54.2: Direct Printed Electrodes of Transparent Conductive Polymers for Flexible Electronic Papers

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Abstract

Direct formation of line-shaped electrodes consisting of transparent conductive polymer of poly(3,4-ethylene dioxythiophene) and poly(styrenesulfonate) (PEDOT/PSS) was successfully achieved onto a flexible polyethylene terephthalate (PET) substrate by using screen printing method. Improvement of the components and the viscosity of the conductive materials enabled to pattern the line electrodes in high resolution. A 4.0 in. diagonal and 88 dpi flexible electronic paper display using quick response liquid-powder technology has been prepared by applying the flexible substrate with the direct printed transparent polymer electrodes.

1. Introduction

Extensive efforts have focused on the development of flexible displays in this decade. Flexible displays have unique properties such as thinness, light weight, and comfortable portability, so that they are considered to be desirable information devices in future. Among the various kinds of the flat panel display technologies, electronic paper is more suitable to the flexible displays compared to the other types because it has some advantages about their reflective properties, wide viewing angle, and relatively simple panel structures [1-7].

We have developed flexible electronic paper displays using quick response liquid powder technology [5-7]. Figure 1 shows the panel structure of the electronic paper. Both the black and white powders with opposite charges are sandwiched between the plastic substrates with patterned electrodes in line shapes. Each particle moves according to the electric fields driven through the passive matrix electrodes.

One of the important technical issues for the development of the flexible electronic papers is to improve durability of the materials in the flexible panels. In many cases, some elements within the flexible panels are still made of inorganic hard materials which may be fragile for the deformation of the flexible panels.

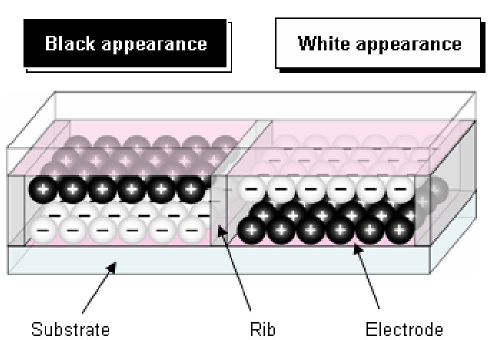

Fig. 1. Panel structure of electronic paper with powders which move between the substrates.

In the previous study, we have reported the possibility of an organic transparent polymer of PEDOT/PSS shown in Fig. 2 for a desirable candidate of a new electrode material in the flexible panels where inorganic oxide of indium-tin oxide (ITO) has been used before [7]. A large number of line-shaped electrodes in the resolution of 88 dpi were successfully formed by using a laser ablation method to a uniformly coated thin layer of PEDOT/PSS. Display properties of the flexible electronic papers with the PEDOT/PSS electrodes were also confirmed to be comparable to those of panels having ITO electrodes [7].

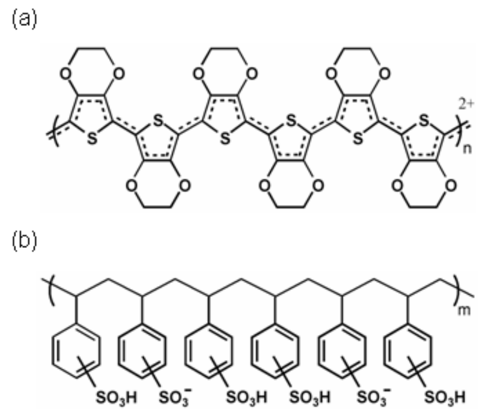

Fig. 2. Chemical structures of PEDOT (a) and PSS (b).

However in practice, for the use of the laser ablation method, expensive apparatuses must be introduced to mass production, which is not considered to be realistic. If we can form the electrodes directly using much simpler methods such as printing, applicability of the transparent conductive materials to the flexible electronic papers should increase drastically in view of cost and mass productivity. Although many approaches forming electrodes by printing of conductive pastes on bottom electric substrates have been extensively developed especially for thin film transistors so far [8, 9], there was no example of preparing electrodes on a front substrate that is necessary to be transparent by using printing methods.

Here, we will report the first example of a flexible display with an upper substrate composed of directly printed conductive polymer electrodes in high resolution. The line-shaped electrodes in a resolution of 88 dpi have been successfully prepared by screen printing. The improvement of the conductive polymers and printing methods has led to the achievement of the fabrication of printed panel electrodes.

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2. Methods

2. 1. Preparation of transparent conductive materials suitable for direct printing

To prepare electrodes directly by a printing method, the printing paste including PEDOT/PSS should desirably have high viscosity. In the previous work, we have coated the conductive transparent polymers of PEDOT/PSS (Fig.2) uniformly by a gravure method followed by laser ablation process [7]. The material used there was an aqueous suspension of the polymers. Its viscosity was 16 mPa·s, which was too low to pattern electrodes directly by a printing method. In case of low viscosity, it is concerned that the spacing areas between the electrodes where the paste must not be located tend to be filled with the flowed paste unwillingly. In this study, we have improved the suspension composed of PEDOT/PSS by mixing other additives which only increase the viscosity of the pastes without decreasing transparency and conductivity of the original suspension. The viscosity of the pastes has elevated to 19,000 mPa·s successfully.

2. 2. Screen printing process

For printing methods, there are many kinds of approaches such as posi printing, screen printing, ink-jet, and so on. Here, we have selected screen printing method to form electrodes on flexible PET substrates. Screen printing has some advantages in regard to the accuracy of aliment which is required during the following assembly processes of the flexible electronic paper panels, and cost of apparatus. The mask of the screen printing used in this study had 640 meshes per inch. The resolution of the test pattern was 82 dpi (line pitch: 310 μm), where the line and space widths were 260 μm and 50 μm, respectively. Patterning of 88 dpi was also conducted for display preparation (line pitch: 290 μm, line/space: 230/60 μm).

3. Results

3. 1. Flexible substrates with direct printed PEDOT/PSS electrodes

Direct printing of the line-shaped electrodes was carried out by using the improved viscous pastes containing the transparent conductive polymers of PEDOT/PSS and the screen printing technique described above. Figure 3 is a photograph of a PET film with printed electrodes in the test pattern. For visibility of the printed area in the photograph, a white paper is located behind the PET film. Screen printing of the pastes containing PEDOT/PSS has been well performed without flow of the pastes.

Figure 4a shows a photomicrograph of line-shaped electrodes prepared from the screen printing method. The same patterned electrode image obtained from laser ablation process in the previous study is also shown in Fig. 4b as a reference. The formation of line-shaped electrodes through screen printing can be obviously observed although the edges of each line are somewhat vague in comparison with those formed by the laser ablation. The line width of the electrodes in Fig. 4a is 268 μm, and the spacing is 42 μm.

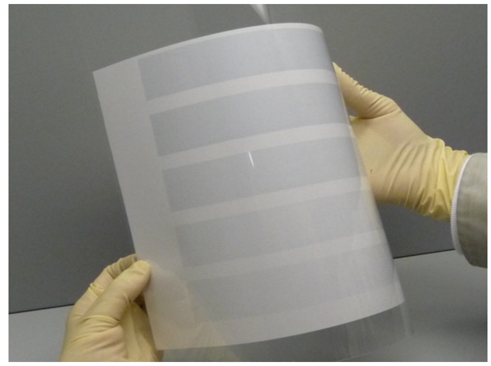
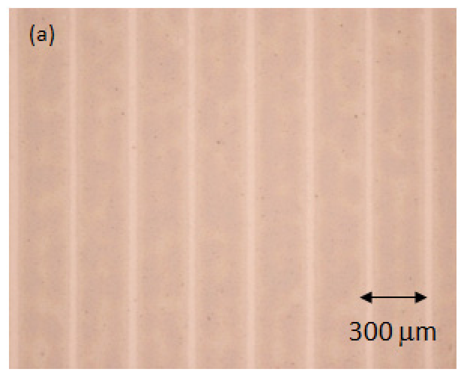


Fig. 3. A Photograph of a PET film with electrodes of PEDOT/PSS obtained through screen printing. A white paper was laid behind the PET film for ease of viewing electrode area.



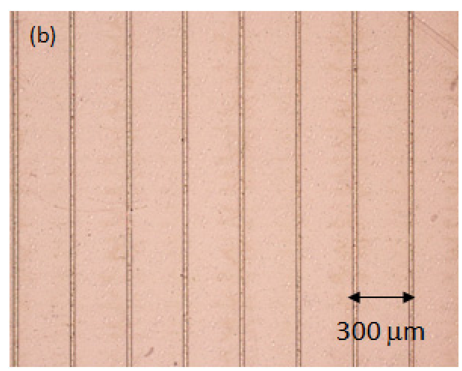


Fig. 4. Photomicrographs of electrodes of PEDOT/PSS obtained through screen printing (a) and laser ablation (b).

3. 2. Optical and electric properties of the printed PEDOT/PSS electrodes

Transmittance spectra of the electrodes formed by screen printing and laser ablation process, and that of an ITO electrode were measured by micro spectroscope as shown in Fig. 5. The spot area measured on each electrode was within the circle of 100 μm diameter. Both electrodes of PEDOT/PSS obtained from screen printing and laser ablation process exhibit almost same transmittances in full ranges of visible region from 80 to 90% (Fig. 5a, b). Conductive polymer of PEDOT/PSS absorbs lights in near IR region in comparison with ITO which results in bluish appearance for the film substrate with patterned electrodes.

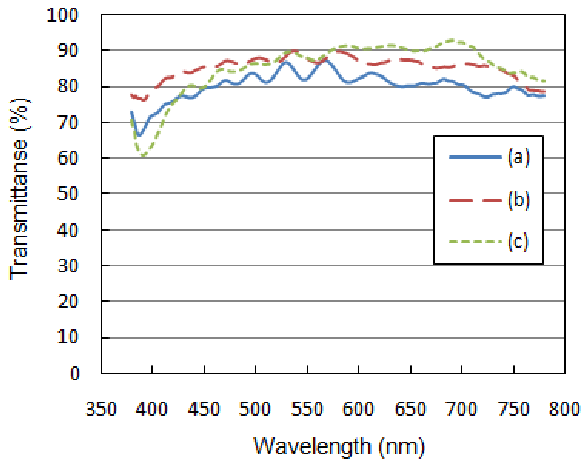


Fig. 5. Transmittance spectra of line electrodes of PEDOT/PSS formed by screen printing (a), laser ablation (b), and a line electrode of ITO (c).

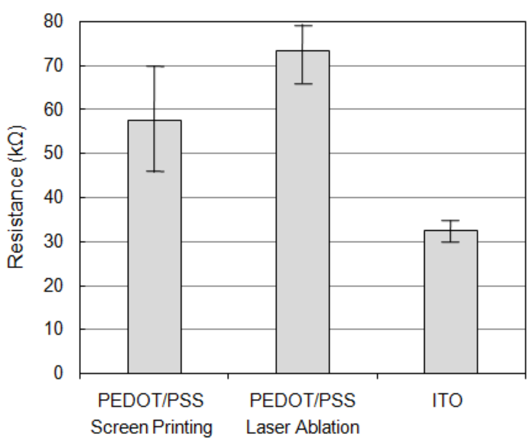


Fig. 6. Resistance of line electrodes of PEDOT/PSS formed by screen printing, laser ablation, and a line electrode of ITO. The length of each line is 30 mm.

Figure 6 is the result of the measured resistances for the line electrodes exhibited in Fig. 5 by the use of manipulator. The length of each line was 30 mm. The resistances of the electrodes composed of PEDOT/PSS prepared by screen printing and laser ablation exhibit 57 and 75 kΩ respectively, those are almost twice of that of ITO electrode. In the previous study, we have succeeded in displaying the flexible electronic papers by using the substrates with the line electrodes of PEDOT/PSS prepared through the laser ablation method. The optical and conductive properties in the case of the screen printing examined in this study are almost similar to those of laser ablation as shown in Fig. 5 and 6. Therefore, we consider it would be possible that the substrates with direct printed PEDOT/PSS electrodes would function in the flexible electronic paper displays of powder moving type.

3. 3. Flexible electronic paper driven through the direct printed polymer electrodes

The flexible PET substrates with the line-shaped electrodes of PEDOT/PSS have been applied for the fabrication of flexible electronic papers utilizing quick response liquid-powder technology. Figure 7 is a picture of a flexible electronic paper display having direct printed PEDOT/PSS electrodes on its upper substrate. The size of the display is 4.0 in. diagonal and it has an array of 281×210 pixels. The resolution is 88 dpi. It is confirmed that a checker pattern has been clearly displayed by passive matrix driving through the printed electrodes composed of the polymer materials. This electronic paper panel also shows good flexibility as shown Fig. 7.

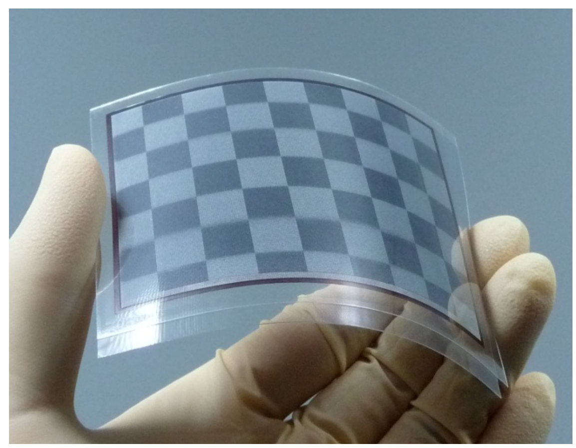


Fig. 7. A flexible electronic paper panel with direct printed PEDOT/PSS electrodes on the upper substrate (4.0 in. diagonal, 281×210 pixels, 88 dpi).

The reflectivity of the flexible display with printed PEDOT/PSS electrodes has been compared to that obtained through the laser ablation method developed in the previous study (Fig. 8). Although the reflectivity of the panel with printed electrode is slightly lower than that having electrodes prepared by laser ablation, similar contrast ratio of black and white states is observed. Further development of the materials and the printing processes will elevate the display properties in near future.

As shown above, we have succeeded in preparing a flexible electronic paper panel with an upper substrate where we only have to print the conductive pastes materials, and it is not necessary to carry out more complicated and cost consumed techniques such as photolithography and laser ablation.

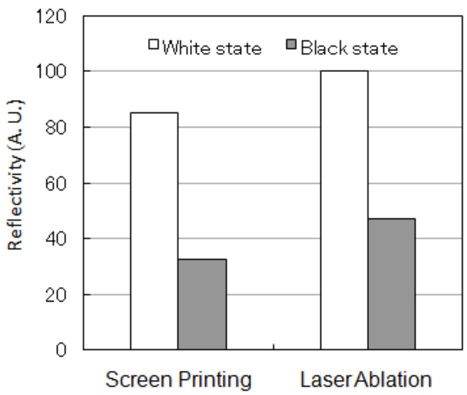


Fig. 8. Reflectivity of the flexible panels with electrodes of PEDOT/PSS prepared from screen printing and laser ablation method.

4. Conclusions

The result described here is the first example of flexible display with electrodes composed of the transparent conductive polymer materials formed directly onto the upper substrates by a screen printing method. Although there were a lot of examples where the classical conductive inks such as silver pastes were used for the fabrications of electric components by direct printing, transparent conductive materials have never been utilized for the patterned electrodes in high resolution to our knowledge. This should be due to the difficulty to develop suitably viscous materials without decrease of transparency and conductivity. In this study, we have solved this problem by improving of the composition of the paste materials including PEDOT/PSS. These results we have shown in this study should progress the development of the materials and processing technologies in the research field of printable electronics which also contributes the advance of flexible display devices.

5. References

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