Effect of Annealing on the Electrical Properties and Morphology of a Conducting Polymer used as an Anode in Organic Light-Emitting Devices

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ABSTRACT: The surface sheet resistance of conducting films of glycerol-doped poly(3,4-ethylenedioxy-thiophene)–poly(styrene sulfonate) is largely dependent on the annealing temperature. The presence of free glycerol in insufficiently baked films, as indicated by infrared spectra and thermogravimetric analysis, results in conducting polymer films with poor morphology and low electrical conductivity. The device performance of organic light-emitting diodes using this modified poly(3,4-ethylenedioxy-thiophene)–poly(styrene sulfonate) as an anode is also greatly affected by the baking conditions of the conducting films. The maximum light output, current density, and luminous power efficiency are observed from devices using anodes baked at a high temperature close to the boiling point of glycerol. © 2003 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 41: 2522–2528, 2003

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INTRODUCTION

Aqueous colloidal dispersions of the conducting polymer poly(3,4-ethylenedioxy-thiophene)–poly(styrene sulfonate) (PEDOT:PSS; Baytron-P, Bayer AG, Germany), first introduced in the 1990s, have been widely used as antistatic coatings in photographic films, as electrode materials for capacitors, and in printed circuit boards and microactuators.[1,2] PEDOT:PSS offers many advantages over other conducting polymers because of its ease of processability, good film-forming properties, high optical transparency in visible light, good mechanical strength, and excellent atmospheric stability. It is known that films of PEDOT:PSS are stable at high temperatures (~100 °C) for a long period of time (~1000 h) without noticeable changes in either their electrical conductivity or optical transparency.[1] An electronic grade of PEDOT:PSS, in its lower conductivity form, has been widely used as a hole-injecting buffer layer in organic light-emitting diodes (OLEDs).[3–5] Polymer light-emitting devices made with a PEDOT:PSS layer on top of an indium tin oxide (ITO) anode have longer lifetime than those using ITO anodes alone. The improvement in device stability has been attributed to the ability of the polymer-coated ITO anode to form a reproducibly clean interface with a hole-transporting layer that substantially slows down device degradation. In addition, the energy barrier for hole injection may be slightly smaller because of the higher work function of the conducting polymers (~5.0 eV) compared with that of untreated ITO (~4.7 eV),[6] which in turn lowers the turn-on and oper-

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ating voltage. This is advantageous because the performance of the OLEDs is greatly affected by a slight change in the charge-injection efficiency.

Much effort has been focused on increasing the conductivity of PEDOT:PSS, including blending with polar host polymers such as poly(vinylpyrrolidone),[7] electrochemical polymerization and subsequent doping,[8,9] and secondary doping with additional acidic molecules such as toluene sulfonate, dodecyl benzene sulfonate, and camphor sulfonate.[10] In most cases, an increase of one to two orders of magnitude in conductivity is observed and is accompanied by a decrease in optical transmittance in some cases. The most surprising results have been obtained from PEDOT:PSS films doped with small amounts of polyalcohols or high-boiling-point solvents.[11–14] In contrast to conventional oxidative (protonic) doping, in which the enhancement of the electrical conductivity (or decrease in surface sheet resistance) is always accompanied by a decrease in optical transmittance due to the absorption of radical cations (polarons) in the visible region,[15] no change in optical transparency has been measured for PEDOT:PSS films doped with polyalcohols or other high-boiling-point liquids. These highly conductive and transparent polymers create new opportunities for fabricating flexible optoelectronic and electronic plastic devices based on polymeric electrodes.

Recently, we have demonstrated that chemically modified conducting polymer films fabricated from aqueous dispersions of glycerol-doped PEDOT:PSS (G-PEDOT) can be used as anodes for organic light-emitting devices.[16,17] The addition of glycerol dramatically decreases the surface sheet resistance while maintaining the optical transparency of the modified polymer films. The device performance with this highly conductive polymer anode is greatly improved compared to that of an OLED with an anode fabricated with standard PEDOT:PSS without any added glycerol. Devices using G-PEDOT as anodes show a good external electroluminescence quantum efficiency of approximately 0.73% at 100 A/m^2, the highest reported for a molecular OLED using a conducting polymer anode without an ITO underlayer. Similar improvements have been observed for polymer light-emitting devices[18] and photovoltaic cells[19] using these highly conductive polymers as electrodes.

The resistivity of unmodified PEDOT:PSS films is largely dependent on the annealing conditions.[20] Baking the films at a low temperature results in as much as three times higher resistivity compared with that of films baked at the optimum temperature. The film morphology can be modified by the drying conditions and is obviously an important parameter in determining the bulk conductivity. The optimization of the baking conditions of G-PEDOT films should be more critical because of the high boiling point of the glycerol (bp = 182 °C/20 mmHg) used as an additive to the polymer dispersion. The performance of an OLED using the highly conductive film as an anode is expected to be largely affected by the baking conditions of the polymer film because its conductivity and possibly morphology may be influenced by the annealing conditions. Here we report the effects of the annealing conditions on the surface sheet resistance and morphology of G-PEDOT films and the performance of OLED devices using G-PEDOT as an anode.

EXPERIMENTAL

The device configuration and chemical structures of the materials used in this study are shown in Figure 1. Dispersions of PEDOT:PSS (Baytron P 4071V) were obtained from Bayer Corp. The hole transporter, *N,N′*-bis(naphthalene-1-yl)-*N,N′*-bis(phenyl)benzidine (α-NPB), and the electron transporter/emitter, tris(8-hydroxyquinolinolato)aluminum(III) (Alq_3), were obtained from H.W. Sands and TCI America, respectively. Alq_3 was purified by vacuum train sublimation, and NPB was used without further purification. The glass substrates (Corning 1737) were thoroughly cleaned with a detergent solution. They were then sequentially sonicated in a detergent solution, deionized water, acetone, and isopropyl alcohol, and this was followed by sonication in deionized water. Finally, the substrates were exposed to vapors of isopropyl alcohol and were O_2-plasma-treated before use.

A small amount of glycerol (0.6 g) was added to 10 mL of the PEDOT:PSS dispersion, and the mixture was stirred overnight. The conducting polymer dispersion was spin-coated onto the cleaned glass substrate after filtration through a 0.45-μm poly(vinyl difluoride) filter. The G-PEDOT polymer films were subsequently baked for 5 min on a hotplate under the ambient atmosphere to remove excess H_2O and glycerol. The baking temperature was varied from 130 to 220 °C (±5 °C). The polymer film thickness, measured with a stylus profilometer (Tencor Alpha-Step 250), was

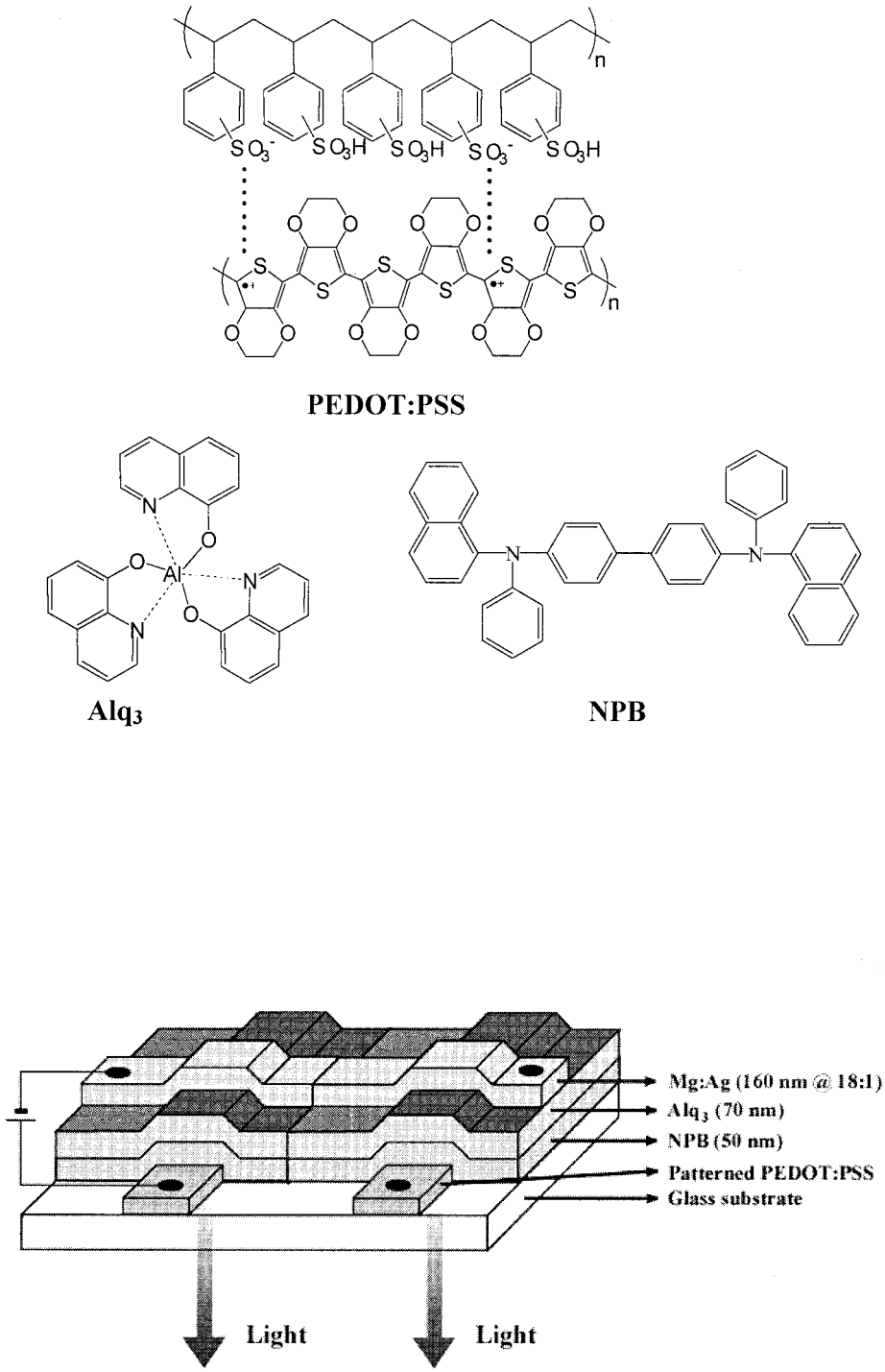

Figure 1. Chemical structures of the materials and the device configuration used in this study.

150 nm ± 5 nm. The sheet resistance was determined by four-point probe measurements. Under the assumption that the thickness of the films was uniform, the film resistivity (ρ) was calculated with a simple relationship, $\rho = R_s t$, where R_s is the sheet resistance and t is the film thickness. The optical spectra were measured with an ultraviolet–visible/near-infrared spectrophotometer (PerkinElmer Lambda 9). Atomic force microscopy (AFM; 3100 series, Digital Instrument)

was used to evaluate the surface morphologies of the polymer films. Fourier transform infrared (FTIR) spectra were taken with a Nicolet 740 spectrophotometer. The thermal stability of the films was measured with thermogravimetric analysis (TGA; TGA 2050, TA instruments).

Details of the device fabrication and characterization have been described elsewhere.[16,21] Briefly, NPB (50 nm), Alq_3 (70 nm), and Mg/Ag (16:1 w/w) alloy films (160 nm) were prepared by sequential vacuum (base pressure $\sim 10^{-7}$ Torr) deposition onto patterned conducting polymer films on glass substrates. A shadow mask was used for the deposition of the cathode materials. The active area of the devices was 2 mm $\times$ 2 mm. All device characterizations were performed inside a glove box under a dry nitrogen atmosphere.

RESULTS

Figure 2 shows the surface sheet resistance of G-PEDOT conducting polymer films annealed at various temperatures. The surface sheet resistance of the 150-nm-thick films of G-PEDOT decreases as the annealing temperature increases. For example, the surface sheet resistance of a film baked at 130 °C is 1270 Ω/□, whereas that of a film annealed at 190 °C is only 860 Ω/□. Annealing beyond 190 °C results in a dramatic increase in the surface sheet resistance of the G-PEDOT conducting films.

Figure 3 shows AFM images (5 μm $\times$ 5 μm) of two G-PEDOT films baked at 130 and 190 °C. The surface roughness of the film baked at 190 °C is smoother [root-mean-square (RMS) roughness = 4.0 nm] than that of the one annealed at 130 °C (RMS roughness of 5.7 nm), showing fewer spikes. Figure 4(a) shows the FTIR spectra of G-PEDOT films baked at 130 and 190 °C. Absorptions around 3500, 2950, and 1050 cm^{-1} are due to the OH, CH, and CO stretching vibrational modes of glycerol, respectively, and can be clearly seen for the film baked at 130 °C. However, these peaks completely disappear upon annealing at 190 °C. This indicates the complete removal of the glycerol from the film when it is baked at a higher temperature. Figure 4(b) shows the TGA results obtained from the films baked at a lower temperature (130 °C) and a higher temperature (190 °C). The TGA results are in good agreement with the FTIR study, in which the existence of the residual glycerol can be clearly seen from the films baked at the lower temperature. The weight loss starting from around 170 °C is due to the residual glycerol remaining in the film baked at 130 °C.

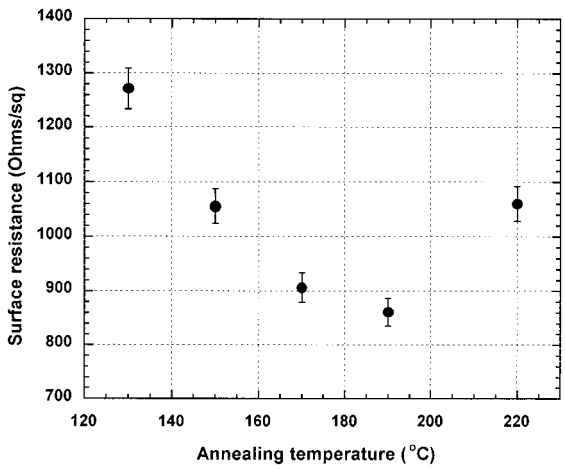

Figure 2. Surface sheet resistance of G-PEDOT films annealed at different temperatures.

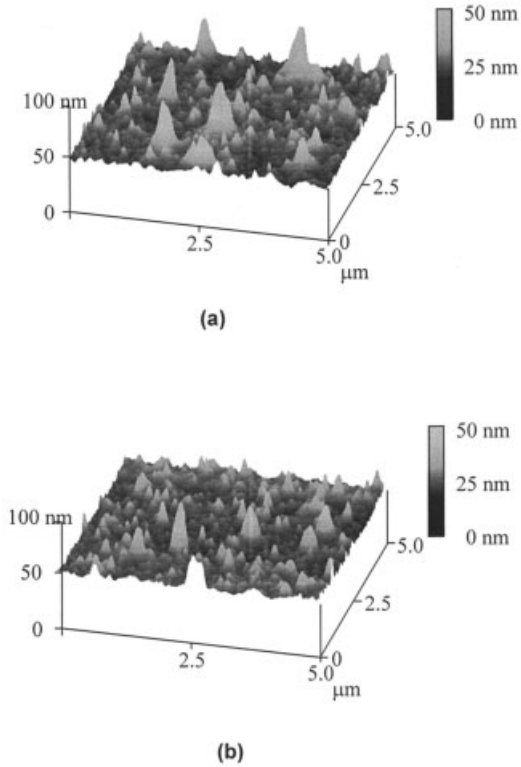

Figure 3. AFM images (5 μm $\times$ 5 μm) of G-PEDOT films (a) baked at 130 °C and (b) baked at 190 °C. The scale in the z direction (50 nm/division) is greatly expanded with respect to the scales in the s and y directions (2.5 μm/division). Therefore, the surface is flat and broad in the lateral direction.

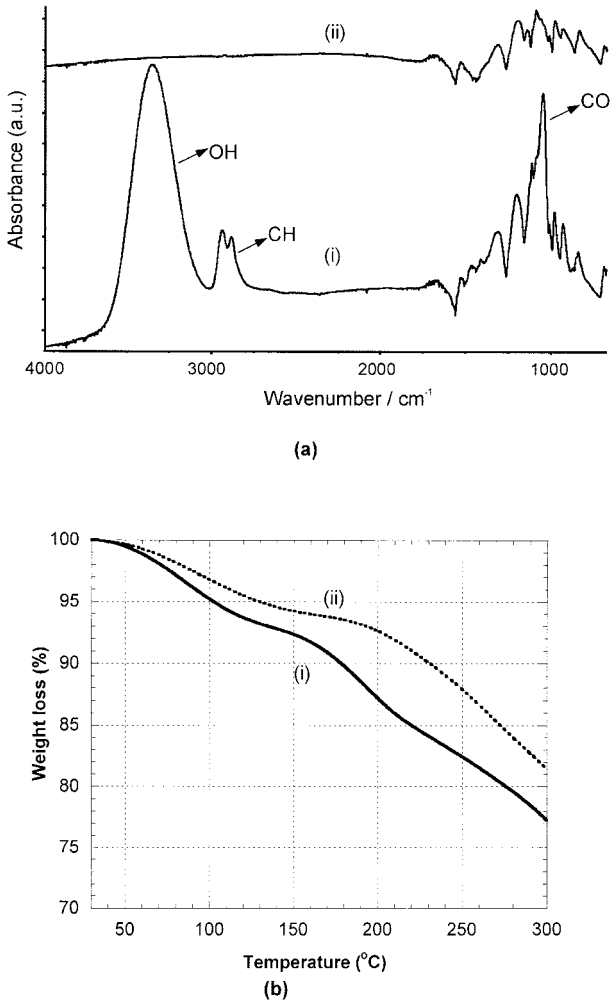

Figure 4. (a) FTIR spectra and (b) TGA of G-PEDOT films baked at (i) 130 and (ii) 190 °C.

Figure 5(a) shows the current density and luminance as functions of the applied voltage for the OLEDs fabricated with G-PEDOT anodes; the G-PEDOT films were baked at different temperatures, ranging from 130 to 190 °C, before being incorporated into the devices. A comparison of the current density, voltage, and luminance characteristics for the four devices clearly indicates that the device performance is greatly improved when the polymer film used as the anode is baked at higher temperatures (170–190 °C). A consistently higher voltage can be observed at the same current density for the devices using the anodes baked at lower temperatures rather than the ones baked at higher temperatures. The devices using anodes baked at temperatures close to the boiling point of glycerol (170 and 190 °C) show higher current density and brightness over the entire voltage range than those OLEDs using the G-PEDOT anodes baked at lower temperatures (130–150 °C). For example, current densities of 210 and 140 A/m^2 were measured at 10 V for the OLEDs using G-PEDOT annealed at 190 and 130 °C, respectively. Brightness values of 490 and 270 cd/m^2 were recorded at the same voltage. A maximum luminance of approximately 1500 cd/m^2 was achieved for an OLED using an anode baked at 190 °C. It is almost a factor of two higher than that measured for OLEDs using PEDOT:PSS anodes baked at 130–150 °C. The latter devices

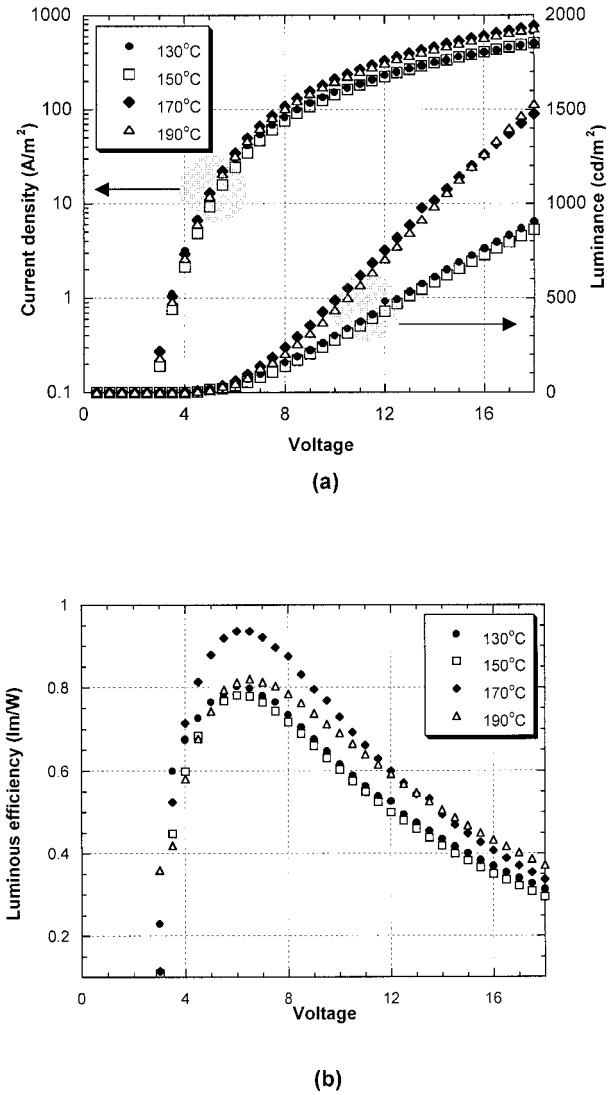

Figure 5. Plots of (a) the current density, applied voltage, and luminance characteristics and (b) the luminous power efficiency as a function of voltage for the OLED devices fabricated with G-PEDOT anodes baked at various temperatures.

start to fail at a relatively low current density. In Figure 5(b), the luminous power efficiency and voltage characteristics for the four OLEDs are shown, and it indicates that the highest efficiency is achieved for the sample annealed at 170 °C.

DISCUSSION

We have studied the effect of annealing the conducting polymer G-PEDOT films on their surface sheet resistance and morphology, and we have found that the annealing temperature is crucial for optimizing these properties and the performance of the OLEDs based on these polymer anodes. The results of this study show that annealing the conducting polymer at a temperature close to the boiling point of the dopant leads to the maximum electrical conductivity and good film uniformity, which, in turn, lead to optimum OLED device performance. These results are in good agreement with a recently reported study in which the resistivity of the undoped PEDOT:PSS films was shown to be largely dependent on its baking and drying conditions.[20] The films annealed at low temperatures exhibited three times higher resistivity than those of the properly baked films.

It is known that spin-coated films of unmodified PEDOT:PSS form grainlike structures with a nonhomogeneous distribution of the PEDOT and PSS species upon spin coating.[22] The surface roughness of the films is higher than that of the bare glass substrates (1.3 nm). This result is not surprising because the mean particle size of PEDOT:PSS (standard grade; Bayer) is in the range of 25–75 nm. Glycerol doping of a PEDOT:PSS dispersion leads to the formation of films with good morphology in which the polymer chains are evenly distributed.[12] Previously, we have shown that the RMS surface roughness of an undoped film of PEDOT:PSS (annealed at 130 °C) is in the range of 4.0–4.6 nm,[17] which is similar to that (4.0 nm) of a glycerol-doped film annealed at a higher temperature (190 °C). In comparison, the RMS roughness of the G-PEDOT film annealed at 130 °C is 5.7 nm. This result clearly indicates that annealing at the proper temperature is critical for achieving the best morphology and the highest bulk conductivity of the film.

The complete removal of the nonconducting free glycerol results in an increase in the G-PEDOT electrical conductivity because the charge carriers can move or hop more easily through these evenly distributed polymer chains. The fact that the optical transparency is not affected by the increase in conductivity suggests that an increase in the charge mobility and not in the concentration of free carriers is responsible for this effect. This proposed mechanism is completely different from the conventional protonic doping in which the enhancement of electrical conductivity is always accompanied by a decrease in optical transmittance due to the increase in the concentration of the highly absorbing charged carriers.[15] This result is in good agreement with the recent report by Ghosh and Inganäs[12] in which the increase in the conductivity of a PEDOT:PSS film upon the addition of high-boiling-point additives is attributed to a plasticizing effect. The additives promote the polymer chains being arranged in a more homogeneous fashion, especially when the films are baked at the optimum temperature. Similar observations have been made of PEDOT:PSS films doped with high-boiling-point solvents such as dimethyl sulfoxide and dimethylformamide.[14]

The morphology and conductivity of G-PEDOT annealed at different temperatures have a strong effect on the performance of OLEDs using G-PEDOT as the anode. The electrical conductivity and charge-injection efficiency of the G-PEDOT anode have a strong influence on the device operating voltage and efficiency. A consistently higher voltage observed at the same current density for the devices using the anodes baked at lower temperatures is due to the poor conductivity and high sheet resistance of the insufficiently baked conducting films. This is consistent with earlier reports in which the OLED device brightness was greatly reduced, especially at a high voltage, when low-conductivity polymers were used as anodes.[4,23] A considerably high sheet resistance limits the current flow through the OLED device and results in a reduced light output. This failure may be due to local Joule heating caused by the high sheet resistance of the conducting polymer anode. The luminous power efficiency, the ratio of the light output power to the electrical input power, is also affected by the conductivity of the G-PEDOT anodes. In general, a higher efficiency is obtained from devices employing the anodes annealed at high temperatures closer to the boiling point of the glycerol. The highest luminous power efficiency (~1 lm/W) has been achieved from devices using the conducting polymer anodes baked at 170 °C.

CONCLUSIONS

We have shown that the surface sheet resistance of films of G-PEDOT is largely dependent on the baking conditions. Studies based on FTIR and TGA have clearly demonstrated the presence of free glycerol in the insufficiently baked films. The OLED device performance is greatly affected by the baking conditions of the conducting film anodes. Higher brightness, current density, and luminous power efficiency have been observed from devices using the anodes baked at temperatures close to the boiling point of glycerol rather than from those using the anodes baked at much lower temperatures (<150 °C). We believe that the increased conductivity and uniformity of the sufficiently baked conducting polymer anode device are responsible for the improvement in the device performance.

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