A THERMALLY ACTUATED ORGANIC DISPLAY DEVICE USING THERMO-CHROMATIC POLYMER COMPOSITE FILM WITH SELF-ALIGNED PATTERNS

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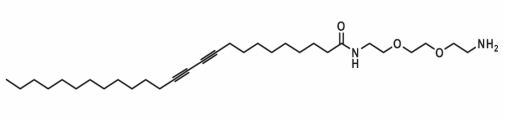
ABSTRACT

A thermally actuated organic display device using UV-sensitive polydiacetylene (PDA)-polyvinyl alcohol (PVA) composite film with self aligned patterns is presented. A novel technique that patterns UV-sensitive organic films on a transparent substrate using a chip-embedded photomask is demonstrated. In contrast to related works regarding PDA and its composites, the current investigation represents the first attempt to realize a PDA derivative film for a thermal-display. Micro-pixels ranging from 200μm to 700μm size were fabricated on a glass substrate. The transition tones of the blue, red and yellow micro-pixels were successfully tuned with embedded micro-heaters under the PDA-PVA layer using both low-temperature (75°C) and high-temperature (180°C) activation processes. The retention time was measured and found to be less than a few hundred milliseconds.

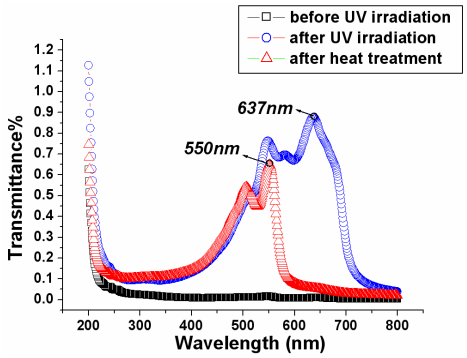
1. INTRODUCTION

Publications in recent display technology show that the interest related to the utilization of polymers is increasing due to the uncomplicated and low-cost fabrication process associated with the use of these polymers [1], [2]. Different polymers possess different chromatic features, i.e. thermochromism, electrochromism, and photochromism. The most common feature among these methods is electrochromism, in which the actuation of the pixels is achieved by applying potential to the electrodes that sandwich the polymer and charge transfer layers. The necessity of using multi-layers in order to satisfy the charge-transfer mechanism makes the device fabrication and integration more difficult compared to the other display structures. Most polymers differ in terms of their degree of difficulty in the solid phase because physical patterning such as wet or dry etching damages the polymer film or other materials included in the device structure. Moreover, in the liquid phase, sealing can be a concern. These problems motivate the many investigations that seek easily patterned, high-contrast solid phase polymer structures that can meet the increasing demand for polymer-based displays.

Thermo-chromatic polymers are the best alternatives for chromatic devices. They do not require charge accumulation and transfer layers as color switching is achieved by alternating the temperature of the material. In this work, utilizing PDA liposome consisting of chemically modified diacetylene monomer, PCDA-EDEA (10, 12– pentacosadiynoic acid – 2, 2´- (ethylenedioxy) bis (ethylamine)) as the chromatic layer, a thermally actuated display device is introduced with self aligned patterning technique. PCDA-EDEA is an amine-ended monomer of the PDA liposome (Fig. 1(a)). Mixing PCDA with PVA and curing the mixed solution result in a UV-sensitive white-opaque film. This film can be polymerized by 254nm UV-light irradiation; via this polymerization, the color of the film shifts to blue. The UV- irradiation is performed through an embedded photomask that generates blue micro patterns on the film with the desired shapes and sizes of the polymerized regions [3]. Following the polymerization step, the blue PDA-PVA patterns dramatically change to red with thermal stress generated by the micro-heaters directly underneath the patterns (Fig. 1(b)). Furthermore, increasing the temperature to higher values provokes a second color shift phase and produces a third color, yellow, from red. With this approach, easy device fabrication, self-aligned patterning and integration compatibility are achieved. These are promising features for the next generation of organic display devices.



(a)



(b)

Figure 1: (a) PCDA-EDEA molecular formula (b) Visible absorption spectra for PDA-PVA film.

2. MATERIALS, STRUCTURE AND FABRICATION OF THE DEVICE

The amine-terminated UV-sensitive diacetylene monomer PCDA-EDEA was obtained by reacting PCDA-NHS with excess amount of EDEA in methylene chloride, as described in the literature [4]. In order to prepare the solid film of the composite polymer, the diacetylene vesicle solution was mixed

with an aqueous 10 % PVA (Aldrich, M_w=89,000-98,000) solution in a volume ratio of 1:1 [5].

A display device simply consists of a transparent substrate, a micro-heater array, a SU-8 layer that separates adjacent micro-heaters, a PDA-PVA composite polymer layer, and a polydimethylsiloxane (PDMS) cover at the top. This is illustrated in Fig. 2.

A 4-inch Pyrex glass wafer with a thickness of 800µm was cleaned with H_2SO_4:H_2O_2 (1:1) solution for 10 minutes. Ti-Au-Ti-Au (10-50-10-200nm) serpentine-type multilayer micro-heaters were fabricated on the substrate with the text pattern "KAIST" and the top Au-Ti layer of only the micro-heater regions were preferentially wet-etched in order to focus the generated heat on the micro-heaters rather than on the connection wires (Fig. 2 and Fig. 3). Using this method, the ratio of the driving heat of the micro-heater to that of the connection wire becomes 5 to 1.

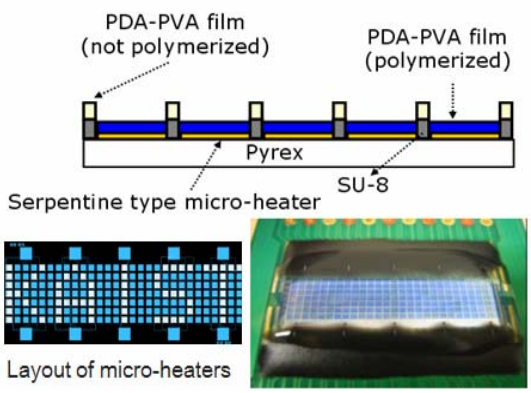


Figure 2: Fabricated organic polymer display device and layout view of the "KAIST" text patterns of micro-heater arrays.

A SU-8 (MicroChem, SU-8 2100) layer with a thickness of 100µm was spin-coated at 500rpm-10secs/ 3000rpm-30secs, soft-baked at 65°C-5mins/ 95°C-60mins, and exposed with I-line (600mJ/cm^2) process. Post-exposure bake was performed at 65°C for 2 min followed by 95°C for 12 min. Finally the layer was developed with MicroChem SU-8 developer to have square patterns with sizes ranging from 200µm to 700µm.

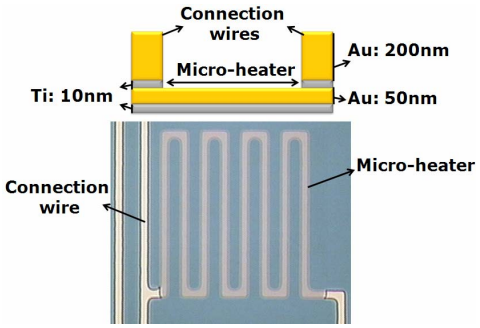


Figure 3: Cross-sectional view and optical microscope image of the micro-heater-only etching profile.

PDA-PVA composite film shows poor adhesion on a glass substrate; therefore, an oxygen plasma treatment is required before the polymer solution can be dispensed onto the substrate. An oxygen plasma treatment was applied to the structure with plasma power of 150 Watts and an oxygen flow rate of 50sccm for 5 minutes. This, in turn, increased the surface energy and improved adhesion, providing better uniformity for the polymer film layer during the injection of the liquid solution on the substrate. 100µl of PCDA-PVA solution was dispensed onto a 2.1cm by 1.1cm patterned glass using a spoid. A 40-µm film layer formed after the polymer composite cured at room temperature for 18 hours.

In order to polymerize and generate pixel patterns on the solid film, the UV-irradiation was performed using 254nm UV-light (710µW/cm^2) through the backside of the Pyrex glass for 10 minutes (VL-6C Vilber Lourmat UV Darkroom). Polymerization changed the color of pixels corresponding to the SU-8 patterns to blue while leaving the organic film on SU-8 non-patterned regions unchanged (Fig. 4). Finally, the chip surface was covered with PDMS (Dow Corning Sylgard 184 10:1) to avoid contamination from the experimental environment.

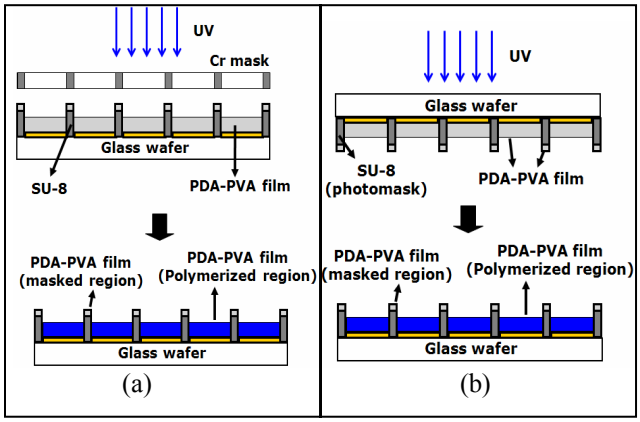


Figure 4: Pattern generation on a polymer film by UV-irradiation a) conventional method b) proposed method.

After connecting the wire-bonded display chip to the power supply, 4V and 10V potentials were applied to the micro-heater array. The color changes of blue patterns to red and then red to yellow were clearly observed by the naked eye. The images of the patterns were taken using a digital color CCD camera.

A temperature-dependent color chart of the PDA-PVA composite was obtained via the following process. A separate glass substrate coated with polymer film was placed on the hotplate. Calibration of the temperature of the film was done using a digital thermometer (TECPEL Thermometer 305B) and a thermocouple that was directly attached to the film. The optical inspection was carried out with a digital color CCD camera while noting the temperature values from the digital thermometer.

3. RESULTS

The backside exposure process used to obtain self-aligned

devices is also common in thin film transistor fabrication technology [6]. The optical and thermal properties as well as the fabrication simplicity of SU-8 on a transparent substrate make it favorable for this type of application. The UV-visible transmission measurements of several materials are presented in Fig. 5. From the measurement data, the masking property of the SU-8 layer (0% transmission) and the transparency of the Pyrex glass (22% transmission) at 254nm of UV light can be extracted. The wavelength of interest is 254nm, as this is the required value to polymerize diacetylene monomers into polydiacetylene molecules. There are very few applications that utilize a SU-8 resist below the 350nm UV range due to its highly actinic absorption property [7]. This property explains why SU-8 behaves as a very good masking layer to sub-350nm UV-light. It can play the same role of an external photomask to simplify the patterning of an underlying layer. It is worthwhile to note that thermal conductivity of the SU-8 layer is 0.2W/mK, which is highly attractive for thermal insulation. It is nearly one-sixth the value of the well-known thermal insulator SiO_2 (1.28W/mK).

In Fig. 5, the transmittance measurements of different materials show that Pyrex glass and Polymethyl-methacrylate (PMMA) are the most suitable substrates, as they have transmittance values of 22% and 18%, respectively. PMMA can be used in a low-temperature range due to its low deformation temperature. The other polymers, Polyethylene terephthalate (PET), Polyethylene naphthalate (PEN) and Polycarbonate (PC), which have a working temperature greater than 180°C, are better for the red-yellow transition but require the use of an external mask in the pattern generation process.

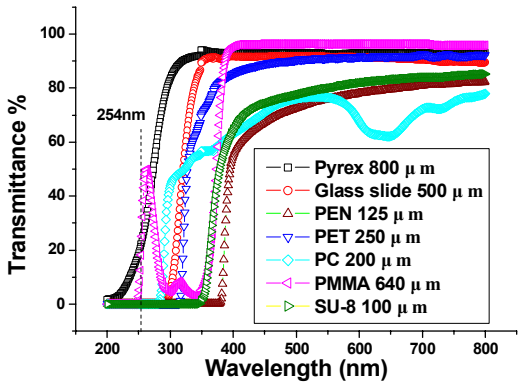


Figure 5: UV-visible transmission spectra for different materials. At 254nm: Pyrex 22%, Glass slide 0%, Polyethylene naphthalate (PEN) 0%, Polyethylene terephthalate (PET) 0%, Polycarbonate 0%, Polymethylmethacrylate (PMMA) 18%, SU-8 0%.

In Fig. 6, it is shown that the blue color of the PDA-PVA film starts to change to red at approximately 55°C, becomes fully red at 75°C, and maintains the same color up to 140°C.

The second phase, the high temperature-yellow phase, starts at 155°C, and an overall transition to yellow is observed at 180°C. Further attempts to increase the temperature resulted in the denaturalizing of the yellow color of the film layer, as illustrated in the image in Fig. 6 at 190°C; beyond 220°C, the film is badly damaged.

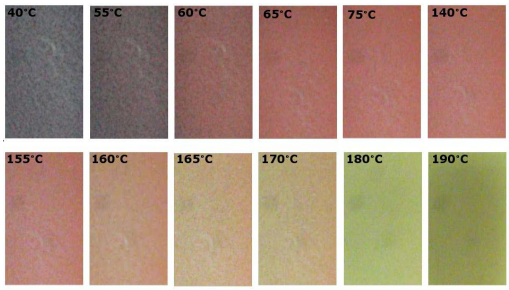


Figure 6: CCD camera images of PDA-PVA film color with respect to the temperature.

Thermally activated display cells with a 700µm by 700µm pattern size and an intercell distance of 100 µm are shown in Fig. 7. The figure includes a CCD camera image of the patterns before polymerization and images of a single cycle activated on/off states of the cell array corresponding to the letter "I". In a simple demonstration, the power supply was switched on and off in less than 500 milliseconds and the images from (b) to (e) were taken with a time interval of approximately 100 milliseconds. Fig. 7(e) shows the inactive states of the cells taken 500 milliseconds after the switch was turned off. The bubble-like shapes inside the patterned cells are attributed to be the poor adhesion between the PDMS cover and the polymer film.

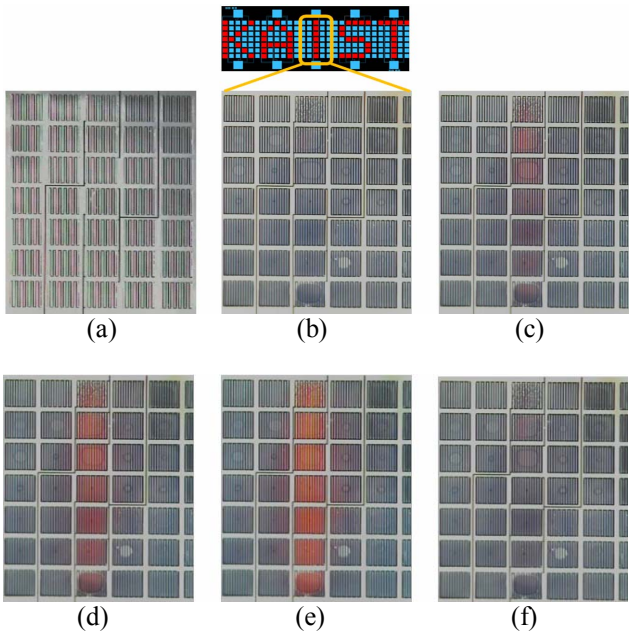


Figure 7: CCD camera images for the letter "I": (a) polymer film before polymerization (b) after polymerization with 10min UV-irradiation (c), (d), (e) sequential images of patterns on activated micro-heaters taken within a few hundred milliseconds (f) recovered-state image taken approximately 500 milliseconds after deactivation of the micro-heaters.

The display chip was continuously heated first without turning off the 10V power supply for approximately 3 seconds in order to allow all the blue polymer patterns turn red. The switching cycles then started in periods of approximately 500 milliseconds when the yellow letters appeared on the red background. The retention time for the red-yellow color variation was measured to be close but relatively less than that of the blue-red shift, as a faster heat exchange of the chip occurs at elevated temperatures. The yellow letters "I" and "S" were successfully ignited on the chip, as shown in Fig. 8. The figure consists of the ON and OFF states of both letters with the timings as stated above. The size of the square cells is 500μm by 500μm and the intercell distance is 200μm.

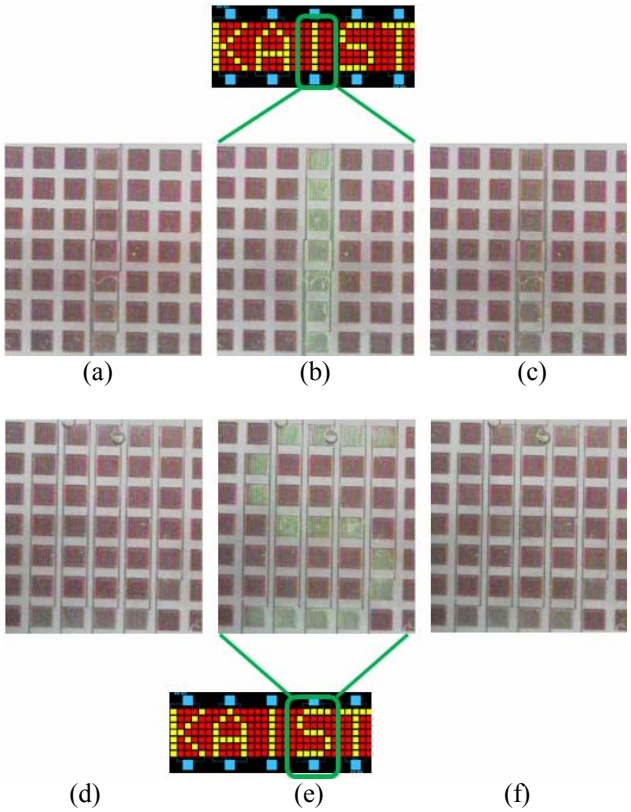


Figure 8: CCD camera images of activated high-temperature cells. Images for the letter "I", (a)-(b)-(c) were taken sequentially at 500 milliseconds. Images for letter "S", (d)-(e)-(f) were taken sequentially at 500 milliseconds.

4. CONCLUSIONS

The thermally activated PDA-PVA composite display has many advantages over the other polymer displays. These include an easy fabrication process, multi-color activation and self-aligned patterning technique. These advantages are mainly due to the UV-sensitive and thermo-chromatic properties of the solid PDA-PVA film.

The substrate of the device fabricated in this study was Pyrex glass with a thickness of 800μm. The substrate selection is very important as the patterning of the display device is done by UV-light irradiation from the backside of the device via the chip-embedded photomask. Substrates with good transmittance to 254nm of UV light can also be used in the current design, but other substrates may be feasible provided that an external photomask is included in the polymer film patterning.

The PDA-PVA mixture can provide three different colors, blue, red and yellow, as well as transition tones. The authors are currently investigating the underlying reasons for the chromatic variations in order to utilize these materials in displays and other applications more efficiently.

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