Displays 34 (2013) 301–314

Contents lists available at SciVerse ScienceDirect

Displays

journal homepage: www.elsevier.com/locate/displa

Transparent electrodes based on conducting polymers for display applications

Pen-Cheng Wang [a,*], Li-Hung Liu [a], Desalegn Alemu Mengistie [a,b,c], Kuan-Hsun Li [a], Bor-Jiunn Wen [d,e], Tzong-Shi Liu [e], Chih-Wei Chu [c,f]

[a] *Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan*
[b] *Nano Science and Technology, Taiwan International Graduate Program, Academia Sinica, Taipei 11529, Taiwan*
[c] *Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan*
[d] *Center for Measurement Standards, Industrial Technology Research Institute, Hsinchu 30011, Taiwan*
[e] *Department of Mechanical Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan*
[f] *Department of Photonics, National Chiao Tung University, Hsinchu 30010, Taiwan*

ARTICLE INFO

Article history:
Available online 10 June 2013

Keywords:
Conducting polymers
Displays
Flexible electronics
Organic electronics
Plastic electronics

ABSTRACT

The materials science and engineering related to the fabrication of conducting polymer thin films and the progress in the development of devices integrated with organic transparent electrodes based on conducting polymers for display applications are reviewed. Transparent electrodes are essential components for many display modules. With the evolution of display technologies, conducting polymers are recently emerging as important alternative materials for the fabrication of transparent electrodes. Conducting polymers offer some advantages, such as light weight, low cost, mechanical flexibility and excellent compatibility with plastic substrates for the development of next-generation display technologies and, in particular, are expected to play an important role in the development of flexible display technologies.

1. Introduction

Conducting polymers are organic materials which exhibit optical, electrical, electronic and magnetic properties of metals, while mechanical properties and processability of conventional polymers [1–11]. The unique and intriguing properties of conducting polymers are widely explored for the development of functional materials/nanomaterials [12–28] and fabrication of advanced technological systems, such as sensors [29–36], transducers [37–43], fuel cells [44–48], organic solar cells [49–54], organic light-emitting diodes [55–71], field-effect transistors [72–77] and displays [78–81]. One of the most attractive applications of conducting polymers in display technologies is their use as transparent electrode materials [82–84]. Compared to other electrode materials, conducting polymers are advantageous because of their low cost, light weight, mechanical flexibility and excellent compatibility with plastic substrates [1,85–89].

Although the iodine-doped polyacetylene initially reported in 1977 could exhibit electrical conductivity comparable to that of silver or copper [1,90,91], this prototype conducting polymer was air-sensitive [92–94]. With the efforts of many researchers in the past three decades, different types of conducting polymers with improved air-stability have been developed [95–99]. Currently, polyaniline (PANI), polypyrrole (PPY) and poly(3,4-ethylenedioxythiophene) (PEDOT) are the three most important conducting polymers. The structures of those three conducting polymers are shown in Fig. 1.

In this article, the potential of conducting polymer thin films deposited on non-conductive substrates as transparent electrode materials for display applications is discussed. In particular, the issues related to the preparation, transparency, conductivity and adhesion of conducting polymer thin films are addressed. Devices integrated only with organic conducting polymer thin films as transparent electrodes for display applications are also reviewed.

2. Transparent conducting polymer thin films

2.1. Properties of conducting polymers

Conducting polymers can be synthesized by electrochemical polymerization or oxidative chemical polymerization methods [1,100]. To synthesize conducting polymers by electrochemical polymerization methods, conductive substrates are required. Electrochemical polymerization can take place when an electrical output from a power supply passes through the conductive substrate immersed in a solution containing the monomer for the synthesis of a conducting polymer. On the other hand, to synthesize conduct-

---

* Corresponding author. Tel.: +886 3 574 2372; fax: +886 3 572 0724.
E-mail address: wangpc@ess.nthu.edu.tw (P.-C. Wang).

0141-9382/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.displa.2013.05.003

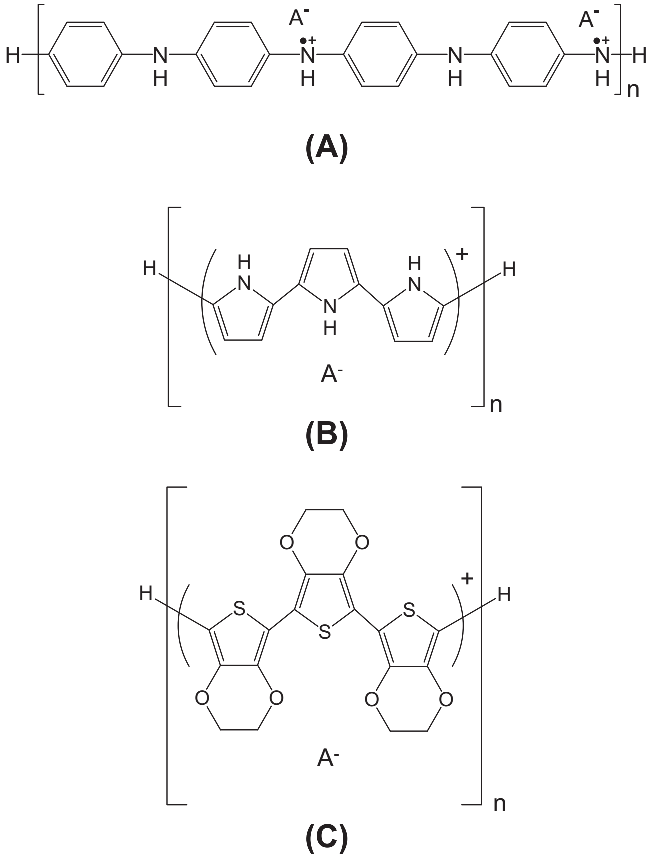

Fig. 1. Structure of (A) doped PANI, (B) doped PPY and (C) doped PEDOT (A^- is an arbitrary dopant species).

ing polymers by oxidative chemical polymerization methods, oxidizing agents are required. Oxidative chemical polymerization can be initiated when the oxidizing agent and the monomer used for the synthesis of a conducting polymer are brought into contact with each other [101–112].

Conducting polymers can undergo reversible doping to change their electrical conductivity [1]. There are two types of doping processes: redox doping and protonic doping [1]. Conductive PPY and PEDOT can be generated by redox doping. As non-conductive neutral PPY and PEDOT are not stable under ambient conditions, the backbones of PPY and PEDOT tend to be partially oxidized [112–114]. In the polymer backbones of PPY and PEDOT, approximately every 3–4 repeat monomer units would bear a unit positive charge [112,114]. As the polymer backbones are positively-charged, they can attract negatively-charged anions. Basically, the anions act as counter ions to balance the charges on the partially oxidized polymer backbones. As significant change in electrical properties of the polymers occurs upon partial oxidation and the concomitant incorporation of counter anions, together with the fact that the change in electrical conductivity can be anion-dependent, the counter anions are also treated as dopant anions of PPY and PEDOT. Conductive PPY and PEDOT can be dedoped to the non-condcutive neutral state by electrochemical reduction [79,113]. On the other hand, conductive PANI is generated by protonic doping (Fig. 2) [99]. When the non-conductive PANI is exposed to protonic acid (HA), the PANI becomes electrically conductive by protonic doping [115]. It should be noted that there is no change in the number of electrons on the polymer backbone when PANI undergoes protonic doping [1]. The HA-doped PANI can be dedoped by a basic solution, such as ammonium hydroxide solution, to its non-conductive state [116,117].

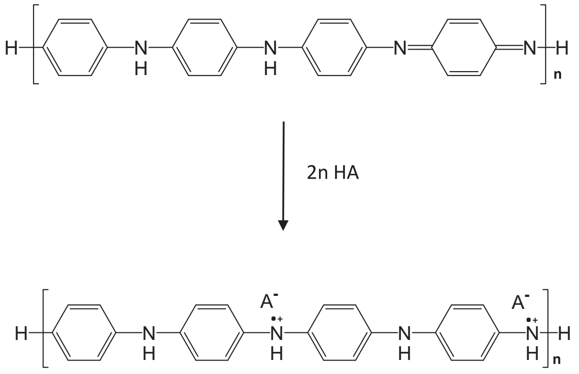

Fig. 2. Protonic doping of PANI (HA is an arbitrary protonic acid).

2.2. Preparation

Conducting polymer thin films can be prepared on non-conductive substrates by (i) coating treatment with a conducting-polymer solution/dispersion, (ii) deposition in a polymerizing solution and (iii) chemical vapor deposition.

2.2.1. Coating treatment with a conducting polymer solution/dispersion

In this method, the conducting polymer thin film is prepared by applying an appropriate amount of conducting polymer solution/dispersion to the non-conductive substrate. It can be done by various coating techniques, such as spread-coating, bar-coating, cast-coating, spin-coating or dip-coating. A conducting polymer thin film can be formed on the non-conductive substrate surface when the solvent evaporates. There are commercial products, such as aqueous dispersions based on PEDOT doped with poly(styrenesulfonic acid-*random*-styrenesulfonate), available from chemical suppliers [118]. The conducting-polymer solutions/dispersions for coating treatment can also be obtained by dissolving custom-synthesized conducting polymers in appropriate solvents, such as dodecylbenzenesulfonate-doped PPY dissolved in *m*-cresol [119] and camphorsulfonic acid-doped PANI dissolved in chloroform or *m*-cresol [120].

2.2.2. Deposition in a polymerizing solution

A conducting polymer thin film can be prepared on a non-conductive substrate by immersing the substrate in a polymerizing solution in which oxidative chemical polymerization of a conducting polymer's monomer is taking place [101,121–123]. The most commonly used oxidizing agents include ferric chloride and ammonium peroxydisulfate, or $FeCl_3$ and $(NH_4)_2S_2O_8$. Depending on the polymerization conditions and the nature of the substrate surfaces, transparent conducting polymer thin films with different properties can be formed on the surfaces of the immersed substrates [123]. As the polymerization of aniline is pH-sensitive, the polymerizing solution must be maintained at $pH < 2$ for the deposition of conductive PANI thin films [124,125]. Preferably, an aqueous medium containing a strong acid, such as hydrochloric acid, with a sufficiently acidic concentration is used to ensure that the reaction will follow the desired polymerization mechanism and the obtained PANI thin films will be instantly doped by the strong acid in the polymerizing solution [101,124,126–130]. As PANI can undergo reversible protonic doping, conductive PANI dedoped by a basic solution, such as ammonium hydroxide solution, can be redoped by another acid of choice if desired [115,117]. To introduce a desired dopant anion to PPY or PEDOT, either the acid or salt containing the dopant anion can be added to the polymerizing solution (Fig. 3) [121,131–138]. The polymerization for the synthesis of