ELECTRICAL PROPERTIES OF ORGANIC DYES

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Abstract: *A roll-to-roll (R2R) photo-lithographic process using a negative dry film photo-resist was used to pattern ITO on a PET film. The roll type of PET film with patterned ITO was used as one of the electrodes for printed organic diodes fabrication. The web width of the roll-to-roll manufacturing line is 2S0mm and the speed can be adjusted from 1 m/min to 3 m/min. The patterned ITO electrode made by the R2R photo-lithographic process showed a feature size less than lOum. A polymer diode device was fabricated by coating a polymer conductor and semiconductor on the patterned ITO electrode followed by thermal evaporating a cathode electrode on the semiconductor layer. The diode DC transfer curve showed a Vt at around O.SVand a ON/OFF ratio above 104 These results demonstrated the feasibility of using the R2R processes for fabricating organic electronics devices.*

1. INTRODUCTION

Different from the method of fabricating integrated circuit on silicon wafer in sheet-by-sheet platform, R2R processing concept has been widely applied to electronics device manufacturing in the past years. One of the key elements that necessitates these different manufacturing platforms is the substrate. The high throughput of R2R process is expected to enable significant cost reduction [1]. It is known that most of electronic device or component- level fabrication is much more complex than traditional R2R manufacturing such as press printing. In addition to precision multi-layer alignment issues, attentions must also be paid on the electrical properties and corresponding reliability of the printed materials for R2R manufacturing processes. Choosing applications with less stringent specifications such as touch panel, light shutter, solar cell, large area sensor array and bi-stable electronic paper [2] are ideal cases of entry for the implementation of R2R continuous process for flexible electronics. Recently, Phillips has made a demonstration of 13.S6J\1Hz RFID transponder made of organic materials [3]. Fraunhofer IZM has demonstrated polymer electronics fabricated by R2R process [4].

In this paper, a printed antenna, printed capacitor and polymer diode were used as the key components to make a flexible rectifier on plastic substrates for wireless transmission applications. A R2R photo-lithography process was introduced to produce patterned ITO electrodes on a PET film for the polymer diode fabrication.

2. R2R Electrode Patterning Process

The ITOIPET substrate used in this work is from CP Films, which has 12Sum thickness and 2S0mm web width. The ITO sheet resistance is approximately 7S Ohm per square with a thickness of about SOO A. Photo-lithographic equipments include R2R laminator, R2R exposure and R2R wet bench (develop, etch, strip called DES) were used for developing, baking, wet etch and wet stripping. The web width for each step was fixed 2S0mm and the process speed for lamination and DES was controlled at 1 meter per minute. Because the ITO is the only layer on PET substrate, the pattern exposure has no precision alignment issue, where the process speed was controlled at less than 20 seconds per shot. Each exposure area is 2S0mm by 2S0mm. The minimum test pattern on the mask was designed to have Sum strips of line and line gap. In this work, the commercial negative dry film resist from Asahi Kasei with 10um thickness was used. Since this resist has lower photo sensitivity, the dose energy used was at 100mJ/cm2 to 140mJ/cm2 After exposure, the unexposed area was developed by a dilute sodium carbonate solution or organic developer of TMAH. ITO was etched out by oxalic acid and the cured photo resist was stripped by an organic stripper composed ofBDG, NMP and MEA.

First of all, a roll type PET ITO was laminated with the dry film resist, where the tension was well controlled below 2Kgf/cm2 Any defect such as scratches, bubbles, wrinkles and even breaks on both dry film and PET webs should be eliminated. The roll edge after winding was controlled within I mrn. Because the dry film was laminated upon ITO surface, laminating conditions by both up and down rollers were controlled with temperature around 110°C and pressure around 4Kgf/cm2 This laminated ITOIPET with dry film resist was fed into R2R exposure machine and exposed shot-by-shot. A collimated light source was imposed on the stage below 4SoC during exposure process. The photo-resist was cured tension-free along machinery direction and transverse direction. The film web during winding was specially taken care to avoid damaging exposed surface and film edges. After proper reaction time for cross-link and stress release, the film web was then fed into wet bench of DES. Because DES machine is about 17 meters in length, the web tension was controlled more tightly; however, it depended on the process web length and could be dynamically adjusted. There was a protection film to cover the patterned surface after stripping. Figure 1 shows the roll type of ITO patterns on PET film by R2R photo-lithographic process. ITOIPET patterning has been done

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by R2R process up to 40 meters in length. Moreover, a continuous transportation in R2R DES has been demonstrated up to 640 meters. Figure 2 shows the pattern ITO/PET film after the patterning processes.

FIG. 1 Roll type ofITO patterns on PET fihn

FIG. 2 640m winding result in DES output

After ITO was patterned, which will be used as the first electrode, the roll web was cut into sheets for PETDOT:PSS and organic semiconductor materials spin coating for diode fabrication. Finally, a thermal evaporation was adapted to form a patterned aluminum as the second electrode to complete the diode fabrication processes.

3. Performance Analysis

ITO electrode patterning features made by the R2R photo-lithographic process has been verified by a set of process test key. As shown in figure 3 and figure 4, the patterns were transferred from the mask into the flexible sheets after been bent many times. The sheet resistance ITO was maintained approximately 75 Ohm per square before and after R2R patterning process.

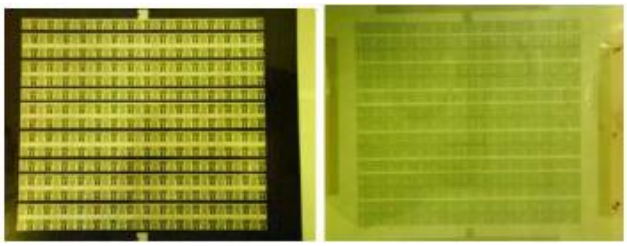

FIG. 3 The left picture is the mask and the right is transferred ITO patterns on PET film

FIG. 4 Bendable ITO patterns on PET fihn

3.1. Electrode Patterning Result

Other commercial available conductive electrode materials such as ITO on PET, IZO on PC, copper on PI and Aluminum on PET have been tested in this R2R patterning pilot line. Although pre-clean step is not necessary for every conductive surface, it may improve the adhesion condition between dry film resist and conductive surface. All the patterning process could be done by these machines except chemical enchants are swapped for corresponding electrode materials. Table 1 shows some physical properties for different conductive electrode patterning.

Electrodes material	Substrate Thickness	Electrode thickness	Minimum line/space
ITO on PET IZO on PC	125um 200um	0.05um O.13um	lOum lOum
Cu on PI	25um	5um	25um
Al on PET	125um	0.3um	10um

Table 1: Patternmg results for different electrode matenals

Figure 5 shows after-etch-inspection (AEI) result There are many square ring patterns which were used to test the resolution limit. Smaller feature size below 10um could be obtained by fine tuning lamination and exposure dosage; however, the dimensions for longer strip of lines and isolated lines and spaces become more difficult to control. The pattern morphology and profile checked by white light interferometer and SEM showed a tapered line edge which was caused by dry film lamination condition. This taper shape also depends on ITO property, where amorphous ITO corresponding to higher receptivity etched by oxalic acid will get sharp edge profile. It is improved by surface treatment before lamination, lamination condition and baking after exposure.

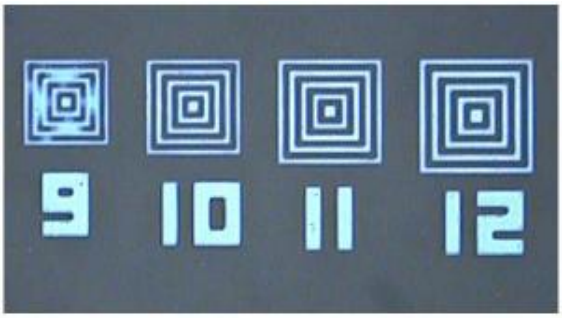

FIG. 5 AEI ofITO patterns on PET film

A nine-point uniformity was measured over the patterned ITOIPET sheet Three kinds of pattern dimensions after etch are collected and showed in Figure 6. Dense bar is a bundle of strip lines with equal line and space. Loose bar is a single strip line of ITO, and loose space is a single strip gap where ITO was etched off Both dense bar and loose bar have slight CD gains above the target 20um, and loose space has a CD lose about 3.5um. These results can be compensated into the mask design as a part of design rule.

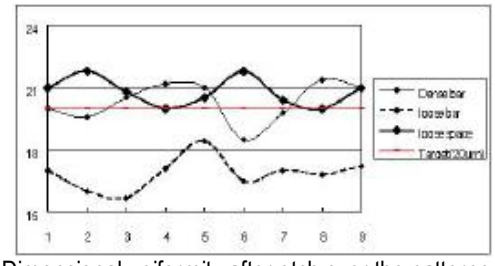

FIG. 6 Dimensional uniformity after etch over the patterned sheet

3.2. Organic Diode Performance

The patterned ITO was used as the anode of an organic diode. Figure 7 shows the diagram of an organic diode structure and its IV curve. A simple test pattern of cross area defines an active area for conducting electrical current For a cross area of 600um by 600um, the forward current of O.lmA voltage at 3V was obtained, whereas the reverse current is approximately 10nA and the voltage is around - 3V The Vt is about 0.5V and ON/OFF ratio is about 104.

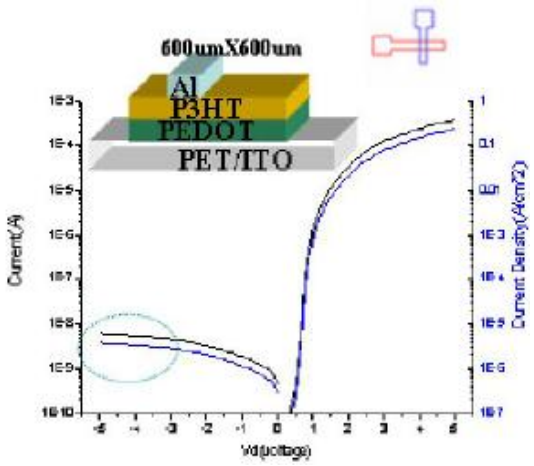

FIG. 7: IV cure and structure of organic diode

4. Conclusions

Electrode patterning is a fundamental step for many organic electronic device fabrication. R2R photo- lithographic process provides a good solution for fine feature electrode patterning manufacturing. However, there are still some issues needed to be addressed such as dimension stability, multi-layer alignment and stress control of multi-layer deposition. This work showed the feasibility of obtaining a fine feature ITO electrode patterning on PET substrate by a R2R process, which provides a low-cost solution for flexible electronics device future development.

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