Organic Thin-Film Transistors with Ink-jet Printed Metal Electrodes

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Abstract

Ink-jet printing technology is widely used in numerous applications. Various inks are developed for the demand of electronic devices. Ink-jet printing conductive metal nanopastes have been used in printed circuit boards and passive components. This technique provides a manufacturing method that can replace more expensive process such as lithography or metal evaporation. In this paper, we demonstrate a new method for manufacturing conductive electrodes of organic thin-film transistors (OTFTs). Adjusting ink properties and jetting performance can control the qualities of the printed nanopaste film. Curing temperature and time are also the key issues which are required for the better morphology of the film. Soluble conjugated polymers such as poly 3-hexylthiophene (P3HT) are very promising candidates for a cheap electronic device on various substrates and suitable for the applications of ink-jet printing technology. We compare the characteristics of OTFTs for the evaporated and the ink-jet printed source-drain electrodes. This approach presents a simple method for fabricating OTFT device and is suitable for a flexible display displays and circuits.

Keywords: OTFT, ink jet printing, nanopaste, piezoelectric printhead, organic semiconductor, P3HT.

Introduction

In recent years, there are two trends for developing new electronic devices: One is minimizing element size to increase the density of devices, and another is reducing the cost of processes or materials.[1] Most of the cost for fabricating an electronic device comes from the processing steps rather than from the cost of the raw materials. Traditional photolithography and high vacuum process can produce devices with scale smaller than 100um, but infrastructures for them are expensive. Low-cost process technologies for fabricating electronic devices include screen printing,[2,3] micromolding in capillaries,[4] soft lithographic stamping, [5]and inkjet printing.[6] The reduction of process steps through direct deposition of the material could reduce the cost and the complexity of the fabrication process further. Inkjet printing is a potential alternative for the existing deposition approaches. Because of being a maskless process, it can reduce the cost of physical molding, chemical waste of material. Moreover, inkjet printing technology is much, more easier extended to process on large area substrate than other processes.

Overarching inks can be used for the process of ink jet printing. These inks involve inorganic and organic electronic materials, and are expected to form wirings, electrodes and many other kinds of components of an electric device. The application of ink-jet printed electronic devices includes thin-film transistors (TFTs), radio-wave frequency identification (RFID), organic light-emitting diode (OLED), and printed circuit board (PCB).[7] Over these various inks used in the past few years, conducting inks are newly developed for forming the electrodes of the devices. Poly(ethylene dioxythiophene), PEDOT, is a good candidate for forming transparent electrode, but the conductivity is several orders lower than metals. The conductivity of the metal nanopastes is 3 to 4 orders higher than that of PEDOT. After low temperature sintering (150^{o}C), the nanoparticles will form aggregations and film thickness can be decided by tuning the drop size and the solid content of the inks. Low temperature processing is very critical to the fabrication processes of the flexible display devices.

Burgi[8] discussed the influence of the work function for the metal to the device performance with P3HT as active layer. The source/drain metal electrode is chosen to be Cr/Au, Ag, or just Au. Other metals form Schottky barriers at the interface so that the resistance is high and the current is blocked therein.

In this paper, we explore the effects on the quality of the printed film according to the various printing conditions setting of Spectra SE-128 piezo printhead. We also discuss the influence of the thin transition metal buffer layer on the TFT device performance. Using a transition metal oxide as the hole injection layer is an effective way to improve the characteristics of OTFTs.[9] At the same time, the contact angle of the nanopaste on the transition metal oxide is smaller than that on P3HT, so the printing quality of metal line is better. Furthermore, the thickness of this buffer layer is so thin that the device performance is not influenced significantly.

Treatment & Fabrication Processes

The structure of the polymer thin-film transistor (PTFT) with ink-jet printed silver electrodes is shown in Fig. 1. The bottom gate with heavily doped Si is selected and thickness of SiO_2 is 300nm as the gate dielectrics. Regioregular poly(3-hexylthiophene) (P3HT) purchased from Rieke is used as the organic active layer. A buffer layer (~3 nm thick), comprised of dielectric materials such as vanadium oxide (V_2O_5), molybdenum oxide (MoO_3) or tungsten trioxide (WO_3), was deposited between the organic layer and each one of the electrodes,. In order to compare the performance of the device with ink jet printed silver nanopaste as the top electrodes, we made the comparative device with evaporated silver film as the top electrodes as well.

The Si/SiO_2 substrate is cleaned sequentially by acetone and IPA in ultrasonic bath. After 150W, 450mtorr, and 5mins oxygen plasma treatment, a monolayer of OTS is self-assembling onto the SiO_2 layer by dipping the substrate (with SiO_2 layer) into the 60^{o}C OTS dilute toluene solution for 20mins. Then, P3HT dissolved in TMB (0.5wt%) is spin-coated on the substrate and baked in 90^{o}C for 90mins. Thickness of this P3HT film is about 50nm. The transition metal buffer layer is thermally evaporated on the P3HT and its thickness is 3 nm. Both inkjet printing and thermal evaporation techniques are separately used for the silver electrode deposition. The inkjet printing platform, developed by our display

technology center (DTC), equipped with spectra SE-128 piezoelectric printhead, is used to discharge the silver nano-particles inks (AG-IJ-G-100-S1), purchased from Cabot. The low resistivity patterned silver film is obtained after being post baked at 150°C for 30 minutes in glove box to sinter the pre-deposited precursor material. The thickness of the buffer layer and the metal layer are 3 nm and 200 nm, respectively. During deposition, the vacuum of the chamber is kept at about $5x10^{-6}$ torr. The measurements of V_d-I_d and V_g-I_d for devices are conducted through a Keithley 4200 semiconductor parameter analyzer.

The field-effect mobility (u) is calculated at the saturation regions from the following equation.

$$I_{DS} = (WC_i/2L)u(V_G - V_T)^2$$

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

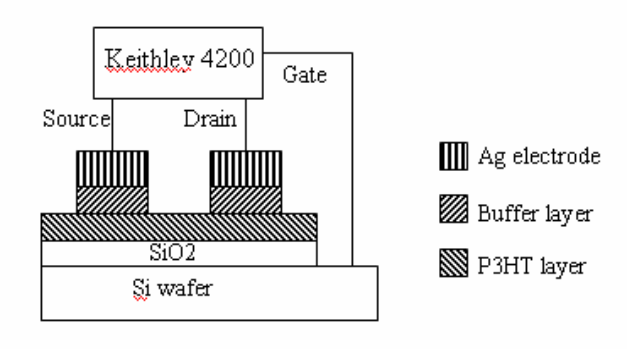


Fig.1 *The structure of the polymer thin-film transistor device (PTFT) with a silver top electrode*

Results and Discussion

Stability of the inkjet printed ink

We can improve the jetting behavior of piezoelectric print heads by three parameters, i.e. pulse waveform, pulse frequency and driving voltage. Suitable range of waveform modulation and pulse frequency are necessary for some driving voltage for appropriate ink discharging. The jetting behavior can be observed by a strobe capturing system integrated in the printing platform. The break-off behavior of the jettable silver nano-particles ink is captured within 60 microseconds and shown in Fig.2. The velocity of the jetted drop is about 6.4 m/s and stable. With a stand-off of 1 mm, we have successfully modulated the ink-jet printing parameters of Spectra SE-128 for silver nano-particles ink, and therefore uniform and continuous silver paste lines are obtained on the pre-cleaned substrate.

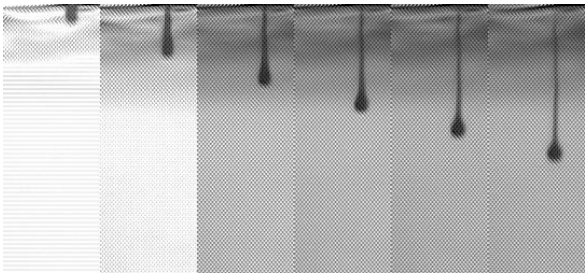


Fig.2 *Observation for the break-off behavior of the printed drop beneath an arbitrary nozzle.*

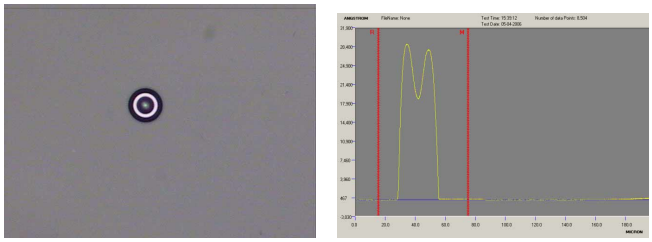
Morphology and profile of the inkjet printed nanopaste on the P3HT/buffer layer

The contact angles of the silver nanopaste between the P3HT film and the V_2O_5 film are shown in Table.1. The contact angle on P3HT film is 65°, which is larger than that on the V_2O_5 film.

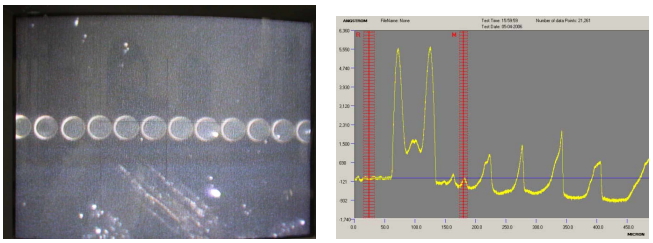
Table.1 The contact angles of the silver nanopaste between the P3HT film and the V_2O_5 film

Substrate	Contact angle
P3HT	65°
V2O5	<10°

The morphology of printed nanopaste relates to the contact angle on the surface. The morphologies of the nanopaste on these two substrates are shown in Fig.3. As the nanopaste is inkjet printed on the the P3HT film and then post-annealed, the dot diameter shrinks to about 30um and forms a coffee-ring structure. The thickness of the ring edge is about 25um. The drop morphology on P3HT is so rough that it is hard to form flat film and to pattern uniform metal electrodes. On the other hand, it is a good choice to print nanopaste on V_2O_5/P3HT film. The dot size is 73um and does not shrink. Coffee-ring still forms, but the morphology of dot is flatter and easier to construct lines and patterns of metal electrodes. Ring thickness is about 500 nm. After the patterned Ag nano-paste being sintered at temperature of 150°C for 30 mins, the resultant resistivity of the inkjet printed electrode is about $3x10^{-8}$ ohm-m, which is 2 to 3 times of that for the normal bulk silver.



(a)



(b)

Fig.3 *Profiles of the sintered silver nanopaste dot formed by inkjet printing on the different substrates: (a)P3HT and (b) V_2O_5.*

Table. 2. Electrical characteristics of the various PTFTs.

S-D Electrodes	Mobility (cm^2/V.s)	Threshold Voltage(V)	On/Off Ratio
Evaporate Au	$3.48x10^{-3}$	-9.49	14268
Evaporate Ag	$1.88x10^{-3}$	-11.17	629
Evaporate V_2O_5/Ag	$2.23x10^{-3}$	-10.63	1398
Evaporate V_2O_5/Ag (with post-annealing)	$1.19x10^{-3}$	-9.95	3107
Evaporate V_2O_5/IJP Ag (with post-annealing)	$2.98x10^{-4}$	-15.27	138

The characteristics of the device with transition metal buffer layer

The source-drain (S-D) electrodes are bilayer electrodes formed on the organic active layer. The channel width and length of each device is the same, 2000 um and 140 um, respectively. There is no difference in device performance between evaporated silver and bilayer V_2O_5/Ag electrodes. The results are shown in Fig.4 (a) and Fig.4 (b). The device with Ag S-D electrode has on-off ratio (I_{on} / I_{off}) and mobility similar to the device with V_2O_5/Ag S-D electrode. The on-off ratio is near 10^3 and the mobility is about 10^{-3} cm^2/V.s. The current of V_2O_5/Ag S-D electrode is about 2 times larger than that of device with Ag S-D electrode, indicating better hole injection after inserting the V_2O_5 , which can also be a hole injection layer, not only surface energy modification. In the case of ink-jet printed silver electrode, the patterned modification of the V_2O_5 buffer layer is necessary for the correct definition of S-D boundary. The Ag nanopaste ink is self-aligned onto the patterned S-D V_2O_5 buffer layer and does not formed on the P3HT due to the different contact angle, i.e. the surface energy. After post-annealing, device performance is shown in Fig.4 (c) and Fig.4 (d). We observed that there is no device performance decreasing for the device with evaporated S-D electrodes after post-annealing the device under 150°C for 30min. Device performance of the device with ink-jet printed Ag electrode is not so well. The mobility and current drops one order of magnitude, which may be due to the conductivity decrease of the inkjet printed Ag electrode and the organic residuals from nanopastes present between the Metal/Semiconductor interface. These results are summarized in Table.2. We note that the choice of S-D electrode and interface engineering are important. The work function of Ag (4.9eV) is smaller than that of Au (5.2eV), Hence the injection barrier for device with Ag electrodes is larger, which is a possible reason for the worse device performance.

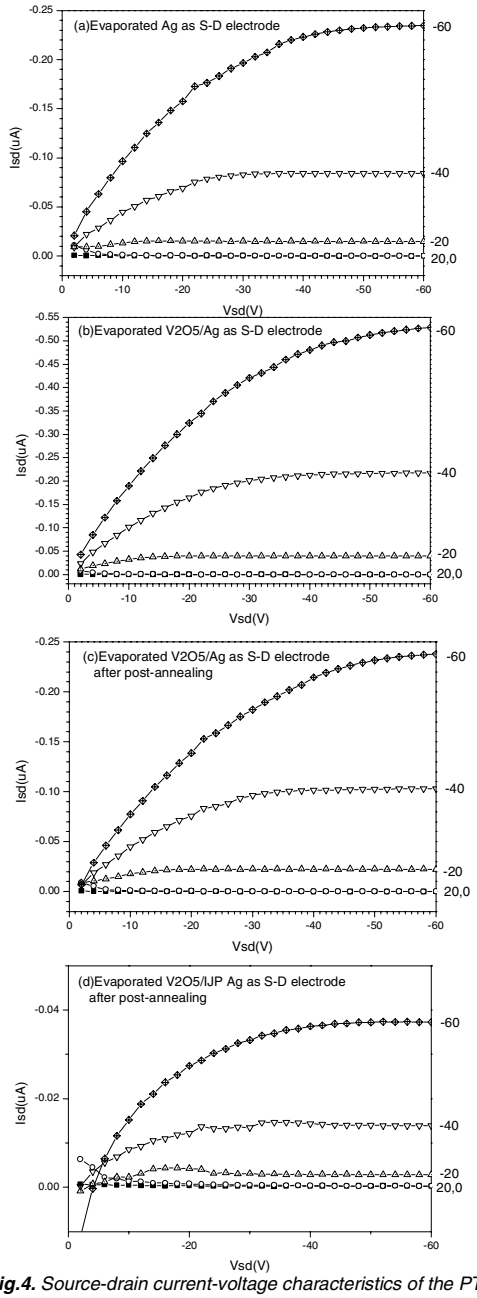


Fig.4. *Source-drain current-voltage characteristics of the PTFT ,wherein the*

source-drain electrodes are: (a) evaporated Ag, (b) evaporated V_2O_5/Ag, (c) evaporated V_2O_5/Ag with post-annealing and (d) evaporate V_2O_5/IJP Ag with post-annealing.

Conclusion

In this paper, we have successfully demonstrated a PTFT device fabricated by inkjet printing top silver nanopaste electrode and thermally evaporating and spin-coating the rest. By modulating the ink-jet printing parameters, a well sintered silver electrode is formed to fabricate a TFT device with a channel width of about 2000um and channel length of about 140um. Furthermore, the sheet resistivity of the inkjet printed electrode can reach down to $3x10^{-8}$ ohm-m, which is only 2 to 3 times of the resistivity of the bulky silver. The morphology of the drop on the P3HT is rough and hard to form flat lines and patterns of the metal electrodes, so we introduce a thin transition metal oxide as the buffer layer. Device performance of the inkjet printed Ag electrode is not as good as evaporated one. The mobility and current drops one order of magnitude, which may be due to the conductivity decrease of the inkjet printed Ag electrode and the organic residuals from nanopastes present between the Metal/Semiconductor interface. In the future, we expect to improve the interface between the S-D electrodes and the semiconductor of printed PTFT device with comparable performance to an evaporated or spin-coating counterpart.

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Kuo-Tong Lin received his Master degree in materials science and engineering from National Tsing Hua University in 2001. He is now a process and integration engineer in the Display Process Integration Technology Division, Display Technology Center of Industrial Technology Research Institute at Taiwan. His works have primarily focused on the reseach and development of the industrial application of the ink-jet printing processes, especially in PLED (polymer light emitting diodes) and OTFT devices.