

Printing of Organic-Based Photonics and Electronics Demonstrated

Functional organic materials have been gaining ground in many technologies including photonics and electronics, most recently in the development of organic light-emitting devices (OLEDs). Because they form the pixels of displays, these are the basis for a class of ultrathin, lightweight, wide-viewing-angle, low-power-consumption displays that can be made on any kind of substrate, including plastic foils, promising displays that can be folded or rolled up.

The two classes of OLEDs are molecular-based and polymeric-based. Regardless of their class, OLEDs have a simple architecture. They consist of a multilayer structure built on a given substrate. A typical polymeric-based OLED structure, or PLED, is shown in Figure 1. The electrically conducting and light-emitting polymer layer is normally spin-coated from solution on the surface of glass coated with indium–tin oxide (ITO), followed by the deposition of a metal electrode. On application of a forward bias, the electrons are injected from the metal side and the holes from the ITO side. The charges drift under the influence of the electric field and recombine on parts of the polymer to form excited states that may result in light-emission upon relaxation to the ground state.

Spin-casting and physical vapor deposition (PVD) have been the most commonly used techniques in the fabrication of OLEDs. However, there is a need for lower-cost and more versatile fabrication techniques. This is particularly required for low-information-content displays including signs and logos as well as general lighting. One added advantage of organic materials is that they lend themselves to simple printing technologies such as screen printing and ink-jet printing. In screen printing, similar to ink-jet printing, the use of materials is minimal because materials are only directed to the printed areas. On the other hand, in spin-coating and vacuum-deposition, no control can be exerted to direct the materials to deposit only on the desired areas without complicated and costly masking systems. Therefore, the ratio of lost materials to that of materials defining the active device area is significant in the latter techniques.

Unlike ink-jet printing, screen printing is relatively rapid and more versatile. The elements of screen printing consist of the

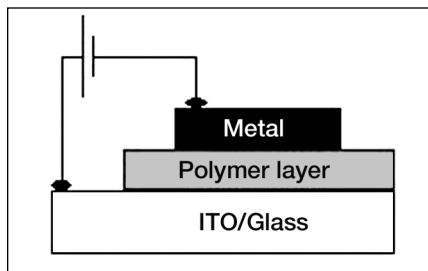


Figure 1. A typical structure of a single-layer polymeric-based light-emitting device.



Figure 2. Screen-printed polymer for light-emitting applications.

screen, stencil, squeegee, ink, press bed, and substrate. Although a relatively simple printing technique, the characteristics and quality of the printed image are greatly affected by a combination of variables including the printing speed, the angle and geometry of the squeegee, the distance between the screen and the substrate, and the mesh material.

As a fabrication process, screen print-

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ing offers the advantages of simplicity, affordability, speed, and adaptability. It can be applied with precision to virtually any surface.

Screen printing has been used as a deposition method for inorganic-based superconductors, solar cells, and sensor materials, for example. The potential benefit of this printing method for photonics was investigated recently when researchers at the Optical Sciences Center (OSC) of the University of Arizona demonstrated that screen printing could be an important tool in fabricating photonic devices that use organic materials. Specifically, fully functional OLEDs with light-emission at <5 V and a peak external quantum efficiency of 2.8% were produced (in unoptimized devices). Furthermore, the first generation of devices with a screen-printed hole-transport layer (HTL) showed an external quantum efficiency similar to that of devices with the same HTL that was deposited by using spin-coating methods.

Prior to this development, screen printing was known to be a relatively thick-film deposition technique. In this work at the OSC, the use of screen printing in the deposition of ultrathin layers of organic materials for OLED and photovoltaic fabrication was demonstrated. Films with a thickness of <20 nm and a surface roughness (rms) as low as 0.6 nm have been obtained. Figure 2 shows a polymeric screen-printed logo for light-emitting applications. The researchers used screen-printing on both hard and flexible substrates. They anticipate that this technique should be useful in roll-to-roll printing of organic photonic and electronic components for low-definition displays, signage, disposable electronics, and lighting.

Opportunities

The Multiscale Photonics and Electronics Group at the Optical Sciences Center, along with collaborators N. Peyghambarian, P. Calvert D. Sarid, and M. Descour, welcome the establishment of industrial collaborations for displays, photovoltaics, nanophotonics, biophotonics, nano data storage, and printing of photonic, electronic, and biomaterials for civilian and military applications.

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Striped Nanobarcodes™ Offer a Nanoscale Counterpart to Conventional Barcodes

Two pervasive trends have emerged in bioanalysis over the last few years: Researchers need to be able to conduct more experiments in parallel within a single sample (multiplexing), and do so in smaller and smaller volumes (miniaturization). Both trends are driven by the need to obtain the most information from diminishingly small volumes of complex samples, such as rare samples obtained from patients in clinical trials or studies designed to identify potential diagnostic markers for diseases, such as cholesterol for heart disease. Researchers at SurroMed of Mountain View, Calif., and the Pennsylvania State University have developed Nanobarcodes™, nano-sized particles that enable multiplexing capabilities in volumes as small as a few microliters or less.

Nanobarcodes are freestanding, cylindrical, metal nanoparticles, self-encoded with submicrometer-sized stripes (Figure 1). They are a nanoscale counterpart of conventional barcodes. While conventional barcodes are identified by the differential contrast of black and white stripes, Nanobarcodes are read under a conventional microscope using the differential reflectivity of various metals. By varying the physical dimensions (length and width), composition (number/type of metals), and striping pattern (number/width/order of stripes) of the nanoparticles, theoretically a library containing billions of different “flavors” can be synthesized. So far, seven different metals (Pt,

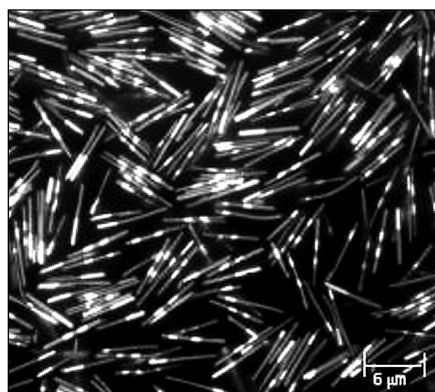


Figure 1. Microscope image of a “five-flavor” library of Nanobarcodes™ (average particle size 6–7 μm). The particles can be identified by their striping patterns due to the differential reflectivity of the metals used. For these pictures, up to eight different stripes and two metals (Au and Ag) were used.

Table I: Combinations of Symmetric Nanobarcode™ Particles with Stripes of Fixed Widths.

# of Stripes	2 Metals	3 Metals	4 Metals	5 Metals
1	2	3	4	5
2	3	6	10	15
3	6	18	40	75
4	10	45	136	325
5	20	135	544	1,625
6	36	378	2,080	7,875
7	72	1,134	8,320	39,375
8	136	3,321	32,896	195,625
9	272	9,963	131,584	978,125
10	528	29,649	524,800	4,884,375
11	1,056	88,938	2,099,200	24,421,875

Pd, Ni, Co, Ag, Cu, and Au) have been used to make particles with up to 13 stripes. Table I shows the possible number of different “flavors” that can be generated using five or fewer metals and 11 or fewer stripes of fixed widths.

Nanobarcode particles are synthesized by electrochemical reduction of metal ions into the cylindrical pores of silica or alumina membranes. Nanorods with specific striping patterns (e.g., gold-silver-gold-platinum) can be produced by alternating electrochemical reduction of the appropriate metal ions. Stripe width can be controlled by the number of coulombs passed in each electroplating step and is therefore—at constant coulombs per time unit—a function of time. After release from the membrane, the nanoparticles can be functionalized with a variety of immobilization chemistries, ranging from non-specific direct adsorption (e.g., of polymers or proteins) to more specific metal-adsorbate interactions such as those that occur in alkanethiol self-assembled monolayers (e.g., via the S atom in 11-mercaptoundecanoic acid). This enables coupling of a wide variety of capture reagents onto the Nanobarcode particles, ranging from specific capture reagents such as antibodies that bind certain proteins with high affinity to non-specific capture chemistries such as hydrophobic/hydrophilic, or acidic/basic interactions for capture based on chemical properties.

Nanobarcodes have a wide range of potential applications because these particles address both bottlenecks in bioanalysis—multiplexing and miniaturization. They also have high sensitivity and a large dynamic range. They combine the advantages of solution arrays—flexibility, scalability, and large dynamic range—with the high level of multiplexing provided by planar arrays (microchips). The technolo-

gy is therefore particularly suited to deconvoluting complex samples using a combination of specific, semispecific, and nonspecific capture chemistries.

Researchers at SurroMed typically utilize microfiltration membranes as templates for the electrochemical synthesis of billions of Nanobarcodes. However, these membranes may have nonideal properties for certain applications, such as a limited range of pore sizes and polydispersity of pore dimensions. To improve the variety and quality of the nanoparticles that can be synthesized, researchers at SurroMed are creating photolithographic methods to generate high-quality polymer templates for electrochemical deposition.

Also under development is a flow reader to identify Nanobarcodes by their striping pattern in flow at a rate of up to several thousand particles per second. The flow reader will enable analysis and sorting of biological samples in a highly multiplexed fashion.

In addition to applications in the life sciences, Nanobarcodes can potentially be used in a variety of non-life-science applications, such as barcoding documents, small parts, or explosives.

Opportunities

SurroMed is interested in licensing or co-development and commercialization partnerships to commercialize its Nanobarcodes for life sciences as well as for non-life-science applications.

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Laser Reactive Processes Produce Nanoscale Inorganic Materials and Coatings

The process of laser pyrolysis (LP) has been developed at NanoGram Corporation in Fremont, Calif., to synthesize complex inorganic compounds with uniform particle size in the range of 5–100 nm. Catalysts and carriers, capacitors, primary and secondary batteries, phosphors, electronically conductive inks, and photonics are a few examples of applications that have benefited from this technology. A range of complex and simple materials can easily be produced due to the versatility of the synthesis process. Materials such as TiO_2 , Si_3N_4 , LiFePO_4 , $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$, and rare-earth-doped glasses exemplify the flexibility of the technique.

In LP, precursors and process gases are combined, fed into a reaction chamber, and passed through a laser reaction zone (LRZ™). The LRZ is a well-defined region of high temperature where the homogeneous nucleation of particles takes place as the material reaches a cooler region and then exits. Using an industrial CO_2 laser, the laser beam is optically configured to create the LRZ. A schematic of the LP process is shown in Figure 1.

Key process-control parameters include system pressure, laser power, gas ratios, and reactant velocity. At least one of the process gases must be laser-absorbing. For CO_2 lasers, typical absorbers include ethylene, 2-propanol, and ammonia. System pressure can be varied, but typically it is below 1 atm. Gas ratios can be used to vary the final product. For example, using VOCl_3 as the precursor, phase-pure V_3C_7 , VO_2 , or V_2O_5 can be obtained by slight modifications of the process gases. The short residence time in the LRZ provides for rapid heating and quenching, thereby minimizing particle growth and producing nanoscale particles.

Starting materials are introduced into the LRZ as gases, vapors, aerosols, or a combination thereof. Using Al_2O_3 as an example, AlCl_3 vapor or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in water can be introduced into the LRZ. Prior to introduction, an aerosol precursor is atomized. For more complex compounds, determining the precursor chemistry becomes more difficult. The process also allows specific phases to be obtained. For example, the rutile (natural TiO_2 that can contain up to 10% iron) and anatase (natural crystallized form) phases of TiO_2 have been isolated independently

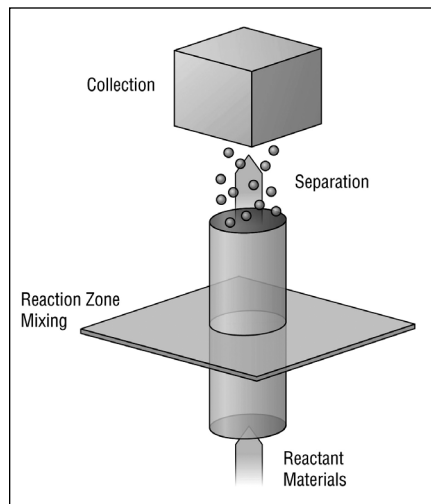


Figure 1. Schematic illustration of the laser pyrolysis (LP) process.

and separately from one another. The ability to tailor specific complex inorganic compounds exemplifies the capabilities of the LP process.

The ability to dope, substitute, and alter compositions of nanomaterial compounds is demonstrated in a series of alkali transition-metal oxides. Using the same starting materials, it is possible to produce varying compositions such as $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, $\text{Li}_2\text{Mn}_4\text{O}_9$, and $\text{Li}_4\text{Mn}_5\text{O}_{12}$. Al can be introduced into the compound, $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, to make $\text{Li}_{1+x}\text{Mn}_{2-y}\text{Al}_y\text{O}_4$. Substituting manganese for cobalt produces LiMnCoO_4 . This versatility can be applied to most complex compounds and applications.

The LP process is characterized by a narrow particle-size distribution. For example, the size of the nanomaterials produced can easily be varied from approximately 5 nm to more than 100 nm, while maintaining a similar distribution profile and the same material properties. The LP process can produce nanomaterials in mass, or the nanomaterials can be coated on a suitable substrate. When coated on a substrate, a variation of the LP process, laser reactive deposition (LRD™), is used. Substrates that can withstand the thermal transients without damage during deposition of nanoparticles include silicon, quartz, and alumina.

The substrate is passed through the LRZ to create a uniform coating of the desired nanomaterial composition. Figure 2 depicts deposition onto a substrate. Film thicknesses can range from 10 μm to 200 μm , with typical deposition times of seconds. Nanoparticle coatings from thin to very thick are obtained by limiting the flow of reactants or translating the substrate multiple times through the reaction zone. The LP process is being applied to the industrial production of complex inorganic nanomaterials. These materials can be coated by LRD processing or collected as a powder.

Opportunities

NanoGram Corporation is interested in establishing development collaborations with industrial companies that can utilize LP and LRD process methods to improve their applications.

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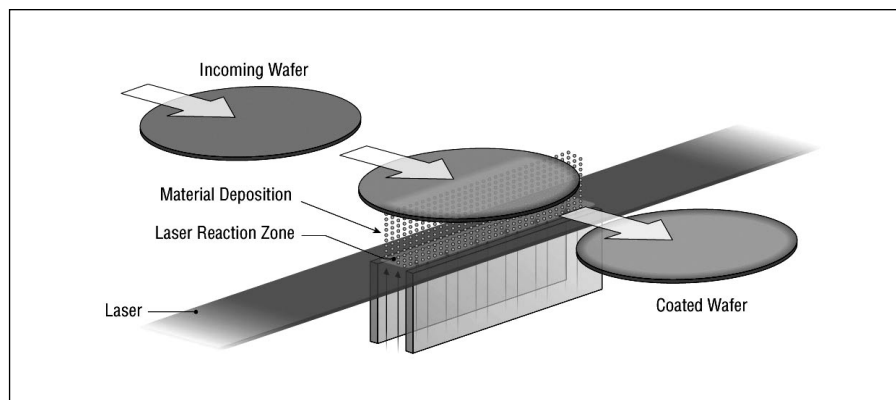


Figure 2. Schematic illustration of the laser reactive deposition (LRD™) process.