

Work function modification of solution-processed tungsten oxide for a hole-injection layer of polymer light-emitting diodes



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ABSTRACT

We report a solution-processed tungsten oxide hole injection layer for polymer light-emitting diodes (PLEDs). Unlike vacuum evaporated tungsten oxide, solution-processed tungsten oxide has a reduced work function due to contamination of the ambient atmosphere. To increase the work function of tungsten oxide layer, an organic ionic solution containing poly(ethylene oxide) and tetra-n-methylammonium tetrafluoroborate was coated on the tungsten oxide layer. Organic ions infiltrated into the tungsten oxide layer and formed an interfacial dipole, increasing the layer's work function by 0.4 eV. As a result, a PLED, which had a hole-injection layer of the tungsten oxide and organic ionic solution, showed a performance equivalent to that of the PEDOT:PSS-based device with even higher maximum luminance of 27,560 cd/m² at 10 V.

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1. Introduction

Polymer light-emitting diodes (PLEDs) show great potential because they can be produced by a cost effective solution process, and they offer the advantages of self and scalable emission, a simple structure and fabrication process [1,2]. The performance of the PLEDs is largely depends on electrode and charge injection into the emitting layer [3,4]. Indium tin oxide (ITO) is almost universally used as a transparent electrode in commercial application due to its high transparency and low sheet resistance [5]. To facilitate hole-injection of ITO, a Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) aqueous solution is generally used as the hole-injection layer of PLEDs since it can reduce the surface roughness and hole-injection barrier of ITO. However, ITO is vulnerable to highly acidic PEDOT:PSS as well as moisture, and the sulfonic acid functionality of PEDOT:PSS also has an adverse effect on ITO. Consequently, the lifetime of PLEDs is reduced by the use of PEDOT:PSS as the hole-injection layer [6,7].

Therefore, many research groups have been attempting to find an alternative to PEDOT:PSS. One of the most promising alternatives is transition metal oxides including molybdenum oxides (MoO₃) [8–11], tungsten oxides (WO₃) [12–15], and vanadium oxide (V₂O₅) [16]. These metal oxides are attractive alternatives due to their high optical transparency, air stability, chemical stability with ITO, and low material cost [17–19]. In particular, due to its excellent ability to increase the lifetime of PLEDs, as was recently

reported [20], tungsten oxide is receiving great attention as a new hole-injection layer in many optoelectronic devices [21]. The hole-injection property of tungsten oxide can be explained by the formation of an interfacial dipole due to its high work function ($\Phi_a(\text{tungsten oxide}) \sim 6.65 \text{ eV}$) [16]. However, unlike a vacuum evaporated tungsten oxide layer which shows the aforementioned high work function, a solution-processed tungsten oxide layer has reduced work function due to contamination of the ambient atmosphere ($\Phi_{a,\text{Air}}(\text{tungsten oxide}) \sim 5.7 \text{ eV}$) [22]. Hence, there have been very few reports about the use of solution-processed tungsten oxide as a hole-injection layer.

More precisely, due to adsorption of oxygen and moisture on the surface, the work function of the transition metal oxide was reduced [23,24]. Therefore, a solution-processed or an air exposed vacuum evaporated transition metal oxide lost its function as a hole-injection layer. The most conventional method to recover the work function of these metal oxides is thermal annealing in ultrahigh vacuum. According to the previous report, the work function of air exposed molybdenum oxide was recovered from 5.6 eV to 6.4 eV [25]. On the other hand, a microwave exposure or Ar plasma bombardment was also used to change the work function of transition metal oxides [26,27]. Although these methods successfully modified the work function of the material, the extra equipment or ultrahigh vacuum, gas environment was required, making an entire fabrication process complicated and less productive. The best way of modifying the work function of transition metal oxide with the minimized adverse effect on the fabrication process is coating another solution on the layer. In this research,

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we modified the work function of the solution-processed tungsten oxide layer by coating of an organic ionic solution, and the resulting tungsten oxide hole-injection layer demonstrated the performance equivalent to that of PEDOT:PSS.

An organic ionic solution containing poly(ethylene oxide) (PEO) and organic ionic salt (tetramethylammonium tetrafluoroborate) was used. The combination of PEO, an ion-transport polymer, and ionic salts is often used for light-emitting electrochemical cells (LECs) [28]. In an LEC, the ionic salts and the ion-transport polymer are mixed with the light-emitting polymer and coated on the electrode. The salt dissociates to form free ions within the light-emitting polymer layer. Under the applied voltage, the free ions move and accumulate on the interfaces of the light-emitting polymer and the electrodes. The ions that accumulate near the electrodes create a region with high ionic space charge, resulting in a large electric field at the polymer-electrode interface that reduces the barrier to charge injection [29]. This principle and, the combination of PEO, ionic salts are also applied to improve the electron injection properties of PLEDs [30–32]. According to a recent report, PEO itself can functionalize Al cathode and improve electron injection [33], thus, PEO and ionic salts are efficient for reducing the electron injection barrier. However, they have not been used to improve the hole-injection properties of PLEDs. In this work, we used the organic ionic solution to improve hole-injection property of the tungsten oxide layer.

2. Experimental

The structure of the PLED fabricated in this study is shown in Fig. 1. A PLED that had the layer structure of ITO/tungsten oxide and Ion/Super yellow (S.Y)/ZnO/Al was fabricated. Patterned ITO glass ($12 \Omega/\square$) was ultrasonically cleaned with deionized water, acetone, and isopropanol. A sol-gel processed tungsten oxide layer that our group previously reported was spin casted [34]. Tungstic acid (H_2WO_4) solution was collected by passing 0.15 M aqueous sodium tungstate (Na_2WO_4) solution through a glass column packed with protonated cation exchange resin (TRILRTE SCR-BH). The tungstic acid solution was mixed with the isopropanol to improve coating quality on glass. The tungstic acid solution was spin coated on ITO glass and baked at $280^\circ C$ for 3 min. The average nanoparticle size was 2 nm (Fig. S1(b) and (c)), and the tungsten oxide layer thickness was approximately 15 nm. Organic ionic acetonitrile solution containing was spin coated and baked at $90^\circ C$ for 3 min. For a fully annealed tungsten oxide layer, baking at $280^\circ C$ for 30 min was followed. Otherwise, a PEDOT:PSS (clevis PVP Al4083, Heraeus precious Metal, Hanau, Germany) aqueous solution was spin coated and baked at $200^\circ C$ for 5 min (approximately 50 nm). A yellow light-emitting polymer (Merck, "Super yellow", PDY-132) dissolved in toluene at 0.5 wt% was spin coated in a nitrogen

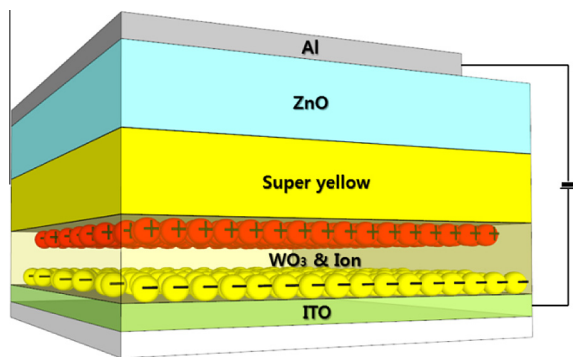


Fig. 1. Structure of the PLEDs: ITO/tungsten oxide & ion/S.Y/ZnO/Al.

glove box and baked at $70^\circ C$ for 30 min. Zinc oxide nanoparticles which synthesized by the method reported by Beek et al. were used as electron injection layer [35]. The zinc oxide nanoparticles were dispersed in the 1-butanol at concentration of 30 mg/ml and spin casted, baked at the $90^\circ C$ for 3 min (approximately 20 nm). Organic ionic acetonitrile solution containing poly(ethylene oxide) (PEO) and tetra-n-butylammonium tetrafluoroborate (TBABF₄) was spin coated and baked at $90^\circ C$ for 3 min [32]. Aluminum cathode was thermally evaporated (approximately 100 nm).

The device characteristics of the current density, voltage, and luminance (J - V - L) curves were recorded with a source measure unit (Keithley 2400, Keithley Instruments Inc, Cleveland, OH, USA) and a calibrated photodiode (CS-100A, Konica Minolta Optics, Inc, Tokyo, Japan). An atomic force microscope (AFM, XE-100, Park systems Corporation, Suwon, South Korea) was used to analyze surface profiles. Transmittance was measured by a UV-Visible spectrophotometer (Evolution 220, Thermo Fischer Scientific, Shanghai, china). Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) measurements were taken with a Sigma probe (Thermo VG Scientific). Refractive indexes were measured with a spectroscopic ellipsometer (M2000D, Woollam).

3. Results and discussion

To form free ions in the tungsten oxide layer, the organic ionic solution must infiltrate into the tungsten oxide layer. However, fully annealed tungsten oxide layer that used in this research is consisted of very tiny nanoparticles [34], and it forms very dense film. Consequently, the fully annealed tungsten oxide layer does not allow efficient infiltration. Therefore, even though 30 min is required for the fully annealed tungsten oxide layer, after only 3 min of annealing, we coated the organic ionic solution on the tungsten oxide layer. We compared infiltration of the organic ions into the semi-annealed (3 min) and the fully annealed (30 min) tungsten oxide layer through the XPS depth profile measurement. In Fig. 2, depth profile measurement results of the semi-annealed and the fully annealed tungsten oxide layer are demonstrated. The relative atomic percent ratio between nitrogen and tungsten as well as the ratio between carbon and tungsten were higher in the semi-annealed tungsten oxide. It means more organic ions were inside of the semi-annealed tungsten layer compared to the fully annealed tungsten oxide layer. As the organic ionic solution was coated before the tungsten oxide layer become dense film, organic ions infiltrated into the semi-annealed tungsten oxide layer.

In Fig. 3, the surface texture measurement was conducted by an atomic force microscope. Coating of the tungsten oxide layer on the ITO layer resulted in a very homogeneous and smooth surface. The RMS roughness of ITO decreased from 1.8 nm to 1.2 nm. Even though coating of the organic ionic solution increased the surface roughness to 3.7 nm, related adverse device performance, including high turn-on voltage and, electrical shorting were not observed. In Fig. 4(a), the transmittances of layers are shown. The tungsten oxide coated glass showed even higher transmittance than bare glass in most visible regions. A sol-gel processed tungsten oxide layer is often used for the dielectric layer for dielectric-metal-dielectric (DMD) transparent electrodes and anti-reflective coatings due to its high refractive index [34,36]. As demonstrated in Fig. 4(b), the tungsten oxide layer has a higher refractive index than glass ($n_{SiO_2} \sim 1.45$). Although we did not optimize the thickness of the tungsten oxide layer for transmittance, it was sufficient to induce antireflection and increase transmittance. Although transmittance decreased after coating of the organic ionic solution, it was much higher than that of the PEDOT:PSS layer. Higher transmittance leads to higher performance PLEDs.

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