

# Photosensitive Materials with Zirconia Nanotechnology

**Hiroki Chisaka<sup>1</sup>, Kouichi Misumi<sup>1</sup>, Dai Shiota<sup>1</sup>, Katsumi Ohmori<sup>1</sup>  
Lei Zheng<sup>2</sup>, Robert J. Wiacek<sup>2</sup>, Z. Serpil Gonen Williams<sup>2</sup>**

<sup>1</sup>Tokyo Ohka Kogyo Co., Ltd., Kanagawa, Japan  
<sup>2</sup> Pixelligent Technologies LLC, Baltimore, US

Keywords: High reflective index (HRI); Zirconia (ZrO2); Flexible; Photo-patternable; Inkjet

### ABSTRACT

The combination of ZrO2 nanocrystals and photosensitive technologies led to new photosensitive materials and inks with high refractive index and inkjet properties superior to conventional materials. Moreover, high resolution and high transparency was achieved even with thick films. This material is useful for next generation applications such as flexible displays.

### 1 INTRODUCTION

In recent years, in the flat panel display (FPD) field, the main panel system has been dramatically undergoing change from liquid crystal (LCD) to organic light emitting diode (OLED) displays. Along with this change, flexibility and weight reduction are required for various OLED materials. For example, in mobile phones, significant efforts have been made to convert a substrate from "heavy and hard" glass to a "light and flexible" transparent polyimide sheet, and the development of rollable and foldable phones has been actively underway. [1]

On the other hand, light extraction in OLEDs is only 20% or less since OLED is an optically isotropic material. Compared to LCD, it is necessary to increase the light extraction efficiency and the orientation of light. this can be achieved using a high refractive index (HRI) material to reduce the amount of light trapped due to index mis-match between device layers. [2][3][4] In order to achieve both material requirements of high flexibility and HRI, a HRI filler is generally used. However, in case of the conventional Zirconia filler with particle size of 50 nm or more, crack issue often happens after film formation. (Figure.1)

The fine patterns lead to increased observations of cracking in poorly designed systems. In this paper, to solve this issue, the photo-patternable material and inks were developed by the combination of the high refractive index PixClear® ZrO2 nanocrystal dispersion developed by Pixelligent Technology LLC and TOK HRI materials. TOK HRI materials is photosensitive material developed over many years with high transparency.[5](Figure.2) With PixClear® ZrO2 nanocrystal cracking and haze issues were not

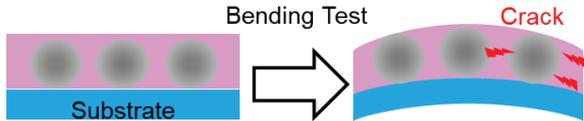
observed because the nanocrystal size in this dispersion was 10 nm (Figure.3) with no particle aggregation. In addition, this material has high flexibility and good chemical resistance. (Table 1)

There are two kinds of photoresists, positive tone and negative tone. In case of the negative tone type, the exposed part is crosslinked by the photoinitiator, and the molecular weight is increased. In contrast, the positive tone type generally has poor resistance as a permanent film such as chemical resistance. For display materials, permanent properties are required, therefore the negative tone type material was selected.

This combination TOK HRI material and PixClear® with its small and uniform nanocrystals is an ideal solution for next-generation displays such as flexible OLED.

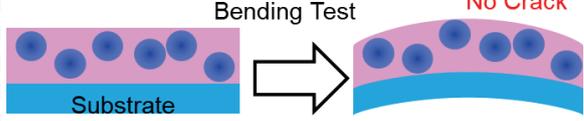
#### Conventional Filler

Filler Size: 50 nm ~



#### PixClear®

Filler Size: 5 ~ 10 nm

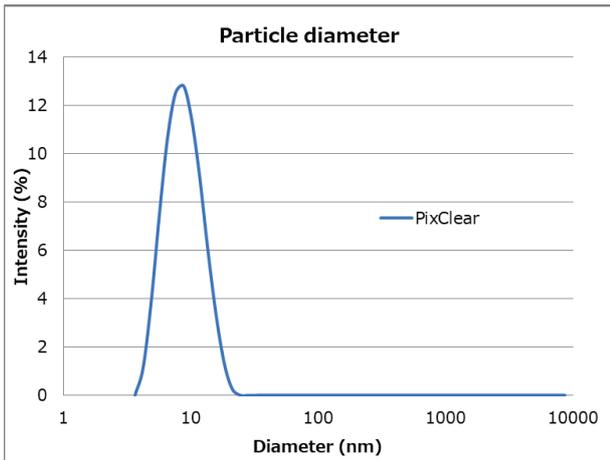


**Smaller filler leads to suppression of cracking.**

Figure.1 Comparison of films with conventional fillers (top) and PixClear® (bottom)



**Figure.2 Comparison of films with conventional fillers (top) and PixClear® (bottom)**



**Figure.3 Particle size distribution of PixClear® measured by DLS**

## 2 EXPERIMENT

### 2.1 HRI photo patternable material preparation

HRI photo patternable material was prepared by mixing negative tone photo resist containing HRI material and HRI ZrO<sub>2</sub> (PixClear®) in 3 : 7 weight ratio.

### 2.2 Flexibility test

HRI photo patternable material was spin-coated onto Kapton® film. The spin-coated film was then baked at 100 deg. C for 2 minutes. After cooling, exposure was executed with broadband ray and 1 J/cm<sup>2</sup>. The film was cured at 230 deg. C for 20 minutes. After film was wrapped around a bar with 2 mm radius (2R), crack observation was performed using optical microscope.

### 2.3 Patterning test

HRI photosensitive material was spin-coated onto Si substrate. Exposure executed with i-line stepper (Nikon). After development by 2.38 % TMAH aq., pattern was observed using scanning electron microscopy (SEM).

### 2.4 Inkjet test

Solvent free ink that HRI and photosensitive

materials was discharged onto glass substrate by inkjet tool. Then, film properties were checked as same as photo patternable film.

## 3 RESULTS

A new material based on the combination of ZrO<sub>2</sub> nanocrystals and TOK HRI material achieved flexible characteristics and higher refractive index with no cracking (Table 1,2 and Figure.4). And since it is a negative type material, resistance to NMP solvent could also be imparted.

In addition, 3 μm resolution with 3 μm film thick was obtained by HRI photosensitive material (Figure 5). Based on this result, we are aiming to form a 1 μm resolution. And also, the solvent free type of HRI ink was prepared.

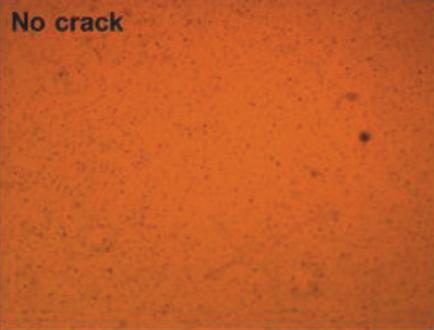
**Table 1 Results of TOK material w/ PixClear®**

Item	Test Method	TOK material	TOK material w/ PixClear®
Refractive Index	VUV-VASE (@ 550 nm)	1.69	1.76
Transmittance	MCPD-3000 (@ 400 nm)	95.0%	95.2%
Dielectric Constant	SSM495 (100 kHz)	4.2	6.5
Flexibility	Bending Test	2 R	2 R
Hardness	Pencil Hardness Test (JIS K5600-5-4)	3 H	4 H
Chemical Resistance	Dipping in NMP for 10min (rt)	No Change	No Change

**Table 2 TOK composition w/ PixClear®**

Item	Test Method	TOK photo patternable w/ PixClear®	Solvent free ink w/ PixClear®
Viscosity	E type (@ 25 °C)	-	20 cP
Refractive Index	VUV-VASE (@ 550 nm)	1.70	1.70
Transmittance	MCPD-3000 (@ 400 nm)	96.4%	96.0%
Flexibility	Bending Test	2 R	2 R
Hardness	Pencil Hardness Test (JIS K5600-5-4)	2 H	-

TOK HRI material w/ PixClear®



Conventional material and filler



Figure.4 Flexibility test

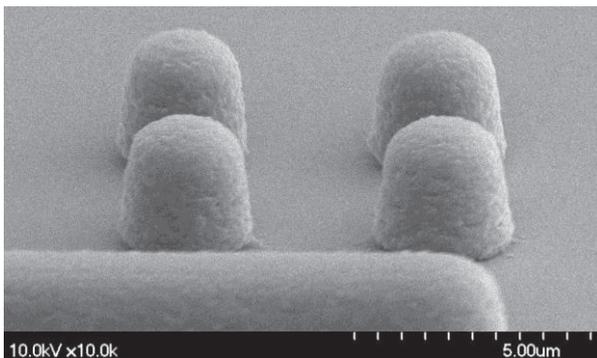


Figure.5 SEM image of photo-patterned TOK Material with PixClear®

#### 4 CONCLUSIONS

We have developed two types of HRI materials for different patterning methods such as photo patterning and ink jetting by combination of HRI ZrO<sub>2</sub> (PixClear®) and TOK HRI material. Both materials also showed good flexibility and high transparency. These results indicated that the new HRI nanocomposite is a promising candidate for next generation flexible displays.

#### REFERENCES

- [1] <https://www.cnet.com/news/samsung-foldable-phone-is-real-and-opens-extends-into-a-tablet-display-specs-galaxy-x-f/>
- [2] <http://www.pixelligent.com/wp-content/files/2015/07/WP-Pixelligent-Zirconia-Nanocrystals-for-OLED-Applications.pdf>
- [3] D. Yokoyama : “ Molecular Orientation in Small - molecule Organic Light - emitting Diodes , ” J. Mater. Chem. , Vol.21 , pp.19187-19202 (2012)
- [4] T. D. Schmidt, B. J. Scholz, C. Mayr and W. Brutting : “Non-isotropic Emitter Orientation in Organic Light-emitting Diodes,” SID 13 Digest, pp.604-607 (2013)
- [5] <http://www.pixelligent.com/wp-content/files/2016/05/Improved-Light-Extraction-For-OLED-Displays-WP.pdf>