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Novel Roll-to-Roll Deposition and Patterning of ITO on Ultra-Thin Glass for Flexible OLEDs

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SUMMARY Novel roll-to-roll (R2R) deposition and patterning of ITO on ultra-thin glass were developed with no photolithography and applied to flexible organic light emitting diodes (OLEDs). The developed deposition consists of low temperature sputtering and annealing. The developed patterning utilizes an etching paste printed by novel R2R screen printing.
key words: *roll-to-roll, ITO, ultra-thin glass, OLED, flexible, photolithography-free*

1. Introduction

"Flexible" is an attractive technical field in organic light emitting diodes (OLEDs) because "flexible" can provide such unique features as thin thickness, light weight, design flexibility, applicability to roll-to-roll (R2R) processes, etc. In flexible OLED technologies, flexible substrates and transparent electrodes are important key technologies.

Candidates for flexible substrate are ultra-thin glass [1], stainless steel foil [2] and barrier film. The comparison among these three substrates is shown in Table 1. Barrier films may be believed as most common flexible substrates for flexible OLED devices at present. Indeed, many flexible OLED displays are reported to utilize flexible barrier films [3]–[5] and R2R fabrication of flexible OLEDs with barrier films has also been reported [6]. However, the gas barrier technologies of barrier films still have issues because of the expensive cost, the difficulty of production, etc. On the other hand, stainless steel foil has perfect gas barrier property in addition to several advantages such as high temperature tolerance, chemical stability, size stability, etc., while the surface roughness and the conductivity of substrate have been issues. Recently, for overcoming these issues, surface planarization technologies were developed and reported, being applied to flexible OLED devices [2], [7]. Ultra-thin glass also has several excellent properties with regard to gas barrier, surface smoothness, transparency, thermal stability, size stability, process stability, etc. However, there are only few reports on the application of ultra-thin glass to flexible OLED devices [8] because of the weak mechanical robustness.

This study investigated treating processes of ultra-thin glass, obtaining useful technologies for applying to R2R processes.

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Table 1 Comparison of three flexible substrates for flexible OLED devices.

	Ultra-thin glass	Stainless steel foil	Barrier film
Specific gravity	~2.5	~7.8	~1.4
Temperature resistance	Excellent	Excellent	Low PET: 110 °C PEN: 150-180 °C
CTE	3-8 ppm/°C	14-16 ppm/°C	PET: 65 ppm/°C PEN: 18-20 ppm/°C
Surface smoothness	Excellent	Not smooth	Not smooth
Problems in handling	Breakable	Conductivity, Optical transparency	Less rigid
Roll to Roll (R2R)	Poor experience	Poor experience	Much experience
Vapor barrier	Excellent	Excellent	Poor

CTE: coefficient of thermal expansion
PET: polyethylene terephthalate
PEN: polyethylene naphthalate

In addition, this study investigated novel R2R technologies for indium tin oxide (ITO), using ultra-thin glass.

As is well known, ITO is the most common transparent electrode for not only OLEDs but also liquid crystal displays (LCDs). While ITO has several advantages such as acceptable conductivity and transparency for OLEDs, chemical and temperature stabilities, etc., one serious issue is the expensive cost. The expensive cost of ITO is mainly attributed to two reasons. The one is the fact that indium is a rare metal, which is closely related to the resource problem. The other is long processes including vacuum deposition of ITO and photolithography, both of which require expensive equipment.

This study proposes novel R2R fabrication processes of ITO for flexible OLED devices, using ultra-thin glass. The novel fabrication technologies include R2R sputtering technologies and R2R patterning technologies with no photolithography. While R2R sputtering of ITO on ultra-thin glass has been reported [9], this study investigated the influence of the deposition temperature and sputtering parameters on not only resistivity and transmittance but also distribution of resistivity, surface smoothness and curl of substrate. While the most common patterning method of ITO is photolithography, this study investigated novel R2R patterning using an etching paste printed by R2R screen printing method. The developed and optimized R2R processes with deposition and patterning of ITO were applied to flexible OLED devices, successfully obtaining uniform emission.

2. Experimental

Ultra-thin glass in this study is OA10G supplied from Nippon Electric Glass [1]. Figure 1 shows a roll-type flexible ultra-thin glass. The width and thickness are 300 mm and 50 μm, respectively. Lead films (PET or PEN, thickness of 100 μm) are attached to the head and the tail of ultra-thin glass. When the ultra-thin glass is wound around a 6-inch core, an insert film (PET with the thickness of 50 μm) is stacked on the ultra-thin glass for preventing contact and/or adhesion between the stacked ultra-thin glasses.

For cleaning ultra-thin glasses, a R2R wet-cleaning equipment developed by FEBACS is used. The equipment has functions of brush cleansing (using detergent, non-contact), pneumatic jet cleaning, air knife and IR drying with this sequence [10].

ITO layers are deposited on the ultra-thin glass by using a R2R sputtering equipment of Kobe Steel [9]. The target is SnO_2(10 wt%)-doped ITO. The DC sputtering power is 1 kW or 3 kW. The speed of substrate movement is 1 m/min, 0.3 m/min or 0.1 m/min. The sputtering temperature is −20°C or 250°C, where the sputtering temperature is defined as the temperature of the rotating drum contacting to ultra-thin glasses under sputtering.

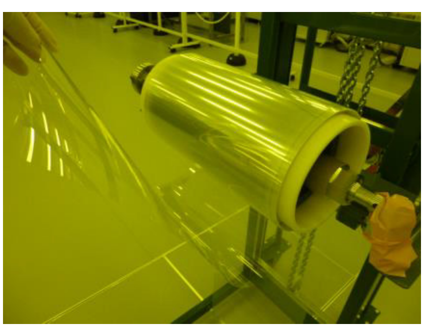


Fig. 1 Roll-type flexible ultra-thin glass OA10G supplied from Nippon Electric Glass.

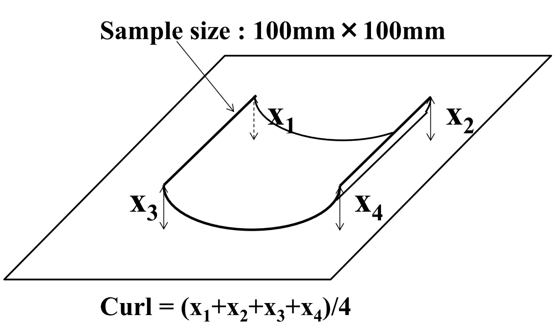


Fig. 2 Evaluation method of substrate curl.

The etching paste was supplied from Noda Screen. The printing equipment of the etching paste is a R2R screen printing developed by SERIA [11].

Curl of substrate is evaluated, according to SEMI D074–0116 standardization "Guide for Measuring Dimensions for Plastic Films/Substrates". In this method, a curled substrate is set on a flat plate as shown in Fig. 2. The size of evaluated samples is 10 cm square. The distances from the four edges of a substrate to a flat plate are measured. The value of curl is defined as the average of the four distances.

The equipment for heat-annealing process is a normal clean oven. The equipment for photo-annealing process is a flash lamp annealing fabricated by DTF Technology.

3. Results and Discussion

3.1 Outline of the Developed R2R Technologies

The developed process for ITO deposition and patterning on ultra-thin glass is shown in Fig. 3. After R2R wet-cleaning of ultra-thin glass, an ITO layer is deposited by using a R2R sputtering equipment, followed by second wet-cleaning. An etching paste is printed by using a R2R screen printing equipment, followed by heating and third wet-cleaning. Before fabricating OLED devices, the substrate with the patterned ITO is heat-annealed or photo-annealed.

3.2 R2R ITO Deposition

In the ITO sputtering, several deposition conditions were evaluated and compared. The thickness of the ITO layer is 100-115 nm. The results are shown in Table 2. First, the sample 1 and sample 2 with different deposition temperatures are compared. When the deposition temperature is 250°C (sample 1), the obtained resistivity is 17 Ω/sq and the transmittance is 94.3%. On the contrary, when the deposition temperature is −20°C (sample 2), the obtained re-

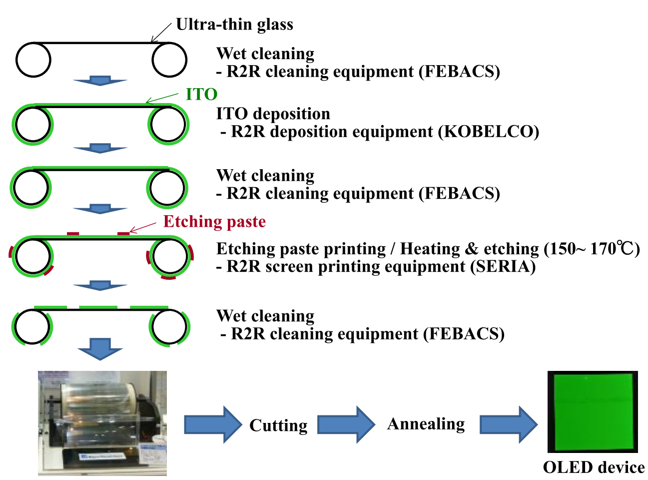


Fig. 3 Schematic illustration of R2R novel processes for ITO on ultra-thin glass.

Table 2 Properties of ITO layers fabricated by R2R sputtering.

	Sample 1	Sample 2		Sample 3	Sample 4	Sample 5
Deposition temperature	250°C	-20°C		-20°C	-20°C	-20°C
Deposition process	3kW 1 pass 0.3m/min	3kW 1 pass 0.3m/min		3kW 3 pass 1m/min	1kW 1 pass 0.1m/min	1kW 1 pass 0.1m/min
Annealing	None	Heat		Heat	Heat	Photo
		Before annealing	After annealing	After annealing	After annealing	After annealing
Surface resistance	17 Ω/sq	19~36 Ω/sq	18 Ω/sq	22 Ω/sq	18 Ω/sq	17 Ω/sq
Transmittance (Max)[1]	94.3%	90.0%	92.4%	98.0%	97.5%	97.0%
Ra (nm)	1.7 nm	0.8 nm	0.8 nm	0.4 nm	0.3 nm	0.3 nm
Curl (Shape)	5.5 mm (Convex)	0.6 mm (Convex)	0.6 mm (Convex)	0 mm	0 mm	0mm

The thickness of ITO: 100-115nm
[1] Reference: Urtra thin Glass

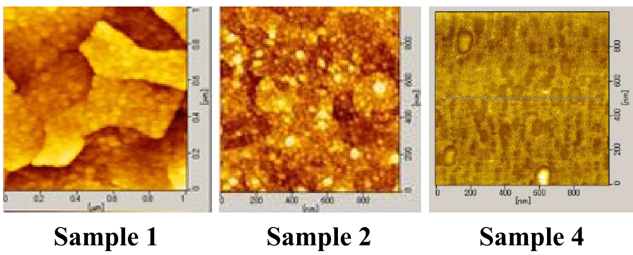


Fig. 4 AFM images of sample 1, sample 2 and sample 4. No annealing is applied.

sistivity is distributed from 19 Ω/sq to 36 Ω/sq and the transmittance is 90.0%. Figure 4 shows the AFM images of the ITO layers with the different sputtering conditions, clearly indicating that the high temperature deposition gives well crystalized ITO but the low temperature deposition gives poor crystallized ITO. Since it is well known that sufficient crystallization is required for obtaining low resistivity and high transparency in ITO deposition, it can be concluded that the poor crystallization obtained at low temperature deposition is the reason for the distributed large resistivity and low transmittance.

Although sample 1 with the high temperature deposition gives low resistivity and high transmittance, it also gives large curl (5.5 mm) and comparably large surface roughness (1.7 nm). Such curl gives rise to a serious problem because it gives large mechanical stress in the following R2R processes, inducing break of ultra-thin glass. When the thickness of glass substrate is 0.5 mm or 0.7 mm, which is general thickness of glass substrate for LCD and OLED devices, such curl scarcely occur because of the rigidity of glass substrate. However, when the thickness of glass substrate is thin such as 50 μm, the mechanical stress induced by ITO gives rise to such curl. The large surface roughness is also an issue because OLED devices tend to require smooth surface. Such curl and surface roughness are attributed to the well crystallized deposition of ITO because such large size of crystallization induces large mechanical tensile stress. On the contrary, low temperature sputtering of ITO gives small curl and smooth surface due to the small size of crystallization of ITO as are shown in the AFM images of sample 2 and 4 in Fig. 4. Especially, two optimized sputtering condition (sample 3 and sample 4) shows no curl. No curl is attractive feature for ultra-thin glass in R2R processes, preventing the break of ultra-thin glass.

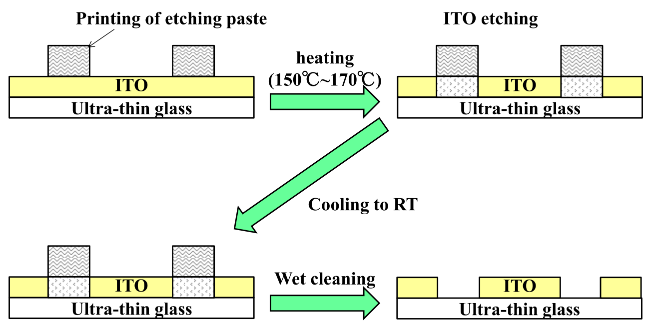


Fig. 5 ITO patterning process by using an etching paste.

In order to obtain low resistivity of ITO layers deposited at −20°C, annealing processes were applied. Two annealing process were investigated. The one is heat-annealing and the other is photo-annealing with flash lamp annealing [12]. As is obvious in Table 2, such annealing processes give drastic improvement in resistivity and transmittance. It is also emphasized that these annealing do not induce any change in surface roughness and curl. These results suggest that the annealing processes accelerate the crystallization of ITO without changing the crystal size of ITO. It can be concluded that the small crystal size of ITO is preferred because it would not induce large stress, giving no large surface roughness and curl.

3.3 R2R ITO Patterning

The ITO layer deposited on ultra-thin glass was patterned by using an etching paste [13] printed by a R2R screen printing equipment with no photolithography process. The patterning process by etching paste is shown in Fig. 5. The etching paste dissolves ITO by heat treatment with 150 ~ 170°C in the R2R screen printing equipment. It should be noted that no fluid material is produced in the etching process. Therefore, the ultra-thin glass with the etched ITO is easily wound up to a core. The substrate is then treated by brush cleansing with no detergent, two fluid cleaning, air knife and IR drying in the R2R wet-cleaning equipment. In this treatment, the ITO area with the printed etching paste and the residual etching paste are removed, resulting in the required pattern of ITO.

Figure 6 shows the comparison of this R2R patterning method with the normal sheet-to-sheet (S2S) photolithographic process. It is obvious that the novel R2R method is drastically shorter than the previous normal one, suggesting that the drastic reduction of investment is possible in mass production.

In this experiment, the novel (0-Gap) R2R screen printing equipment is applied. Figure 7 shows the mechanism of the 0-Gap R2R equipment. Classical screen equipment use

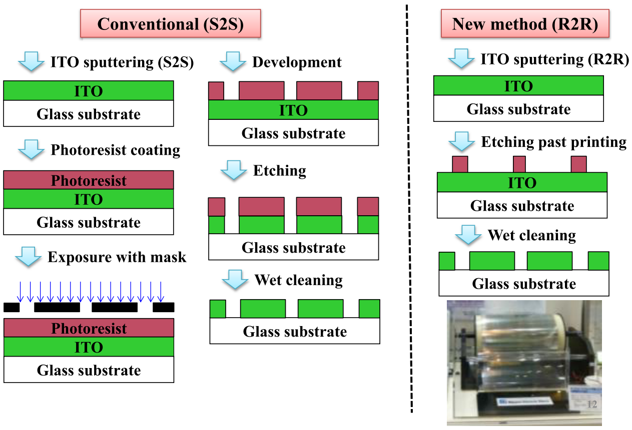


Fig. 6 Comparison of the novel roll-to-roll (R2R) ITO patterning process by an etching paste with the normal sheet-to-sheet (S2S) photolithographic process.

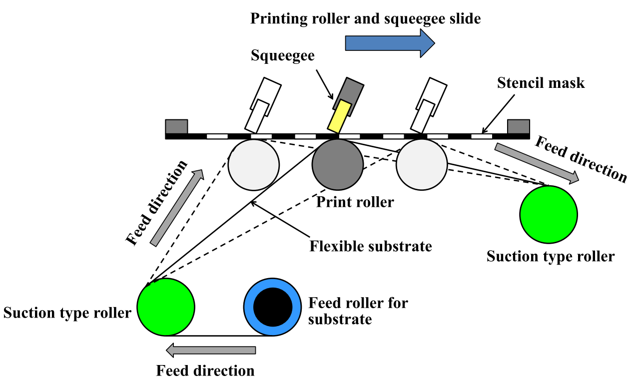
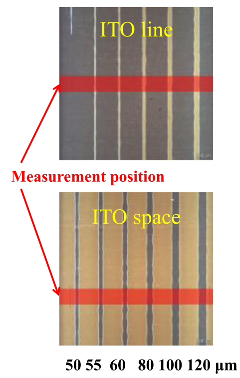


Fig. 7 Novel roll-to-roll (R2R) screen equipment with no gap between the stencil mask and the flexible substrate [7].

a flat stage and a flat stencil mask, which is deformed by a press of squeegee at screen printing process. On the contrary, the 0-Gap R2R equipment in this study has a print roller instead of a flat stage. Flexible substrates are sandwiched between a print roller and a flat stencil mask. In this equipment, the gap between a stencil mask and a flexible substrate is zero because of no deformation of stencil mask, while the gap in the classical screen printing is not zero. The zero gap induces small error of accuracy of position and size of patterns [11].

The patterning results of ITO are shown in Fig. 8. The patterning accuracy is around 50 ∼ 60 μm. Although such resolution is not suitable for display applications, it is acceptable in OLED lighting. In addition, the patterning by using an etching paste gives gentle sloop at the edge of the patterned ITO. The sloop length is around 17 μm, which was measured by a white light interferometric microscope. Since the thickness of the ITO is 100-115 nm, it is obvious that the taper angle at the ITO edge is very low, being suitable for preventing the current leakage and/or short between an anode and a cathode in OLED devices.



Design (µm)	Average (µm)	Max. (µm)	Min. (µm)
55	31.4	44.9	22.7
60	37.6	43.0	32.4
80	66.7	77.3	58.9
100	84.6	93.5	77.9
120	101.9	108.6	97.4

Design (µm)	Average (µm)	Max. (µm)	Min. (µm)
50	49.8	55.9	43.2
55	60.6	66.9	51.0
60	75.6	90.6	61.0
80	106.0	121.5	98.0
100	125.3	136.0	118.9
120	142.6	149.1	136.3

Fig. 8 Results of ITO patterning.

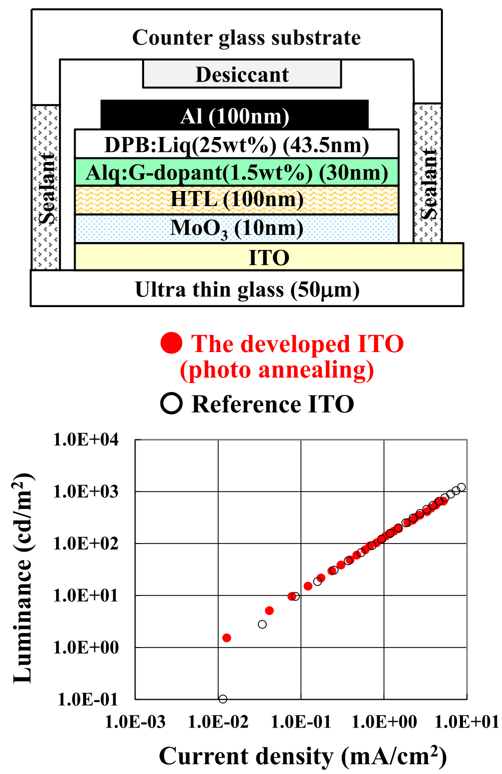


Fig. 9 Device structure and I-L characteristic of the OLED device fabricated by using the process shown in Fig. 3, where the annealing process is photo annealing.

3.4 Applications to OLED Devices

The ultra-thin glass with the developed ITO pattern was applied to OLED devices. Figure 9 shows the device structure of an OLED device fabricated by the process shown in Fig. 3, accompanying the I-L characteristics. The I-L characteristic of the developed OLED device is comparable with the reference OLED device with normal ITO, indicating that the developed ITO can be applied to OLED devices.

The device shown in Fig. 9 is not flexible but one can fabricate flexible OLED devices, combining a flexible en-

Fig. 10 Device structure and an emitting picture of the developed flexible OLED device. The roll type ultra-thin glass with ITO fabricated by the process shown in Fig. 3 is also shown.

capsulation. The device structure and an emitting picture of the developed flexible OLED device are shown in Fig. 10.

4. Conclusion

A novel roll-to-roll (R2R) process for deposition and patterning of ITO with no photolithography on ultra-thin glass was developed, investigating the effect of process conditions. The developed technologies can contribute to not only the cost reduction in OLED manufacturing but also the application of ultra-thin glass to flexible OLED devise.

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