Printed Invisible Silver-Grid Transparent Electrode on Flexible Epoxy Film and Application to Powder Electroluminescent Device

Masato Ohsawa[1], Natsuki Hashimoto[1], Naoki Takeda[2], Shota Tsuneyasu[2], Toshifumi Satoh[2]

[1]Institute for Super Materials, ULVAC, Inc., 5-9-6 Tohkohdai, Tsukuba, Ibaraki 300-2635, Japan
[2]Department of Media Engineering, Graduate School of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan
Keywords: Invisible Ag-grid, PEDOT:PSS, Gravure offset printing, Epoxy film, Electroluminescence

ABSTRACT

Invisible Ag-grid transparent electrodes have been printed on a flexible epoxy film. The Ag-grid electrode were laminated with a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) layer. The electrode shows no noticeable resistance change throughout the bending cycles at a bending radius of 1.0 mm. The transparent electrode-based powder electroluminescent device develops excellent flexibility.

1 INTRODUCTION

A conventional indium tin oxide (ITO) has been usually used as a transparent electrode owing to high transparency and electrical conductivity [1]. However, the ITO is not favorable in flexible electronic devices due to its intrinsic brittleness. Invisible metal-grid electrodes have been suggested as an alternative and flexible material for ITO replacement. The metal-grid electrodes become very valuable if the grid electrodes are able to be fabricated by printing processes at lower costs since the printing methods help to improve the efficiency of material utilization and simplify the fabrication processes [2].

Alternating-current powder electroluminescent devices (ACPELDs) are promising as flexible lighting sources for commercial application because of the fabrication method with simple printing processes and low cost materials. ACPELDs can be used in flexible lighting devices. ACPELDs are composed of phosphor and dielectric layers sandwiched between a transparent electrode and a back electrode [3].

In spite of invisible metal-grid electrodes are promising as flexible transparent electrodes, research on the bending durability of the metal-grid transparent electrodes and those-based electroluminescent devices is still limited.

In this study, invisible Ag-grid transparent electrodes have been fabricated on a flexible epoxy film substrate and a polyethylene naphthalate (PEN) film substrate by a conventional gravure offset printing using our newly developed Ag nanoparticle ink based on our previous study [4,5]. The Ag-grid electrodes were laminated with a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) layer. Bending reliability of the transparent electrodes of Ag grid laminated with PEDOT:PSS (Ag-grid/PEDOT) on the flexible epoxy film substrate was evaluated and compared to that of the transparent electrodes on the polyethylene naphthalate (PEN) film substrate. Furthermore, the fabricated epoxy film-based Ag-grid/PEDOT:PSS transparent electrode has been applied to an ACPELD as an ITO replacement. Bending durability of the fabricated ACPELD was evaluated.

2 EXPERIMENT

Transparent electrodes of printed invisible Ag-grid laminated with conductive polymer were fabricated by a conventional gravure offset printing and an applicator shown in our previous study [4,5]. Our developed Ag nanoparticle ink (L-Ag Nano Metal Ink, ULVAC) was applied to fabricate a fine Ag-grid electrode pattern on an epoxy film substrate (YX-7200, Mitsubishi Chemical Corporation) or a polyethylene naphthalate (PEN) film substrate (Teonex-Q65HA, TEIJIN), the thickness of both of which is 50 μm, by a gravure offset printing unit. Using the printing unit, the Ag-grid electrodes were fabricated with the Ag-grid line width of 5 μm, spacing between the Ag-grid lines of 200 μm and the thickness of the lines of 0.6 μm. The printed area of the grid electrode patterns was 40 mm × 80 mm. The printed grid electrodes were annealed at 180℃ for 60 min. Then the Ag-grid electrodes were over-coated with a conductive polymer PEDOT:PSS dispersion (composed of ARACOAT AS601D and CL910, Arakawa Chemical Industry) by an applicator and cured at 100℃ for 1 min. The whole area of the fabricated Ag-grid electrode pattern was laminated with the PEDOT:PSS layer.

The ACPELD was fabricated by a gap coating method, except for the back electrode. The fabricated ACPELD consists of the epoxy film substrate / the Ag-grid laminated with PEDOT:PSS / phosphor layer / dielectric layer / back electrode. A doped ZnS powder phosphor paste (IZTA01, Image Tech) was coated on the Ag-grid/PEDOT:PSS electrode by the applicator and dried at 110℃ for 15 min. The phosphor layer is 30 μm thick. A dielectric $BaTiO_3$ paste (IBTA01, Image Tech) was coated upon the phosphor layer by the applicator and dried at 110℃ for 15 min. The thickness of dielectric layer is 20 μm. An evaporated aluminum film was deposited onto the dielectric layer as the back electrode. The thickness of back electrode is 0.2 μm. The luminescent areas of the ACPELDs were 35 mm × 60 mm.

The bending durabilities of the fabricated electrodes of the Ag-grid/PEDOT and the ACPELD were evaluated by a bending endurance test machine (Tension-Free Folding Clamshell-type, YUASA SYSTEM). The electrode and ACPELD samples were bended in the bending angle range from 180° (flat state) to 0° at the prescribed bending radius. The repeated bending tests were carried out in the bending condition at a bending cycle rate of 30 rpm. In the bending tests, the electrode and ACPELD samples were placed with the Ag-grid side outwards. Electrical resistance changes of the fabricated electrodes were measured throughout the bending tests. The gauge length of the electrode sample loaded by bending, L_g is written with the following equation [5]:

$$L_g = \pi r \tag{1}$$

where r is the bending radius of the electrode. The electrical resistance changes of the electrodes were evaluated in the areas corresponding to L_g.

Focused ion beam (FIB)-prepared cross-sections of the Ag-grid/PEDOT electrodes were observed by a field emission scanning electron microscope (FE-SEM S-5500, Hitachi).

3 RESULTS AND DISCSSION

3.1 Outer bending durability of Ag-grid laminated with PEDOT:PSS transparent electrode

Fig. 1(a) shows a bended image of the fabricated Ag-grid transparent electrode. Shown in Fig. 1(b) is a microscope image of the fabricated Ag-grid electrodes with the line width of 5 μm, the thickness of 0.6 μm and spacing between the Ag-grid lines of 200 μm. The sheet resistance values of Ag-grid/PEDOT transparent electrodes on the epoxy film substrate and the PEN film substrate are 4.4 Ω/□ and 4.9 Ω/□, respectively.

Outer bending durabilities of the Ag-grid/PEDOT electrodes on both the epoxy film and PEN film substrates have been evaluated at a variety of the bending radius. The change in resistance of the electrode samples is expressed as R/R_0, where R_0 is the resistance of initial flat state and R is the resistance after bending at the prescribed bending radius. The corresponding bending strain of the transparent electrode is calculated by the following equation [5]:

$$Strain = (h_f + h_s) / 2r \approx h_s / 2r, \tag{2}$$

where, h_f, h_s and r denote the transparent electrode thickness, the substrate thickness and the bending radius, respectively. Fig. 2 shows R/R_0 of the Ag-grid/PEDOT electrodes on the epoxy film and PEN film in the outer bending state as a function of bending strain. R in the bending state almost remains unchanged in the bending strain range up to 2.0%, which corresponds to the bending radius of 1.25 mm, in the electrodes on both the epoxy film and PEN film substrates. Increase of R in the bending state of the electrode on the epoxy film substrate is suppressed in the bending strain range over 2% compared to that on the PEN film substrate.

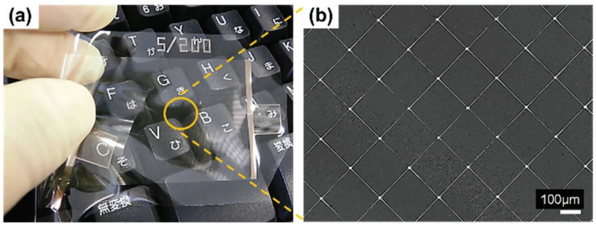

Fig. 1 (a) Image of the epoxy film-based Ag-grid electrode. (b) An optical microscopic image of the Ag-grid electrode with the line width of 5 μm and the spacing between the lines of 200 μm on the epoxy film substrate.

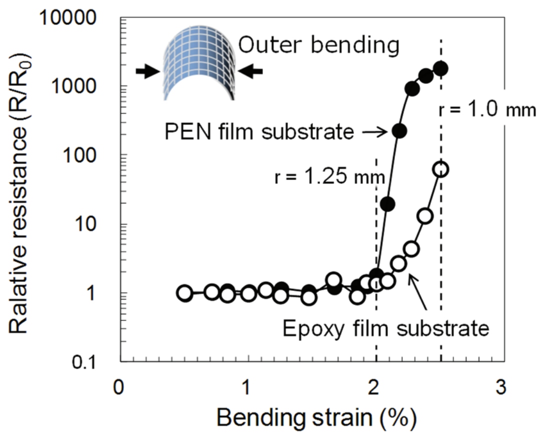

Fig. 2 Resistance of the Ag-grid/PEDOT electrodes on the epoxy film and PEN film substrates measured in the bending state, normalized to the resistance measured in the initial flat state, as a function of outer bending strain. The "r" means the corresponding bending radius. The inset shows the relationship between the direction of the Ag-grid and the bending direction.

The repeated bending durabilities of the Ag-grid/PEDOT on both the epoxy film and PEN film substrates have been evaluated at bending radius of 1.0 mm, which corresponds to an outer bending strain of 2.5%. Fig. 3 shows R/R_0 in the re-flat state after bending of the electrodes as a function of the bending cycles. R of the electrode on the PEN film substrate in the re-flat state after bending increases with increasing the number of bending cycle in the range above 100 cycles and reaches 300 times as high as R_0 after 20,000 bending cycles. In contrast, R of the electrode on the epoxy film substrate in the re-flat state after bending shows no noticeable change throughout the 20,000 bending cycles.

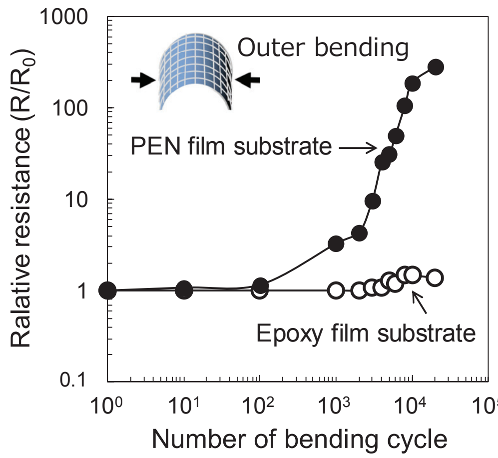

Fig. 3 Resistance of the Ag-grid/PEDOT on the epoxy film and PEN film substrates measured in the re-flat state after bending, normalized to the resistance measured in the initial flat state, during repeated outer bending (bending at a radius of 1.0 mm). The inset shows the relationship between the direction of the Ag-grid and the bending direction.

FIB-prepared cross-sectional SEM images of the Ag-grid/PEDOT electrodes on the epoxy film and PEN film substrates after the 20,000 outer bending cycles at a bending radius of 1.0 mm are shown in Fig.4. Fractures and cracks are not observed in the repeatedly bended electrode on the epoxy film substrate (Fig. 4(a)). On the other hand, horizontal intralaminar fracture propagation accompanied by cracks is clearly observed in the Ag-grid layer of electrode on the PEN film substrate (Fig. 4(b)). The epoxy film surface would strongly adhere the Ag-grid electrode and PEDOT:PSS layer compared to the PEN film surface. The adhesion characteristic of the epoxy film substrate contributes the excellent bending durability of the Ag-grid/PEDOT electrode.

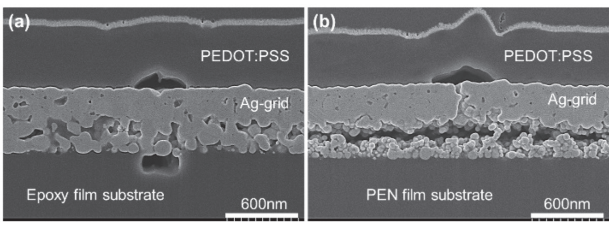

Fig. 4 FIB-prepared cross sectional SEM images of the Ag-grid/PEDOT electrodes: (a) on the epoxy film substrate, (b) on the PEN film substrate, after the 20,000 outer bending cycles at a bending radius of 1.0 mm.

R/R_0 in the bending state of the Ag-grid/PEDOT electrode on the epoxy film substrate has also been evaluated throughout the 20,000 outer bending cycles at a bending radius of 1.0 mm. Fig. 5 shows *R/R_0* in the bending state and the re-flat state after bending of the Ag-grid/PEDOT electrode on the epoxy film substrate as a function of the bending cycles. *R* in the bending state increases with increasing the bending cycles and reaches 3,000 times higher than *R_0* after 20,000 bending cycles. However, R in the re-flat state after bending shows no noticeable change throughout the 20,000 bending cycles. This indicates that adequate recovery of electrical resistance arises in the re-flat state after repeated outer bending.

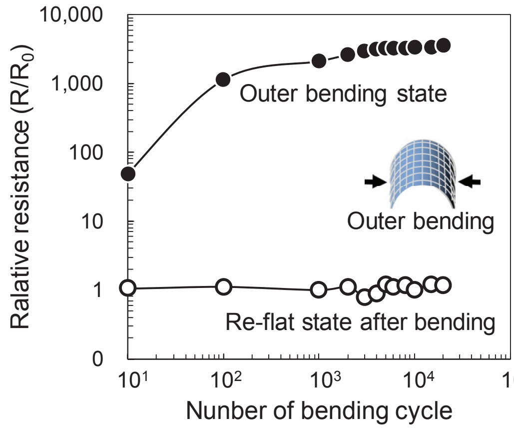

Fig. 5 Resistance of the Ag-grid/PEDOT on the epoxy film substrate measured in the bending state and re-flat state after bending, normalized to the resistance measured in the initial flat state, during repeated outer bending (bending at a radius of 1.0 mm). The inset shows the relationship between the direction of the Ag-grid and the bending direction.

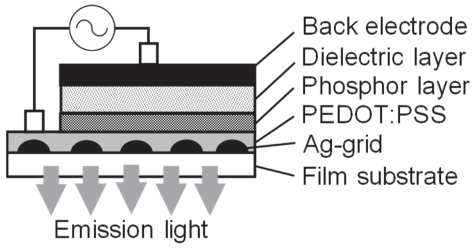

Fig. 6 Structure of the fabricated ACPELD.

3.2 Characteristic and repeated bending durability of ACPELD

The Ag-grid/PEDOT:PSS electrode on the epoxy film substrate has been applied to the ACPELD as the transparent electrode. Fig. 6 shows the structure of fabricated ACPELD in this study. The fabricated ACPELD consists of the epoxy film substrate / The Ag-grid laminated with PEDOT:PSS transparent electrode / phosphor layer / dielectric layer / back electrode. Fig. 7(a) shows a lighting image of the bended ACPELD. The Ag-grid/PEDOT transparent electrode on the epoxy film-based ACPELD develops stable uniform luminescence and flexibility. Shown in Fig. 7(b) is a microscope image of light emission from the fabricated ACPELD on the Ag-grid/PEDOT transparent electrode at 150 $V_{0\text{-}p}$ (zero-to-peak voltage value) and 2 kHz. Luminescence is uniform in the whole area except that the Ag-grid lines are blocking the light. Fig. 8 shows luminance versus applied voltage (L-V) for the as-prepared ACPELD with the Ag-grid/PEDOT on the epoxy film substrate. The L-V characteristic indicates that the ACPELD is caused by a well-known electroluminescence mechanism using the doped ZnS phosphor [3].

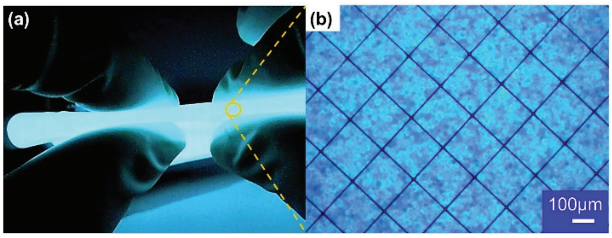

Fig. 7 Lighting images of the ACPELD with the Ag-grid/PEDOT transparent electrode fabricated on the epoxy film substrate: (a) the bended ACPELD, (b) a microscope image of light emission from the ACPELD at 150 $V_{0\text{-}p}$ and 2 kHz.

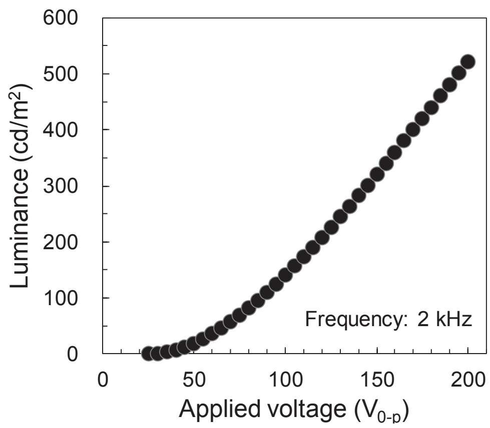

Fig. 8 Luminance versus applied voltage for the as-prepared Ag-grid/PEDOT-based ACPELD fabricated on the epoxy film substrate.

The repeated bending durability of the fabricated ACPELD with the Ag-grid/PEDOT electrode on the epoxy film substrate has been evaluated at bending radius of 1.0 mm. Fig. 9 shows the luminance change of the fabricated ACPELD at 150 $V_{0\text{-}p}$ and 2 kHz as a function of number of the bending cycles. The luminance of the fabricated ACPELD shows no noticeable change throughout the 30,000 bending cycles. The luminance maintenance, L/L_0 (where L is the luminance of as-prepared ACPELD, L_0 is the luminance of repeatedly bended ACPELD) is kept at 96% after the 30,000 bending cycles. The ACPELD with the Ag-grid/PEDOT transparent electrode on the epoxy film develops excellent repeated bending durability.

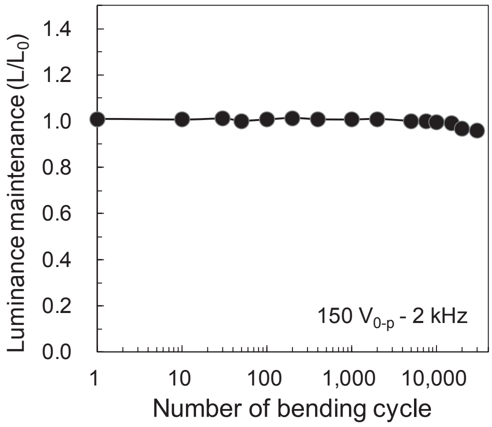

Fig. 9 Luminance maintenance, as a function of number of bending cycle, of the Ag-grid/PEDOT-based ACPELD fabricated on the epoxy film substrate at a bending radius of 1.0 mm.

4 CONCLUSIONS

The Ag-grid laminated with PEDOT:PSS transparent electrodes have been fabricated on a flexible epoxy film. The electrode shows no noticeable resistance change throughout the 20,000 bending cycles at a bending radius of 1.0 mm. The transparent electrode-based ACPELD develops excellent flexibility. Luminance maintenance of the ACPELD is kept 96% after the 30,000 bending cycles at a bending radius of 1.0 mm.

REFERENCES

[1] S.K. Park, J.I. Han, W.K. Kim, and M.G. Kwak, “Deposition of indium–tin-oxide films on polymer substrates for application in plastic-based flat panel displays”, Thin Solid Films, vol. 397, pp. 49-55 (2001).

[2] Z. Xin, Y. Liu, X. Li, S. Liu, Y. Fang, Y. Deng, C. Bao and L. Li, “Conductive grid patterns prepared by microcontact printing silver nanoparticles ink”, Mater. Res. Express, Vol. 4, p. 015021 (2017).

[3] K.W. Park, H.S. Jeong, J.H. Park, G. Deressa, Y.T. Jeong, K.T. Lim, J.H. Park, and J.S. Kim, “Flexible powder electroluminescent device on silver nanowire electrode”, J. Lumin. vol. 165, pp. 216-219 (2015).

[4] M. Ohsawa and N. Hashimoto, “Flexible transparent electrode of gravure offset printed invisible silver-grid laminated with conductive polymer”, Mater. Res. Express, Vol. 5, p. 085030 (2018).

[5] M. Ohsawa and N. Hashimoto, “Bending reliability of flexible transparent electrode of gravure offset printed invisible silver-grid laminated with conductive polymer”, Microelectron. Reliab., Vol. 98, pp. 124-130 (2019).