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Enhanced electrical properties of PEDOT:PSS films using solvent treatment and its application to ITO-free organic light-emitting diodes

Yoon Kyung Seo [a,1], Chul Woong Joo [b,1], Jonghee Lee [b,1], Joo Won Han [a], Dong Jin Lee [a], Siti Aisyah Nurmaulia Entifar [a], Soukyoon Kim [a], Nam Sung Cho [b], Yong Hyun Kim [a,*]

[a] Department of Display Engineering, Pukyong National University, Busan 48513, Republic of Korea
[b] Flexible Information Device Research Center, Electronics and Telecommunications Research Institute (ETRI), Daejeon 34129, Republic of Korea

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ABSTRACT

Highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films are prepared by introducing a new solvent 2-ethoxyethanol and are optimized by acid-free solvent post treatment. The behavior of samples are investigated with various coating conditions. The change of electrical performance for 2-ethoxyethanol added PEDOT:PSS films with various post treatment methods is studied. Upon post treatment, the sheet resistance greatly decreases attributed to a structural change with removal of insulating PSS in the film. Based on these conductive films, we demonstrate efficient ITO-free green phosphorescent organic light-emitting diodes (OLEDs). The efficiency of OLEDs with post-treated PEDOT:PSS electrodes is greater than that of OLEDs with untreated PEDOT:PSS electrodes. The results illustrate a promising future for flexible, low-cost, ITO-free OLEDs employing PEDOT:PSS electrodes optimized by 2-ethoxyethaol with acid-free solvent post treatment.

1. Introduction

Recent advances on the organic light-emitting diodes (OLEDs) have led to broad applications in lighting sources and displays due to the potential for low-cost roll-to-roll processing, mechanical flexibility, thin and lightweight form-factor, optically transparency, and energy-efficient emission [1,2]. The general bottom-emitting OLEDs consist of thin-film organic semiconductors including hole/electron transport and emissive materials are sandwiched between the transparent electrode and the opaque metal electrode. Injected holes and electrons from both electrodes can generate photons by going through charge transport and recombination processes, etc [3,4]. Not to mention, indium din oxide (ITO) is the most common transparent electrode material for conventional OLEDs owing to its high conductivity and transmittance as well as well-established fabrication process. However, ITO is fabricated by vacuum process and needs elevated processing temperature (> 300 °C). In addition, ITO suffers from poor mechanical flexibility and high material costs [5,6]. These obstacles of ITO make it challenging its application to flexible, low-cost OLEDs. In this regard, various alternative transparent electrodes such as conductive polymers [7,8], carbon nanotubes [9,10], graphenes [11,12], silver nanowires [13,14], and metal grids [15,16] have been extensively investigated to replace ITO. Among candidates for alternative transparent electrodes, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has attracted significant interest as a promising transparent electrode because of its excellent mechanical flexibility, high conductivity, high transmittance, and compatibility with low-cost solution-processing [17,18]. Such benefits of highly conductive PEDOT:PSS enable for PEDOT:PSS-based ITO-free OLEDs which can lead to high device performance by careful optimization process for PEDOT:PSS electrodes [7,19,20].

To increase the low electrical conductivity of below 1 S/cm for the pristine PEDOT:PSS, various techniques have been investigated. The most widely used method is to introduce polar organic compounds having a high boiling point such as ethylene glycol (EG) and dimethyl sulfoxide (DMSO) into PEDOT:PSS formulation, which significantly increase the conductivity higher than 700 S/cm [8,21]. In addition, the introduction of mannitol, ionic liquid, acids, anionic surfactants, ultrasonic method, and in-situ grafting method etc in PEDOT:PSS solutions also increases the conductivity of PEDOT:PSS films [22–26]. To further enhance the conductivity, various solvent post treatments have been performed by several groups [8,27–30]. We have reported conductivity enhanced PEDOT:PSS films (1417 S/cm), which are post-treated in an EG bath [8]. The resulting post-treated PEDOT:PSS transparent electrodes are successfully employed into OLEDs and OPV cells and show comparable performance to reference devices with ITO transparent electrodes [8,31]. Furthermore, methanol,

* Corresponding author.
E-mail address: yhkim113@pknu.ac.kr (Y.H. Kim).
[1] These authors contributed equally to this work.

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hexafluoroacetone, or sulfuric acid are used as solvents for post treatment to improve the conductivity of PEDOT:PSS films [28,29,32].

In this study, highly conductive PEDOT:PSS transparent electrodes prepared with 2-ethoxyethanol, which is a newly investigated solvent for highly conductive PEDOT:PSS films, have been reported. The electrical and optical properties for PEDOT:PSS thin films added by 2-ethoxyethanol are studied with conditions for film processing. The acid-free solvent post treatment considerably enhances the electrical performance of PEDOT:PSS films mixed with 2-ethoxyethanol. The change of electrical performance for 2-ethoxyethanol added PEDOT:PSS films with various post treatment methods is studied. The PEDOT:PSS with 2-ethoxyethanol films greatly reduce a sheet resistance from 312.5 to 210.7 Ω/sq after solvent post-treatment. The optimized PEDOT:PSS-based OLEDs with solvent post-treated PEDOT:PSS films achieve the higher device efficiency compared to OLEDs with untreated PEDOT:PSS electrodes. The results demonstrate that the PEDOT:PSS films optimized with the new solvent of 2-ethoxyethanol and acid-free post treatment are highly promising to replace the conventional ITO electrodes for low-cost, flexible ITO-free OLEDs.

2. Experimental

2.1. Fabrication and characterization of PEDOT:PSS electrodes

6 vol% of ethylene glycol or 20 vol% of 2-ethoxyethanol are added into PEDOT:PSS (Clevios PH1000, Heraeus, Germany) formulations. The formulations are spin-coated on glass substrates at 1500 rpm for 30 s. Subsequently, the films are baked on a hot plate at 120 °C for 15 min in air ambient [8,33]. For various solvent post treatment, several PEDOT:PSS films are immersed in solvent bath (dip treatment) or solvent is dropped on the films (drop treatment). The solvents used for post treatment are methanol, 2-ethoxyethanol, and EG. The post-treated films are baked on a hot plate at 120 °C for 15 min. Sheet resistance of films is examined by a van der Pauw method. We perform transmittance measurements by using a spectrophotometer (Optizen POP). The values of transmittances in this work include the glass substrate absorption. The film thickness is examined by a surface profilometer (Alphastep 500, Tencor). The AFM images are recorded in tapping mode (Icon-PT, Bruker).

2.2. Fabrication and characterization of OLEDs

All devices are fabricated by thermal evaporation in a high vacuum chamber (base pressure $\sim 10^{-8}$ mbar). The structure of devices is as follows (bottom to top): ITO or PEDOT:PSS films as a bottom electrode/10 nm 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN)/50 nm N,N′-di(naphthalene-1-yl)N,N′-diphenyl-benzidine (NPB)/10 nm HAT-CN/50 nm NPB/10 nm HAT-CN/40 nm NPB (total HTL thickness: 170 nm)/10 nm 4,4′,4′′-tris(N-carbazolyl)-triphenylamine (TCTA)/20 nm 2,6-bis(3-(carbazol-9-yl) phenyl) pyridine (DCzPPy): tris (2-phenylpyridine)iridium ($Ir(ppy)_3$) (7 wt.%)/60 nm 1,3-bis(3,5-dipyrid-3-yl-phenyl)benzene (BmPyPB)/1 nm LiF/100 nm Al. The film thickness, doping concentration, and material are carefully optimized by optical simulation and several experiments for high performance [34]. The devices are encapsulated with an additional glass using epoxy glue in nitrogen atmosphere. The device areas are 2×2 mm^2. The current-voltage-luminance characteristics and electroluminescence spectra are obtained using a source-measure unit and a goniometer-equipped spectroradiometer (Minolta CS-2000).

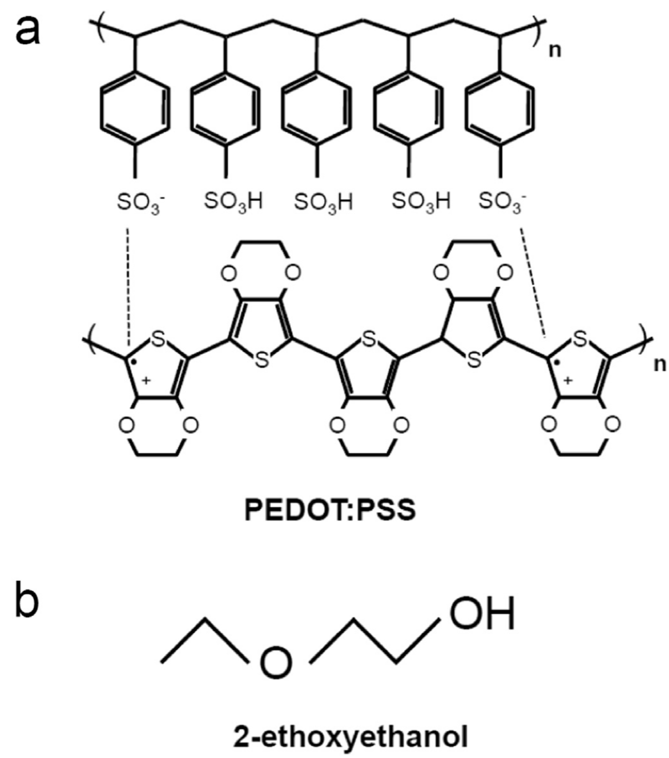

Fig. 1. Chemical structures of a) PEDOT:PSS and b) 2-ethoxyethanol.

3. Results and discussion

Fig. 1 exhibits chemical structures of PEDOT:PSS and 2-ethoxyethanol which is used as a conductivity enhancement agent. Due to the high-boiling point (about 135 °C) and the polar nature of 2-ethoxyethanol, the conductivity of PEDOT:PSS films can be greatly improved to 761.7 S/cm by introducing 20 vol% of 2-ethoxyethanol as reported in our previous work [35]. The high-boiling point polar solvents such as DMSO and EG significantly increase the conductivity of PEDOT:PSS films by a strong screening effect and favorable morphological changes as reported elsewhere [21,36].

Fig. 2 shows the behavior of sheet resistance and average transmittance at visible wavelengths (400–800 nm) of multi-layered PEDOT:PSS films mixed with 20 vol% of 2-ethoxyethanol ($PEDOT:PSS_{2ee}$) with respect to the number of PEDOT:PSS layers. The layers are spin-coated at 1000 rpm. The sheet resistance and transmittance of films monotonically decrease with increasing the number of layers as expected. It is worth noting that the $PEDOT:PSS_{2ee}$ film has an excellent wettability so that multilayer coating

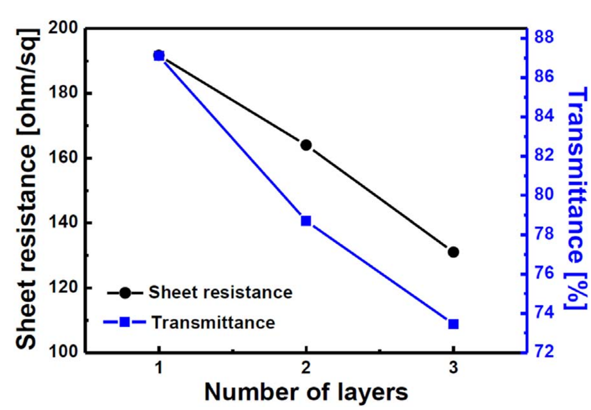

Fig. 2. Sheet resistances and transmittances for 2-ethoxyethanol doped PEDOT:PSS films with respect to the number of layers.