Journal of Imaging Science and Technology® 51(5): 461–464, 2007.

Ring Edge in Film Morphology: Benefit or Obstacle for Ink Jet Fabrication of Organic Thin Film Transistors

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Abstract. *In this study, a novel process using ink jet printing with dilute PMMA [poly(methylmethacrylate)] solution to form fine separation banks as confined boundaries for the subsequent depositing poly(3,4–ethylene dioxythiophene) (PEDOT) was proposed. The PEDOT comprised the source and drained electrodes with a gap of several micrometers due to the innate characteristic of the ring edge of ink jetted PMMA. Using this technique, the organic device was designed with a bottom gate and evaporated pentacene as the channel material. The device mobility and on/off ratio were about 3.6×10^{-4} and 2×10^{2} cm^2/V sec, respectively. © 2007 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.(2007)51:5(461)]

INTRODUCTION

Inorganic semiconductor technology and related applications have already attained a mature stage in the past decades. Because of this revolutionary advancement, science and technology have grown vigorously. The demand for lightweight and flexible electronic products is gradually increasing. However, high temperature processing of inorganic semiconductors is difficult to apply to this demand. Low temperature direct patterning technology and organic electronics have accordingly been intensively developed.[1] With respect to organic electronics, pentacene and regioregular poly(3-hexylthiophene) (RR-P3HT) are the most popular materials used in fabrication of organic thin film transistors (OTFT). The electrical performance of pentacene is superior among the present organic materials, but it is processed by vacuum evaporation, e.g., thermal evaporation[2] or organic vapor phase deposition.[3] Despite of the lower mobility of the polymeric material, the solubility of P3HT, compared to pentacene, makes it compatible with the printing process, which has the advantages of low temperature processing, large area manufacturing capability, etc.

Among patterning technologies, ink jet printing is considered the most promising potential candidate for industrial mass production. In recent years, ink jet printing is used not only on paper and wide format media, but also widely applied to patterning deposition of organic and inorganic electronics. There are many investigations of ink jet printing patterning, such as deposition of insulators, organic semiconductors,[4] or formation of conductive paste circuits,[5] and microlens array.[6] Fabrication of organic TFT (OTFT), a stacked device, needs to integrate several printing steps; thus, it is more difficult and complicated than a single material deposition process. In spite of these challenges, the use of ink jet printing to make good polymer TFT devices has already been discussed in many papers.[7,8]

Most research on OTFT has been concerned with new material development, surface modification or structural design for improving the electric characteristics.[9] As is well known, the current from drain to source is inversely proportional to the channel length. It is favorable to shorten channel length instead of increasing channel width W for better TFT array resolution. However, the printing feature is limited by the drop size and directionality of the ink jet droplet. The printed line width is usually greater than 80 μm with the use of a print head with 35 pl droplet, such as a Spectra SE-128. The variation of ink jet printing directionality also makes it difficult to obtain small and uniform gate channel

Received Jan. 17, 2007; accepted for publication Jun. 20, 2007.
1062-3701/2007/51(5)/461/4/$20.00.

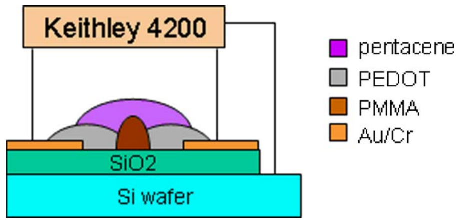

Figure 1. Structure of the organic thin film transistor (OTFT) device with a ridge of PMMA ring edge.

length over the whole printing area. In this study, we separated the organic electrodes by a poly(methyl methacrylate) (PMMA) ridge, formed by the natural phenomenon of capillary flow to obtain gate lengths of $<10\ \mu m$ using an ink jet printing method.

PMMA PARTITION TO SEPARATE CHANNELS

The phenomenon of ring shaped patterns from dried solution is common in our daily life. When a liquid droplet lands on a substrate, there are three interface interactions governing the droplet drying behavior. These interactions occur between the individual interface of solid to liquid, liquid to gas, or gas to solid. When the solvent gradually evaporates, liquid droplets are dried to the solid state. Finally, the solute accumulates around the peripheral boundary as ridges, much thicker than that of the center area and is called the "coffee ring shape."

Much effort has been devoted to explain the coffee ring phenomenon. Deegan et al.'s hypothesis[10] is the most acceptable to describe the ring shaped formation behavior. He assumed that the liquid evaporates faster around the periphery than at the center part. This makes the peripheral boundary easier to dry than the center area and, therefore, to form a contact line around the liquid peripheral. This results in a concentration gradient of dissolving solute, and the solution accompanying the solute begins to diffuse from the center to the edge. When the drying process is completed, most solute in the liquid has been carried to the edge and formed into a ring shaped profile. The natural behavior of ridge formation is an obstacle for obtaining smooth films for organic electronics, such as polymer light emitting diodes (PLED) and organic thin film transistors. As an alternative, this study exploited this behavior as a beneficial micropatterning method to define the gate length of OTFT. Through this method, OTFTs with a several micrometer channel length are fabricated.

EXPERIMENTAL

The structure of the organic thin film transistor (OTFT) used in this study is shown in Figure 1. The bottom gate is heavily doped Si on which thermal oxide, SiO_2, 300 nm thick is formed. Sputtered Au 70 nm thick and Cr 30 nm, as an adhesive layer, was used to form the interconnection tracks with spacing of $\sim 100\ \mu m$, as defined by a stainless shadow mask. Poly(methylmethacrylate) (PMMA) ridge several micrometers wide was formed by the coffee-ring edge effect. The statistical data for the ring width distribution yield a mean value of $7.88\ \mu m$ and a standard deviation of $1.68\ \mu m$ for 25 devices. After suitable plasma treatment to remove the thinner PMMA film from the surface, the diluted poly(ethylene dioxythiophene) (PEDOT 4071, purchased from Bayer) was ink jet printed on both sides of the ridge as source and drain electrodes, using a thermal bubble print head capable of 80 pl droplets as developed by our institute (ITRI).

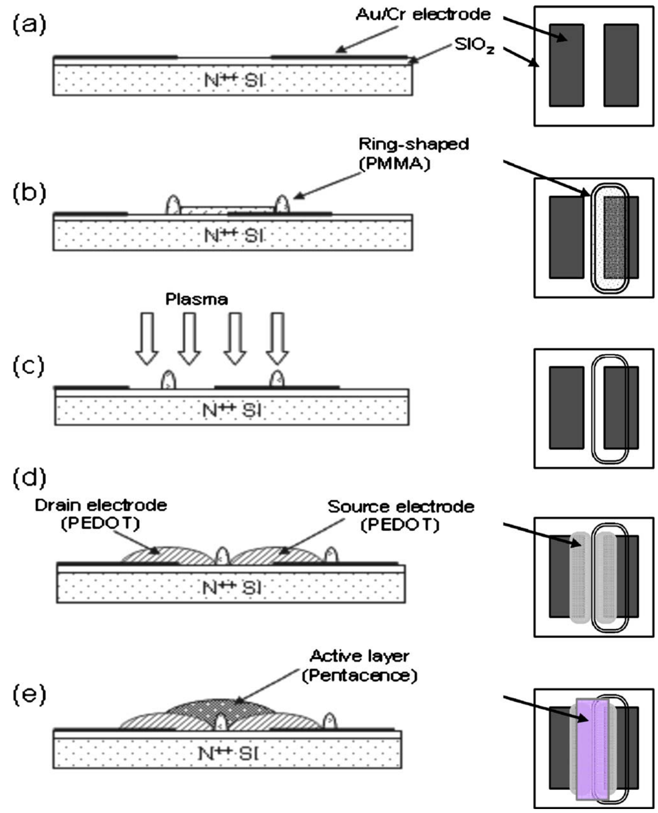

Figure 2. Side and top views of the process flow schematic illustration of ring ridge patterned organic thin film transistors.

The fabricating procedures for ring ridges, electrodes, and the pentacene active layer are shown in Figure 2. As shown in Fig. 2(a), the Si/SiO_2 substrate with Au/Cr interconnection pads were treated with O_2 plasma at 200 W, 800 SCCM (standard cubic centimeter per minute) for 1 min to improve the surface wettability. In Fig. 2(b), 1 wt. % PMMA solution dissolved in anisole was printed and there was one ridge located between the two Au/Cr pads. An ion-coupled plasma was used to etch the thinner part inside the ring ridge by treating 50 sec O_2 plasma with etching rate 6.78 Å/sec, and therefore, two thicker ridges were left on both sides. Sequentially, carbon tetrafluoride plasma was applied to make the PMMA surface liquid repellent as shown in Fig. 2(c). The residual ridge was treated with CF_4 plasma for 100 sec under a pressure of 1 torr with a small etching rate of 0.3 Å/sec. The treated PMMA surface then had contact angles of 106° and 60° for water and anisole, respectively. Therefore, after the dry etching and repellent treatment, a ridge with width of $5.37\ \mu m$ was made as shown in Figure 3. Then PEDOT solution was ink jet printed on both sides of the ridge to connect to each of the Au/Cr pads,

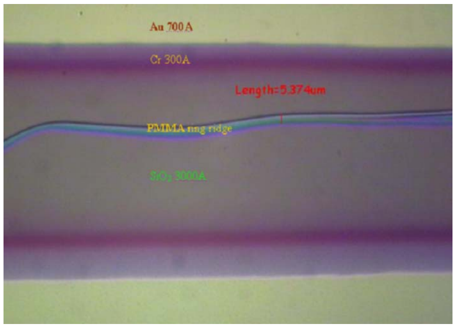

Figure 3. Microscopy of a PMMA residual ridge after plasma etching.

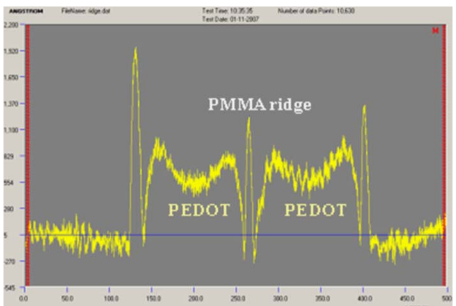

Figure 4. Profile of printed PEDOT by ink jet printing on both sides of the etched repellant PMMA ridge.

which were used as a source or drain electrode as shown in Fig. 2(d). Figure 4 shows the profile of PEDOT, which was printed on both sides of the etched PMMA ridge. This profile was obtained by XP-1 profilometer (AMBIOS technology). From the profile, we can see that the printed PEDOT can be adequately confined between ridges, and the height of PEDOT domains and ridges are around 70 nm and 110 nm, respectively. Hexamethyldisilazane (HMDS) and pentacene were thermally evaporated in sequence onto the above substrate to complete the OTFT devices, as shown in Fig. 2(e). In order to prevent source/drain electrodes from interconnecting, it is better to make the PMMA ridge as repellent to the PEDOT solution as possible.

RESULTS AND DISCUSSION

According to the above procedures, utilizing the ink jet printing technique incorporated with ring edge effect we were able to produce a narrow line of $<10\ \mu$m width, for which the mean and standard deviation are 5.16 μm and 0.31 μm for 25 samples. Applying this patterning method to fabricate an OTFT device, better MOS (metal-oxide semiconductor) characteristics could be obtained. The I_d versus V_d and I_d versus V_g measured using a Keithley 4200 semiconductor parameter analyzer are shown in Figure 5. The field effect mobility can be calculated at the saturation region from the following equation:

$$\mathrm{IDS} = \left(\frac{WC_i}{2L}\right)\mu(V_G - V_T)^2, \tag{1}$$

where C_i is the capacitance per unit area of the insulator, and V_T is the threshold voltage.

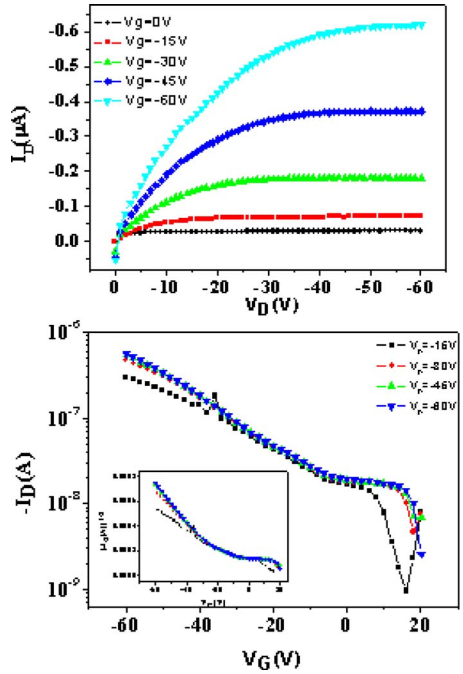

Figure 5. Organic thin film transistor characteristics of a ring ridge patterned with pentacene as the active layer.

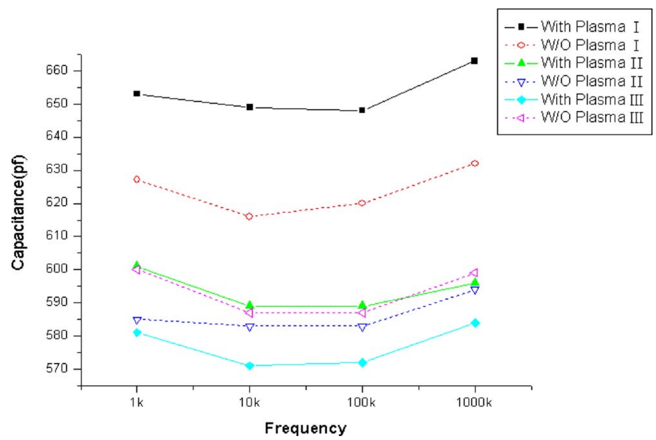

Figure 6. Capacitance comparison of plasma treatment on the oxide layer.

The mobility, on/off ratio and threshold voltage are about 3.6×10^{-4} cm^2/V sec, 2×10^2, and 22 V, respectively. It is found that the off-current and threshold voltage are relatively high in this device, which may be attributed to the negative charging into the PMMA ridge after the plasma treatment. In addition, pentacene cannot form a better alignment on the HMDS/PMMA ring ridge owing to the poor mobility of these devices. Further study is needed to clarify the above problems.

Besides the patterning process, the plasma charging effect on an oxide layer should be considered because the insulator layer was also treated during the etching and repellent treatment. This issue was addressed in terms of the capacitance variation of devices with MIM structure, doped Si/oxide/Al, with or without plasma treatment on the oxide layer. After examination with an HP 4194 impedance analyzer, we found the capacitance to be without dramatic change after plasma treatment under the conditions used in the patterning process, as shown in Figure 6. Most devices have similar capacitance, even though some have a maximum variation of $<5\%$.[11]

CONCLUSION

In this paper, we overcame the restriction of line width by using the direct ink jet printing technique (with droplets of 35 pl the line width is generally around $80-150\ \mu$m) to obtain fine lines of 5 μm using the ring-edge effect. We successfully applied this novel method to fabricate OTFT devices with small channel lengths of several micrometers. This patterning method was proven feasible. Devices with common characteristics of transistors were proposed, though the results have yet to be optimized, where the mobility and on/off ratio were about 3.6×10^{-4} cm^2/V sec and 2×10^2 cm^2/V sec, respectively. It is evident that this patterning method of ink jet printing can be widely applied after additional studies in the future.

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