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| Citation | 電気材料技術雑誌. 2005, 14(2), p. 43-46 |
| Version Type | VoR |
| URL | https://hdl.handle.net/11094/76801 |
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Polymer Light-Emitting Device with a Cathode Fabricated from Silver Nanoparticles by Wet Processing

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Recently, organic light emitting diodes (OLEDs) utilizing fluorescent dye [1] or conducting polymer [2] have been realized to have a long lifetime and excellent durability for flat panel display applications. Organic devices utilizing conducting polymers have attracted considerable interest because of their advantages in large-area device fabrication. An additional advantage for OLED is that they are simply fabricated by wet-process, including spin coating and ink-jet printing method on various kinds of substrates.

Recently, electrodes fabricated from metal nanoparticles have been attracting considerable attention due to their simple and low-cost processes. Each metal nanoparticle is covered with a dispersing agent, because each metal nanoparticle coheres easily. Therefore, a nanopaste with high metal content formed from many metal nanoparticles acts as a liquid. As its formation temperature is approximately 200 °C, a super-fine circuit can be formed on an organic board using a simple printing process such as inkjet printing. Metal nanoparticles are also expected to be applied as electrodes of organic devices such as transistors [3]. To create the patterning of devices by wet processing, cathode formation using nanopaste plays an important role.

In this study, we investigated the fabrication and characteristics of a polymer device utilizing a cathode fabricated from Ag nanoparticles by wet processing to realize organic devices simply fabricated by wet-process as an initial step.

Figure 1 indicates the annealing temperature dependence of the resistivity of the Ag films which were fabricated by spin coating the Ag nanopaste on a glass substrate and annealing for 1 h in N₂ atmosphere. Ag nanopaste (NPS-J) was purchased from Harima chemicals Inc. The average diameter of Ag nanoparticles was about 5 nm. The resistivity of the Ag film fabricated from the Ag nanopaste (nano-Ag film) rapidly decreased at temperatures between 180 and 190 °C. The resistivity of the nano-Ag film reached $1.65 \times 10^{-5} \Omega\text{cm}$ at an annealing temperature of 210 °C and is ten times the value of the deposited Ag film. The surface color of the nano-Ag film at 210 °C is metallic. The AFM images of Ag films at annealing temperatures of 180 and 190 °C are shown in Fig. 2. The grain size of Ag

nanoparticles at a substrate temperature of 180 °C is estimated to be about 50 ~ 100 nm from the AFM image. Each grain boundary between Ag nanoparticles at 190 °C is fused compared with that at 180 °C. This result suggested that the dispersing agent on the Ag nanoparticles decomposes at an annealing temperature between 180 and 190 °C. The fusion of the Ag nanoparticle grain boundaries results in the decrease in the resistivity of the nano-Ag films.

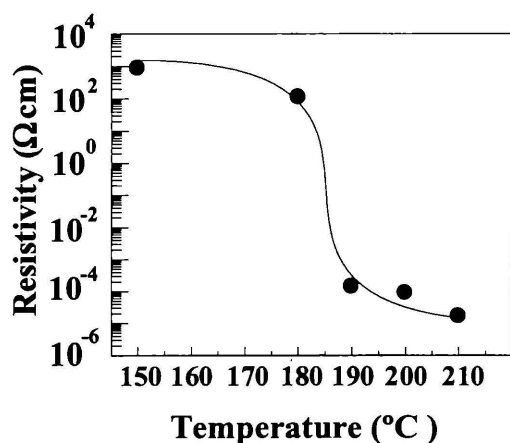


Fig.1. Annealing temperature dependence of resistivity in Ag films. The line is a guide for the eye.

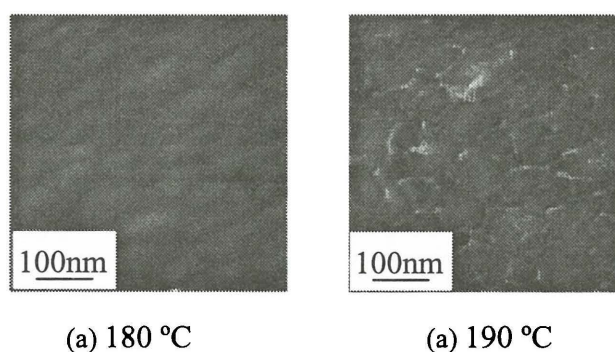


Fig.2. AFM images of Ag films at annealing temperatures of 180 and 190 °C.

Organic layers were fabricated by spin coating on an indium tin oxide (ITO)-coated glass substrate. The substrate was degreased with solvents and cleaned in a UV ozone chamber. First, a poly(ethylenedioxythiophene) : poly(styrene sulfonic acid) (PEDOT:PSS) hole injection layer was spun over the ITO-coated glass substrate at 35 nm thickness. A regioregular poly(3-hexylthiophene-2,5-diyl) (PAT6) film and poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) film was spin-coated from chloroform solution, respectively. The typical thickness of the PAT6 and MEH-PPV film was about 140 and 150 nm, respectively. The a-C:N buffer layer which prevents Ag nanoparticles from penetrating into the organic layer was deposited using a mirrortron-type sputtering system (Thin-Film Process Soft Inc., Japan) with facing targets under a pure Ar flow rate of 45 sccm and a N₂ flow rate of 20 sccm. Finally, the Ag nanopaste was dropped using a micropipette or ink brush on the patterned organic layer and then baked at 210 °C for 1 h in N₂ atmosphere. Figure 3 shows the EL spectra of polymer OLEDs with an amorphous carbon nitride (a-C:N) buffer layer and a Ag cathode fabricated from the Ag nanopaste. The PAT6 and MEH-PPV device emits a red EL band centered at about 700 and an orange EL band at 650nm, respectively.

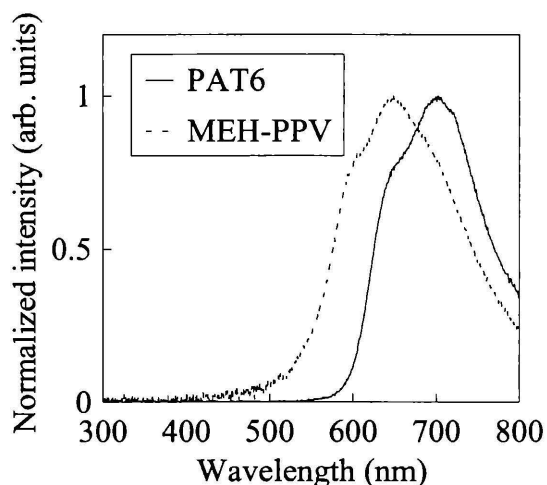


Fig.3. EL spectra of EL spectra of PAT6 and MEH-PPV devices with a nano-Ag cathode.

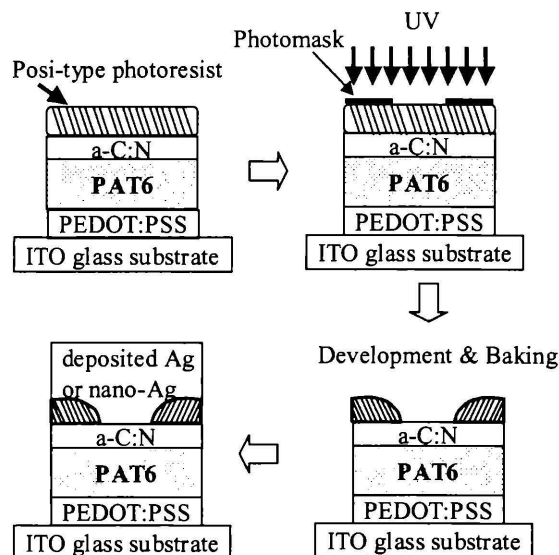


Fig.4. Fabrication process for the patterned polymer device in this study.

The patterned polymer device with the cathode using Ag nanoparticles was fabricated as follows. After spin-coating the organic layer and depositing an a-C:N buffer layer, the surface of the organic layer with the a-C:N buffer layer was patterned using photolithography as shown in Fig. 4. First, the positive-tone photoresist used to make the insulator layer was spun onto a film of PEDOT:PSS / PAT6 / a-C:N (10 nm) and baked at 110 °C for 5 min in an ambient atmosphere. The thickness of the photoresist was approximately 500 nm. We reported the a-C:N buffer layer on the organic layer is also useful for blocking the photodegradation influence of UV light, and this effect was improved further in vacuum [4]. Next, a UV light was irradiated on the photoresist for 15 s under a base pressure of 2 Pa. After prebaking the devices at 110 °C in an ambient atmosphere, these were developed by solvent, cleaned by deionized water and then baked at 210 °C in N₂ atmosphere. The Ag nanopaste was dropped using a micropipette or ink brush on the patterned organic layer and then baked at 210 °C for 1 h in N₂ atmosphere. The typical thickness of an Ag cathode fabricated from the Ag nanopaste (nano-Ag cathode) was about 400 ± 100 nm. The active area of the devices has a diameter of 400 or 500 μm. For comparison, the Ag cathode was vapor-deposited at a background pressure of 10⁻⁶ torr. Finally, these devices were covered with a glass plate and encapsulated by epoxy resin in an Ar gas atmosphere.

Figure 5 shows the dependence of the current density and luminance on the applied voltage for the PAT6 devices with the nano-Ag and deposited Ag cathodes. Both devices have the same turn-on voltage. The luminance increased superlinearly with increasing applied voltage. The patterning of the emission from the PAT6 device with the nano-Ag cathode can

be carried out as shown in Fig. 6. In the case of the device with the nano-Ag cathode, a luminance of about 2 cd/m² has been obtained at an applied voltage of 13 V. The luminance of the device with the nano-Ag cathode is half that with the deposited Ag cathode. On the other hand, the current density of the device with the nano-Ag cathode is similar to that with the deposited Ag cathode. This result indicates that decreased device performance is attributed to the lowering of electron injection from the nano-Ag cathode. We demonstrated the possibility of polymer OLEDs using a cathode fabricated from Ag nanoparticles by wet processing.

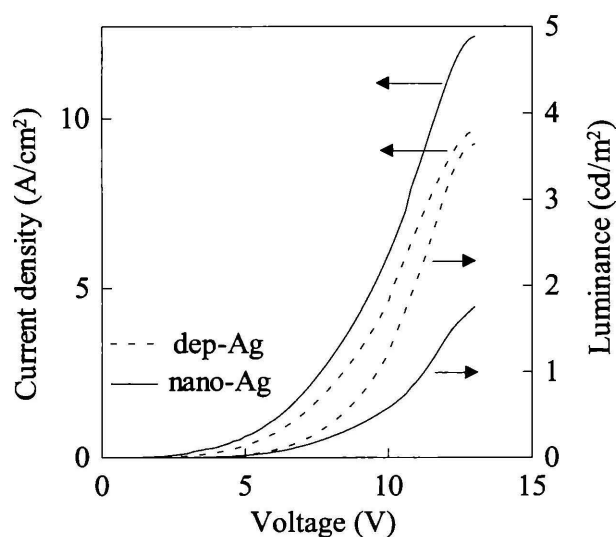


Fig.5. Dependence of current density and luminance on applied voltage for PAT6 devices with nano-Ag and deposited Ag cathodes.

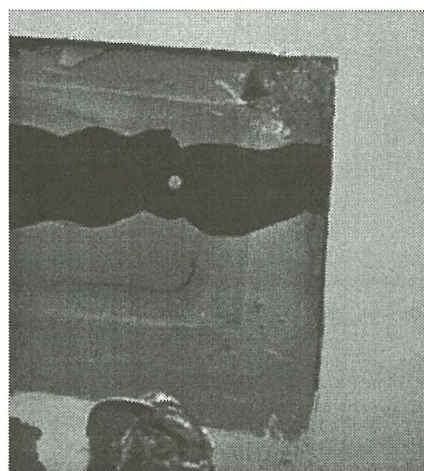


Fig.6. Photograph of the patterned emission from an OLED of an ITO / PEDOT:PSS / PAT6 / a-C:N / nano-Ag cathode with an active area

Acknowledgments

Part of this work was financially supported by the Ministry of Education, Culture, Sports, Science and Technology under a Grant-in-Aid for Scientific Research (No. 16360173). The authors would like to thank S. Uesugi and M. Adachi of Cluster Technology Co., Ltd. for AFM measurements.

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