Ink-Jet Printed Electrodes for Passive Fluid Based Display

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Abstract

There is an urgent need for change to meet the requirements of green technology for printed circuits for printed electronics and displays. In this paper, a novel and simple process to manufacture electrodes of fluidic base display at room temperature was proposed. Following our prior researches, the processes combined self-assembly polyelectrolyte (SAP) layer deposition, ink-jet patterning of palladium catalyst, and electroless plating to form an electrode pattern on a polyimide substrate. The patterned, high conductive circuit is applied to fluid based displays, such as cholesterol liquid crystal or electro-wetting displays, which are also color patterned by the printing process to discharge the individual color media onto predetermined flexible substrates. This study demonstrates the ink-jet printing electrodes for a 10.4" cholesterol liquid crystal display on a polycarbonate substrate. The thickness and resistivity of the electrode pattern were measured at about 400±50 nm and o.15 ohm/square, respectively. The Flexure-angular examination indicated, after a 2 mm curvature and 2000 tests, that the variation of resistivity variation was less than 1%.

Introduction

In recent years, there has been great interest in plastic substrate display, such as e-paper, due to their light weight and flexibility. Generally, this display is driven using an active matrix or passive matrix mode. Although the active matrix mode has high resolution and brightness, the passive matrix mode has lower manufacturing costs and driver voltage. Whether using active matrix or passive matrix, currently the electrodes are patterned by conventional photolithography. However, it has a downfall due to the pollution, waste, and expansive process. Some alternative processes have been proposed latterly, for example, screen printing [1], direct writing [2], micro-contact [3], and so on.

Inkjet printing [4], as a derivative of direct-write processing, offers the advantages of low capitalization, very high materials efficiency, an atmospheric process, and non-contact processing [5]. Using this process to immediately pattern electrodes on flexible substrates has been established by ink-jet printing with Cu, Au, and Ag nanoparticles [6,7,8] or organometallic inks [9]. In order to develop the electronic properties of inks, it is necessary to sinter inks at temperatures over 150^{o}C for at least 30 minutes. However, general plastic flexible substrates will be damaged or deformed easily at this high temperature. In addition, the reliability and the cost of inks are also challenged frequently. In our prior researches [10,11], a specific approach that combined self-assembled polyelectrolytes, ink-jet printing catalyst, and electroless metal plating technologies for the fabrication of electrical circuits was successfully established. The hybrid process has great potential as a result of the use of a room temperature process and cheap materials. In these combined processes, the deposited metal film grew smoothly and the thickness could be controlled below a micrometer. It conforms exactly to the requirements of the display cell design.

Taking steps from our prior researches, the electrodes of fluidic base display are further patterned on a polycarbonate (PC) substrate by use of the hybrid processes reported in this paper. The patterned, high conductive electrodes are applied to fluid based displays, such as cholesterol liquid crystal or an electro-wetting display, which is also color patterned by the printing process to discharge the individual color media onto predetermined flexible substrates.

Experiment

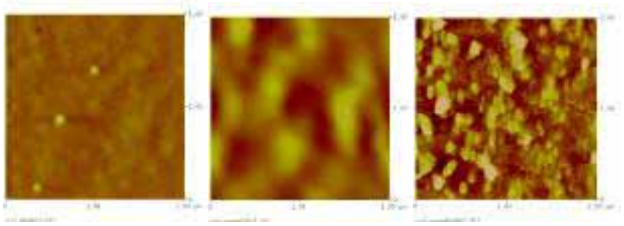
The ink-jet platform ITRI 3GU series is equipped with a four-axis X-Y-Z-theta platform, an optical system used for alignment, and a maintenance system to recycle ink fluidics. All of the components are set upon the granite base (AA Grade) with four vibration isolators to absorb the vibration. The printing speed is up to 25 in /s. An optical-interferometry 3-D surface profiler is used to measure the thin film profile (SNU Precision Co., Korea). It has a vertical resolution of 0.1 nm, and lateral resolution of 0.5 micron. Scanning range can be adjusted from a micro to a nanometer, depending on the interferometric optics (2x-5x, Michelson interferometry, 10x-50x, Mirau interferometry). The contact angle of water on the self-assembled films is measured using a KRUSS drop shape analysis system (DSA 10 MK2). The surface morphology and surface roughness of dip and spin self-assembled multilayer films are investigated using the tapping mode of atomic force measurement (AFM Nanoscope). An optical microscopy Leica MZ12 is used to observe the surface morphology of circuits.

Surface Modified and Analysis

In our prior researches, we demonstrated that the ink jet printing process has been successfully used to pattern circuits. Substrates were modified with porous PEMs membrane organized by several Polyelectrolytes cation / anion bi-layers to bind the metal film and substrate. However, this traditional PEMs multilayer membrane was weak polyelectrolyte films,

which was sensitive to the pH of solution.[12] The basic electroless electrolyte (pH>10) might damage it and effect the adhesion between substrate and metal film. In this study, the PEMs multilayer membrane formed by strong electrolyte was the alternative choice. It could provide a uniformity and more stable surface. In this study, we utilized strong electrolytes PEMs instead of the weak electrolytes PEMs used in prior studies. Characterizations of the PEMs on PC substrate were accomplished by atomic force microscopy (AFM) analysis. Fig.1 (A) and (B) show that the AFM images depicted the surface morphology of the PC substrate treated by ozone plasma and PEMs membrane in 7 double layers, respectively. The surface RMS (root-mean-square) roughness was about 0.7 nm on PC substrate and about 2.5 nm on a multilayer membrane.

The process of heat-treatment was used to enhance the adhesion of metal on the multilayer membrane. Fig.1(C) reveals a shrinking multilayer membrane after 90°C annealing for 1 hr. The surface RMS roughness increased to about 7.8 nm. This was possible because the heating could provide the energy necessary for overcoming the electrostatic attraction between oppositely charged polyelectrolyte groups. At the elevated temperature, the PEMs become capable of changing their largely two dimensional arrangement corresponding to a low entropy state to a more coiled arrangement which is equivalent to a configuration entropy increase [13]. Comparing this with Fig.1(B), we can clearly observe that the grain size of PEMs decreases and the morphology of the membrane moved from loose transforming into compact transforming. The compact structure can offer more surface area to enhance adhesion strength.

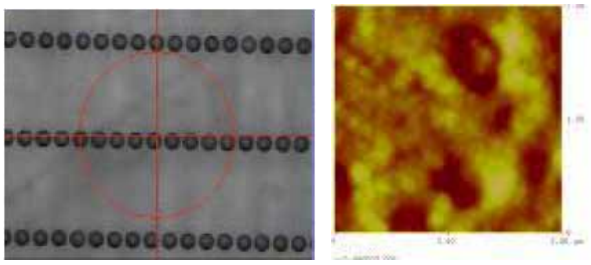


(A) **(B)** **(C)**

Fig 1: *AFM tapping mode images of the surface morphology (A) PC substrate; (B) multilayer membrane on PC substrate (C) multilayer membrane on PC substrate after annealing at 90°C for 1 hr.*

Ink-Jet Patterning and Electroless Deposition

The catalyst, Pd-complex, bound to the free carboxylic acid group of PAA and formed the Pd nanoparticles to catalyze the electroless metal plating reaction was demonstrated [14]. However, PEMs layers had no COOH functional group with which to exchange protons to form Pd nanoparticles. Recently, nanoscaled Pd or Pd-Ag nanoparticles have been synthesized as a catalyst for electroless copper and nickel. Therefore, we adjusted the nano-Pd ink by using a suitable lower molecular weight thickening agent and nonionic surfactant to correspond with the printed head specification. The viscosity and surface tension of the ink were controlled at 10 cps and 40 dyne/cm, respectively. As can be seen in Figure 2(A), the drop size, approximately 80um in diameter, is printed landing on PC substrate. The contact angle of catalyst ink on PC substrate also was measured at about 65±5 degrees by the drop shape analysis system. This was appropriate for the inkjet printing process. Figure 2(B) shows the AFM tapping mode images of Pd nanoparticles ink printed on PEMs membrane. The numerous tiny white spots which are about 50 nm are suspected to be clusters of Pd nanoparticles on the surface.



(A) **(B)**

Fig.2 *(A) Optical micrographic of catalyst ink-jetted droplet on the PI substrate; (B) Pd nanoparticles printed on the surface of multilayer membrane / PC substrate.*

A 10.4" reflecting CHLCD electrode pattern is selected for demonstrating this process (see Fig. 3(A)). The line width/space are 140 micron/120 micron (see section I), 140 micron /120 micron (see section II), and 600 micron /50 micron (see section III), individually. The PC substrate, which had been patterned, was immersed in electroless electrolyte at 30°C for 10 minutes. As a result of using Pd nanoparticles ink, the traditional pretreated steps, for example, sensitized or acceleration process, can be ignored before plating. Figure 3(B, C, D) illustrate the performance of metal lines deposition on PC substrate. The plating results nearly conformed to the original design. The thickness of this metal film was measured at about 400±50 nm by use of the SNU system, and the resistivity was measured about 0.15 ohm/square by 4-point probe. In addition, the adhesion strength between copper film and PC substrate passed 3M 600 tape peeling test.

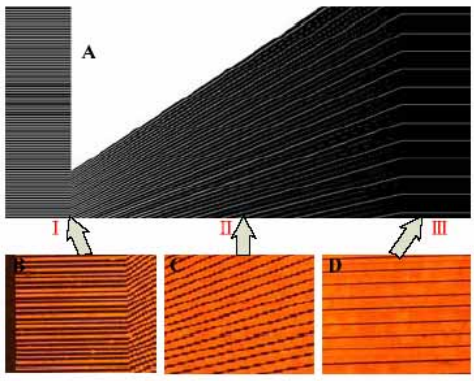


Fig.3: (A). *10.4" reflecting CHLCD electrode pattern; (B) region I; (C)*

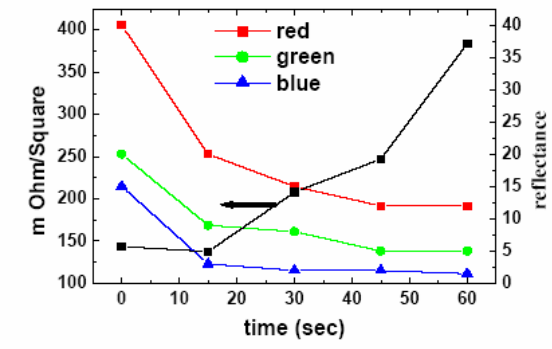
region II; (D) region III were different parts in the electrode pattern.

Results and Discussion

Electrode Reflection Reduction

In order to be applicable to reflecting CH-LCD, different with the prior circuit preparation, the electrodes need dark in order to prevent destructive interference and enhance contrast ratio. In this criterion, copper film has high reflectivity, so that it isn't suited for this reflecting CH-LCD and needs further modifying treatment. Brown oxide treatment is usually utilized to enhance adhesion between the metal and binder in PCB process [14]. This process can change the color of copper to brown, but it also influences the copper conductivity. Fig.4 (A) shows the conspicuous difference between a non-treated region (see Fig. 4 (A) right) and a brown oxide region (see Fig. 4 (A) left), where the brown region was immersed into a brown oxide bath. Fig. 4 (B) shows electrodes resistivity (marked as black square, left vertical axis) and reflectance (verified at different spectrum region, right vertical axis, red spectrum: square, green spectrum: circle, blue spectrum: triangle) for copper film as a result of immersing time. The resistivity increased with the increase in immersing time, but the reflectance decreased. The maximum values were 0.38 ohm/square in resistivity for the 60 sec. immersing time. It is enough to apply in reflecting CHLCD. Furthermore, the reflectance values in the red, green, and blue light regions, decreased with the increase in immersion time. The reflectance tended to become gentle after immersing for over 45 seconds. It is worth mentioning that samples would be damaged after immersing for over 75 seconds. This is attributed to the thin copper film being corroded. Therefore, the optimum recipe was immersing for 45 seconds.

(A)



(B)

Fig. 4: *(A). The difference between the non-treated region and the brown oxide region; (B) resistivity (marked as a black square, left vertical axis) and reflectance (verified at different spectrum regions, right vertical axis) for a copper electrode treated by the brown oxide process as a function of immersing time*

Flexure-Angular Testing

The flexure-angular test pattern circuit that was established is referred to in prior research. The radius of the curvature is 2 mm, and the push-pull strength is 4.9 NT. After performing the flexure test 2000 times, circuits have no evident defect in their circuits and the variations of resistivity were measured below 1%. The substrate, however, cracked during the 2213th flexure-angular test. This PC substrate was so brittle that it was less resistant to breakage and generally much weaker in tensile strength. Figure 5 shows the result of using crevice substrate.

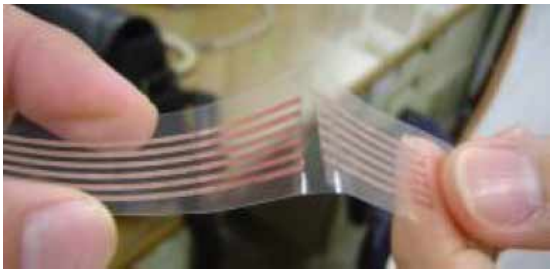


Fig 5:*. The metal film cracks were formed after flexure-angular verification.*

Conclusions

In this paper, we succeeded to demonstrate a novel and simple process to manufacture electrodes of fluidic base display. The patterned high conductive electrodes were accomplished with a hybrid method combining self-assembly polyelectrolyte (SAP) multilayer deposition, ink-jet patterning of nano-palladium ink, and electroless plating electrode pattern on a polycarbonate substrate. The thickness and resistivity of the electrode pattern were measured at about 400±50 nm and 0.15 ohm/square, respectively. Moreover, the adhesion strength between metal and substrate passed the general peeling test. High conductivity and low reflectance are both important requirements in the reflecting display. The brown oxide treatment successfully developed the high reflecting copper surface. Finally, this hybrid method was attributed to having a high potential in the reflecting display field to be a cheaper and more environmentally friendly process.

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Biography

Ming-Huan Yang received his Masters degree in Chemistry from National Cheng Kung University in 2002, and now he is a Ph.D candidate in the Materials Science Institute of National Qing-Hua University. He is now in charge of chemistry formulation for ink-jet printing of inorganic materials and metal in the Printable Science Department, Display Technology Center of Industrial Technology Research Institute at Taiwan. His research interest covers industrial ink-jet printing processes development especially in flexible electronics and flexible display fabrication.