

1997

Conducting polymer substrates for plastic liquid crystal display

Ling Huang*, Catherine O'Ferrall, Terrance Vargo and Ranganathan Shashidhar
Code 6900, Naval Research Laboratory, Washington, DC 20375-6900

William Fritz, Steve Smith, Richard Hewitt and William Doane
Liquid Crystal Institute, Kent State University, Kent, OH 44242

ABSTRACT

In a conventional liquid crystal display device (LCD), glass substrates coated with an indium tin oxide (ITO) layer are typically used for the application of an electric field to the liquid crystal material. For many applications, there is a need for a LCD with a plastic substrate. Polypyrrole is a well known conducting polymer for its high conductivity and chemical stability. Compared with the currently used ITO conducting layer, polypyrrole is more compatible mechanically with plastic. Because it is an organic material, it should be able to bend and flex with the substrate. Therefore, it is a good candidate for the conducting surface needed in a plastic LCD. Here we present the preparation of polypyrrole films on a polyethylene terephthalate (PET) substrate by an *in-situ* solution deposition process and their patterning by conventional photolithography techniques. We will discuss their important physical properties, such as surface resistance and optical transmission, and their suitability as a substitute for ITO as an electrode for a plastic reflective Ch-LCD.

Keywords: reflective display, plastic display, conducting polymer, polypyrrole, photolithography

1. INTRODUCTION

Reflective cholesteric liquid crystal displays (Ch-LCDs) have attracted a great deal of interest (Ch-LCDs) because they are lightweight, low power flat-panel displays. Because of their unique optical properties, reflective Ch-LCDs allow one to use optically birefringent material, such as plastic, as substrates. Furthermore, the Ch-LCD can be made bistable, which allows for the manufacture of large area, high-resolution displays without an active matrix and thus can be processed at low temperatures compatible with most plastic materials¹⁻⁴. By taking advantage of these characteristics, the use of a plastic substrate would make a display even lighter in weight, more rugged (i.e., nonbreakable), and possibly flexible.

Currently, the transparent metal indium tin oxide (ITO) is used as the conducting electrode on glass as well as plastic substrates. While ITO works well with glass, it does not adhere as well to plastic, is brittle, and has a tendency to break under constant bend conditions. A conducting polymer such as polypyrrole should be able to overcome these shortcomings. As an organic material, polypyrrole is not only flexible and bendable, but also more compatible with the plastic substrate.

Polypyrrole has attracted great interest in the last ten years because of its high electrical conductivity and environmental stability, making it a good candidate for many possible applications⁵. Extensive studies have been done to improve the conductivity of the material. Some efforts focus on the relationship between the conductivity and the chemical structure of the material as summarized in reference 6. Others focus on the effect of the polymerization conditions, such as the stoichiometry of the reactants, selection of dopants, reaction media, and temperature, on the conductivity of the material prepared⁷⁻¹⁰. In this paper, we investigate the preparation and patterning of a polypyrrole film as a substitute for ITO as the display electrode for a reflective Ch-LCD.

One can prepare polypyrrole films either chemically or electrochemically. While providing films with good quality, the latter technique suffers from the limitation that it requires a conductive substrate. Also, the dimension of the film grown by this technique is limited to the size of an electrode. In contrast, *in-situ* chemical solution deposition is applicable to a variety of surfaces including nonconductive ones¹¹. It is especially suitable where a substrate of large area or with various kinds of geometric shapes is required. By optimizing the deposition conditions, we have been able to use the chemical solution deposition technique

DTIC QUALITY INSPECTED 2

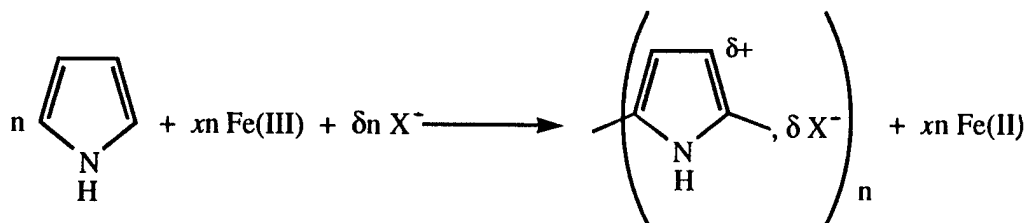
DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

19990401 005

to prepare uniform and adhesive films on a plastic substrate. We have also been able to adapt conventional lithography techniques to pattern these films to fabricate conducting polymer electrodes.

2. EXPERIMENT

An *in-situ* solution deposition used to prepare polypyrrole films is based on the following polymerization reaction,



where X- is a doping anion with one negative charge; n is the number of units in a polypyrrole chain; x is the stoichiometric ratio between pyrrole monomers and Fe(III); and δ is the fraction of positive charge distributed in each pyrrole unit in the polymer.

When a solution containing an oxidizing agent like Fe(III) is mixed with a solution of pyrrole monomer, a chemical reaction occurs, forming polypyrrole. Since this product is not soluble, it precipitates from the solution as it forms. When the reaction proceeds at a controlled rate, a homogeneous film can grow on a substrate that is immersed in the reaction solution. By controlling the growth time, one can prepare films of different thicknesses, and therefore, with different surface resistances and different optical transmissivities.

Polypyrrole cannot be dissolved in common solvents. However, the conjugation of the polymer chain can be destroyed by strong oxidizing agents, resulting in smaller species which are soluble in common solvents. That forms the basis for patterning of a polypyrrole film by photolithography. The process is demonstrated in Fig. 1.

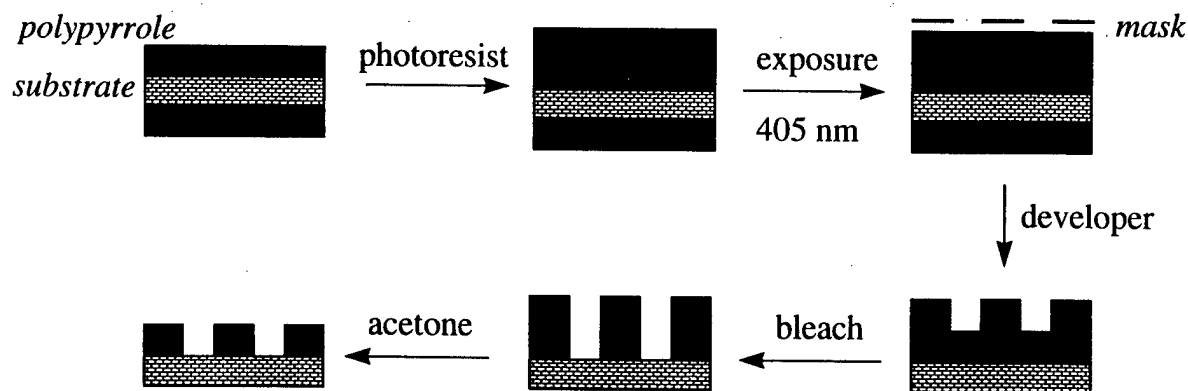


Fig. 1. Patterning of a polypyrrole film with photolithography

The polypyrrole film is first coated with a photoresist and then exposed to UV light through a photomask. After the exposure, the photoresist in the exposed area is rinsed off in a developer while the unexposed photoresist remains. Since protected by photoresist in the unexposed area, only the polypyrrole in the exposed area is etched by soaking the substrate in a bleach solution. Finally the photoresist is rinsed off, and a patterned conducting polymer emerges.

To prevent electrical shorting between the top and the bottom substrates of a LCD cell, an SiO₂ layer of 400 angstroms is deposited onto the patterned substrates by e-beam deposition at room temperature.

3. RESULTS

Polypyrrole cannot be dissolved or melted, so the material must be synthesized directly in the desired shape and location. For that reason, when a deposition solution is to be developed, at least two more factors should be taken into consideration besides optimizing the conductivity. One is the adhesion and the other is the uniformity of the film. Many factors, such as the surface properties of the substrate, the deposition rate, the chemistry of the solution and the reaction media, can affect the nucleation and the formation of the film, and ultimately affect the quality of the film.

By optimizing the deposition solution, we have been able to prepare films with both good adhesion and homogeneity. The film can withstand the standard peeling test. SEM reveals that the film is homogenous and the typical particle size is about 100 nm (Fig. 2, left). However, there are some larger particles up to several microns on the surface (Fig. 2, right). These particles are suspected to be particulation accumulated during the film growth process. A study to control the size and eventually eliminate these particles is in progress.

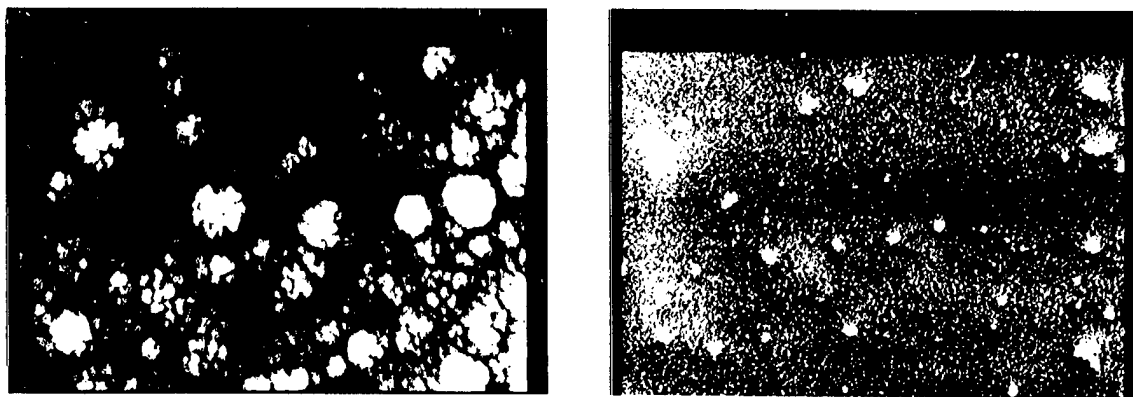


Fig. 2. SEM of a polypyrrole film prepared by *in-situ* solution deposition

A plastic substrate with 2"x2", 80 lpi patterned conducting polymer electrodes (see Fig. 3, left) has been achieved with photolithography techniques. As illustrated by SEM (see Fig. 3, right) the lines and spaces on the patterned substrate are well defined with a clean-cut edge. The lighter area is the polypyrrole and the darker area is where the polypyrrole has been removed by chemical etching.

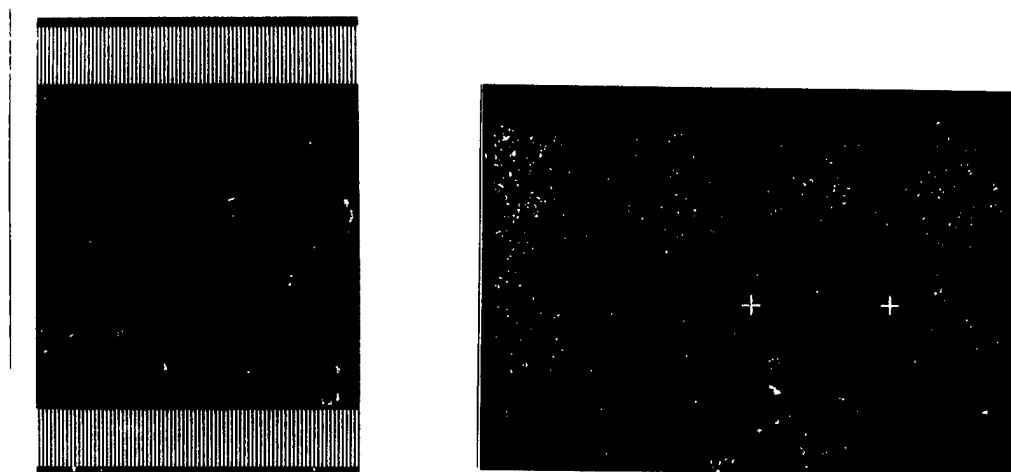


Fig. 3. A patterned substrate (left, entire substrate; right, localized area by SEM)

In a reflective LCD device, two substrates are needed, a light or transparent one for the top and a dark or opaque one for the bottom. By varying the deposition time, we can prepare films with surface resistances ranging from 2000 ohm/sq to 250 ohm/sq with corresponding transmittance from 86 to 12%. The typical light substrates prepared possess about 2-3 kohm/sq with nominal 70-80% transmission. Better display properties are achieved as the top substrate is made more transparent and more conductive. Consequently, an investigation to improve these properties of the material is in progress. The dark substrate, prepared from a thicker polypyrrole film, is ideal for the bottom substrate of a reflective LCD device. It possesses a surface resistance as low as 200-400 ohm/sq with an optical transmission less than 15%. It functions as both the electrode and a black absorber which helps improve the contrast. A more detailed discussion related to the device and demonstration of a working reflective Ch-LCD made with plastic substrates using conducting polymer electrodes is presented in a separate paper [3015-23].

4. CONCLUSIONS

We have demonstrated the feasibility of producing a reflective Ch-LCD using plastic substrates with conducting polymer electrodes. By utilizing a simple process of *in-situ* solution deposition, we are able to prepare a uniform polypyrrole film with good adhesion on the plastic substrate. The important physical properties of these films, such as surface resistance and optical transmission, satisfy the needs of a reflective LCD device. By adapting conventional photolithography techniques, we are able to pattern conducting polymer films with a resolution of 80 lpi and are currently developing approaches to extend this resolution to much higher values. The use of the robust conducting polymer electrode on plastic substrates opens up new areas of applications for Ch-LCD technology.

5. ACKNOWLEDGMENT

This work was supported in part by Office of Naval Research contract no. N00014-95-1-1254. Authors would also like to thank Mr. Peter Isaacson for the SiO₂ deposition.

6. REFERENCES

1. D. K. Yang and J. W. Doane, *SID Digest XXIII*, 759-761 (1992)
2. W. J. Fritz, D. St. John, D. Yang, and J. W. Doane, *SID Digest XXV*, 841-844 (1994)
3. D. Yang, J. West, L. Chien, and J. W. Doane, *J. Appl. Phys.* **76**, 1331-1333 (1994)
4. Z. Lu, W. St. John, X. Huang, D. Yang, and J. Doane, *SID Digest XXVI*, 173 (1995)
5. A. G. MacDiarmid, *Conjugated Polymers and Related Materials*, Ch. 6, Eds., W. R. Salaneck, I. Lundstrom, and B. Ranby (Oxford University Press, 1993)
6. G. B. Street, *Handbook of conducting polymers*, edited by T. A. Skotheim, vol 1, p. 265 (Marcel Dekker, Inc., 1986)
7. R. E. Myers *J. Electron. Mater.* **15**, 61 (1986).
8. S. Machida, S. Miysta, A. Techagumpuch, *Synth. Met.*, **31**, 3119 (1989).
9. Y. A. Dubitsky, B. A. Zhubanov and G. G. Maresch, *Synth. Met.*, **41-43**, 373 (1991).
10. D. Stanke, M. L. Hallensleben and L. Toppare, *Synth. Met.*, **72**, 159 (1995).
11. R. V. Gregory, W. C. Kimbrell and H. H. Kuhn, *Synth. Met.*, **28**, C823 (1989).