Nanostructuring Plastic Displays within the Flexible Electronics Paradigm

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ABSTRACT

This presentation describes our advances in fabricating a fully functional color, plastic liquid crystal display that uses an all-inorganic thin film transistor array based on a nanocrystalline II-VI semiconductor. The display itself represents an interesting context in which to explore the ways in which the key attributes of a flexible electronics platform are enhanced with nanostructured materials and processes, including inorganic nano-printing inks, nanocrystalline materials and nanocomposites, and nanostructured interfaces.

Keywords: flexible displays, flexible electronics, smart plastic, plastic LCD, nanocomposite, nanocrystalline semiconductor

1 BACKGROUND

It is likely that the transformations anticipated by flexible electronics will be achieved by merging not only large-scale electronic platforms with traditional materials and industries, but also by recruiting nanotechnologies, and hybrid combinations of organic and inorganic materials into the service of device fabrication. There is widespread consensus that the transformational potential of flexible electronics is enormous. In applications like RFID tags, sensors, lighting, logic and memory, authentication, anti-tampering, energy and displays, a simple basis set of drivers can be identified that gives major impetus to market applications estimated to be on the order of $136 B [1]. Plastic Knowledge has been engaged in developing a variety of electronic devices on plastics with a strong focus on manufacturing potential. Our long term perspective on flexible electronics emphasizes manufacturable embedded functionality (embedded intelligence) in plastics.

The plastic film manufacturing industry is mature. Plastics and plastic composites have long been printed on (inked), electroplated, metallized by evaporative coating, and supported all manner of dielectrics, in discrete panel, roll-to-roll processes, and in 3D geometries. Nevertheless, plastic substrates for flexible electronics create new manufacturing challenges not only in creating dense arrays of electronic devices, but in elaborating those devices through volume manufacturing into hyphenated plastic structures like smart cards and displays. Successful implementations of flexible electronics require judicious recruitment of interdisciplinary solutions. These are likely to include nanotechnologies, and hybrid combinations of organic and inorganic materials in the service of flexible electronics. Currently, the nascent industry of flexible electronics is attracting a plethora of potentially scalable solutions based on printing technologies and re-tooled versions of standard patterning technologies. Solutions will also emerge from resolving conflicting demands of scale that on the one hand might, for example, demand conductors on the scale of microns to perhaps kilometers. These conflicting demands declare themselves when flexible electronics is called upon to do more than just create devices. The flexible display is an interesting context in which to examine some of the requirements that must be met to realize functionality. Indeed, nano-, micro-, meso- and macro-scale structures must all converge properly to make a functional plastic display. The presentation below outlines some of the features that are important in this context.

2 EXPERIMENTAL

As in previous experiments [2] we used 200 μm thick films of a custom-formulated polyarylester compound. The plastic film was modified so that micron scale devices could be fabricated with multilevel mask registrations despite the fact that films were heated to temperatures on the order of 220 ^{o}C. The plastic has a thermal expansion coefficient of ~50 ppm/^{o}C and exhibits optical transparency better than 90% across the visible wavelength range. The polymer was hard-coated with a propriety silica nanoparticle composite. Processing was conducted on samples up to 5 inch diagonal. Plastic substrates were first degassed in a preparatory chamber to remove primarily water, residual organic solvents and unreacted monomer by a programmed slow ramp to 250 ^{0}C, followed by baking for 6 h at that temperature, and then slow cooling under vacuum to room temperature. The plastic is quite hydrophobic, absorbing a maximum 0.4% water, which is easily removed during the baking cycle. After this treatment, films were then rapidly transferred in a clean room environment. The transistor consists of an aluminum gate, aluminum oxide dielectric layer, custom silicon oxynitride dielectric (PECVD), a II-VI semiconductor and aluminum source and drain electrodes. Processing was done under class 100 conditions. Aluminum was deposited on the plasma roughened substrate by sputter deposition. Films on the order of 0.75 μm thickness were subsequently patterned by photolithography and wet etched to create the gate lines.

The gate region was quantitatively anodized at neutral pH. This gate dielectric was subsequently annealed to give the required isolation layers. Leakage currents were on the order of 10^{-10} A or smaller. For aluminum surface quality studies, aluminum was deposited by argon ion sputter deposition (4 mTorr, 1000W) onto substrates that were uncooled or cooled to ~ 6 ^{o}C. Foils were characterized by reflectivity at 632.8 nm (HeNe laser). CdS was chosen to prototype the initial experiments, despite the lower mobilities compared with CdSe. CdS films were formed at 70 ^{o}C by reaction of thiourea, ammonia (complexant) and $CdCl_2$. Pixel electrodes were fabricated from gold films or from ITO. Liquid crystal material was vertically aligned with a polyimide alignment layer. The LC was sandwiched between the lower (TFT equipped) plastic substrate and the upper plastic layer coated with ITO. Spacers maintained a uniform 3 μm cell gap. Color switching under the control of off-board electronics was achieved by flashing side illuminating red, blue and green light emitting diodes. Atomic force microscopy, focused ion beam (FIB), and SEM experiments were conducted at the Thin Films Group facilities of the Ecole Polytechnique in Montreal. Ink jet printing was carried out in collaboration with Optomec using the M^3D Aerosol Jet® printer system. Organic TFTs were printed according to designs and formulations developed by Frisbie and coworkers [5].

3   RESULTS AND DISCUSSION

One of the first length scales we encounter in fabricaging a plastic LCD is associated with free volume and structural relaxations in the plastic substrate. In polymer films, glassy-state structural relaxation, often referred to as physical aging, can produce a time dependence of the modulus, brittleness, permeability, and dimensional stability. Structural relaxations are often associated with redistributions of free (excluded) volume in the polymer, whose dimensions are frequently on the nanoscale. Summed over the dimensions of a polymer film, nanoscale relaxations can interfere with photolithography, where mask-to-mask registration can be crucial to device fabrication. As others have found, we observe that it is important to impart dimensional stability to polymer substrates by annealing out short and longer term relaxation mechanisms. Algorithms have been developed for optical steppers for partial compensation of dimensional changes in plastic substrates, but it is not clear yet to what extent or how robust these compensation schemes are, or how dependent they are on the type of polymer film or individual film properties. Dimensional stability in our hands has been worked into our program of developing Smart Plastic™ substrates with a kind of "shape memory" that permits the substrate to return to its original dimensions

after each processing step, independent of whether the process involves heating, exposure to aqueous acid, base, organic solvents or photoresist and strippers. The Smart Plastic™ strategy reduces manufacturing constraints by having the polymer itself resolve some of the conflicting demands placed on it through processing, rather than requiring that the manufacturing method do so. In our hands, multilayer polymer films offer wider latitude for solving problems of dimensional stability during device fabrication.

Forces on a TFT plastic backplane can be divided broadly into those that are internal and those that are external. External forces are those associated with macroscopic deformations like bending or shaping. Internal forces are those that are introduced by microlithography, including photoresist deposition and patterning, metal film deposition, wet and dry etching, solvent development, stripping (lift-off) and thermal annealing. These forces, which are difficult to control, result in differential thermal expansion and contraction and dimensional changes caused by water and organic solvent absorption and evaporation, and also by differences in thermo-mechanical properties of deposited inorganic and organic devices. Stiff device films
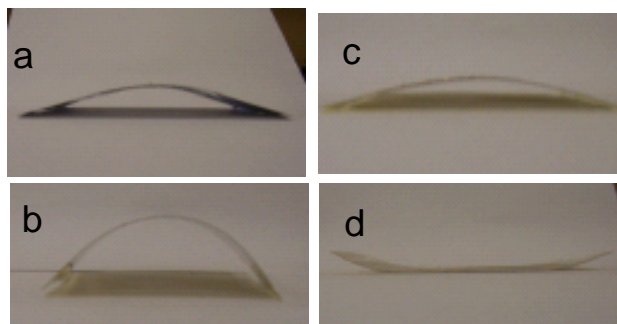

Figure 1. Changes in curvature due to differential stresses after different processing steps in improperly conditioned plastic substrates (TFT side is on top). a) after deposition of aluminum data lines; b) after lift-off (acetone solvent exposure); c) after 5 min standing in ambient atmosphere; d) after 250°C heat treatment in air, 20 min.

on compliant polymer substrates therefore place significant demands on the TFT backplane in terms of stress control. .Figure 1 above shows a sequence of deformations that result when there is stress mismatch during strain following several TFT fabrication steps on a plastic film that has not been properly stressed compensated. Significant effort has gone into developing stress management schemes [3]. These include applications of stress compensating dielectric layers and the fabrication of devices at island points of zero stress on films. Another compensation strategy that has not be much discussed in the literature is to build up multilayer
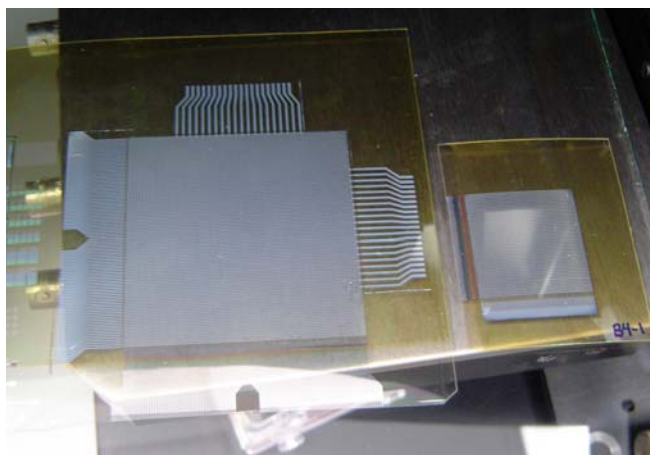
Figure 2. Active matrix backplane developed on stress compensated plastic substrate.

composite plastic films with built-in stress compensation. When this is done, as in our approach, the deformations observed in Figure 1 disappear to give the result shown in Figure 2.

Interfaces, like those between polymer and semiconductor materials, dielectrics, metal and metal oxide conductors, and even photoresists can modify polymer mechanical motions over nanometer scales at device interfaces. For example, there is substantial evidence that the effects of nano-confinement on polymer chain dynamics depend on the surfaces and interfaces to which polymers are attached. Interfacial interactions are now known to modify dynamics in the interior regions of glass formers [4], but the implications for surface adhesion and stress response of overlaid electronic components extending over the nanometer scale are not yet understood. Interfaces can affect adhesion and film quality in other areas. Differences in thermo-mechanical properties of polymers and inorganic electronic components – including gate and data lines - deposited on them can lead to mechanical failure through cracking and delamination. Polycrystalline aluminum films in the range 0.1-10 μm belong to the so-called mesoscale, and are highly inhomogeneous, so that local stress and structural variations may play important roles in lithographic patterning, electronic transport properties and mechanical performance. Specular reflectance R_s gives a measure of aluminum film quality through the rms surface roughness

$$\frac{R_s}{R_0} = e^{-(4\pi\delta\cos\vartheta_0/\lambda)^2} \quad (1)$$

Where R_0 is the total reflectance and θ_0 is the angle of incidence of the light on the surface. Figure 3 shows that reflectance of Al from the uncooled films is about 20% lower than that of the mirror-finish obtained on cooled plastic substrates. Plastic films that were not cooled during aluminization emerged from the sample chamber with a

milky appearance, despite the fact that deposition on neighboring pristine silicon wafer test pieces gave mirror-like finishes. We attribute the milky appearance to poor thermal conductivity of the plastic, differential thermal expansion of the polymer/hard coat surface, and enhanced physical and chemical reactions between high energy projectiles with the composite hardcoat. Adventitious contaminants released from the substrate polymer tend to generate large numbers of large grain boundaries. Surface scattering shows up more clearly in the right hand plots in Figure 3 where we observe significant anisotropic scattering around the central reflectivity peak for the uncooled sample. It is known that aluminum films can suffer from hillock formation and significant degradation in
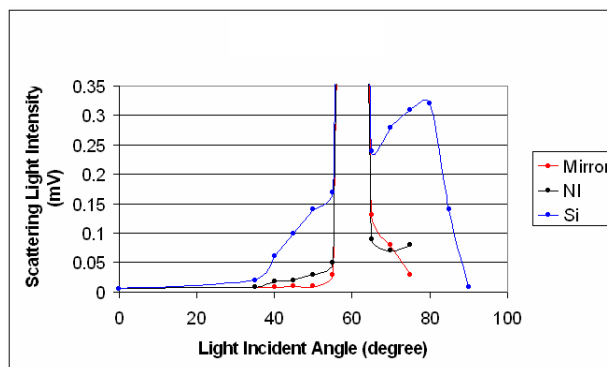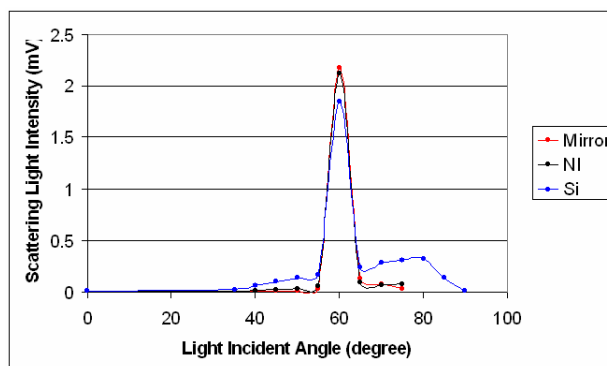

Figure 3. Reflectivity measurements for plasma-deposited aluminum on uncooled (Si) and cooled (Nl) polymer substrates as compared with a high quality optical mirror (Mirror). Top figure shows complete reflectance spectra. Bottom figure shows expanded zone at the base of the peaks in the maxima of the reflectance spectra.

reflectivity [4]. Hillock formation leading to diffuse light scattering can start at temperatures on the order of 70-80 °C. Moreover, films incorporating impurities from interfacial reactions may be brittle, fracturing and delaminating more easily. During deposition, the optical quality and physical properties of the resulting aluminum film on the plastic depend on the degree of outgassing from the polymer, substrate temperature, microstructural responses of the plastic during thermal cycling in and out of

the vacuum chamber, aluminum deposition rate and uniformity, and thickness of the metal layer. The organosilica nanoparticle hardcoat can exhibit surface topography that differs with etch conditions due to differential etch rates of the silica and polymer binder matrix. Roughness at the hardcoat surface due to the plasma etch will be transferred to the Al film, hence it is important to minimize etch-related roughness. AFM analysis revealed that the hardcoat overlayer exhibits an rms surface roughness < 2 nm. The AFM measurements indicate good surface uniformity with no contamination by larger silica particles that might act as significant Al nucleation sites. Al overcoatings show approximately 15 nm rms roughness and good film uniformity, but we note that there are occasional hillocks and imperfections on the order of 150 nm in height by ~ 500 nm in diametrer. The polycrystalline Al films are typically nanograin materials. Thicker Al films have larger grains and are also somewhat more elastic. Differences in mechanical properties at the mesoscale depend on intergrain and intragrain (size dependent) deformations and interactions, and these in turn affect adhesion, ductility and the quality of surface anodization during formation of the gate dielectric of the TFT. With mirror-finish films, Al gate regions (conductance ~3.5 x 10^{-6} Ωcm) could be quantitatively anodized at neutral pH. Annealing of the gate dielectric gave isolation layers with breakdown voltages on the order of 8 MV/cm. Capacitance measurements yielded a dielectric constant of ~9 for the annealed anodized oxide. Focused ion beam analysis showed that there was no diffusion of aluminum across the hardcoat barrier.

Thin film transistors that we have developed from II-VI semiconductors also have features that scale from nanometers to microns. Our method uses an ion-by-ion chemical bath technique [1] that was developed as a low temperature alternative to vapor deposition. As discussed previously [1], the ion growth mechanism yields CdS (or CdSe) films that can exhibit lattice orientation perpendicular to the substrate. CdS, for example, is deposited as a mixture of hexagonal close packing cubic phases. Not unexpectedly, the interfaces between the nano-grains are metastable so that brief periods of annealing at 250 ^{o}C improved the I-V characteristics of the transistors. Figure 4 is an optical micrograph showing the source and drain electrodes with the II-VI nanocrystalline semiconductors (yellow band) interposed. These TFTs were then incorporated into a 3 inch diagonal QVGA all plastic display. The display uses RGB LEDs and off-board field sequential color (FSC) drive electronics to achieve color mixing. The FSC architecture requires 2/3 less transistors than conventional LCDs, and there is no need for a color filter. Without optimization of the liquid crystal, switching speeds of 120 subframes/sec over a 3 μm cell gap have been achieved. In a similar manner, we have fabricated a plastic display that embodies the key features of FSC color mixing in a display that has been shaped into
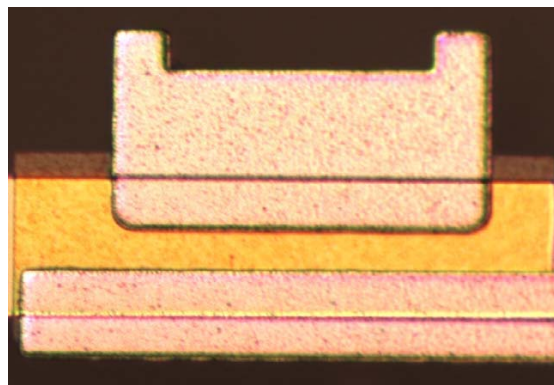

Figure 4. Optical micrograph of the source/drain region of a II-VI semiconductor (yellow band) TFT created by low temperature ion-by-ion chemical bath deposition

a convex curvature. While the display is not intended to be reversibly flexed once the shape has been defined, the achievement advances a basic principle of flexible electronics, namely that devices embedded in plastic can be elaborated into sophisticated value-added systems like functional curved (conformal) displays.

In an effort to develop Smart Plastic™ substrates that are agnostic to the choice device fabrication process, we fabricated arrays of low and high performance devices by hybridizing vapor deposition techniques with inkjet printing. For example, nanoparticle silver and dielectric inks were used to create capacitors on the plastic substrate (Figure 5).
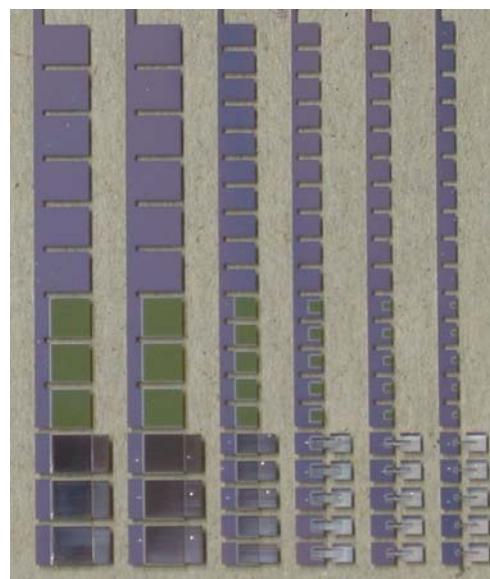

Figure 5. Capacitors created by inkjet printing silver and dielectric nanoparticle inks on bottom electrode lithographically patterned aluminum electrodes.

After sintering at ~80°C in a convection oven, the silver electrodes emerged some 5x rougher (80 nm rms) by AFM

than the aluminum electrodes. Surface plasma treatment of the plastic gave strongly adherent devices (tape test). No attempt was made to optimize the dielectric used to make the capacitors, since the objective was to determine that functioning multilevel structures could be obtained by precision overprinting of dielectric and conductor.

A primary objective of organic electronics is to develop inexpensive materials and methods to make high performance devices on flexible substrates. Accordingly, functional organic (ion gel) TFTs (Figure 6) were successfully printed by inkjet onto the Smart Plastic[TM] substrate. The material compositions and performance characteristics of these OTFTs have been published elsewhere [5].
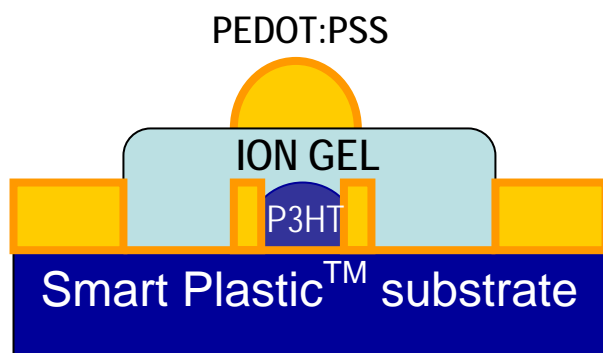

Figure 6. Schematic of an organic TFT deposited by inkjet printing onto a Smart Plastic[TM] substrate.

In summary, examination of selected materials and processes required to create a functional color plastic liquid crystal display identifies ways that nanostructures feature in the flexible electronics paradigm. In the display context, nanostructures are recruited to scale across micron, meso- and macro-dimensions. For displays of the type discussed in this paper, relevant nanostructured materials and processes include inorganic nano-printing inks, nanocrystalline materials and nanocomposites, and nanostructured bulk polymer films and their structure determining interfaces. In this perspective, the elaboration of flexible electronics into commodity products will benefit from ongoing research in nanoscience and nanotechnology. Finally, since there no common polymer platform for flexible electronics, a useful strategy we are pursuing is to create (smart) polymer composite substrates that are more or less agnostic to device fabrication processes. This was illustrated in simplified form by building TFTs using both standard lithographic processing and inkjet printing techniques on the same substrate.

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