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Polymer Electronic Devices and Materials

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Polymer Electronic Devices and Materials

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Abstract

Polymer electronic devices and materials have vast potential for future microsystems and could have many advantages over conventional inorganic semiconductor based systems, including ease of manufacturing, cost, weight, flexibility, and the ability to integrate a wide variety of functions on a single platform. Starting materials and substrates are relatively inexpensive and amenable to mass manufacturing methods. This project attempted to plant the seeds for a new core competency in polymer electronics at Sandia National Laboratories. As part of this effort a wide variety of polymer components and devices, ranging from simple resistors to infrared sensitive devices, were fabricated and characterized. Ink jet printing capabilities were established. In addition to promising results on prototype devices the project highlighted the directions where future investments must be made to establish a viable polymer electronics competency.

Acknowledgements

The work presented in this report was conducted by a large team of capable Sandians, including Dan Barton, Ron Anderson, Doug Chinn, Paul Baca, Val Shulfer, Bev Silva, Patrick Doty, Tiffany Wilson, and Robert Burr, along with many others. In addition several student interns made valuable contributions, including especially Nathan Lowrie and Aaron Ferreira.

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Executive Summary:

Polymer electronics technology has several potential advantages over conventional inorganic (silicon and compound semiconductor) devices. One advantage should be lower cost and ease of manufacturing. In addition, devices can be flexible and can be built up on a variety of substrates by relatively inexpensive methods in comparison to semiconductor processing. In principle, both electronic and mechanical properties can be controlled through chemistry and processing since the entire library of organic chemistry is available. The polymer electronics industry is on the brink of volume production for a few select applications. The promise is great, but the risk is still high. The goals of this LDRD project were to develop polymer electronics as a core competency at Sandia National Laboratories. This entailed development of appropriate polymer electronics materials expertise, device design and processing capabilities. One of the first tasks was to explore the readiness and suitability of polymer electronics for national security applications, such as chemical and radiation sensors, light emitting diodes, lasers, large area electronics, photovoltaics, batteries, and actuators. The breadth of these applications and their relevance to Sandia's national security mission provide strong motivation for advancing polymer electronic technology, yet much progress will be required to realize the potential. As a rough yardstick for the level of effort required, one need only reflect on the investment in the semiconductor industry to bring it to its current state. With this in mind it is clear that this LDRD effort has been only a first small step in the investment that will be required to significantly advance the technology base and to position Sandia as a viable participant.

Over the course of the LDRD project the team explored the feasibility of a variety of polymer based electronic circuit components that are common to a number of applications. These elements included conductors, dielectrics, and semiconductors. During the early part of the project much of the work centered on understanding the availability, quality, and consistency of various component materials, and in particular their compatibility with ink jet printing. Although promising early results were obtained with syringe printing, ink jet printing was viewed as a key technology for achieving finer dimensions and mass manufacturing. The team developed an ink jet printer as a baseline deposition capability compatible with a variety of substrates and polymer formulations. Considerable progress was made in making the materials more printable and promising results were obtained, but much work is still needed to achieve more consistent results and durable devices.

During the latter part of the project, attention was focused on the development of polymer-based infrared (IR) devices (photodiodes or IR photovoltaics). Various bias driven assembly techniques were demonstrated for both the manipulation of the electronic behavior of indium tin oxide (ITO) and to simplify the fabrication of IR photovoltaic devices. Photoactive devices were assembled using conducting polymer and photosensitive lead sulfide nanocrystals. In one version, novel surface modification techniques based on diazonium attachment chemistry developed at Sandia National Laboratories were used. Ideally, this approach will eventually enable production of cheap polymer sensors and photovoltaics that can utilize IR radiation.

Acronyms and Abbreviations

BARF – boron salt (sodium tetrakis(3,5-bis (trifluoromethyl) phenyl) borate)

IR – infrared

PPy – polypyrrole

PEDOT - poly-ethylene-dioxythiophene

PANI – polyaniline

PVP – polyvinylpyrrolidone

PPV – polyphenylenevinylene

PVC – polyvinylchloride

ITO – indium tin oxide

TNAP - 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane

UV – ultraviolet

UV-Vis – ultraviolet – visible spectroscopy

CPD – contact potential difference

EIS – electrochemical impedance spectroscopy

I(V) or I-V – current voltage

1. Introduction

Polymer electronics is a unique micro-device technology utilizing plastic diodes, transistors, sensors, light-emitting devices, and photovoltaics among others. One of the advantages of organic or polymer semiconductors over more traditional materials involves the number of materials available. Inorganic electronics have roughly 20 elements available, many of which must be formed into crystalline structures to be useful. In contrast materials for organic electronics are almost unlimited. Since dopants are typically acids, there are literally thousands available. There are countless side groups that can be added to the polymer backbones to fine tune particular materials properties. Polymer materials can be synthesized chemically, electrochemically and in plasmas. Structural order can be varied from purely amorphous to highly crystalline. Substrate shapes can range from fibers to films. In summary, organic materials have more degrees of freedom to work with than inorganic semiconductors and can be tailored for specific physical, electrical and optical properties; therefore a broader range of devices can potentially be integrated with this technology.

Ease and cost of fabrication may be other advantages for polymer electronics. Polymer processing can be done at low temperatures using a variety of solvents. Furthermore, low-cost fabrication is possible because multi-billion dollar fabs, high-priced vacuum equipment and expensive, rare materials may not be needed. Rapid turn-around and custom circuits can be made by mask-less manufacturing as circuits are built up layer-by-layer using common “printing” techniques.

In addition, the combination of an active polymer electronic backplane with more traditional high-performance silicon and compound semiconductor technologies opens a whole new and powerful multi-technology integration approach. Integration onto flexible substrates with on-board, polymer-based power supplies and full color, flexible organic light emitting diode displays makes it possible to imagine an inexpensive, credit card sized plastic microsystem. Printing on large areas (many square meters) is also possible with this technology because local registration can be used and printing can be done at (or close to) room temperature.

With its unique characteristics, polymer electronics has the potential to become an enabling technology for many applications of interest to Sandia and the nation. Of course all of the potential advantages of organic electronics mentioned above are accompanied by major challenges. Solvent and material interactions, microstructure-property relationships, material lifetime and durability all must be understood to develop a viable technology. All of these things are affected by the purity and consistency of starting materials. Materials suppliers are used to purities on the order of 90%. The variability of results reported in the literature for nominally identical materials indicates that this level of purity is probably not sufficient for reliable electronics applications. The lack of consistency in the characteristics of polymer-based electronic devices also results in a lack of basic understanding of electron and hole transport mechanisms in these materials.

As part of this project, the team gained an understanding of the state of the art in the development of polymer electronics. While there are countless possible device possibilities to pursue in the polymer electronics arena, the latter part of the project concentrated on the feasibility of polymer-based infrared sensitive devices as detectors or power generation elements. Such devices have wide applicability, from sensed microsystems to larger-scale power generation. For example, solar power generation offers the potential to produce a renewable source of power. In the year 2002 photovoltaic devices accounted for between 427 MW² and 560 MW³ of power worldwide. Devices based on crystalline Si have reached efficiencies of 24%, however, the cost of manufacturing still remains high.² Sandia also develops on-chip silicon solar cell arrays as microsystem power elements. Despite the high cost of production, Si devices account for 99% of all photovoltaic devices.² Hybrid cells also exist including the Gratzel (photoelectrochemical) that consist of hybrid inorganic semiconductors and a sensitizing dye molecule. An alternative to the Si based or silicon hybrid device is the all organic based device (all organic active area).

Typically, the solar cell devices work in the visible region of the power spectrum. About half of the sun's spectral power falls in the infrared (IR) range.⁴ As a result conventional solar cells are not collecting the full amount of spectral power available. An improved method of making photovoltaic devices would include the IR region of the power spectrum. The incorporation of IR absorbing PbS nanoparticles is one method that has received much attention recently.^{1, 4-6}

2. Development of Basic Polymer Electronic Components and High-Volume Compatible Fabrication Capabilities

In early work the team identified a promising all polymer diode configuration from the literature. Reported construction used a vertical layer structure with more conductive polymers like polypyrrole (PPy), PEDOT, or polyaniline sandwiching less conductive polymers like MEH-PPV or polyfluorene. The literature also reported the use of a polymer insulator, PVP. We procured several variations of each of these materials, and built lateral and vertical structures for feasibility testing of performance. The most promising results were achieved with a PEDOT/PPV/PPy stack. The device was fabricated using a Robocast syringe dispense system already available at Sandia (this system was developed for ceramic slurry applications) on a polyvinylchloride (PVC) substrate. A picture of the structure is shown in Figure 1 below, and typical performance curves for this type of construction are shown in Figure 2.

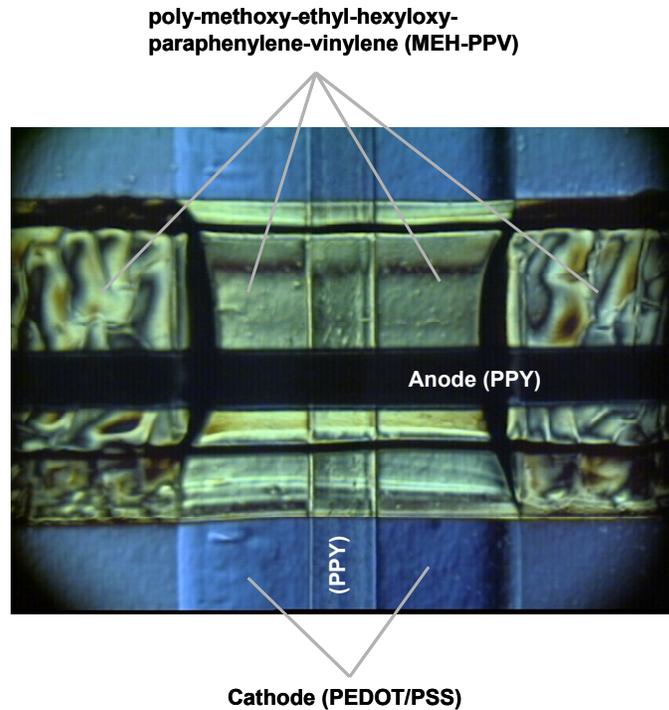


Figure 1. An early all-polymer Schottky barrier diode printed with syringe dispensing on a PVC substrate. The vertical PPy cathode is drawn first, followed by the wider vertical stripe of PEDOT material. Next the horizontal stripe of PPV semiconducting material was deposited, followed by the horizontal top contact of PPy.

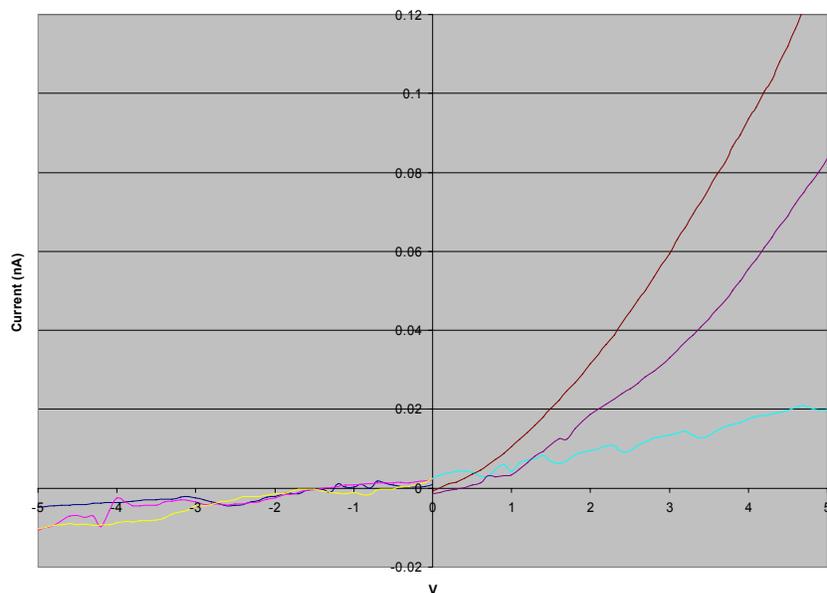


Figure 2. Current voltage characteristics of an early PPy/PEDOT/PPV/PPy all polymer diode fabricated with syringe dispensing on a PVC substrate. The different colored curves are the characteristics of nominally identically processed diodes. Variability in the performance characteristics reflects the lack of control over device dimensions (both area and thickness).

As mentioned these promising early results were obtained with syringe printing that is similar in many ways to pen plotters from the past, except that the ink is forced from the pen by the syringe pump. Figure 3 shows 3 x 4 and 15 x 25 diode arrays printed using the same fabrication methods.

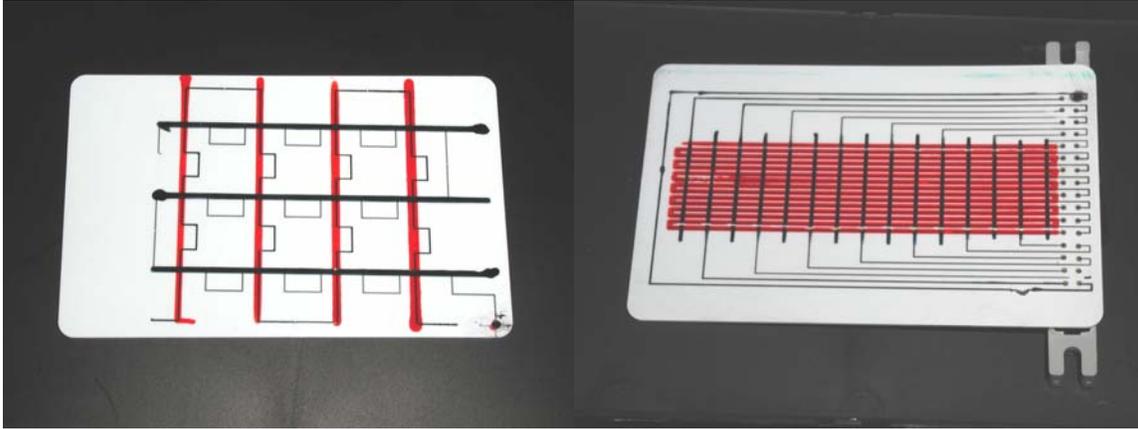


Figure 3. Diode arrays fabricated with syringe dispensing on PVC, illustrating the potential to create electronic circuitry on a flexible substrate. These diodes are the same basic construction as that shown in Figure 2 above.

While these early results were promising, syringe printing has limited potential for printing finer features in ever thinner layers, as envisioned for polymer electronics. Inkjet printing was identified early on as a promising fabrication approach for polymer-based electronics that could be scaled up for higher volume applications and could achieve finer dimensions and smoother topographies.

Therefore, an ink-jet printer and appropriate dispensing processes were developed for fabrication of electronic components and circuits onto various substrates. By direct-write application of insulating and conductive polymer materials in fluid formulations of either aqueous dispersions or organic solvent solutions, lines and layers may be sequentially added to the construction, building up a complete electronic circuit. The equipment dispenses various polymer fluids using piezo-electric actuated glass capillary nozzles mounted onto a print head controlled by a height adjustable motorized stage. Ink can be dispensed from nozzles that are heated to $< 40^{\circ}\text{C}$ in order to optimize printability. Various pneumatics and electrical controllers regulate the ink supply. A motion controller programs X-Y substrate stage movement so that circuit elements can be drawn. A heated vacuum chuck holds substrates in position, and enhances drying of applied inks for faster dispensing. Barrel reservoirs (Luer tip syringes) mounted on a rail above the print head feed fluid (inks) into nozzles, with atmospheric range pressure pneumatics controlling nozzle meniscus by application of house nitrogen or vacuum in order to optimize ink jetting results. Pneumatic valves are used to enable pressure relief, purging, nozzle selection, stage vacuum, and nitrogen excess flow control. Polymer material (ink) is normally supplied in 5cc, 10cc, or larger barrel reservoirs from a separate fluid formulation laboratory. Reservoir tips are connected to Luer fittings on nozzle tubing, uncapped and connected to pneumatics adapter, and clipped in place for use. A system of cameras and monitors makes possible adjustment of the dispense gap and alignment of

the computer generated pattern to fiducial marks on the substrate. High voltage ink jet actuation pulse levels and timing are set up through a serial cable from a computer to the ink jet controller. This interface also controls set up for drop frequency and source of triggering, as well as LED strobing of drops in flight. Another serial cable from the computer transfers programming of stage motion and ink jet droplet actuation triggers. High voltage actuation pulses are triggered from the motion controller program to the JetDrive controller over a trigger signal cable. The system continues to be refined with software and automated for process variable control and operator ease of use, including direct importation of patterns from AutoCAD.

A picture of the ink jet printer is shown in Figure 4 below. The entire printer is enclosed in an exhausted enclosure to eliminate odors and operator exposure to the volatile ink formulations.

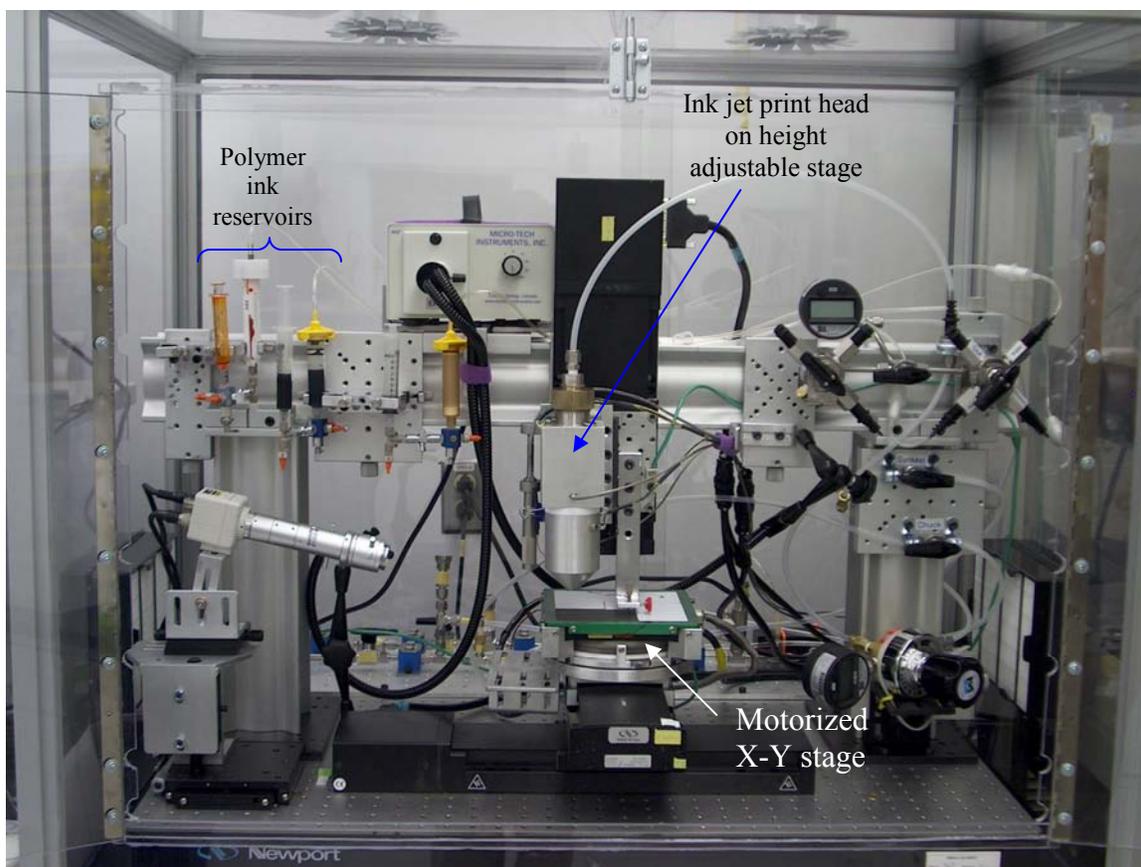


Figure 4. The ink jet printer developed as part of the project is depicted here. The printer is located in an exhausted plexiglas enclosure (doors are open in this photo) to eliminate odors and solvent exposure. Various components of the printer are labeled. The system can also be converted to syringe-dispense printing.

While ink jet printing has greater potential for finer dimensions and smoother topographies, it does place increased demands on the ink properties. In the early efforts mentioned above we procured several variations of each of the polymers. Several of these inks come delivered in ink-jettable formulations. Others arrive in powdered form and must be dissolved or suspended in appropriate solvents. Solubility parameters had to

be worked out for the powdered starting materials. As it turned out, achieving consistent and suitable ink properties for jet printing turned out to be one of the biggest challenges and highest risks of this project. Ink development is still an area where much improvement is needed to make polymer electronics viable. As an example, one of the many issues with ink formulation involves too rapid evaporation of a low-boiling solvent in the nozzle orifice, causing clogging by the solid polymer residue. Such problems can prevent one from printing complex circuits. Other key challenges include controlling wetting properties on the initial substrate and over previously deposited polymer layers (Figure 5). Figure 6 below depicts some common blistering and peeling problems with PPy when printing one layer over another. Redissolving of underlying layers and cross contamination of layers also proved to be troublesome.

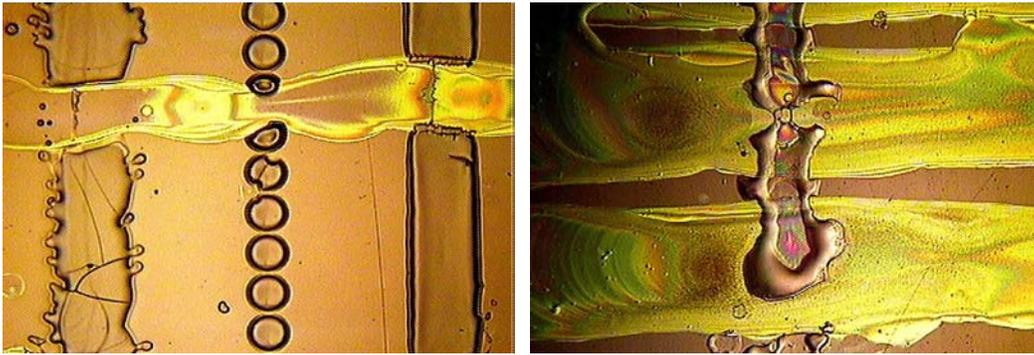


Figure 5. PPy (vertical) printed over PPV (horizontal) at various velocities. Some progress in improved wetting achieved through such techniques as plasma etching of the surface and heating the substrate while printing. Considerable progress is still needed.

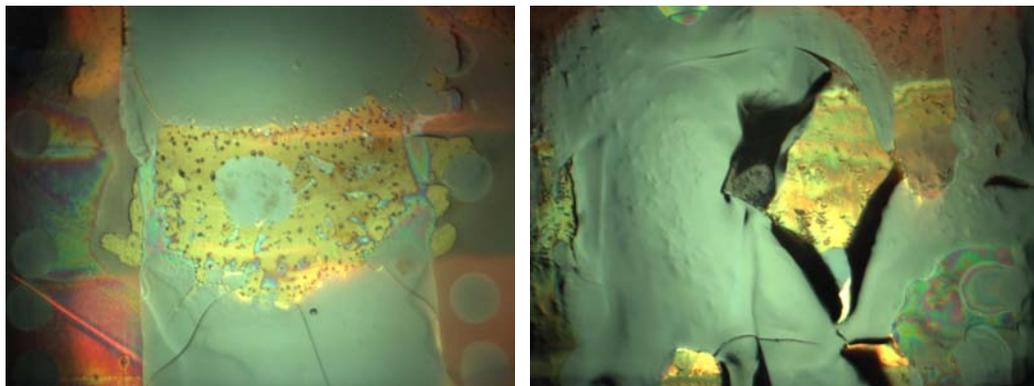


Figure 6. These micrographs depict common problems with ink jetted PPy films. The picture on the left shows cracking and crazing of the film. On the right the film has blistered and peeled.

Certain materials that we evaluated exhibited a prevalence of crazing in the deposited film usually through the entire width and thickness of the line interrupting electrical continuity. This happened anywhere from immediately after printing and drying, to a few weeks later. In some instances heat from the microscope light used to examine devices induced cracks while we inspected otherwise pristine films. Some ability to control this crazing by the addition of polymer matrix stabilizing agents into the ink formulation was demonstrated. Poor adhesion compounded the problem of crazing, as the films would also blister and curl into a flaked and spiked appearance. This occurred

between the top polypyrrole and polyaniline layers on some test devices within three weeks after a performance demonstration of the best array yield and output levels to that date.

Practical circuits require relatively high conductivities of traces to avoid excessive voltage drops due to current resistance. Some ways to address this are to increase cross-sectional area with wider or thicker lines, or increasing the solids weight percentage loading of the dispensed fluid. Another possibility is to choose materials that have doping or other species that enhance conductivity. As an example, one polypyrrole material with supplier proprietary organic acid doping for conductivity has proven to be poorly conductive and very prone to crazing in thicker films, so that more than a few built-up layers of ink-jet deposited lines begin to craze and measure drastic increases in resistance. A different polypyrrole material from another manufacturer was made with a doped conductive polypyrrole shell surrounding a waterborne polyurethane core binder resin. This version was doped with toluenesulfonic acid. Not only did this second material demonstrate several orders of magnitude greater film conductivity when deposited with the same parameters, but it also did not suffer from crazing even with over one hundred built-up layers of ink-jet deposited lines, and even though it was dispensed with greater weight percentage of solids loading. This PPy ink is formulated with methanol for better wetting to hydrophobic surfaces and poly(ethylene glycol) as a stabilizer and for higher viscosity control of straight un-forked streams through ink jetting.

In order to minimize voltage drop across diode lead resistance and establish a higher operating point nearer to normal electronic circuit supply voltages, one of the attempts at developing a better conductor material combined an inherently conductive pi-conjugated polymer, regio-regular polythiophene, with a conductive nanoparticle, C61. Both of these commercially available materials were added to promote hopping transport. A third ingredient, a boron salt known as BARF (sodium tetrakis(3,5-bis (trifluoromethyl) phenyl) borate) added ionic conduction.

Diode performance curves with the “synthetic metal” mixture initially exhibited a very high output current levels (~ 10 microamps at a few volts) in simple electrical measurements. However, the electrical characteristics were strongly dependent upon voltage sweep rates and results were not repeatable. It was determined that the high current levels were actually transients associated with ion transport and the formation of charge double layers around electrodes. These attempts failed to achieve reproducible conductive polymers, and we reverted back to commercially characterized and produced organic inks for cost and performance reasons.

One other problem that the team ran into in this area was with the availability of the inks. Over the course of the project it was not unusual to find that an ink was no longer available from a manufacturer, or that the formulation had been changed slightly for reasons unrelated to Sandia’s applications. For example, the most conductive of the polypyrrole inks became unavailable for further distribution through Aldrich, because its maker, the Dutch company DSM, lost the employee who knew how to make it and the

processing formula along with him. Polyaniline similarly failed further supply through Aldrich from its Japanese makers. (However, polyaniline also fell into disfavor because of its notorious susceptibility to humidity effects on conductivity.)

Furthermore, the purity of commercially available materials is typically only 90%. Based on the experience of the semiconductor industry, higher levels of purity will be required to make significant advances in understanding. Getting the attention and commitment of manufacturers to a particular product with tight specifications will require higher volume use than current activities. A steady and consistent supply of the various inks will be a key requirement for establishing a viable polymer electronics technology.

The table below provides a list of the main polymers investigated during this project. Various processes implemented to achieve higher yields and reproducibility are documented in the appendices.

Table I. Polymers Utilized During the Course of the Project

Polymer	Function
PPV (p-phenylenevinylene)	Semiconductor
PPy (Polypyrrole)	Conductor
PEDOT (poly-ethylene-dioxythiophene)	Conductor
PANI (polyaniline)	Conductor
Shellac	Dielectric
PVP (Polyvinylpyrrolidone)	Dielectric
Synthetic metal (mixture of regio-regular polythiophene, C60 nanoparticles, and a boron salt)	Conductor

3. Infrared sensitive device development

During the latter part of the project, attention was focused on the development of polymer-based infrared (IR) devices. Such devices could be either IR photodiodes or IR photovoltaics. Nanocrystalline composite photovoltaics (shown schematically in Figure 7) built by solution-based processing could provide a light-weight, flexible, low cost energy harvesting platform that is difficult to achieve with conventional inorganic photovoltaic materials. A comparison of the two fabrication approaches is shown in Table II. Correct choice of nanocrystals allows one to span the spectrum from visible to infrared and enables applications in heat-into-power as well as traditional solar photovoltaics.

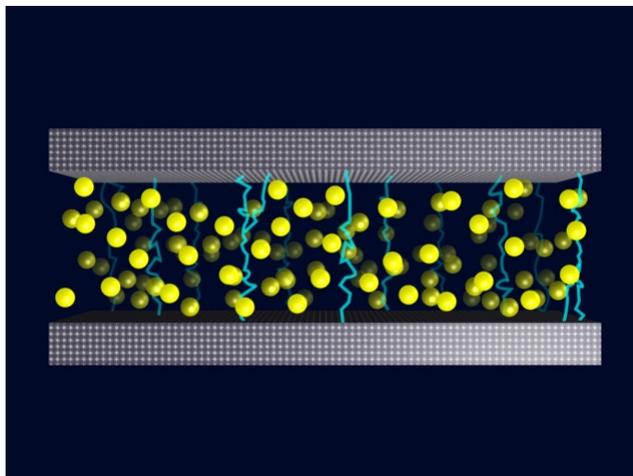


Figure 7. Schematic representation of a composite polymer-nanoparticle solar cell. The nanocrystals impart photosensitivity, while conductive polymeric material allows one to conduct electrons and holes to the electrodes and thus extract power.

Table II. Manufacturing advantages and disadvantages for solution-based processing as compared to traditional semiconductor processing.

<ul style="list-style-type: none"> • Solution Process <ul style="list-style-type: none"> – No substrate: can be incorporated into thin, flexible films – Atmospheric pressure – Low temperature <ul style="list-style-type: none"> • <100°C – Potentially Inexpensive precursors <ul style="list-style-type: none"> • Surfactants • Solvents • Conducting Polymers – Recoverable precursors <ul style="list-style-type: none"> • Solvent, surfactant – Large scale films possible 	<ul style="list-style-type: none"> • Semiconductor Process <ul style="list-style-type: none"> – Wafer substrate ~ 500mm thick, must be removed to achieve thin films – Vacuum systems – High temperature <ul style="list-style-type: none"> • >600°C – Expensive precursors <ul style="list-style-type: none"> • Trimethylgallium • Trimethylaluminum • Tertiarybutylarsine – No recoverable precursors – Somewhat Limited to substrate diameter: 12" for Si, 6" for GaAs, 4" for InP
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Solution processed nanocrystals have advantages over equivalent semiconductor devices for applications requiring large scale, flexible, low-cost devices

In simple organic photovoltaic devices the primary exciton dissociation site is at the electrode interface (Spanggaard, *et al*²). In order to improve on current devices we chose to modify the electrode surfaces in order to reduce these exciton dissociation sites and improve efficiency. Since indium tin oxide is a transparent conductor, it has played a crucial role in the construction of photovoltaic devices.⁷ Our work focused on the functionalization of ITO. Several reports have shown successful modification of ITO using dipolar phosphonic acids,^{8,9} chlorosilanes,¹⁰ C60,¹¹ 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP),¹¹ tetraalkoxytin¹² and thiol coated gold monolayers.¹³ Recently it was reported that ITO may be functionalized with the use of diazonium salts.¹⁴ In this report we chose to examine electron rich and electron poor diazonium salts as a tool to modify the work function of ITO in an easily manufacturable manner for IR photodevices. We chose to use the IR absorbing PbS nanoparticles as the method to realize IR response.

Experimental Aspects

Materials and reagents:

Tetrabutylammonium tetrafluoroborate was purchased from Acros Organics. Acetonitrile, poly[2-methoxy-5-(2'-ethylhexyloxy-p-phenylenevinylene)] (MEH-PPV), poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene] (MMO-PPV), oleic acid, octadecene, bistrimethylsilyl sulfide, potassium ferric cyanide, potassium ferrous cyanide, and toluene were purchased from Aldrich. Lead oxide was purchased from Fisher Scientific Company. Indium tin oxide on glass (25 Ohm) was purchased from Aldrich. Ultrajet carbon dioxide spray cans were used to dry substrates. 4-perfluorocadecylbenzene diazonium; tetrafluoro borate was prepared according to the method of Dirk et al.¹⁵ 4-(4-tert-Butoxycarbonyloxy-phenylethynyl)-benzenediazonium; tetrafluoro borate was prepared in a similar method. All electrochemical procedures were performed on a Voltalab PZG 100 potentiostat. The reference electrode was silver silver nitrate. UV-Vis analysis was performed using a Perkin-Elmer Lambda 25 spectrophotometer. NIR analysis was performed using a Perkin-Elmer UV-Vis-NIR spectrophotometer. Thin films were prepared using a Specialty Coating Systems, Inc. Model P6700 spin coater. Nanoparticles were precipitated with the use of a Fisher Scientific Marathon 8K centrifuge.

Measurement Set Up:

Photo-active device evaluation was performed using a Voltalab PZG 100 potentiostat with the reference and auxiliary leads tied together. A 200 W light bulb was used as the light source when evaluating photo-active devices. Contact potential difference (CPD) measurements (Kelvin probe) were performed using a Monroe Electronics Isoprobe Electrostatic Voltmeter, model 244A with a model 1017AS probe under flowing N₂. Measurements are made relative to the untreated ITO substrates and demonstrate a relative change in CPD or work function. Electrochemical impedance spectroscopy (EIS) measurements were performed with a Voltalab PZG 100 potentiostat. Curve fitting was performed with the associated Voltalab software.

Nanoparticle synthesis:

Lead sulfide nanoparticles were synthesized according to the method of Hines and Scholes.¹⁶ Lead oxide (90 mg, 0.40 mmol), and oleic acid (4.0 mL, 12 mmol) were heated under argon at 150 °C. The heat source was removed and to the resulting clear solution was added bistrimethylsilyl sulfide (50 μL, 0.24 mmol) dissolved in octadecene (2 mL). The resulting black solution was held at 80 °C for 15 min. The solution was cooled and methanol was added to precipitate the lead sulfide nanoparticles. The mixture was transferred to a centrifuge tube and spun at 2000 RPM for 10 min. The supernate was decanted and discarded. The black nanoparticles were re-dissolved with a minimum amount of toluene and re-precipitated using methanol.

Photodiode device assembly:

Photoactive devices were prepared in a method similar to that of McDonald et al.¹ A hole transport layer was fabricated on one-half of a 10 mm × 25 mm ITO coated glass substrate. A lead sulfide nanoparticle/MEH-PPV blend (90% nanoparticles by weight) dissolved in toluene were spun-cast at 1000 RPM for 30 seconds. The top contact was prepared by pressing one-half of a 10 mm × 25 mm ITO coated glass substrate coated with an electron transport layer. The final device was secured with spring-loaded binder clip.

Measurement of Photocurrent:

Device evaluation was performed using a Voltalab PZG 100 potentiostat with the reference and auxiliary leads tied together and connected via an alligator clip to the un-functionalized portion of the electron transport coated ITO substrate. The working electrode was connected via alligator clip to the un-functionalized portion of the hole transport coated ITO substrate. A 200 W light bulb was placed four inches in front of the sandwiched device. A constant voltage was applied with the light turned off to establish a baseline. After 30 seconds the light was turned on and after 30 seconds of light exposure the light was turned off. Current was measured for greater than 2 min. after the light was turned off.

ITO Cleaning:

The ITO surface was first cleaned using a (1:1 30% H₂O₂: H₂SO₄) piranha solution for 2.5 min. *CAUTION: PIRANHA IS A VERY STRONG OXIDIZER AND REACTS VIOLENTLY WITH ORGANICS.* After incubation in the piranha solution the piranha was decanted into a clean beaker and water was added to the beaker containing the ITO substrate. The ITO was removed from the water solution and washed with fresh water and dried using a stream of CO₂

Silanization procedure:

The ITO substrate was first cleaned according to the ITO cleaning procedure above. The substrate was then incubated in a solution of (N,N-dimethylamino)phenyldimethylsilane (50 μL) dissolved in toluene for 10 min. The substrate was then removed and washed with additional toluene and dried under a stream of CO₂.

Diazonium Assembly:

Assembly onto ITO was performed according to the method of Maldonado.¹⁴ An ITO coated glass slide was connected via an alligator clip to the working electrode of a potentiostat and immersed into a 1 mmol/L diazonium salt solution in 0.1 mol/L tetrabutylammonium tetrafluoroborate in acetonitrile. The potential was repetitively cycled from 0 V to -1 V to 0 V for the desired number of cycles. The substrate was washed with additional pure acetonitrile and dried with a carbon dioxide stream.

Results and Discussion

Initially, a system was chosen so as to provide a means to take advantage of a wider range of optoelectronic materials. The system chosen was based on the conjugated

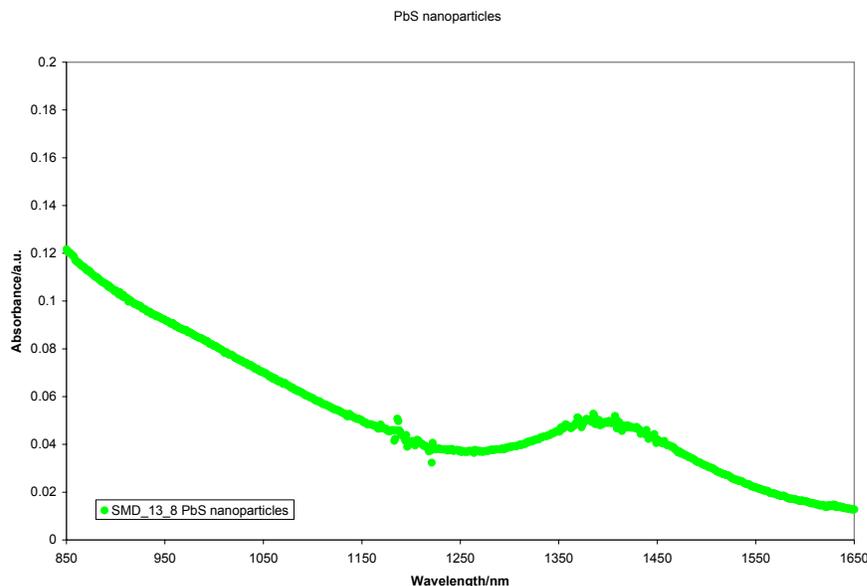


Figure 8. NIR spectrum of PbS nanoparticles prepared by the reduction of a PbO salt with the use of bistrimethylsilylsulfide in a single phase system of nanoparticle stabilizers including oleic acid and undecene.

polymer poly[2-methoxy-5-(2'-ethylhexyloxy-*p*-phenylenevinylene)] (MEH-PPV) sensitized by IR absorbing PbS nanoparticles.¹ Initially, PbS nanoparticles were synthesized according to the method of Hines and Scholes.¹⁶ The PbS nanoparticles were characterized by NIR as shown in Figure 8. The lead sulfide nanoparticles were also characterized using transmission electron microscopy and showed a narrow size distribution and uniform crystallinity.

Photo active devices were assembled using MMO-PPV and PbS/MEH-PPV. The device was operated at 3 V since dissimilar materials were not used as the electrodes. If dissimilar materials (for example, Al and ITO) were used, the generated field would help to separate the hole and the electron in the photogenerated excitons. The use of dissimilar electrode materials for charge separation has been demonstrated in the literature, but was not pursued in the present work because of time and budget constraints near the end of the project. At 3 volts of bias the difference between light and dark current was about 200%. A plot of current vs. time is shown in Figure 9. The slow response of the device requires further study. This type of behavior could arise from capacitive effects (double layer formation in the polymer capacitor) exacerbated by the relatively thick polymer layers of the device. Slow response on this scale is certainly unusual for a conventional solar cell.

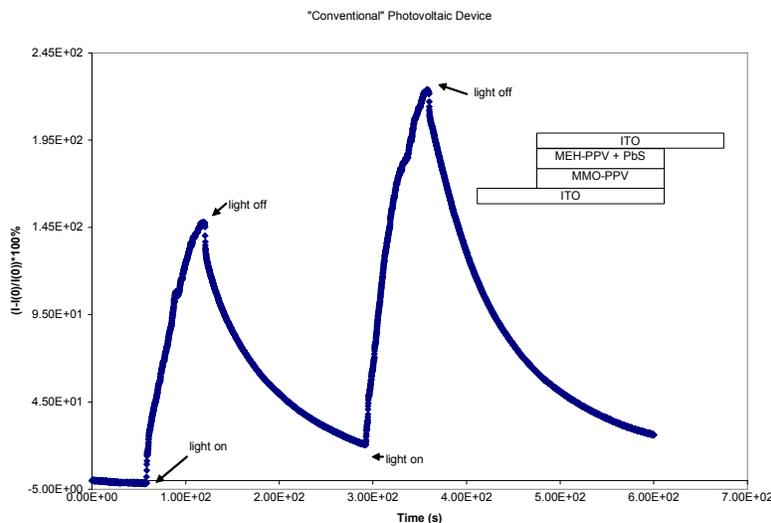


Figure 9 Response of an ITO/MMO-PPV/MEH-PPV + PbS/ITO photo active device exposed to a 200 W wide range light source.

In an effort to improve on the device described above we began the evaluation of diazonium treated ITO. Initially we chose to treat the ITO with (dimethylamino)-dimethylphenylsilane. We have previously determined that the thickness of a molecular layer attached to semiconducting and conducting surfaces can be precisely controlled by the number of cyclic voltammetry cycles. We have also shown that multilayer structures may be created on phenylated surfaces generated from diazoniums. Consequently, we chose to attach additional layers to a silyl amine generated phenylated ITO surface. The ITO surface was first cleaned using piranha solution and then treated with (N,N-dimethylamino)dimethylphenylsilane. After silanization, the ITO substrate was immersed into a solution of 1 mmol mixture of potassium ferricyanide and potassium ferrous cyanide, and an I(V) curve (blue) was generated using cyclic voltammetry from 0 mV to 600 mV, at a scan rate of 100 mV/s. 4-Perfluorooctylbenzene diazonium tetrafluoroborate was then assembled onto the silanized ITO. The assembly was accomplished using cyclic voltammetry scanning from 0 V to -1 V, at rate of 100 mV/s. After 50 cycles the functionalized ITO was immersed in the potassium ferricyanide and potassium ferrous cyanide solutions and the I(V) curve (pink) was generated. The results are shown in Figure 10a and 10b. The blocking of the redox couple of the iron $\text{Fe}^{+2}/\text{Fe}^{+3}$ (decreased current response) clearly demonstrates the formation of a semiconducting surface on the ITO. EIS spectra clearly demonstrate increased capacitance with additional coating steps.

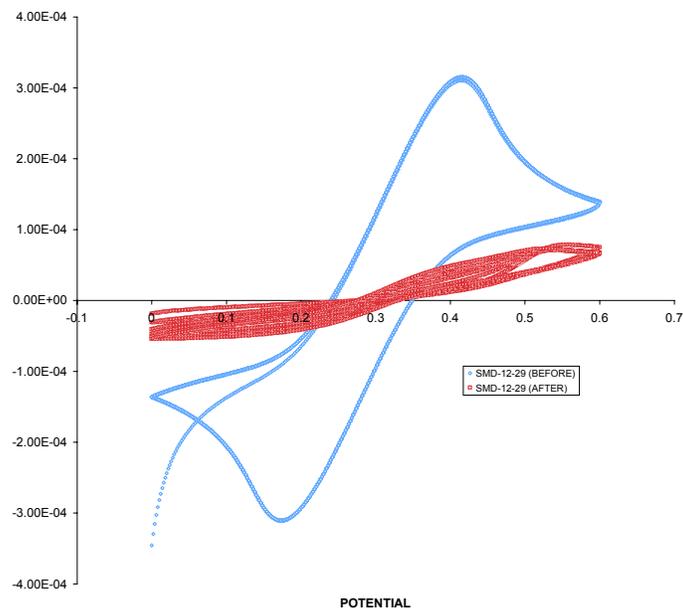


Figure 10 (a). Electrochemical evidence of diazonium layer formation. The assembly of the diazonium layer blocks the redox site on the ITO surface. The blocking of the redox couple of the iron $\text{Fe}^{+2}/\text{Fe}^{+3}$ (decreased current response) clearly demonstrates the formation of a semiconducting surface on the ITO.

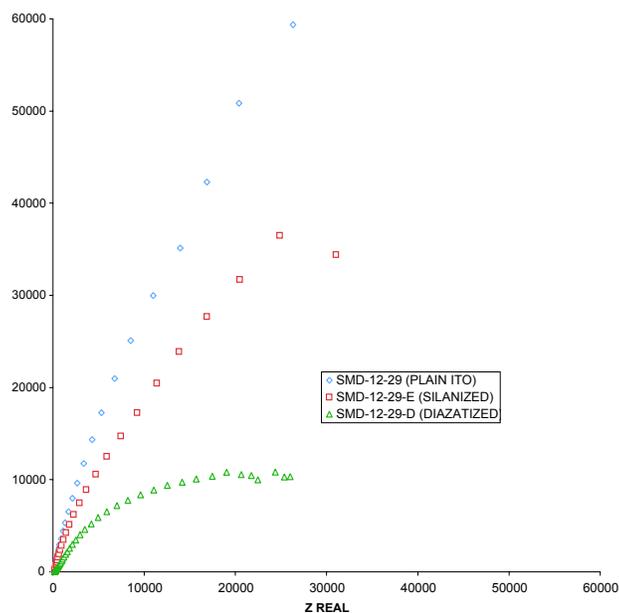


Figure 10 (b). Electrochemical evidence of diazonium layer formation. Electrochemical Impedance Spectra of ITO (blue) and ITO after (N,N-dimethylamino)-dimethylphenylsilane treatment (red) and after electrografting 4-perfluorooctylbenzene diazonium tetrafluoro borate (green). Most simply, the increased resistance of the film (decreasing slope) and increased capacitance (curvature) of the films is clear and tracks with each functionalization step.

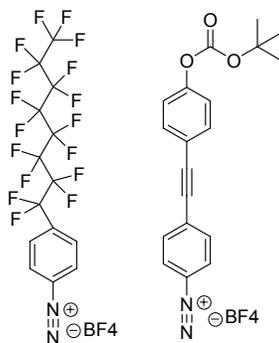


Figure 11. Diagrams of an electron deficient diazonium salt (left) and an electron rich salt (right)

It was then determined that the ITO can be functionalized directly based on the method of Maldondo.¹⁴ Two diazonium salts were chosen for assembly; an electron deficient and electron rich diazonium salt (see Figure 11). Assembly was performed using the cyclic voltammetry method, sweeping from 0 V to -1.0 V for 50 cycles. Upon removal from the assembly solutions the apparent contact angles of each substrate were very different. The ITO substrate that was functionalized with the electron deficient salt was very hydrophobic whereas the ITO substrate functionalized with electron rich salt was very hydrophilic (Figure 12). Kelvin probe measurements of the work function of the ITO surface indicated that assembly of different molecules changed the work function of ITO by 0.9 V (Figure 13). The electron rich diazonium salt demonstrated a work function value of 0.5 V (~0.1 V higher than bare ITO). The electron poor diazonium demonstrated a work function of -0.4 V. The addition of 45 extra cyclic voltammetry cycles did not change the work function value by much (<0.05 V).

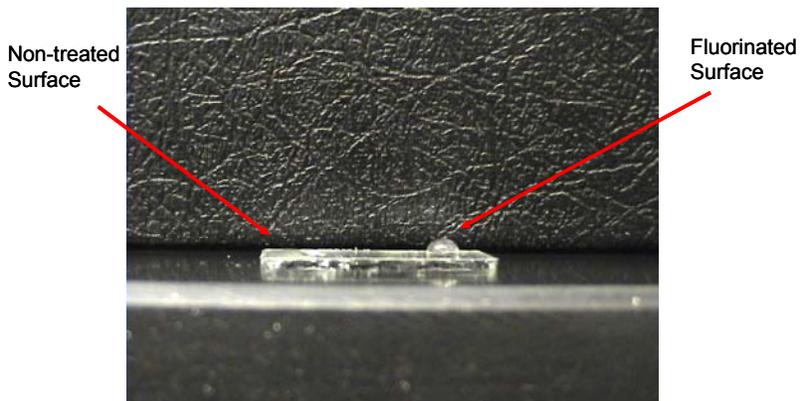


Figure 12. Hydrophilic surfaces on the left prepared using the electron rich salt, and hydrophobic surface on the right with the electron deficient salt.

Contact Potential Difference (CPD) for surface treated ITO

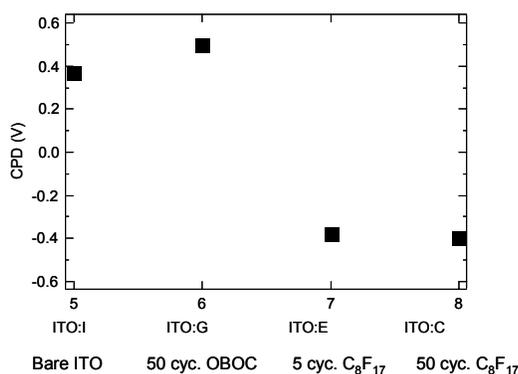


Figure 13. Kelvin probe measurements to determine the work function as a function of surface modification.

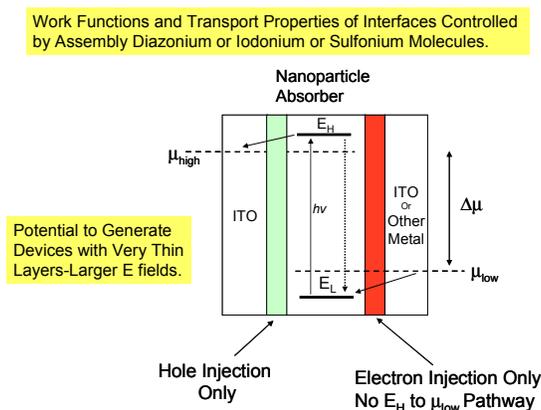


Figure 14. Idealized schematic of device structure to be achieved using the surface modification processes associated with bias directed assembly processes.

The goal of this final effort was to use diazoniums to modify surfaces to generate a device that behaves as shown schematically in Figure 14. This would result in a simpler manufacturing process and higher efficiency. Therefore, photovoltaic-like devices were constructed using the diazonium modified ITO surface as the electrodes. We believed we could improve the quantum efficiency of the device by minimizing exciton quenching and hole/electron recombination events using a blocking layer constructed from our layer-by-layer diazonium assembly processes. In this way devices were fabricated having the structure ITO/electron deficient diazonium/MEH-PPV + PbS/electron rich diazonium/ITO. The device was biased at 1 V and the photo-response was measured as the 200-W light source was turned on and off. Without bias, the device responded very slowly at current levels at the detection limit of our potentiostat. Bias was applied to speed the measurement process. The device response is shown in Figure 15. As with the earlier results, the slow response is presumably due to the relatively thick layers of the device. MEH-PPV is a very poor conductor with very low carrier mobilities. Additionally, the device contained significant parasitic capacitances from the experimental setup. The current change is 6% when exposed to the 200W light. Most

significantly, no switching was observed at 1 V without the diazonium functionalization (i.e. with only the MEH-PPV + PbS nanocrystals). This strongly suggests the validity of our hypothesis that the diazoniums could provide both an internal electric field and blocking layer, though considerable additional work will be required to fully realize this dream.

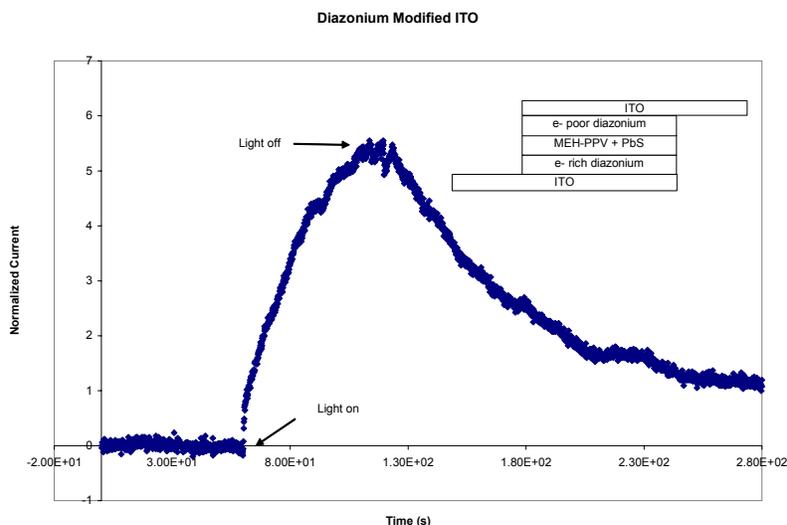


Figure 15. Response of an ITO/C8F17 diazonium/MEH-PPV + PbS/hydroxyl terminated diazonium/ITO photovoltaic device exposed to a 200 W wide spectrum light source.

4. Summary and Future Directions

This project resulted in the development of several new capabilities and clearly highlighted some areas for further research and development that will be required to develop a viable core competency in polymer electronics at Sandia National Laboratories. The team successfully demonstrated several all polymer electronic components, such as conductors, resistors, and diodes. The best performing devices were fabricated using syringe dispensing techniques. An ink jet printing capability was brought on line that has the potential to produce circuits with finer dimensions. However, jet-printable inks proved to be a larger challenge than originally anticipated, particularly for highly conductive and semiconductor polymers. Much better understanding of the materials science of these inks will be required to adequately address processing issues like line and thickness control, surface wetting, adhesion, and the like, along with the required electrical properties. Furthermore, air stability is a critical requirement. These things must be addressed before repeatable and robust versions of even the simplest electronic components will be realized.

The work on polymer based infrared sensitive devices looks promising, but again much work is still needed. We have developed a unique bias driven assembly method to create ultra thin photovoltaic-like devices by modifying ITO electrode surfaces using diazonium salts. A far-from-optimized device showed 6% change in current when exposed to a 200-W bulb. This technology has the capability to provide many advantages including the higher efficiencies and easier, lower-cost fabrication. Ideally, this approach will provide a means to realize cheap polymer photovoltaics that can utilize IR radiation. Such devices would be useful for both large and small scale power applications.

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Appendix A. Procedure for Handling and Use of DOW Z6030 Coupling Agent

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Dow Z6030 is available to us from Aldrich as # 440159. This material is classified as an organosiloxane, and is typically used to improve the adhesion between inorganic and organic surfaces.

For our purposes, it may be used to improve the adhesion between a plastic substrate such as PVC and various semi conducting aqueous based polymers suspensions such as PPY and PEDOT. It may also be used to improve bonding between materials such as FR4 circuit board material and various coupon materials.

Solutions of this silane in water are not stable for long periods of time, and should be discarded after a week. Store all reagent material and all solutions made from this material under inert gas.

Aqueous solutions of this material are typically 1% for our applications. In order to prepare this solution first make up a pH adjusted water base. To purified water begin adding glacial acetic acid drop wise until a pH of 4 is reached. You can then use this acidified water to make the silane solution.

Since these solutions have such a short shelf life it is best to make small batches, 30 ml quantities are ideal for this purpose. For a 1% solution, add 0.03 grams of silane to 29.07 grams of the pH-adjusted water.

Place the solution on a stirrer for at least 30 minutes, or until it hydrolyzes and forms a clear solution. After stirring, store under inert gas, and re-blanket with gas every time the bottle is opened.

Application of this material may be by brushing, wiping, airbrushing or any similar method that does not leave excess material on the substrate. After applying the silane, dry the surface at 100 degrees Centigrade for 15 minutes. The optimum application and drying conditions may vary for a particular process and material.

Semi conducting polymers are known for their unique electrical properties. However, these properties come at a price because of the unusual methods used to synthesize them. Electro deposition is often used to synthesize these materials. Because of this, these materials are highly insoluble in all but the most aggressive solvents.

Therefore, these materials are prepared as suspensions. Colloidal suspensions are dispersions of insoluble materials (usually less than 1 um) in a liquid that is suitable for delivery of the colloid to a substrate.

In order to prepare diodes using conjugated materials discreet amounts of one material must be deposited adjacent to another while maintaining electrical contact. Therefore, it is imperative that the surface properties of these materials conform to the design specifications of the diode.

As provided by the manufacturer these semiconductors are usually in the form of dry powders. They must then be sized for suspension by milling. In the past we have milled these materials using a mortar and pestle. While this method will reduce particle size, it often results in a “smearing” of the polymer on the walls of the mortar. This smeared polymer is very difficult to remove. Cold milling using dry ice and methanol in a mortar and pestle gives better results but collection is still difficult. The use of a cryo mill is an improvement, but even the smallest mills require fairly large amounts (two grams or more) of polymer and since these materials are very expensive this becomes a factor.

Once enough of the polymer has been milled it must be sized prior to deposition. Sizing is important because the suspension will fall out if the particle size exceeds the ability of the liquid it is suspended in to disperse it. Also, deposition equipment such as the Microfab Microjets we use relies on small diameter capillaries to deliver these liquids. Sizing is usually done by placing the polymer in the suspending/delivery liquid and then syringe filtering.

Addition of viscosity modifiers and wetting agents

The ideal polymer for semiconductor use must meet certain criteria:

- It must be a stable suspension
- It must be suitable for the deposition method being used
- It must wet the substrate if necessary, and wet the adjoining polymer
- It must be cost effective to produce and deposit
- It must have a reasonable shelf life
- It must produce a stable diode

Occasionally, methanol or other low boiling point solvents are added in order to enhance the ability of the suspension to wet the substrate or the adjacent polymer that has been previously deposited. It is noteworthy that solvent selection may be critical in these applications because while polymers must be located next to each other, they may not have certain electrical and physical interactions. Electrical shorting may occur when particles from one polymer layer are allowed to protrude into the adjacent layer. This may be the case when suspension liquids for one polymer have a high affinity to a previously deposited layer. The physical interaction between adjacent layers should be a subject of further study.

Wetting agents such as amines have also been used in order to promote adhesion of the first polymer layer to the substrate, and to “tie” interlaminar layers together. Again, the physical, chemical, and electrical interaction of adjacent layers is poorly understood and should be looked at in detail.

Viscosity modifiers such as cellulose, higher molecular weight alcohols, and clays have also been added to polymer suspensions to modify viscosity and improve deposition. Techniques such as this may reduce the intended electrical properties of a polymer because its volume fraction is reduced.

Suspension Processing

Cleanliness is of high importance in the preparation and deposition of these materials. Ideally, the highest level of cleanliness available and the separation of material streams will only add value to this process. Contamination of these materials while in production must always be assumed and a study must be conducted in order to assess the minimum requirements necessary to produce efficient stable diodes.

As mentioned above the cross contamination of discreet polymer layers may occur when one polymer layer is deposited next to another. Our experience has shown that this difficulty may be minimized by the post treatment of one layer before the addition of the next. Vacuum drying of deposited layers has shown that the thorough removal of a polymer's suspending fluid improves the interlaminar boundary characteristics of adjacent polymers. This improvement is probably the result of the surface conditioning that occurs as the polymer line dries, the surface tension effectively pulling the particles more closely together into a more organized packet and smoothing out the outer surfaces.

Addition of conductivity Modifiers:

Polypyrrole (PPY) has been our first choice as a conducting polymer. We have had the most success using polyaniline doped PPY which is dispersed in a polyurethane binder. Loadings of as high as 10% PPY have been deposited on a PVC substrate. We have experimented with two materials in order to improve the conductivity of the conductor, gold colloid, and carbon nano particles.

Water based colloidal suspensions of gold from 2-5 um have been added at loadings as high as 20 %. These materials have been easy to work with, go into suspension with the PPY and are not lost in filtration. In addition they do not degrade the physical properties of the deposited PPY. Their benefit is still being evaluated.

The addition of carbon nano particles in the form of tubes and spheres has also been the subject of experimentation. Although the single particles are very small, these materials are usually clumped together and must be processed before being added to a conductor. Some form of milling is usually required as is particle sizing of the milled material.

If the nano particles cannot be evenly dispersed in the polymer they will be removed during the filtration step. Also, addition of the nano particles lowers the liquid fraction significantly, which raises the viscosity. The viscosity must not exceed 20 cps or it becomes very difficult to deposit by Microjet or EFD system. Preliminary tests have shown that carbon nano particles improve the conductivity of the PPY but not significantly.

Single wall carbon nano tubes are highly conductive when placed in a dispersion that allows them to physically contact each other. Ongoing work should include experiments in which nano particles alone are dispersed in a binder, which is then deposited as a conductor in a diode.

Appendix B. Polymer Diode Process Description - Ink Formulation

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EQUIPMENT USED:

Fume hood, Three place balance, calculator, Ionized dusting source, Magnetic stirrer, Spin coater, Hypodermic syringes; Spatulas, Glassware, Notebook, Disposable polyethylene pipettes, Magnetic stir bars, Butyl rubber gloves, Wiping cloths, Syringe filters, Disposable screw cap beakers

MATERIALS USED:

Solvents: Methanol, Ethanol, Isopropyl alcohol, Methylene chloride, Water, Acetone, Chlorobenzene

Polymers:

PVP, Poly Vinyl Phenol, Aldrich # 43622-4
PPV, Poly Phenylene Vinylene (MEH), Aldrich # 54646-1
PPY, Poly Pyrrole, Aldrich # 48109-2
PEDOT, Poly ethylene dioxythiophene, HC Starck, Baytron P

MATERIALS STORAGE:

Store all organic solvents in a flammable storage container.

Store all polymer materials in a cool dry place.

DISCRIPTION OF PROCESS:

All balance weights are made to three decimal places.

PVP: A 3% suspension in ethanol. Place an uncapped disposable beaker on the balance and tare it. Weigh out 0.900 grams of the polymer into the beaker. Add 29.100 grams of ethanol to prepare a 3% solution by weight. Add a one inch magnetic stir bar, replace the cap. Label and date the cap. Place the suspension on the stirrer and blend for one hour at room temperature and a setting of four.

Stop the stirrer. Place a one micron syringe filter on a 50 milliliter syringe. Remove the plunger and pour the PVP suspension into the syringe barrel. Filter the suspension into a 30 milliliter amber wide mouth bottle with a Teflon gasket in the lid. Label and date the cap.

PPV: Prepare a 1% suspension. Place an open disposable beaker in the balance and tare it. Weigh out 0.300 grams of the polymer. Add 29.700 grams of chlorobenzene to the beaker. Add a one inch stir bar. Cap the beaker. Label and date the cap. Place the beaker on the stirrer and blend for four hours at room temperature at a setting of four.

Place a five micron syringe filter on a 50 milliliter syringe. Remove the plunger and pour the PPV suspension into the syringe barrel. Filter the suspension into a 30 milliliter amber wide mouth bottle with a Teflon gasket in the lid. Label and date the cap.

PPY: Prepare a 50% dilution. Place the polymer reagent container on a wrist shaker and shake for one half hour. Place 15 milliliters of the polymer material in an open disposable beaker. Add 15 milliliters of 2:1 solution of methanol to distilled water and a one inch magnetic stirrer. Cap the beaker. Label and date the cap. Place the beaker on the stirrer and blend for one half hour at a setting of four at room temperature.

Place a five micron syringe filter on a 50 milliliter syringe. Remove the plunger and pour the PPY suspension into the syringe barrel. Filter the suspension into a 30 milliliter amber wide mouth bottle with a Teflon gasket in the lid. Label and date the cap.

PEDOT: Remove the reagent from the bottle by pipette. Use care not to collect any dried material that may be on the sides of the bottle or floating on the surface. Place an open beaker on the balance and tare it. Weigh out thirty grams of the reagent.

Place a five micron syringe filter on a 50 milliliter syringe. Remove the plunger and pour the PEDOT suspension into the syringe barrel. Filter the suspension into a 30 milliliter amber wide mouth bottle with a Teflon gasket in the lid. Label and date the cap.

MEASUREMENT:

These materials must be printable using a 30 um Microjet. A Microfab Microjet controller and the proper software and jetting parameters must demonstrate that the material can be successfully printed before delivery to the printing facility.

PVP is an insulator. When applied and cured to a thickness of between 50 and 100 microns between two gold surfaces resistivity should be in the Mohm range.

PPY is a conductor. When applied and cured to a thickness of between 50 and 100 microns on a non conductive surface such as glass, conductivity should be in the Kohm range.

PPV is a semiconductor. Applied and cured to a thickness of between 50 and 100 microns on a glass surface.

PEDOT is a semiconductor. Applied and cured to a thickness of between 50 and 100 microns on a glass surface.

Appendix C. Preparation and Dispersion of Polymers for Use as Diodes when Applied to Organic Substrates

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POLYMERS CURRENTLY IN USE ARE:

- PVP, Poly (4-vinylphenol), CAS # 24979-70-2
- PPV, Poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-vinylene], CAS # 177716-59-5
- PPY, Polypyrrole, CAS # 51325-03-2
- PEDOT, A mixture of: Poly (styrene sulfonate), and, Poly (2,3-dihydrothieno[3,4-b]-1,4-dioxin), CAS # 155090-83-8

The above materials are purchased from Aldrich Chemical Co.

SUSPENSIONS ARE MADE AS FOLLOWS:

- PVP, 3% in methanol
- PPY, 10% in a 2:1 solution of methanol and water
- PPV, 1% in chlorobenzene
- PEDOT, diluted 1:3 with water

The above suspensions are filtered using Teflon media syringe filters with polypropylene holders. The PVP, PPY, and PEDOT suspensions are filtered with 1-micron filters, while the PPV suspension is filtered with a 5-micron filter.

Density measurements are made of the filtrates and this information is then used in calculating the viscosity of each filtered suspension. Currently, density and viscosity measurements are available for the following suspensions:

<u>Polymer</u>	<u>Density g/ml</u>	<u>Viscosity cps</u>
PEDOT	0.993	6.26
PVP	0.817	2.05
PPY	0.989	1.266
PPV	1.107	23.6

The following are suspension costs/ml based on current pricing from Aldrich including the price of solvents:

- 3% PVP in methanol = \$0.085
- 10% PPY in 2:1 methanol: water = \$0.053
- 1% PPV in chlorobenzene = \$3.47
- 33% PEDOT in water = \$0.136

PROCEDURE FOR PREPARING SUSPENSIONS:

Polymer materials are considered to be light and temperature sensitive. All materials should be processed at the lowest temperature possible. Store all neat polymers and suspensions in amber glass containers. Subsequent storage shall be in "inert" materials such as glass, Teflon, or polyethylene. All procedures utilize clean glassware and facilities. Follow all standard safety practices in using chlorinated solvents including hand and eye protection and the use of a fume hood. Treat all waste as hazardous material and dispose of properly.

All polymers are taken from their original containers and placed in clean covered beakers where they are diluted with the appropriate solvent on a weight-to-weight basis. A stirring bar is added and the suspensions are made on magnetic stirrers.

After the entire polymer has dispersed, the suspensions are placed in glass syringes and filtered using syringe filters. Filtrates are collected in amber glass bottles with Teflon gasketed lids and labeled.

Portions of the filtrate are then taken and measured for density using one and two milliliter volumetrics. After calculating the density, Gilmont style viscometers are then used to calculate the viscosity.

Suspensions are then taken from these bottles in order to fill the supply syringes located on the Newport/Microfab dispensing equipment.

Appendix D. Preparation of an Insulator For polymer Diodes using Shellac and Ethanol

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Department 06245
8/23/05

POLYMER:

- Shellac, available from Pangaea as “Flake shellac, dewaxed SSB56 Pharma, CAS #Nr. 9000-59-3

COLORANT:

- Coomassie brilliant blue G-250, available from Acros #1914-0050, CAS #6104-58-1

SOLVENT:

- Ethanol, Available from McCormick Distilling, CAS #64-17-5

EQUIPMENT:

- Chemical fume hood
- Nitrile rubber gloves
- Safety glasses
- Analytical balance
- Spatulas
- 20 ml borosilicate glass vials with polyethylene lined lids. Available from VWR as #66022-130
- 10 ml polypropylene syringe
- Filter, Pall Acrodisc 25 mm 5 um acrylic copolymer media
- Magnetic stir bar, VWR #58948-116
- Burrell wrist action shaker, model 75, set to hold vials at a 7” radius

PROCEDURE:

- Weigh out 0.75 grams of shellac into a vial.
- Weigh out 0.075 grams of Coomassie blur into the same vial.
- Weigh out 14.25 grams of ethanol into the same vial.
- Place a stir bar into the vial and replace the lid.
- Place the vial on the shaker and shake for one hour.
- Filter the solution into a clean vial.

YIELD:

Approximately 15 ml of a bright blue translucent free flowing liquid.

NOTES:

In most cases 0-.75 grams of shellac will dissolve in this amount of ethanol in one hour on the shaker. The shellac flakes from the manufacturer may vary from small particles to flakes the size of a dime. To aid dissolution you may wish to break-up or grind the flakes with a mortar and pestle.

Appendix E. Preparation of Synthetic Metal using Agitation

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8/22/05

Polymer diodes are currently being deposited on polymer substrates. Several types of semi conducting polymers as well as polymer insulators are deposited by ink jetting on PVC. The most conductive material we are currently using is called "Synthetic Metal". It is a mixture of three compounds including solvents designed to disperse and solubilize the polymers resulting in a synergistic effect between polymers which improves conductivity.

POLYMERS:

- Regioregular poly 3 hexyl thiophene. Available from Plextronics as Plexcore #P3HT, Lot # 05-10289, phone #724-612-1708.
- BARF, Sodium Tetrakis(3,5-bis (trifluoromethyl) phenyl) borate. Available from Sigma-Aldrich, CAS #79060-88-1, phone # 314-771-5765.
- MC60, Modified Fullerene, Available from American Dye Source as #ADS61BFA, phone # 514-457-0070.

SOLVENTS:

- THF, Tetrahydrofuran. Available from Acros as #326970010, CAS #109-99-9.
- Styrene, available from Acros as #13279-0010, CAS #100-42-5.

EQUIPMENT:

- Chemical fume hood
- Nitrile gloves
- Analytical balance
- Spatulas
- Polypropylene syringe
- National Scientific Target 25 mm syringe filters, 5 um, Teflon media with polypropylene body
- 20 ml borosilicate glass vials with polyethylene lined lids. Available from VWR as #66022-130
- Magnetic stir bar, VWR #58948-116
- Burrell wrist action shaker, Model 75, set to hold vials at a 7" radius

PROCEDURE:

- Weigh out 0.1672 grams of the poly 3 hexyl thiophene in the first vial. Add 3.1 grams of THF. Add a stir bar to the vial, cap, and shake for 15 minutes.
- Weigh out 0.2053 grams of BARF into the second vial, add 3.1 grams of THF. Cap the vial and shake for 15 minutes
- Weigh out 0.1664 grams of MC60 into the third vial, add 3.0 grams of styrene, add a stir bar to the vial, cap, and shake for 15 minutes.
- Next combine the MC60 solution with the thiophene solution, and finally add the BARF solution to the first two. Add one stir bar, cap, and shake for 15 minutes.
- Filter this mixture into a clean vial using the syringe and the 5 um syringe filters. It may take two filters to do so.

YIELD:

Approximately 10 ml of a blood red/purple free flowing liquid.

NOTES:

- The National Scientific filters used in this procedure are no longer available. Due to the highly polar nature of these solvents an inert media such as Teflon, glass or perhaps cellulose may be used.
- BARF is currently synthesized by David Wheeler at Sandia National Laboratories.
- Store styrene under refrigeration.

Appendix F. Procedure for Preparing a PPV Ink with Cyclohexanone

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8/22/05

PPV is one of the polymers used in the fabrication of polymer diodes. This material is very difficult to dissolve due to its inert chemical structure. At this time it is not clear if some of the semi conductors we use are deposited as suspensions or true solutions. In the past many highly polar solvents such as chlorobenzene, chlorostyrene, and methylene chloride have been used in an effort to dissolve these materials. Unfortunately these solvents often re-dissolve previously deposited polymer inks or the polymer substrates they are printed on. In an effort to eliminate some of these issues we are constantly searching for solvents which can solubilize the polymer without adversely effecting previously printed lines or substrates. We are also interested in solvents that are more user and environmentally friendly. Cyclohexanone has been shown initially to have these benefits.

POLYMER:

- D1 PPV, Poly[2,5-bis(3,7-dimethyloctyloxy)-1,4-phenylenevinylene]. Available from American Dye Source as #ADS300RE, phone # 514-457-0070.

SOLVENT:

- Cyclohexanone, available from Fisher as #02109-1, CAS #108-94-1

EQUIPMENT:

- Chemical fume hood
- Nitrile gloves
- Safety glasses
- Analytical Balance
- Spatulas
- 20 ml borosilicate glass vials with polyethylene lined lids. Available from VWR as #66022-130
- Mortar and pestle
- Burrell shaker model 75, set to hold vials at a radius of 7"
- Hot plate/stirrer available from VWR as # 33920-236
- Magnetic stir bar available from VWR as #58948-116
- Polypropylene 10 ml syringe
- 25 mm syringe filter with an acrylic copolymer 5um membrane available from Pall as Acrodisc #4489T

PROCEDURE:

- Place the mortar and pestle in the freezer for at least one hour.
- Take about 0.250 grams of PPV and place in the mortar and pestle. Gently grind the polymer up in such a way as to minimize the appearance of large granules without smearing the polymer on the surface of the mortar and pestle.
- Weigh out 0.156 grams of PPV into a vial.
- Add 9.844 grams of cyclohexanone to the vial.
- Place a stir bar in the vial and replace the cap.
- Shake for one hour.
- Allow mixture to stir on a magnetic stirrer at a setting of 5 overnight or for about 16 hours.
- Place vial on shaker for one hour.
- Filter solution into a clean vial using the syringe and syringe filter.

YIELD:

- Approximately 10 ml of a bright orange free flowing liquid.

NOTES:

- It is helpful to chill the mortar and pestle before grinding the PPV. The cold surfaces tend to keep the polymer from smearing as it is being ground.
- The PPV as supplied from ADS is granular. It is not uncommon to see particles as large as small peas to some as fine as dust. This procedure makes a 1.5% solution. Higher concentrations may be possible; however it is best to grind up any large clumps of polymer to aid dissolution.
- The acrylic copolymer syringe filters are used because the cyclohexanone does not appear to dissolve this material. Use caution when selecting filters and laboratory apparatus that come in contact with solvents to prevent cross contamination.

Appendix G. The Preparation and Production of Semiconducting Polymers for Ink Jet Application

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Currently there are four materials being printed by the ink jet technique in order to produce electronic devices. These materials are:

- Shellac,
- “Synthetic metal”,
- Poly(anilinesulfonic acid), or PANI
- Polyphenylenevinylene, or PPV

Since the beginning of this project various materials have been tried. Practitioners of this art are constantly contrasting electrical properties with “jet ability” in order to obtain the most highly efficient devices. MSDS information for these compounds are included as part of this report

In most cases semi conducting polymers are difficult to synthesize (usually by electrodeposition), and are consequently difficult to dissolve. Many of the inks we have formulated are actually suspensions. Because of this difficulty, it behooves the practitioner to precondition polymers and “solvents” whenever possible.

The PPV is provided to us as small clumps and fines. Solvents or suspension liquids are chosen which will not adversely dissolve a previous line while still having the ability to solubilize or suspend the polymer. In addition viscosities which work best are in the one to two hundred centipoise range.

Preconditioning of the polymer may include cry grinding, wet milling, and particle size segregation in order to ease difficulties in suspending or solubilizing and to produce more uniform particle size inks. Milling equipment such as a Bel Art Micro Mill, a ball mill, or a Dentsply Wiggle Bug is often used to break down polymer clumps. An Andersen Impactor may then be used to size and segregate the particles. Techniques such as sieving are not feasible because it requires large amounts of polymer which can be very expensive. Sieving also becomes ineffective when particle sizes less than 100 microns are needed.

Most semi conducting polymers are photo and temperature sensitive. After preparation it is best to store all inks in amber bottles which have Teflon gaskets. A Teflon gasket will prevent some of the very polar solvents used from dissolving gasket material.

Other than some of the above mentioned equipment, a traditional chemical laboratory environment is all that is necessary to safely prepare these materials. A fume hood, an analytical balance, hot plate, sonicator and sink are a must. Remember also that many of the solvents and polymers are considered hazardous and must be disposed of appropriately. Personal safety measures include the proper training of personnel, the use of gloves, lab coats and safety glasses, as well as conducting all chemical processing in the hood.

Most often we use 80 micron Microjets to dispense these inks. Typical jetting parameters for these materials are as follows:

- PANI 0.42 psi, 40 Hz, and 4 mm/sec.
- PPV 0.55 psi, 30 Hz, and 4 mm/sec.
- Shellac 0.21 psi, 30 Hz, and 4 mm/sec.
- SM 0.25 psi, 30 Hz, and 8 mm/sec.

The pressure refers to the head pressure applied to the syringe reservoir, and the speed is the traverse rate of the x-y table under the jet.

SHELLAC

This material is provided by Pangaea Sciences, 2962 Saint Malo Circle, Mississauga, Ontario, L5N 1S9, Tel 905-814-0798. A 5% solution is made up in pure ethanol, part # A406F-1GAL, available from Fisher.

Shellac flakes are first weighed into a vial after which the ethanol is added. The vial is capped and placed in a wrist shaker for one hour. After this time the flakes will have dissolved. To the raw solution a sufficient quantity of Arcos # 1914-0050 Coomassie Brilliant Blue is added to form a 0.5% solution. This product is available from Fisher Scientific, 1-800-766-7000. This coloring agent is added so that the printing staff may more easily see the shellac line as it is being printed, and so that optical micrographs will reveal the shellac line as well. The vial is then placed on the wrist shaker for 45 minutes. The solution is then placed in a syringe and filtered using a 25 mm syringe filter such as the Gelman Acrodisc PN 4489T. This material is then stored at room temperature in amber glass bottles with Teflon gaskets.

SYNTHETIC METAL

This material is a combination of:

- Regioregular poly 3 hexyl thiophene from ADS located at 555 Morgan Blvd., Baie d'Urfe, Quebec, Canada.
- Tetrahydrofuran, part # 320970010 by Acros/Fisher.
- Sodium tetrakis (3, 5-bis (trifluoro methyl) phenyl) borate, known as BARF, part # 72017, made by Fluka, available from Sigma-Aldrich through Fisher.
- Modified Fullerenes or MC60, # ADS61BFA, available from ADS.
- Styrene, # S-497-2, from Aldrich/Fisher
- 4-Chlorostyrene, known as 4CS, part # C71203-50G available from Aldrich/Fisher

To 0.1672 grams of regioregular poly 3 hexyl thiophene add 3.1 grams of THF. With a bit of heat on the hot plate it will readily dissolve. This is about a 5.4% solution. In another vial mix 0.2053 grams of BARF with 3.1 grams of THF which dissolves instantly. This is about a 6.5% solution.

In a third vial place 0.1664 grams of modified fullerenes and add 3.0 grams of styrene to this. Use ultrasonics and low heat several times to effect a consistent mixture.

Pour all three solutions into one of the bottles, shake it and filter using a glass syringe and a 5 micron Teflon membrane filter. Gelling is typical of polythiophene, but not generally in such dilute solutions. Add 4 grams of styrene to the mixture and 2 grams of 4-chlorostyrene to resolubilize. Store this material in amber glass containers with Teflon gaskets and refrigerate.

POLY (ANILINESULFONIC ACID)

This material is available from ADS as # ADS650WP and used straight from the bottle. Store this material in amber glass containers.

POLYPHENYLENEVINYLENE

This material, PPV, is available from ADS as # ADS300RE. It is combined with 4-chlorostyrene. To prepare a 1.5% solution. Combine 0.154 grams of the PPV with 0.946 grams of 4CS. Place on the wrist shaker for one hour, remove, and sonicate cold for 15 minutes. Place back on the wrist shaker for one hour, remove and sonicate for 15 minutes cold. Transfer the solution to a 10 cc syringe and filter through a Teflon membrane 5 micron filter. Store this material in the refrigerator in an amber glass container.

PRELIMINARY TESTING

Several methods may be used in order to evaluate an inks suitability as an electronic component. At best it should be a stable compound not prone to degradation. Since these solutions consist of mainly organic substances they tend to be susceptible to thermal and ultraviolet cross linking and cleavage. Storage in amber glass bottles at room temperature or below room temperature in some cases is necessary. And, since some of the solvents used to dissolve the polymers may be very polar, inert materials such as Teflon should be used for the storage containers and for the bottle lid gaskets.

During processing when using very polar solvents care must be taken to ensure only inert materials are allowed to contact the ingredients. For example during filtration syringes with polypropylene barrels and plunger rods are usually sufficient. Most medical type syringes use butyl rubber plungers which may dissolve in some of these solvents. In that case, syringes with polyethylene plungers or glass syringes with Teflon plungers are best. As discussed earlier, filtration may be difficult if the pore size of the filter is less than 5 microns. Some solutions/suspensions of PPV at greater than 1.5% regardless of solvent have been very viscous. Also, due to the cost of the polymer only small quantities are

prepared. Therefore syringe filtering is best. When solvents such as chlorostyrene or chlorobenzene are used a Teflon filter media is a must. The only supplier of these filters in the 5 micron size is National Scientific's Target brand. These filters are no longer available. We may have to either use break-down filter holders with Teflon media, or reformulate with less polar solvents.

It is always best to pretest a new ink prior to delivery to the printing lab. Ensuring that the ink will jet properly and that it has the basic electrical properties necessary to be successful in printing will save time and expense. Most often a line of ink may be hand applied to a substrate such as PVC with a syringe or small brush to assess its ability to wet the surface. Its physical characteristics after it dries should also be noted. If these parameters meet standards, ink lines are then drawn which after drying may be tested electrically. This testing may be done using a volt-ohm meter and gold contacts. This test is very crude and will only indicate trends in conductivity. If this test meets standards a film of the material may be spun. Four point probe testing may then be done to establish its value as a semi conductor

If the ink in question passes these preliminary tests it is then placed in the formulating lab's printer and tested to establish parameters such as traverse speed, frequency of the piezo oscillator, and head pressure. Lines must also be examined for width, height, wetting, and boundary. If the ink meets these requirements application over other ink lines should also be checked to verify compatibility in the stack. Diode or other types of electrical testing may then be done before transferring the ink to the printing staff.

Distribution

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