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Performance Improvement of Polymer Light Emitting Diodes by Insertion of a Silane Layer

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Abstract

The influence of a silane layer on the performances of polymer light emitting diode(PLED)s has been studied. Glycidoxypropyltrimethoxysilane(GPS) with an epoxy functional group was used as a surface modifier for ITO substrates. The GPS layer was inserted between an ITO and a poly(3,4)-ethylenedioxythiophene/polystyrenesulfonate(PEDOT) by wet process and the performances of PLEDs were investigated. The introduction of GPS layer increased the brightness and efficiency of PLEDs by 30%. In addition, the lifetime of PLEDs was also improved considerably by using GPS as a surface modifier.

Keywords : Polymer light emitting diode, Silane modification, Efficiency, Lifetime

1. Introduction

Polymer light emitting diode(PLED)s have been studied extensively for the past 10 years for application in the field of full color flat panel displays. They have several advantages over small molecule light emitting diode(SMLED)s such as low operating voltage, low power consumption, low manufacturing cost, large size fabrication and easy processing. However, the performances of PLEDs still need to be improved further to expand the commercialization of PLEDs. The light efficiency of polymer EL materials is quite low compared with small molecular EL materials and the lifetime of polymer LED also have to be improved.

There have been many efforts to improve device performances of PLEDs by modifying device structures or materials. In general, PLEDs are made up of an anode, a hole transport layer(HTL), a light emitting layer(EML), and a cathode[1]. Sometimes electron transport layer(ETL) is inserted between EML and cathode to enhance efficiency and lifetime. Many studies have been focused on the development of new light emitting polymers and cathode modification because electron injection from the cathode is a limiting factor for device performances. Insertion of an insulating layer such as LiF, CsF and metal alloys such as Mg:Ag have been applied to enhance the electron injection[2,3,4].

Similar to the concept applied in electron injection layer, there have been several reports about the insertion of an insulating layer between an ITO and a hole transport layer. Qiu et al. improved the device performances of SMLEDs by introducing a thin praseodymium oxide film[5]. The thin film prevented the surface leakage current and increased electroluminescence efficiency of the devices. Zhu et al. introduced LiF thin layer on ITO and increased light efficiency and brightness of PLEDs[6]

In this work, we introduced a thin silane layer between an ITO and a hole transport layer as an ITO surface modifier to improve device performances of PLEDs. The silane layer was deposited by simple dipping process and device performances of PLEDs were investigated according to a silane concentration.

2. Experiments

The device structure of PLED used in this work is shown in Fig. 1. The ITO coated glass substrate was a product of Samsung Corning Co. and had a sheet resistance of 10 Ω/square. Glycidoxypropyltrimethoxysilane(GPS) which was used as an interlayer between ITO and PEDOT

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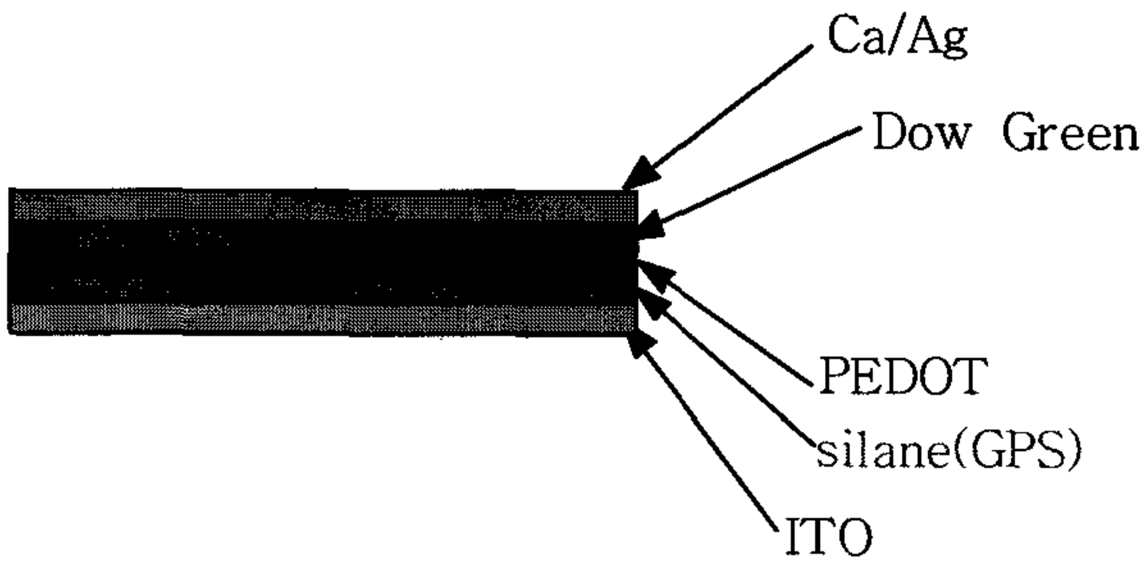


Fig. 1. Device configuration of polymer light emitting diodes.

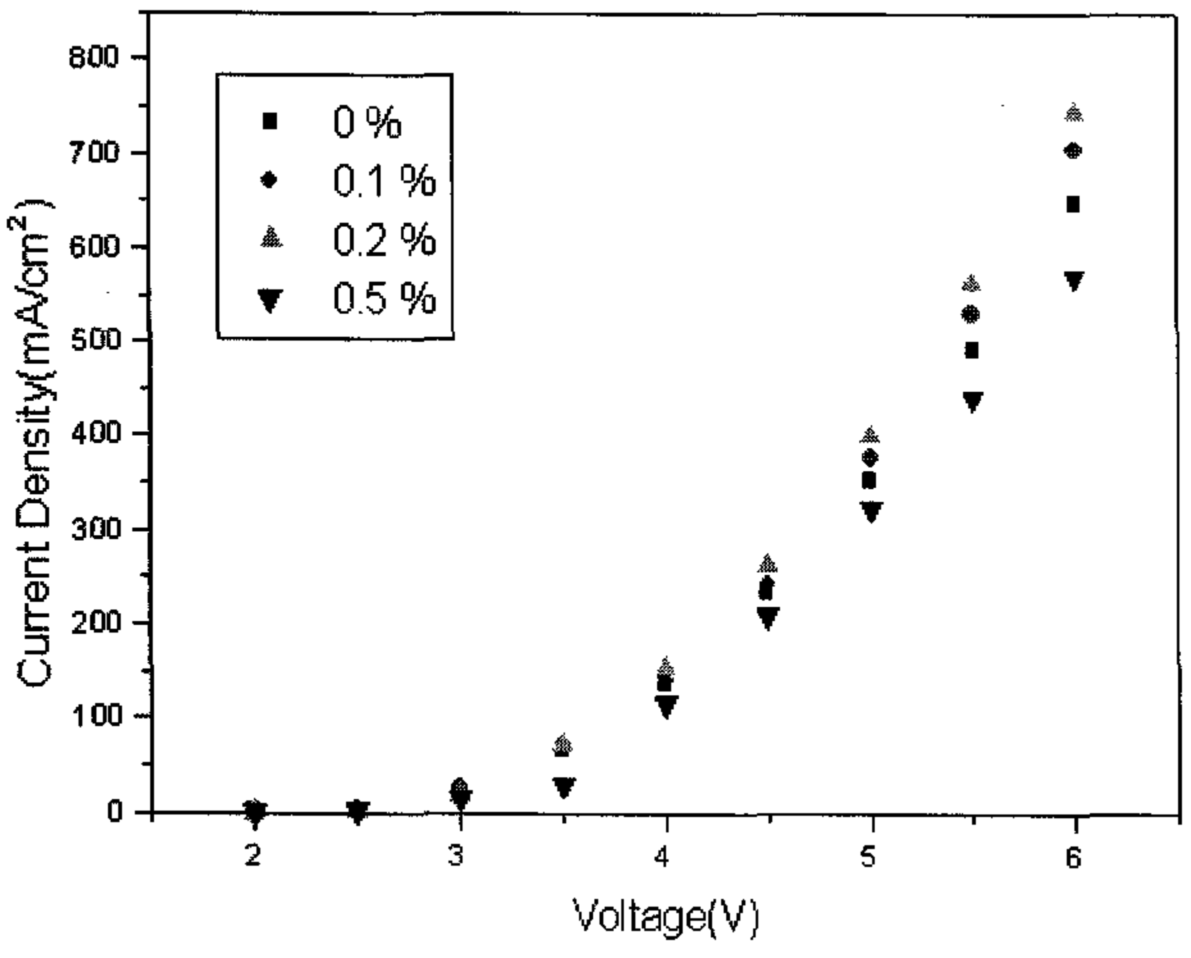
was purchased from Dow Corning Co.. Poly(3,4)-ethylenedioxythiophene/polystyrenesulfonate(PEDOT) was purchased from Bayer Co. and used as a HTL and polyfluorene type Dow green polymer was used as an EML. Ca/Ag double layer was applied as a cathode for PLEDs

ITO coated glass substrates were cleaned with acetone and isopropyl alcohol in an ultrasonic bath for 15 min respectively and were dried at 120 °C for 2 hr prior to use. The ITO coated glasses were treated with UV-ozone for 15 min and was dip coated with an aqueous GPS solution. The GPS solution was prepared by dissolving GPS in butanol/H_2O(95/5) solution at a concentration of 0.1, 0.2 and 0.5 wt%. The solution was stirred for 60 min to hydrolyze GPS and then the UV-ozone treated ITO substrates were dip coated with the hydrolyzed GPS solution. After that, the GPS treated ITO substrates were dried at 200 °C for 5 min to remove residual solvents. PEDOT was spin coated on the GPS coated substrates at a thickness of 50 nm and baked at 200 °C for 5 min. Spin coating of EML was carried out at a spin speed of 3000 rpm and 80 nm EML thin film was obtained. After baking the EML film at 135 °C for 60 min, Ca was deposited on EML layer at a rate of 0.5 Å/s followed by Ag evaporation at a rate of 5 Å/s in a high vacuum chamber($\approx 10^{-7}$ torr) through a metal shadow mask with 2 mm by 2 mm opening. The thickness of Ca and Ag was 30 nm and 230 nm respectively. After cathode deposition, the devices were encapsulated with a metal can and a barium oxide. Current density-voltage-luminance characteristics of the devices were measured with PR 650 spectrophotometer and lifetime results were obtained at a constant current mode at a brightness of 500 cd/m^2.

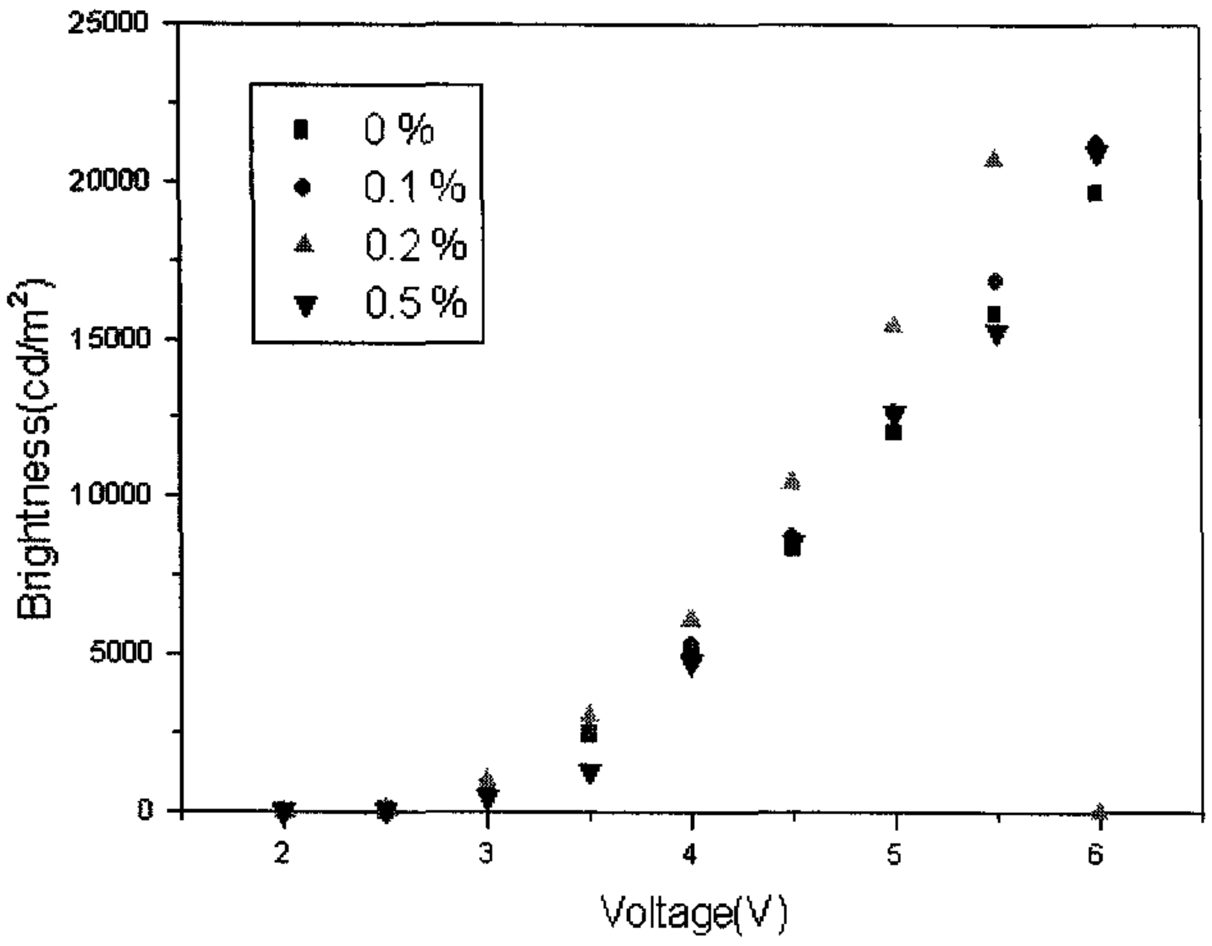
3. Results and Discussion

It is well known from extensive researches that silane type materials adsorb chemically and physically on inorganic surfaces through a chemical bonding, a hydrogen bonding, and a physical interaction[7]. Silanol groups produced from hydrolysis of silane materials react with a surface hydroxyl group on inorganic materials to form siloxane linkage or hydrogen bonding. In addition, GPS has a polar epoxide functional group which is compatible with aqueous PEDOT solution. Therefore, the GPS layer is expected to strengthen the interface between ITO and PEDOT. In addition, GPS molecules can be crosslinked through condensation reaction between silanol groups, which leads to the formation of a crosslinked network structure. The network structure is resistant to thermal and chemical attack and can contribute to the lifetime enhancement of PLEDs.

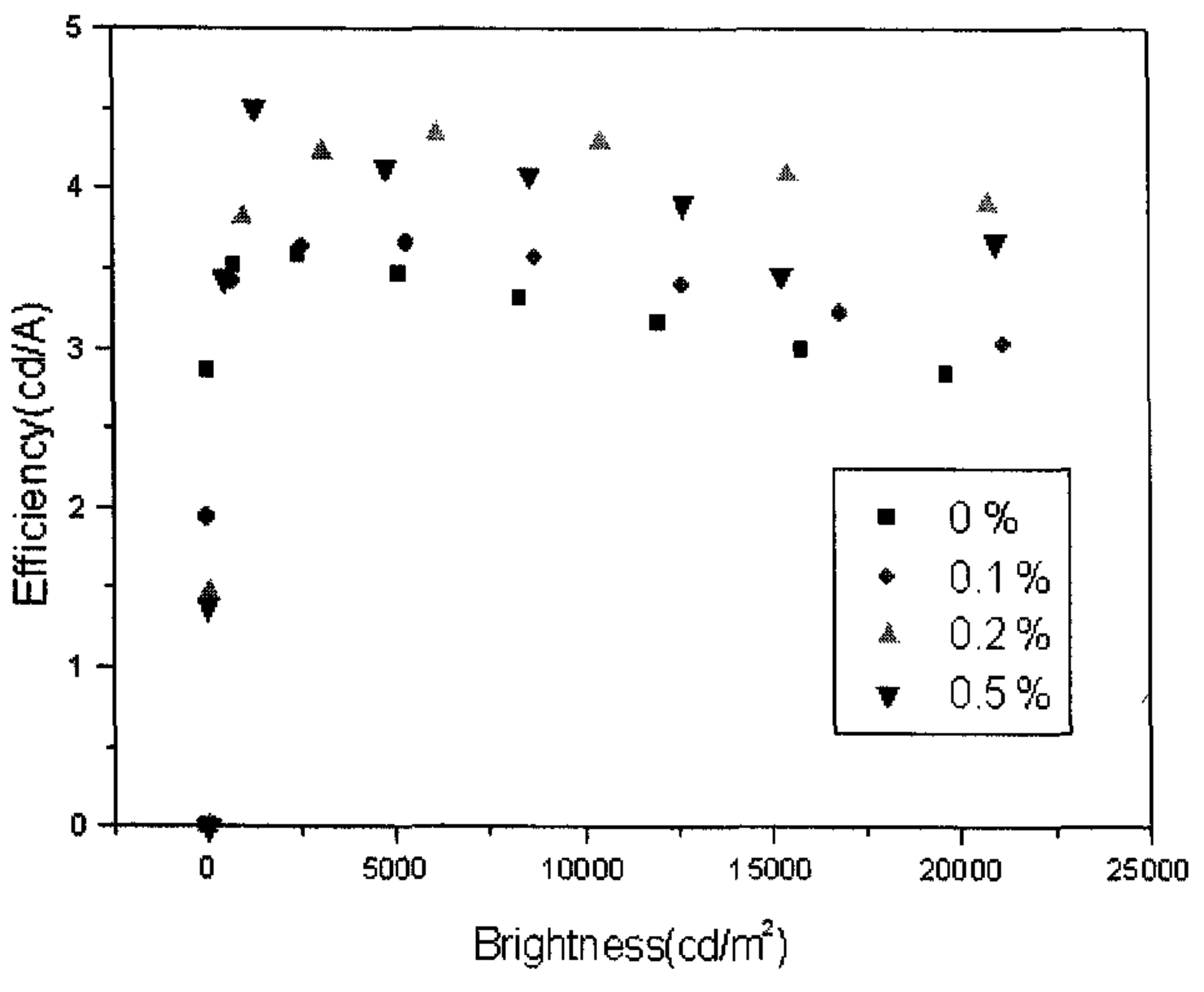
Fig. 2 shows the I-V-L characteristics of the ITO/GPS/PEDOT/EML/Ca/Ag devices according to GPS concentration. The current density of the devices increased according to the GPS concentration and showed a maximum value at 0.2 wt% and brightness also showed the same tendency. In general, the current density of organic EL devices is mostly determined by a majority carrier, that is, by a hole in PLEDs. The presence of a GPS layer on ITO surfaces enhances the hole injection from ITO to PEDOT up to a GPS concentration of 0.2 wt%, while it prevents the hole injection above 0.2 wt%. The increase in the current density at low GPS concentration results from the decrease of interfacial defects and traps originated from poor wetting between PEDOT and ITO. A few nm thick GPS layer fills the defects and gaps between ITO and PEDOT and smoothen the ITO surface. Compared with inorganic ITO, physically adsorbed GPS layer forms a stronger interface with PEDOT because it has organic functional group which is compatible with PEDOT as well as inorganic functional group. That is, the GPS layer acts as a bridge between ITO and PEDOT, resulting in the improvement of interfacial adhesion in the PLEDs. The decrease in the current density above 0.2 wt% is due to hole blocking of thick GPS insulating layer because tunneling of holes is possible only within a few nm thickness range. The GPS thickness on ITO layer was 0.5, 1.1 and 2.5 nm for 0.1, 0.2 and 0.5 wt% respectively. The brightness of the devices showed the same tendency as the current density as the brightness of EL devices is proportional to the current density. The brightness of the devices with GPS layer was higher than that of the devices without GPS by 30 %.



(a) I-V



(b) L-V



(c) E-L

Fig. 2. I-V-L curves of PLEDs according to GPS concentration

The efficiency of the devices is shown in Fig. 2(c). It is apparent from the figure that the GPS layer enhances the light efficiency at all brightness range investigated. It showed a maximum value at 0.2 wt% GPS concentration. The efficiency of the devices with GPS layer was 4.5 cd/A at 1000 cd/m^2 compared with 3.5 cd/A for the GPS free devices. Trap filling and defects removal by GPS layer are thought to result in the increase in the light emitting efficiency. The relatively high efficiency of the device with 0.5 wt% GPS hole injection layer compared with a GPS free device may be due to balanced hole and electron injection as well as defect removal. It is well known that hole mobility is much higher than electron mobility in PLEDs, leading to an imbalance in the hole and electron in light emitting layer[8]. One way to enhance the efficiency of PLEDs is to control the hole injection from ITO side, which results in improved hole and electron balance in the devices. As shown in Fig. 2, hole injection from ITO side is retarded at GPS concentration of 0.5 wt%, which is favorable to light efficiency of PLEDs.

The lifetime and reliability of PLEDs are largely dependent on the characteristics of the interface between an ITO electrode and HTL materials because the interface adhesion is poor for inorganic-organic interface. Silane materials have long been applied as coupling agents for inorganic-organic interfaces as they have both silicon inorganic moiety and organic moiety. Therefore, highly polar GPS can act as a coupling agent for ITO and PEDOT, leading to the improvement of the interfacial adhesion between ITO and PEDOT. In addition, uniform GPS thin coating reduces ITO defect sites and hole traps and can block the incorporation of indium in PEDOT layer through crosslinked network structure formation. The lifetime of PLEDs was compared at 500 cd/m^2 to study the effect of GPS layer on the long time performances of PLEDs. There was a sharp drop in the brightness of all devices in the initial stage and followed by a gradual decrease. The lifetime of the devices increased noticeably by introducing GPS layer between ITO and PEDOT. The lifetime of pristine device was 33 h at 500 cd/m^2, while that of 0.5 % GPS treated PLED was 130 h at 500 cd/m^2. There are many reasons involved for the increase of lifetime for the device with GPS layer. Interfacial adhesion promotion effect of GPS layer mentioned earlier reduces the probability of interfacial failure for the PLED devices during operation. Improved adhesion through GPS layer can prevent the

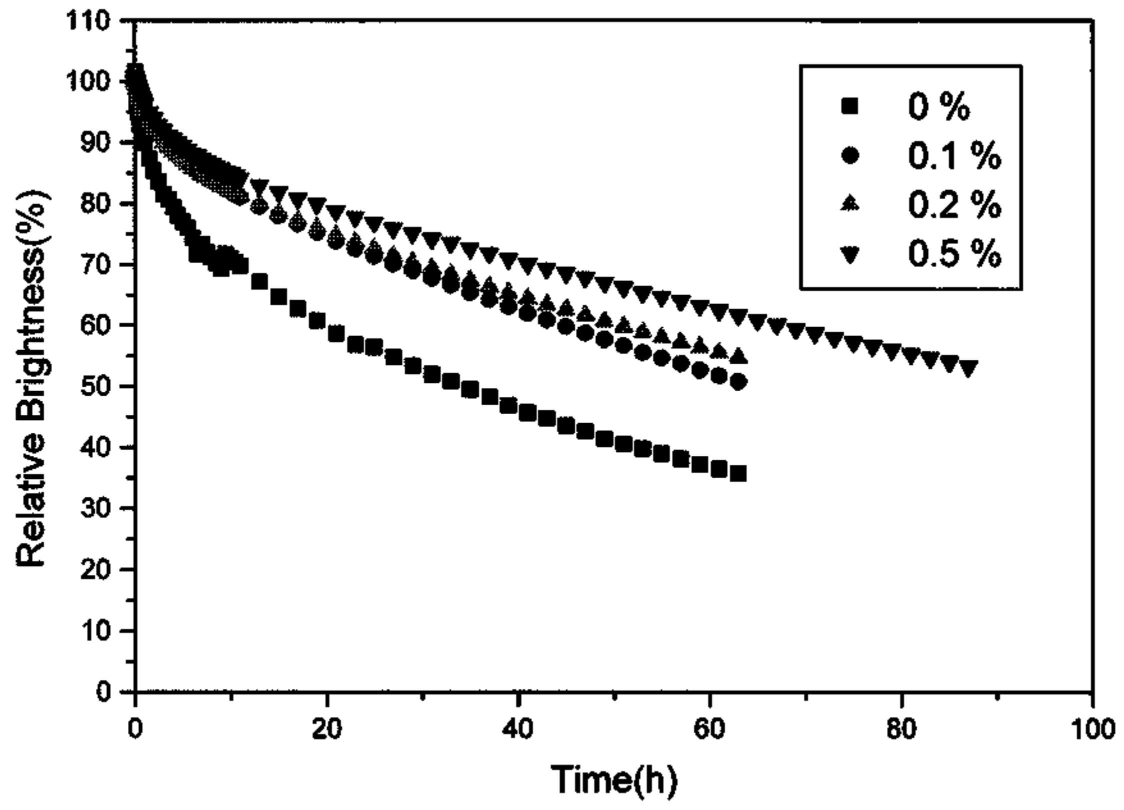


Fig. 3. Lifetime curves of PLEDs according to GPS concentration

delamination of PEDOT thin film from ITO surface which causes a rapid drop in the brightness and increase in voltage. The relatively low initial decay of brightness within 5 h in GPS containing devices compared with GPS free device confirms the improved interfacial contact between ITO and PEDOT. Another advantage of using GPS layer is that it can be used as a barrier for indium contamination from ITO. As GPS forms a crosslinked network through curing reaction between themselves and with hydroxyl groups on ITO surface, it pevents the indium incorporation in PEDOT layer which is also a cause of device failure. In our X-ray photoelectron spectroscopic analysis, the indium content in PEDOT layer without GPS layer was 8 %, while the indium content in PEDOT layer with GPS interlayer on ITO was less than 1 %. The thin GPS layer protects the ITO electrodes from acidic attack by PEDOT which is a strong acid(pH=1.23) and high thermal stability of crosslinked GPS network also has a positive influence on device lifetime.

4. Conclusions

In summary, the insertion of a GPS layer between ITO and PEDOT enhanced the light emitting efficiency and brightness through improved interfacial contact. In addition, the long-term stability of PLED was also improved greatly by blocking the indium incorporation in PEDOT layer.

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