Ink-Jet Printed Passive Electronic Components: Metal-Insulator-Metal Device

Chia-Hsun Chen, Yuh-Zheng Lee, Chung-Wei Wang, Ming-Huan Yang, Kevin Cheng, and Jane Chang, OES Lab/ITRI, Taiwan, R.O.C.; Chung-Ping Liu, and Sha-Man Wang, Yuan-Ze University, Taiwan, R.O.C.

Abstract

In this study, an ink-jet printed poly(methylmethacrylate)(PMMA) solution with mixed organic solvent to form insulator was presented. A detail observation of ring edge behavior for Ink-Jet Printing (IJP) device and its process parameters relation had been evaluated. One of the layer structure consisted of a thin layer of adhesive polymer (polyvinyl acetate: PVA) between bottom electrode and printed insulator layer, and then to treat the spincoated thin PVA with CF₄-plasma to raise the contact angle up to 40~50 degrees. Besides, a mixed solvent comprised of one solvent having lower boiling point and another one having higher boiling point was used to improve the ring-effect as well. Heating the platform as the droplet is landing also mitigates the effect of coffee-ring. Single-layer insulator device is very easy to be leakage, so triple-layered insulator device is made and then has better capacitance characteristic. Experimental results indicated that the leakage current for ink-jet fabricated multi-layered insulator was about 10nA/cm² at 3V, and the dielectric constant for the printed insulator was about 3.0.

Introduction

In recent years, there is growing need for low cost Radio Frequency Identification (RFID) technology comparable to barcode[1] for its better convenience and more functionality. But the processes involved with silicon-based technology have no much room for further cost-down. Among the alternatives, ink jet printing process is a competitive candidate because of its low-cost and ease of fabrication potentials. In ink jet printing process, the coffee-ring formation of the printed droplet is a major issue, which troubled many researchers who have attempted to form an uniform thin film layer with this method. In this work, we developed a series of processes to reduce the coffee-ring effect to fabricate embedded capacitor with soluble insulator by ink-jet printing platform, which is composed of a plate with three high accuracy moving axes, and a thermal bubble print head. Both of them are developed by OES Laboratory of ITRI. A spin-coated PVA layer with plasma treatment can help to improve the film formation for the printed droplet. The effects for the solvents with and without mixing with higher boiling point solvent have been explored. We also studied the results in various kinds of printing schemes. The devices with triple-layered printed insulators show more stable and definite capacitance characteristics with a dielectric constant of about 3.0.

Experimental Chemicals Preparation

We have fabricated capacitor with ITO as the bottom electrode, silver as the top metal, and PMMA as the insulator.² The insulator

was spin-coated with 500 rpm for 13 seconds at first then with 1000 rpm for 30 seconds. Two kinds of solvent are prepared, one is pure anisole, and another is anisole mixed with 1,2,4-trimethoxybenzene (TMB) by 1:1 weight ratio. Figure 1 shows the I-V and C-V for a MIM device with about 300~400nm thick of spun-on PMMA layer, wherein (a), (b) are for the case with anisole, and (c), (d) are for the case of mixed solvent. The current density of the device is of the order of 10nA/cm² at 3V, and the capacitance of the spun-on device will be taken as a standard for comparison with that of ink-jet printed devices in this work.



Figure 1. The (a)(c) I-V and the (b)(d) C-V diagrams of the MIM device with ITO as the bottom electrode, silver as the top metal, and spun-on PMMA as the insulator layer. (a) and (b) are from the pure anisol as solvent. (c) and (d) are from the mixed solvent of anisol and TMB.

Jetting Observation

In order to print the solution for PMMA by the thermal bubble ink jet print head developed by OES/ITRI, proper viscosity and surface tension for the solution are necessary. We found that the solution with 10 to 15 wt% of PMMA in pure anisole and anisole-TMB mixed solvent are all suitable for printing. In the case of pure anisole, the surface tension is about 29.58 to 33.14 mN/m and the viscosity is about 5.30 to 12.00 cps. Figure 2 shows the consecutive pictures with time interval of 2 µs for the droplets with pure anisole as solvent just printed out of the nozzles of the spinting head. Each picture is taken from the overlap of the shots

for thousands printed droplets from the same nozzle; hence the clear shape of the printed droplet exhibits the stability for the printed droplet.



Figure 2. Strobes for printed droplet of 14 wt% PMMA solution with pure anisole as the solvent. The strobe for the case with mixed solvent is not significantly different from the above case.

Device Structure

Figure 3 shows the structure and layout of the printed MIM device. The substrate is ITO glass. The ITO is etched to form five individual stripes on a $3 \text{ cm} \times 3 \text{ cm}$ substrate for use as electrode and electrical connection. The insulator is printed on ITO to cover the intersection between the bottom ITO and the top silver stripe.



Figure 3. The device layout structure of the MIM device.

Due to the non-uniformity of printing PMMA on ITO, a thin layer of PVA was spun upon the patterned ITO to raise the contact angle for the printed insulator droplet. The PVA is dissolved in DI water with 12 wt %, and it is necessary to heat it up to 96.3°C in the stirrer to afford the better solubility. The solution was spin-coated with 500 rpm for 13 seconds, then with 1,500 rpm for 30 seconds. The PVA layer was baked with hot plate (HP-303DN) at 70°C for 90 minutes, because the glass transition temperature for PVA is around 61.3°C. The baked PVA layer was treated by CF₄-plasma (Tepla 300) to increase the liquid-repellant tendency. The gas flow rate is 300 sccm, the power is 600 Watt, and the treatment time is lasting for 60 seconds. The contact angle for the anisole droplet on the ITO surface treated by plasma is 8.2±0.67 degrees, it is 13.82±0.1 degrees on the PVA coated ITO without plasma treatment, and is 45.1± 0.09 degrees on the PVA coated ITO with CF,-plasma treatment. The larger contact angle can cause the printed droplet not to spread too far from the landing position to prevent further "coffee-ring" formation. The coffee-ring formation will cause the printed film very non-uniform.²

Ring Edge Behavior

After surface treatment for the thin PVA layer, insulator solution with 10 wt% of PMMA was printed to cover the cross section

between the bottom and the top electrodes. The printed films were baked with hot plate (HP-303DN) under 90°C for 20 minutes. The moving plate was kept at 55°C as the droplet was landing on it, this will suppress the coffee-ring formation as well. Figure 4 shows the droplet formation at different landing conditions. The coffeering formation is very obvious for the case without surface treatment [Fig. 4(a)], and it was mitigated for the case with treatment [Fig. 4(b)]. In Fig. 4(c), the coffee-ring is not so obvious for the case of mixed solvent without surface treatment, and after surface treatment, Fig. 4(d) shows actual improvement in suppressing coffee-ring formation. Silver was deposited as the top metal with thickness of 3000Å. The silver stripe was extended to reach an ITO pad reserved on the glass substrates; hence the silver film can be kept well as we measure the device (Fig. 3).



Figure 4. The profiles for the printed droplet with pure anisole as solvent, (a) without and (b) with surface treatment. The profiles for the printed droplet with mixed anisole-TMB as solvent, (c) without and (d) with surface treatment.

Results

No obvious difference can be recognized between the profiles of printed single-layered film of the solution with pure and that of mixed solvent. But the I-V curves[Fig.5(a) and (b)] of the devices fabricated through pure anisole shows that both of them suffer from leakage current. However, in the case of the devices for mixed solvent, there is one device performing low leakage current characteristic. Although the mixed solvent can improve the film formation in one drop test, the final resulting devices still perform leakage behavior. This indicates that for an area printing, the uncovered defects still dominate and therefore result in electrically short phenomenon. No matter what solvent was used, the printed single PMMA insulator layer was too rough to prevent the leakage in these devices. Hence we printed two more layers to overlap the first printed bottom layer.



Figure 5. I-V curves for the case with (a) pure solvent and (b) with mixed solvent in single-layer device. (c) The C-V curve for low leakage-current device[IJP TMB_4 in Fig.5(b)] in the case of mixed solvent.

Figure 6(a) is the I-V diagrams for the triple-layered device with pure solvent. Fig.6(b) shows its C-V characteristic. Figure 6(c) and (d) are the I-V and C-V curves for the triple-layered devices with mixed solvent, respectively. All of the eight devices show very low leakage current, hence the triple-layered devices perform much better than the devices with single-layer insulator. Fig.6(e) and (f) are the profile for the printed films with triple-layer insulator for the case of pure and mixed solvent, respectively. The vertical axis are magnified, in fact, the variation of the film is only about several percents.

Discussions and Conclusions

Suitable surface treatment by CF4-plasma on the PVA layer is a key process to improve the film formation of the printed solution. Further tests on the PVA layer formation and plasma conditions are expected to improve the performances of the printed devices in the future. Mixed solvent comprised with lower and higher boiling point solvent can help to mitigate the coffee-ring effect as well. Further works on choosing more suitable solvent combination and proper mixing ratio are expected to improve the results further as well. The other method to improve the performance of the printed device is to overlap the insulator layer to be multi-layer. The roughness due to coffee-ring formation can be lowered to just several percents, then the low leakage current and the definite capacitance characteristics are obtainable.

In summary, the ink-jet printed device by OES/ITRI has demonstrated definite capacitance characteristics with PMMA solution as soluble insulator. The resulting dielectric constant is about 3.0.



Figure 6. The (a) I-V and (b) C-V diagrams for the printed triple-layered devices with pure solvent. The (c) I-V and (d) C-V diagrams are for the printed triple-layered devices with mixed solvent. The profile for the printed triple-layered film with (e) pure and (f) mixed solvent. The scale for the vertical axis (film thickness) are magnified, actually the roughness is just about ten micrometer across one millimeter, i.e. just several percents.

References

- P. Harrop and R. Das, *Printed Electronics: Where, why and what next* (ID TechEX, Cambridge, 2004), website: <u>http://www.idtechex.com/</u>.
- 2. N. Stutzmann et al., Science 299, 1881(2003).
- 3. R. Deegan et al., Natural 389, 827 (1997).

Author Biography

Chia-Haun Chen received his Ph.D degree in the Institute of Physics from National Chiao Tung University in 2004. He is now a process engineer in the Printing Technology Division, Opto-Electronics and Systems Laboratories of Industrial Technology Research Institute at Taiwan. His work has primarily focused on the industrial ink-jet printing processes development, especially in color filter, polymer light-emitting diodes, organic thin film transistor, organic memory device, and passive electronic components devices fabrication by ink-jet printing and device simulation related with organic memory device involved as well. chenchiahs@itri.org.tw