battery. In all cases, the hybrid structure can be made thin and flexible. We now review the electrical behavior of the cells, as well as their cabability for providing bias voltage to thin film transistors on flexible substrates.



(a) Cross section of single
And multiple stacks



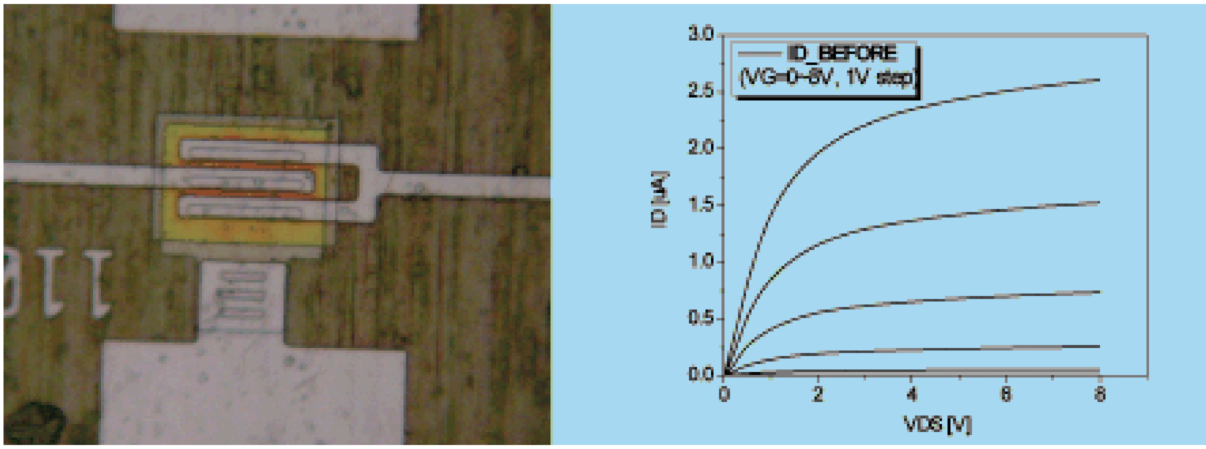
(b) Top surface structure showing the position of the anode and cathode

Fig. 3. (a) Cross-section of the constructed flexible battery. (b) The top view of the same structure is shown.

Experimental Results

The $RuO_2 \cdot xH_2O$ cells are capable of performing routine electronic system power sourcing operations, such as the flexible cell lighting based on LEDs, as well as providing bias voltage to drive transistors for flexible displays. The capability for challenging source requirements such as power for integrated circuits is also achievable. Perfect IV characteristics for enhancement mode transistors have been obtained, as well as for transistors configured as an inverter chain. The surface geometry (15 micron gate widths) and typical current-voltage (IV) characteristics of these transistors are shown in Figure 4. These transistors were within a test wafer on a flexible pen substrate which was processed as part of our flexible display development project. These characteristics are indicative of excellent transistor action, showing a low series resistance and well behaved drain current versus drain voltage saturation.

Electrical Assessment of Power Cell Performance. Perhaps the most interesting aspect of the $RuO_2 \cdot xH_2O$ cells is their short-term discharge capacity. The source current remains high (10-15 mA for the 16 cm^2 cell) for over ten minutes of operation. On average, this leads to a specific capacity of 0.2 mA-h/cm^2 over the ten minute period. The long term discharge behavior of the battery through a large load (as would be typical of operation in an ultra-low power system) was examined. Note that the current remains higher than 0.4 μA for over 110 days. The integration to 110 days yields a 2.32 mA-h/cm^2 specific storage capacity. When extrapolated to 150 days, this results in a specific storage capacity of 2.43 mW-h/cm^2.



(a) **(b)**

Fig. 4. (a) A top view of a flexible electronics thin film drive transistor. The substrate is stainless steel and the active material is amorphous silicon. (b) IV-characteristics of the nMOS transistor.

The discharge plots of a $RuO_2 \cdot xH_2O/Zn$ cell for various loads are shown in Figure 5, showing traces taken over a 4 h time interval. These results were obtained on single sheets of a flexible power cell with a 16 cm^2 active area.

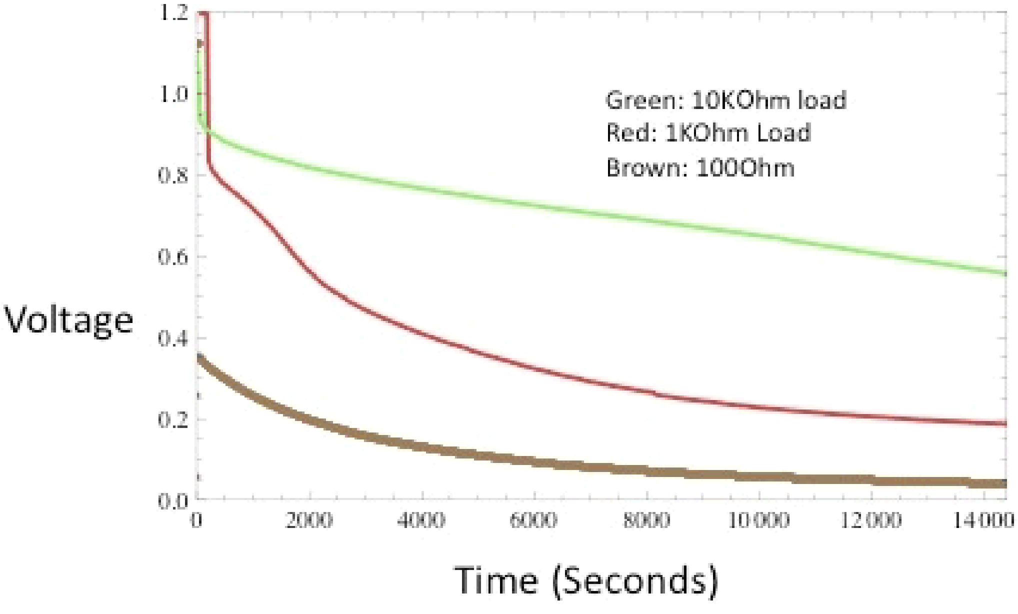


Fig. 5. Voltage versus time discharge plots for different loads.

The energy delivered for the zinc cell in a 24 h period corresponded to a power source of 0.7 mW/cm^2. For a 10 K load, the voltage reduced linearly over time from 0.9 V to 0.6 V. The 10 K load is about the load a source would see looking into the supply interconnects of a typical low-power integrated circuit. Similar discharge plots were obtained for the $RuO_2 \cdot xH_2O/Al$ cell. In this case, the energy delivered in 24 h corresponded to a power density 0.3 mW/cm^2 (Figure 6). The $RuO_2 \cdot xH_2O$ system is suitable for extremely low charging voltages. When an aluminum counter-electrode is substituted for zinc, the requisite charge voltage reduces to 0.8 volts, as shown in Figure 6, where a discharge plot following a 2 hour charge at a constant 0.8 V for the $RuO_2 \cdot xH_2O/Al$ system is shown. The discharge voltage saturates to 0.2 volts after 80,000 seconds.

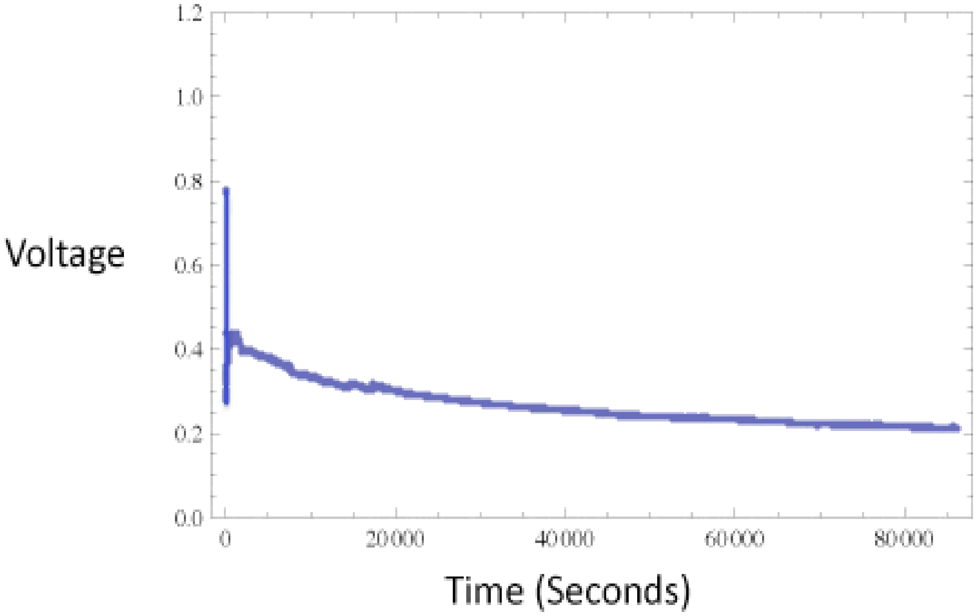


Fig.6. A 24-hour discharge plot for a $RuO_2 \cdot xH_2O/Al$ cell,(.5mW-h/cm2). Note that this 0.3 V voltage is fairly constant over the 24 h discharge.

Therefore, the results indicate that the $RuO_2 \cdot xH_2O$-based redox cell can be configured as an electrochemical battery/super-capacitor hybrid resulting in excellent performance. A composite structure made of cells of this battery type was able to supply over 30 mA for over 4.5 minutes into the bias supply interconnects of the input node in any type of distributed network, fully powering the node for that period of time. Furthermore, when the battery was taken off-line (terminals disconnected) for half an hour, the cell can fully power the node for an additional 4 minutes when re-connected.

In addition, the cells are environmentally benign and are easy to manufacture. No expensive processing or material handling equipment is required. While the ruthenium oxide is relatively expensive, it is but a percentage of the cathode, the rest being made up of activated carbon. We estimate the cost of fabrication of the cell to be less than $2 per square centimeter. Other advantages of this cell can be outlined as follows:

- Having an electrode of large surface area allows for the the passage of a relatively large current.
- The multiplicity of valence states allows for a “graceful” reduction in cell potential.
- This same multiplicity is likely to make the chemistry reversible.

So far, we have discussed electrical performance. However, we have determined that the main limitations to power integrated flexible electronics are strain effects induced by bending the substrate as well as strain from thermal expansion mismatch of materials. In the following section we present the discussion of these mechanical effects on flexible electronics performance.

Discussion of Nano Mechanical Effects

Amorphous Si TFTs and Thin Film Battery. Since Organic TFTs do not currently match the performance of inorganic devices, amorphous silicon or nanocrystalline silicon has been used in the near term to fabricate the TFTs. It has been shown that the failure limit for a:Si TFTs is ~0.5% in tension and up to 2% in compression, which is comparable to other inorganic materials [9].

Patterning the blanket a-Si layer into islands on the polymer substrate reduces the local strain on the islands, which is compensated in the polymer substrate between them [10]. A major challenge is the electrical interconnect to each TFT, but this may be a future approach for extending the mechanical limits in flexible electronics.

The mobility of TFTs is also affected by strain. It has been shown that for predictable, uniaxial strain, orienting the TFTs such that the channel current flows perpendicular to the applied stress reduces the drain current sensitivity by an order of magnitude relative to the parallel orientation [11]. The voltage output of the battery is expected to decrease due to strain effects from the substrate. A decrease in bias voltage may not turn on one of the bias transistors, resulting in dark line defects in a typical display. We expect therefore significant degradation in performance due to strain effects in flexible displays and in flexible electronics in general.

Metal Conductors. Unlike oxide materials, metal films do not experience brittle failure modes. Instead, metal films fail by localized deformation. The failure mode is initiated by the formation of a neck that becomes elongated and eventually leads to a rupture. The two most critical parameters that determine the rupture strain are (1) the modulus of the substrate and (2) the film adhesion. At 3% strain, an Au film on a low modulus silicone substrate shall start to fail. This figure is comparable to a freestanding film. Also, it has been noted that the substrate does not confine the elongation of the neck. If the substrate has a higher modulus, then deformation is more uniform and films can survive strains of greater than 10% - with the condition that the film and substrate have good adhesion.

Interlayer Effects. Once a failure occurs in a thin film, stress is relaxed locally and transferred to adjacent layers [12]. This means that while a device layer may withstand a uniform stress when tested alone, the same layer in a multilayer device may fail because of a failure in another layer of the stack. This effect is shown schematically in Figure 7. The implication is that, for example, while a single crack may not be catastrophic for an interconnect layer (such as Indium Tin Oxide layer, ITO), it may result in premature failure in a neighboring TFT that does result in catastrophic failure.

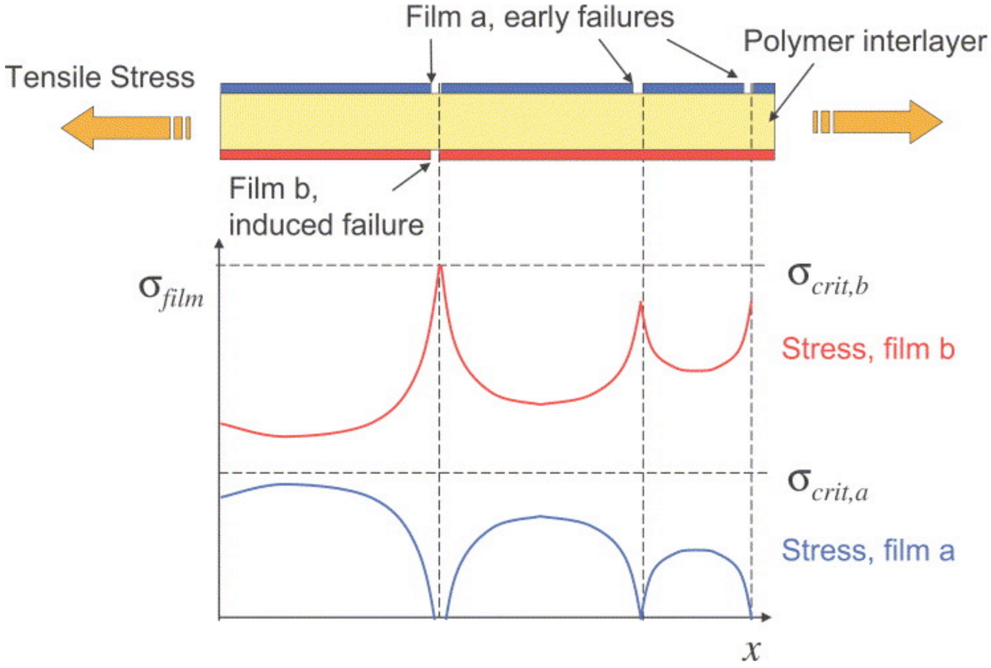


Fig.7. Layer interactions in thin films

Stress Reduction. There are several strategies for reducing stress from device fabrication: modifying device materials, film thicknesses, geometry, deposition methods, deposition temperatures, and also film annealing. An alternate strategy to reduce mechanical stresses pertinent to the process integration of molybdenum/hydrogenated amorphous silicon TFTs was performed [13]. The previous approach was to minimize the intrinsic stress in the Mo layer through appropriate process conditions and film thicknesses – this resulted in narrow process latitude and a compromise in the performance of the resulting TFT. Alternatively, the stress was shown to be reduced by reducing the extrinsic stress by the underlying films through a different masking sequence in the fabrication. A 120°C process was developed that used a He-diluted 2.5% SiH_4 + 97.5% (NH_3+N_2) mixture for the deposition of a-SiN_x:H. This resulted in film densification and hydrogen release from SiH bonds – creating improved dielectric films that had smaller compressive stresses [14]. The quantification of mechanical stress effects on flexible substrates is a topic under intense investigation and will be reported in a future publication.

Summary

In this paper, the advanced nanoparticle processing technologies that can create “stackable” layers of nanoparticles a single layer thick have been reported. Nano-particulate “hetero-structures” can thus be formed with well-controlled material dimensions and properties. As an example, it was shown that one can make layer mixtures of activated carbon and ruthenium (IV) oxide to create super capacitors. The exact control and dispersion of controlled amounts of the oxide “enables” this process to be achieved with high yield. The mono-particulate layer process described here is a modified Langmuir-Blodgett trough. The particle dimensions were between 10-100 nm. No high-vacuum equipment or clean facility is required. Furthermore, it was shown how a spray-coated zinc powder electrode can be used as a counter-electrode forming a galvanic cell of extremely high charge storage capacity (>40A-hr/cm^2). Both types of components can be made in the same process line, yielding a battery/super-capacitor hybrid. The resulting cells are flexible and thin (<0.3mm thick.).

The nanoparticle based flexible batteries integrated with thin film transistors as part of a flexible display is reported. In such a technology, a flexible flat panel display is enabled by an active matrix of devices and the flexible which replaces the conventional glass substrate (usually plastic or stainless steel**)**. The most common type of active matrix is a thin-film transistor (TFT) array. The TFT array is also called a backplane, and display materials, such as electrophoretic displays (EPDs), liquid crystal displays (LCDs), and organic light-emitting diodes (OLEDs), are added on top. A required driving or bias voltage from the flexible, thin film battery is applied at each pixel between the backplane and the common electrode which is the top electrode. We have successfully shown that the flexible power source is capable to bias the display drive transistors.

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