White Paper: Inkjet Printing of Zirconia Nanocomposite Materials

Peter Guschl, Ph.D., Applications Engineering Lab Manager

Xinyu Wang, Ph.D., Research Scientist

Michael Weinstein, M.Eng., Associate Product Manager

Pixelligent Technologies

6411 Beckley Street, Baltimore, Maryland 21224

Email: pguschl@pixelligent.com

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Abstract

The application of Pixelligent's PixClear® high-refractive index (> 1.7) zirconia nanocomposite films onto glass substrates by way of inkjet printing is discussed in this white paper. Two formulations are highlighted within: one formulation for optically clear films, and the other for OLED lighting internal extraction layers (IEL). The optically-clear nanocomposite formulation comprises zirconia nanocrystals (< 10 nm in diameter), a UV-curable binder material, and a high-boiling point solvent (DPG). The IEL formulation also contains zirconia nanocrystals, the binder and solvent but has added scattering particles. In this white paper clear films (> 90% transmission over the visible light range) and films containing scattering particles have been printed as uniform layers and patterned structures.

Introduction

When applying films on glass substrates for organic light-emitting diodes (OLED) for lighting and display purposes, there are a few common coating techniques: spin-coating, slot-die coating and inkjet printing. While each method offers discreet benefits and challenges within laboratory and manufacturing environments, PixClear® nanocrystals are compatible with each of these tools for application.

Spin-coating is a simple technique that deposits films on flat substrates by way of centrifugal forces generated by high rotational speeds [1]. Desired film thicknesses (on the order of 0.1 – 10 micrometers) are achieved for materials with specific viscosities at fixed spin speeds. Thicker films require slower spin speeds or an increase in the material's viscosity. The deposition of thin, sub-micron films on small substrates are also achievable for this technique. Spin-coating is a laboratory tool which is useful in manufacturing in a limited number of applications, most notably semiconductor photolithography. For most spin-coaters the substrate's length/width is limited to several inches, and even the most advanced spin coaters are not suitable for large substrates used in display or solar panel manufacturing. Similar to spin-coating, inkjetted specimens are subject to variations and defects that are dependent upon substrate cleanliness, the placement of the coating material and substrate, and the formulation consistency (e. g. viscosity, solvent content, drying rates) [2]. Finally, changes made to the formulation require adjustments of the spin coating speeds to maintain desired film thicknesses which increases the amount of time needed to produce multiple coated parts of consistent thicknesses.

Slot-die coating operates under the principle of metered flow of a coating material through a die with a slot at specific web velocities. Process control systems built into the slot-die apparatus allow for constant fluid temperature, uniform distribution of the fluid and a well-defined film layer width [3]. The advantages of slot-die coating make it appropriate for high throughput production and offers an efficient, economical coating process. Slot-die coaters can handle material viscosities in the 1 – 100,000 cP range, yielding film thickness from 1 – 1,000 micrometers. One disadvantage is that submicron films can be challenging for slot-die coaters, because the slot is required to be closer to the substrate. Close proximity of the slot to the substrate can magnify film thickness variations if the substrates themselves have surface variations.

Inkjet printing utilizes pressure-driven flow of a coating material through narrow (~10 – 20 microns in diameter) nozzles controlled by voltage changes on a piezoelectric membrane. This deposition method requires an optimized coating formulation that permits consistent ejection of droplets from the nozzles (i. e. no clogging, sufficiently low viscosity, etc.). Usually this requires proper solvent and co-solvent selection such that evaporation rates are balanced over the entire wet film after printing. A broad range of film thicknesses are achievable for inkjet printing, ranging as low as tens of nanometers and up to 100 microns for viscosity values from 1 – 25 cP. With heat applied to the inkjet cartridge higher viscosity materials could be deposited. As for other coating techniques the solids content and viscosity dictate the resultant dry film thicknesses. Some of the main advantages of inkjet printing are material conservation during deposition (i. e. the material is printed to where it is needed) and complex patterning of the printed material is entirely possible [4]. The advantage of patternability opens up possibilities for materials to be: 1.) printed only on defined regions of a substrate, 2.) applied in unique three-dimensional arrays including the use of different inks to build 3-D structures with spatial variations in their properties and 3.) deposited as specialized structures when employing appropriate surface chemistries between the ink and substrate. As is applicable for slot-die coating, direct heating applied to the intended substrate is extremely useful in preventing excessive wetting of formulations with high solvent content and high wettability to the substrate.

For this study, we demonstrate the ability of Pixelligent's zirconia nanocomposites to be inkjet-printed, emphasizing a new way in which high-refractive index materials are being incorporated into devices for OLED lighting and displays.

Methods

Substrate Cleaning

All substrates were glass and subjected to a cleaning procedure involving washing with a solution of detergent and water and isopropyl alcohol rinse followed by drying at room temperature.

Ink Preparation

Pixelligent PixClear® ink formulations used for inkjet printing are Pixelligent's Gen 1 and Gen 2 formulations for OLED lighting. The Gen 1 and Gen 2 formulations consist of zirconia nanocrystals with a UV-curable binder and solvent. The Gen 2 ink contains a scatterer, whereas the Gen 1 ink does not. The inks were prepared in the laboratory with appropriate dilution with propylene glycol methyl ether acetate (PGMEA) and dipropylene glycol methyl ether (DPGME) solvents to achieve viscosities for inkjet printing (1 – 20 cP). PGMEA and DPGME have boiling points of 146 and 190°C, respectively.

Film Drying and Curing

After inkjet printing the films were dried at 50°C for 5 to 10 minutes followed by an additional 1 minute at 100°C to remove the majority of solvent from the films. The dried films were UV-cured with an "H"-type Hg lamp at an exposure of 6 J/cm^2.

Instrumentation

The inks were printed on a Dimatix DMP 2800 inkjet printer (see Figure 1), using 1 and 10 picoliter (pL) cartridges. The nominal nozzle diameter for the 1 and 10 pL cartridges are 9 and 20 microns. Film thicknesses and film quality were affected by key inkjet parameters, such as, applied voltage for each nozzle, the slew rate (how fast the voltage is applied), the drop spacing on the substrate and applied heat of the printing surface/substrate.

Film thicknesses, non-uniformity and other film dimensions were measured with a Tencor Instruments P-2Long Scan Profiler. Film non-uniformity was calculated with the following equation

$$\%NU = \frac{L_{max} - L_{min}}{2 * L_{avg}} * 100\%$$

L_{max}, L_{min} and L_{avg} are the maximum, minimum and average film thicknesses. Fifteen thickness measurements were taken with the Tencor profiler. Micrographs were taken with an AmScope binocular compound microscope and Canon PowerShot S100 digital camera. Pictures of inkjet-printed Gen 2 films were taken with an Epson Perfection V600 photo scanner.

Figure 1. Dimatix DMP 2800 inkjet printer

Results and Discussion

Inkjet printing requires information regarding the ink formulation's wettability to the substrate. By printing an array of droplets onto the intended substrate, one can determine the size of the droplets after they have wetted and dried. Figure 2 shows 254-micron drop arrays for the Gen 1ink formulations. For the Gen 1 formulation the droplets were estimated to have diameters of around 120 microns after wetting onto a cleaned glass substrate. Drop spacing is a crucial parameter for ink jet printing and can affect overall film thickness (for blanket films) and film uniformity. By adjusting the drop spacing between 5 and 60 microns (Figure 2), a wide range of film thicknesses between 70 nm and 7 microns resulted for the Gen 1 inks. High drop spacings can affect the film quality and give rise to visible non-uniformities in the form of lines in the film, suggesting that there was insufficient overlap of adjacent droplets. Conversely, when the drop spacing is low (~ 5 – 10 microns) the overlap between neighboring droplets is quite significant and gives rise to high wet film thicknesses. When wet film thicknesses are high, then a lot of solvent is required to evaporate. Film qualities tend to be poor when films require long times to dry. The majority of uniform films (with calculated non-uniformity between 10 – 20%) were printed with drop spacings of 15 – 25 microns.

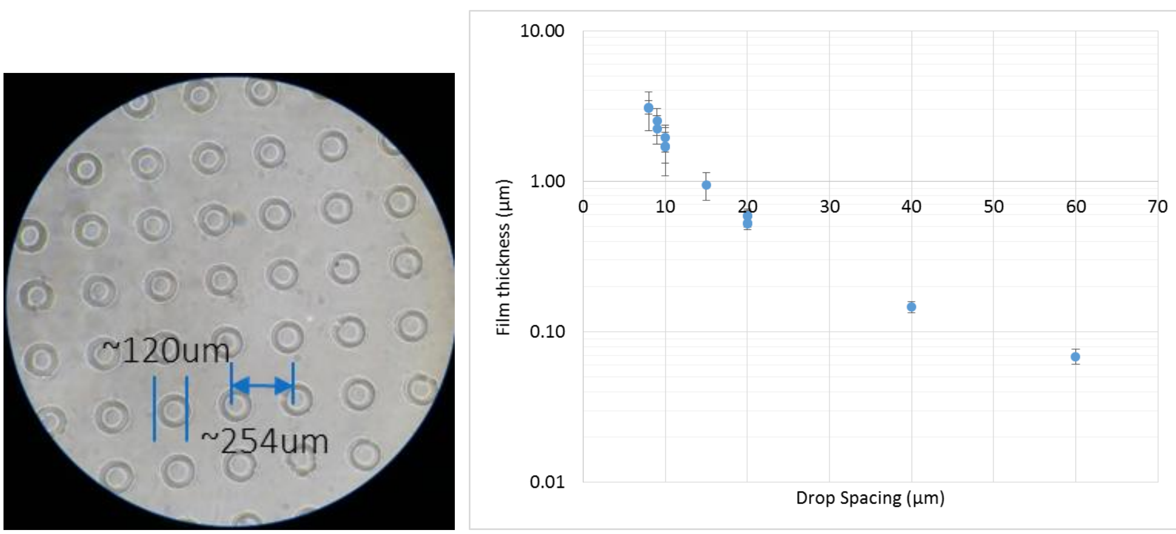

Figure 2. Optical micrographs of drop arrays of Gen 1 ink on glass at 40x magnification (left) and film thickness dependence on drop spacing for Gen 1 inks

Another important property of inks that are printable via inkjet is latency. Latency refers to the ability of an ink to be printed at a moment and subsequently printed at later moments without any adverse issues with the nozzles of the inkjet cartridge. In order to demonstrate latency for our Gen 1 ink, an experiment was initiated by printing at four different time intervals over a 5-hour time period. Thin films of 0.55 microns were printed initially at t = 0, 15, 60 and 300 minutes, by using the ink in a single cartridge. Figure 3 demonstrates the consistency of producing film thicknesses between 0.5 and 0.6 microns with film non-uniformities of less than 12%.

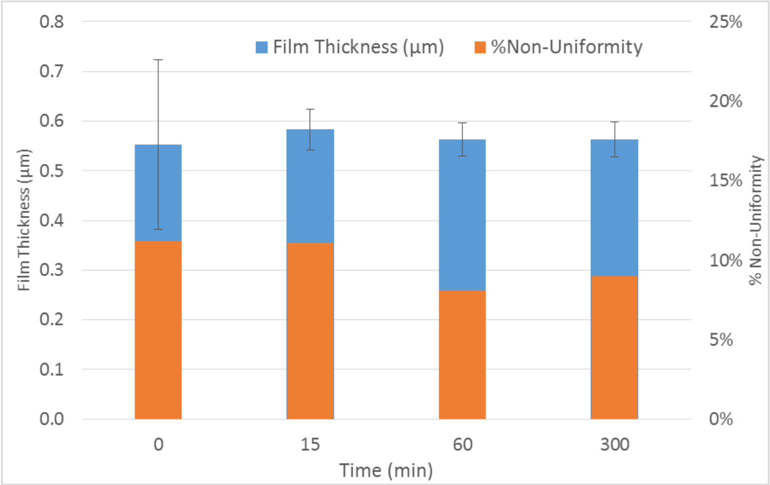

Figure 3. Graph of latency experiment for Gen 1 ink

Gen 2 inks can be inkjet-printed as films and structures for the purpose of improved light extraction in devices for OLED display and lighting. For consistent firing of the inkjet nozzles in the cartridges the use of DPG as the main solvent has proven to be most beneficial. Figure 4 shows four different patterns of the Gen 2 ink material at thicknesses of approximately 2 – 3 microns.

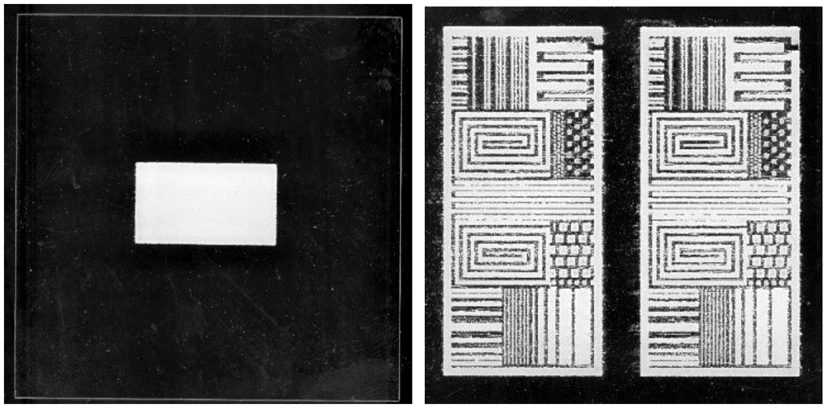

Figure 4. Examples of patterns printed with Gen 2 formulations: a small rectangle (left), Dimatix preset pattern on 2.5” x 2.5” glass substrates (right)

Conclusions

The Pixelligent Gen 1 and Gen 2 formulations are effective inks for inkjet-printing. Inkjet-printed, optically-clear films with high-refractive index containing Pixelligent’s PixClear® zirconia nanocrystals show excellent uniformity and are achievable with Gen 1 inks that can be printed numerous times with remarkable consistency (latency). We have also demonstrated that films comprising scattering particles in addition to the PixClear® zirconia nanocrystals can be printed into various simple and complex patterns. Information from this white paper give strong support that these materials can be extremely useful as light extraction layers in optoelectronic devices.

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