Printing Light Harvesting Biological "Devices" and other Functional Materials Applicable to Organic Photovoltaics

Jan L. Sumerel, FUJIFILM Dimatix, Inc., Santa Clara, California USA

Abstract

Many processing steps in the manufacturing of organic photovoltaics require solution processing. Inkjet printing is a facile method for depositing solutions into patterned thin films. Piezoelectric inkjet printing is a thermally consistent process, thereby protecting the tertiary structure of organic molecules that convert optical power to electrical power. We have taken several steps back from device manufacturing and worked out the details of inkjet printing light harvesting bacteria, more specifically photosynthetic cyanobacteria. Each individual single-celled organism is a functioning biological photovoltaic device that works with only the input of water as an electron donor for the photosynthetic reaction. In addition, these cells harvest photons from a variety of wavelengths so that they function more efficiently in heterogeneous light environments. An added bonus is that their byproduct is pure oxygen and conversely, they use C02 as a food source, thus removing carbon dioxide from the atmosphere. In these biological organic photovoltaic devices, a series of photochemical reactions occur through a thylakoid-containing internal membrane structure underneath their gelatinous cell wall. We will show the successful thin film patterning of these cells, and we will also show their light emission characteristics. In addition, we will show their carbohydrate production yields highlighting their ability to use light to form energy that can be converted easily into electricity. Finally, we will show other patterned thinfilms of organic photovoltaic relevant materials including conductive silver used in cathodes, carbon nanotubes used as transparent conductors, conjugated polymers used in the active layer and quantum dots, band gap acceptor materials that also function in non-white light environments. Finally, this talk will discuss the impact of inkjet printing on the photovoltaic market and highlight the research efforts of leaders in this field.

Introduction

It is no surprise that the advent of electronic displays has found such attractiveness to the general population. The impact of high resolution visual displays has been apparent as computer screens of all sizes beckon attention and compete with displays on TVs, cell phones, MP3 players, dashboards, exercise equipment, advertising media and cameras. Displays are here to stay, and new methods that facilitate high throughput production of these visually stimulating devices are dominating production lines. Inkjet printing is inherently compatible to high throughput. [1] Already, interesting technological phenomena have spawned from the patterning of structurally and functionally different materials including high performance ceramics. [2] For this reason, drop-on-demand inkjet printing, a simple fabrication process, has become a prominent player in materials processing for display components. The inkjet printable electronics market for these types of products is expected to reach over $30 billion by 2013. [3] However, it is a big step for display developers to jump into robust in-line manufacturing production systems. [4] This type of equipment requires a sizable financial investment plus sufficient experience so that manufacturing specifications and in-house knowledge can be established. Thus, a low cost, easy-to-use laboratory scale system is required for preliminary experimentation. This strategy then allows both substrate evaluation and on-site development and manufacturing of specific jettable fluids to occur simultaneously. FUJIFILM Dimatix has addressed this need for an R&D tool with the DMP that offers printhead maintenance, substrate alignment, nozzle inspection and drop analysis, and its ease-of-use for a variety of fluids has been demonstrated. [5]

New Wave Manufacturing: Low Cost Inkjet Printing

Just push print, the most common command for the desktop printer, can now be used in the laboratory or in manufacturing lines. Inkjet printing is a simple and cost effective technique with applications in the fields of electronics and biomedicine and has been shown to have specific applications in these industries. [6-8] In contrast to other multi-step production methods, inkjet printing is an additive process that precisely deposits metered quantities of fluid onto a variety of substrates including glass, silicon, plastics, organic thinfilms, and metals based on a user generated pattern. The resolution of the printed pattern is determined by a number of factors, including substrate/fluid contact angle, nozzle size, and lateral resolution of the printhead. [9] Inkjet printers can dispense fluid drops with volumes in the picoliter (pL) to microliter (mL) range, and an integral step in bringing this processing technique from the laboratory to manufacturing systems is the development of jettable fluids. The chemical properties of the fluid, including density, surface tension and viscosity, determine its jettability in a printer. [2] During drop formation, energy is distributed between the fluid's viscous flow, surface tension, and kinetic energy. [10] The deposited fluid volume is directly proportional to nozzle size. This flexibility enables microscopic patterned thinfilms of functional materials at a variety of resolutions. The physical properties of the patterned thinfilms (film thickness and pixel values) are dependent on the fluids coupled with the drive electronics of the printing device. In general, 2D drawings, pictures or structures, formatted as a bitmap image, can be translated into X and Y print coordinates for materials deposition (drop-on-demand). Each individual nozzle ejects a drop with a ligament. The ligament and the drop coalesce during flight to make a volumetric sphere and upon contact with the substrate, the sphere alters its three dimensional structure to become columnar. A resulting printed image is a compilation of drops where the third dimension is equal to film thickness, a physical property that is dependent on particle loading, drop spacing and drop spread. Once this critical but iterative R&D phase of process and material evaluation is complete to allow sustainable inkjet printing, the fluids are scaleable for production use.

Inkjet Printing Employing MEMS Devices

The required heating process for thermal inkjet printing (300°C) will damage thermally-sensitive materials, thereby limiting their use in devising functional devices. [7, 10] In contrast, using piezoelectric inkjet printing, temperature sensitive, functional materials are deposited under ambient conditions. Piezoelectric printheads contain a lead zirconate titanate (PZT) piezoelectric ceramic, nozzles, and a fluid chamber. When a voltage is applied to the PZT, mechanical vibrations create acoustic waves that in turn force fluid out of the chamber through the nozzles. [11] Piezoelectric printheads are categorized based on the deformation mode of the PZT (e.g., squeeze mode, bend mode, push mode, or shear mode). [12] At FUJIFILM Dimatix, the MEMS fabrication method for printhead production was adopted to increase the precision and resolution of the deposited materials. [13] These silicon devices increase jet-to-jet uniformity and drop placement accuracy. The inertness of the silicon expands the operating ranges to allow higher chemical diversity and fluid throughput expanding piezoelectric inkjet printing from the ability to print graphic inks to the realm of printing functional fluids required for display manufacturing.

With regards to the technological advances incorporated into the DMP from FUJIFILM Dimatix, a unique feature of this table-top printing system is the printhead itself. For the first time, FUJIFILM Dimatix is producing high performance MEMS printheads that are intended to have a limited lifetime, filled once by the user, and then discarded. The silicon chip that comprises the disposable printhead consists of 16 individually addressable jets that generate drops. These nozzles are spaced 254 mm apart, but actual drop spacing during printing is determined by the lateral resolution with tuned head angle. The inkjet printhead is powered by a piezoelectric unimorph, which is constructed in the plane of the wafer and consists of patterned PZT bonded to a silicon diaphragm. [11] The silicon chip is bonded to a molded liquid crystal polymer frame with an electrical interface. This construct is the jetting module portion of the printhead and snaps to the fluid module to complete the FUJIFILM Dimatix disposable cartridge. The fluid module is fabricated with a flexible polypropylene reservoir and protective rigid polypropylene housing. The volume of the reservoir is small (1.5 mL) to conserve expensive fluids. Fluid flows directly from the reservoir through a small column into the device in the plane of the wafer through a silicon acoustic terminator and then into a pumping chamber. The fluid then flows down a descender and out the nozzles perpendicular to the wafer plane. The silicon nozzle/air interface is coated with a proprietary non-wetting material to reduce wetting of low surface tension fluids and to facilitate printhead maintenance. The effective diameter of the nozzle is 21.5 mm; this nozzle size is approximated to generate 10 pL drops. An important operating parameter of this device is the negligible void volume due to the direct fluid/printhead interface.

Employing the Disposable Printhead for Fluid Development

Fluid flow properties like low viscosities, low boiling points, high surface tensions and non-Newtonian behaviors are hallmarks functional materials required for patterned thinfilms for display processing and are all generally unfavorable chemical characteristics for printing. For this reason, the Dimatix Drop Manager software was created to tune jetting parameters for these liquids. This software manipulates the parameters that generate the electronic signal to drive the movement of the PZT, including its frequency, wave shape, wave duration and voltage. Directing these parameters has provided a significant advancement in printing an array of functional materials and has been one of the areas of our research.

Printing Bacteria

In this paper, we have inkjet printed single celled bacteria. These single celled organisms were printed in growth medium as the fluid carrier. They were printed on both agar plates and silicon wafers and imaging was obtained using light microscopy.

Materials and Methods

Inks

Bacteria were grown in growth medium and then loaded into the cartridge for inkjet printing.

Substrates

Clean glass wafers were purchased from VWR (VWR Scientific, West Chester, PA). Single-side polished 150 mm silicon 100 wafers were obtained from Silicon Quest International (Santa Clara, CA) and sputtered with 300 nm gold layer using an Au target and a converted TES sputterer.

Printer

The DMP-2831 (FUJIFILM Dimatix, Santa Clara, CA) was used according to packaging instructions. The DMC-11610 (10 pL) and DMC-11601 (1 pL) cartridges were removed from their storage bags and after degassing, 1.5 mL of fluid was injected into the cartridge. The cartridge was manually placed into the DMP carriage. The Drop Watcher camera system was activated utilizing the Drop Manager software. The default spit purge spit cycle was repeated until pulsating fluid could be seen at the nozzle plate. The time of flight (TOF) of the ~10 pL drops was recorded using a built-in stroboscopic broad band white light emitting diode and a charge coupled device camera with a high resolution 4x magnification lens that has a spectral response of greater than 60% between 400 and 700 nm. The camera's field of view is approximately 1.2 x 1.6 mm. The strobe frequency was matched to the firing pulse frequency (1 kHz for this application), and the motion control software's built-in variable delay and drop refresh rates were employed for visualization.

Contact Angle Measurements

Contact angle measurements were carried out using a VCA Optima XE (AST, Billerica, MA). 2 µL samples were manually pipetted for the measurements. The sample position between the LED backlight and the computer-interfaced camera was adjusted for optimal height and focus and then video captured. The associated software fit the silhouette and calculated the contact angle.

Atomic Force Microscopy

Tapping mode AFM was conducted on a Digital Instruments Dimension 3100 using an etched silicon tip with a nominal radius of curvature of 10 - 20 nm. Scan sizes were varied, depending on the feature size. The scan rate was 0.1 - 0.3 Hz. The set point was set to 60 - 70% of the free-standing root mean square of the voltage of the oscillating tip.

Conclusion

The software interface and waveform tuning features make the DMP an ideal research and development inkjet printing tool that allows fluid process development. It possesses the features required to make inkjet printing of bacteria a cost-effective manufacturing process. The printing parameters have been demonstrated. Established operating parameters can now be translatable to production line systems with built in versatility, uniformity and scalability.

References

[1] H. Antoniadis, Low-Cost Solar Cells Exploiting Solar Ink, IEEE San Francisco Bay Area Nanotechnology Council Monthly Meeting, 2007, Santa Clara, CA, USA.

[2] J.A. Lewis, et al., Direct Ink Writing of Three-Dimensional Ceramic Structures, J. Am. Ceram. So, 2006, 89: p. 3599-3609.

[3] [cited 2007 January 20]; Available from: http://www.nanomarkets.net/news/pr_detail.cfm?PRID=195.

[4] [cited 2007 January 18]; Available from: http://www.cdtltd.co.uk/products__solutions/ink_jet_printing/91.asp.

[5] J. Sumerel, et al., Piezoelectric Inkjet Processing of Materials for Medical and Biological Applications, Biotechnol J, 2006, 1(9): p. 976-87.

[6] H. Sirringhaus, et al., High-Resolution Inkjet Printing of All-Polymer Transistor Circuits, Science, 2000, 290(5499): p. 2123-6.

[7] P. Calvert, Inkjet Printing for Materials and Devices, Chem. Mater., 2001, 13: p. 3299-3305.

[8] C. Haber, M. Boillat, and B. van der Schoot, Precise Nanoliter Fluid Handling System with Integrated High-Speed Flow Sensor, Assay Drug Dev Technol, 2005, 3(2): p. 203-12.

[9] J.H. Song, and H.M. Nur, Defects and Prevention in Ceramic Components Fabricated by Inkjet Printing, Mater. Proc. Technol., 2004, 155: p. 1286-1292.

[10] T. Xu, et al., Inkjet Printing of Viable Mammalian Cells, Biomaterials, 2005, 26(1): p. 93-9.

[11] J. Brünahl, and A.M. Grishij, Piezoelectric Shear Mode Drop-on-Demand Inkjet Actuator, Sens. Act. A, 2002, 101: p. 371-382.

Author Biography

Dr. Jan Sumerel is Manager for Biomedical Sciences at FUJIFILM Dimatix. Dr. Sumerel received her Ph.D. in Biochemistry and Biophysics at the University of North Carolina. She did her postdoctoral work at the University of California, Santa Barbara. As Director of Process Development at Invenios, Dr. Sumerel used 266 nm lasers to three-dimensionally micromachine photostructurable glass for the wafer fabrication of MEMS devices including printheads and biochips. She has a number of technical publications and US patents in the fields of biochemistry, molecular biology, and nanotechnology.