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A conductive polymer composite was used in fabrication of field emission(FE) electrode array. The FE electrode was prepared by using a template: polycarbonate membrane filter of 0.4 ~ 1.2 μm diameter pores. Initially, the conductive polymer was spin-coated on the ITO glass. Polymer tubules were molded by capillary action of the polymer solution into the template. After removing the template, metal were deposited by sputtering or electroplating onto the polymer to enhance the field emission. The micro structure was then observed by using SEM and analyzed via EDAX step by step along the fabrication procedure. This structure showed that FE started at 0.6 V/μm under vacuum condition of 10^{-6} Torr.

Keywords: conductive polymer; field emission; molded-by-capillary action; template

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1. INTRODUCTION

The field emission display(FED), as a flat CRT(cathode ray tube), is expected to create a high marketing demand in near future because of its prominent features such as wide view angle, low power consumption, short response time, high resolution, and a wide range of temperature capabilities [1]. However, the practical use of FED has been delayed because of technical difficulties related to the fabrication of metal emission electrode tips in array forms. Many of research teams in the world have concentrated their efforts to develop an effective emitter tip array with the variety of materials. Most efforts were focused on fabricating metal cathode tips on silicon substrate by adopting the procedure used in micro-chip fabrications [2–4]. Recently, a great deal of research work have been focused to the usage of conducting polymers, because of easiness and simplicity in the manufacturing procedure. A lot of work using conducting polymers as a cathode material have been reported; Musa *et al.* used poly(3-octylthiophene), Wang *et al.*, employed polyaniline, and Kim *et al.* utilized PEDOT [5–7].

In this study, a field emissive tip array was fabricated from a conductive polymer composite utilizing a new method called molded-by-capillary action method. This method allowed us a simple procedure of fabricating polymer tubules into a template by placing the template on to the spin coated polymer film. The micro tubule structures were then observed and analyzed by SEM (scanning electron microscope) and EDAX (energy-dispersive analysis of X-rays) step by step along the fabrication procedure. Finally, the result achieved was a measured field emission at the atmospheric condition of 10^{-6} Torr.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

All chemicals used in this work were of ACS grade. These chemicals were purchased from Sigma-Aldrich Korea Ltd. and used without further purification. The templates used directly for fabricating conducting polymer tubule array were track etched polycarbonate membranes holding pores of relatively constant diameter, e.g., Polycarbonate membrane filter holding 1.2 μm pores or 0.4 μm pores and both of them are 10 μm thick (Millipore Corp.). Transparent indium-tin oxide (ITO) glass electrode (Samsung Corning, Korea) was used as a supporting electrode after several cleaning steps. The polymer coating was done by employing a vacuum spin coater (Headway). Vacuum oven (VO-20X, Jeio Tech, Korea) was used for drying

purposes. All SEM and EDAX images were obtained by using JSM 6700 F (JEOL, Japan) and JSM 7000 F (JEOL, Japan), respectively. For FE measurements, an ammeter (KEITHLEY 2001) and a voltage source (FUG HCN 700–3500) were used.

2.2. Fabrication and Characterization of Conducting Polymer Emitters

An FE electrode was fabricated by conductive polymer complexes by using a simple molded-by-capillary action method. Through the procedure that appears in Figure 1, we prepared the ITO glass electrode onto which a polycarbonate membrane has to be cling. We first formulate a conducting adhesive glue from PEDOT/PSS [poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate)] and PVA [poly(vinyl alcohol)]. This glue was spin-coated onto an ITO glass then a piece of membrane template was carefully placed on top of it before the glue was dried out completely. While the membrane was putting on the glue, the basic tubule structure was formed by the capillary action into the template. This structure was completely dried out in vacuum oven for 24 hours. Methylene Chloride (MC) was used to remove the membrane to investigate the shape of tubule structure and measure field emission measurements. After removing the template, the polymer tubules were sputtered with Au/Pd on the polymer structure in 10^{-6} Torr or plated with Au by using chemical reduction method to enhance emission property [8–9]. Finally, the field emission current was measured using the field emission cell depicted in the same figure. A piece of stainless steel was used as an anode and kept 1000 μm or 700 μm away from the cathode by using glass spacers. This measurement was carried out in a vacuum chamber at 10^{-6} Torr.

3. RESULTS AND DISCUSSION

The use of molded-by-capillary action method leads us to formulate a conductive polymer adhesive first. When the polycarbonate membrane was sitting on the gluing polymer coating, the polymer got into the pores of the template by capillary action and formed tubule structures. In this procedure, the template has to be placed before the glue polymer hardened completely. When a 10 μm thick template possessing pores of diameters either 1.2 μm or 0.4 μm placed onto the damp glue polymer, it produced polymer tubule structure in Figure 2. As shown in (a) of the figure, the template of 1.2 μm pores produced well aligned independent tubule array on the substrate ITO and thickness of the tubule was estimated as $\sim$50 nm. Each tubule stands well by itself

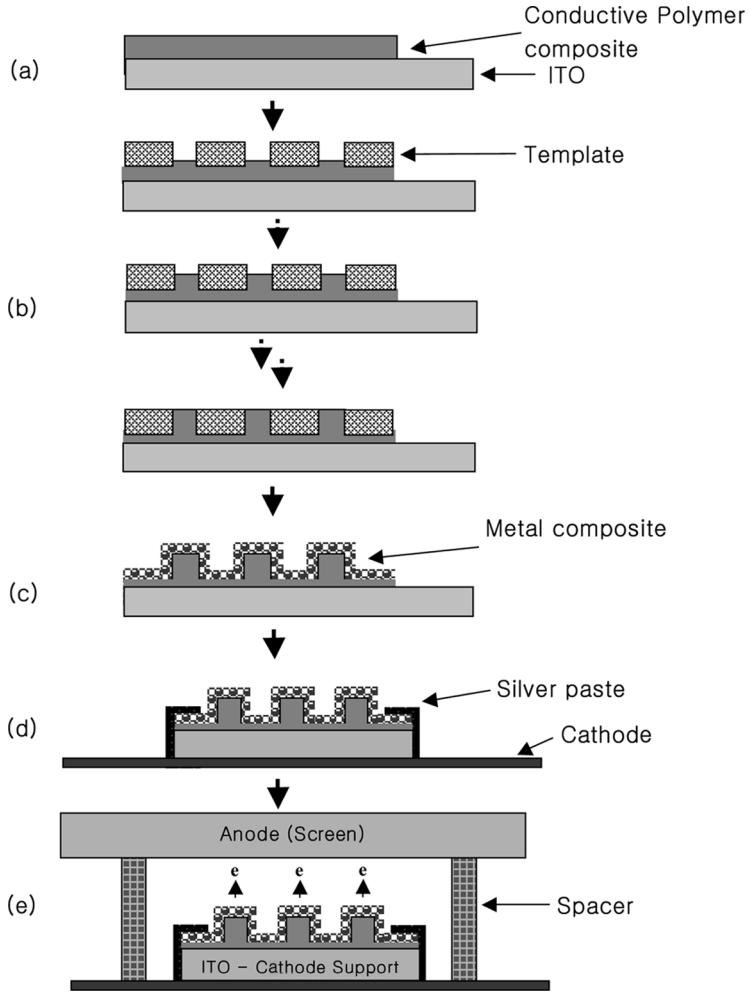
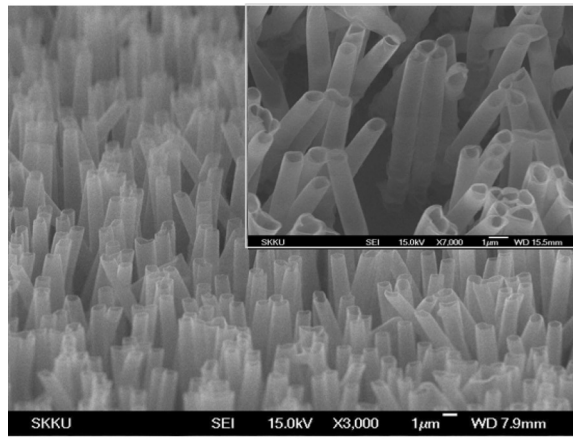
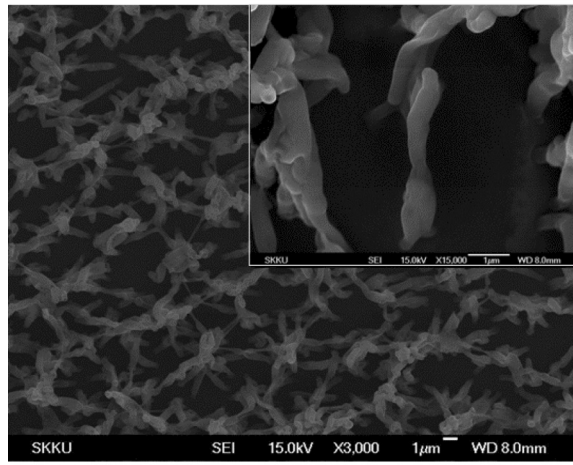


FIGURE 1 Schematic diagram of experimental procedures includes fabrication of micro tubule structures and emission measurement. (a) after casting polymer glue polymer on the supporting ITO electrode, (b) tubule formation by placing the PC membrane, (c) Au deposition after dissolving the template, (d) electrical connection to electrode, (e) total FE measuring set up.

with its thin thickness. Most of them have regular shapes in height and diameter because the template has such a regular shape. But the template of 0.4 μm pores provided tubules of smaller diameter and those tubules were cling together at the top as in (b) of the same figure. The latter structure was almost in shape of wire. At this



(a)



(b)

FIGURE 2 SEM images of conductive polymer electrodes: (a) 1.2 μm diameter membrane used (tube type), (b) 0.4 μm diameter membrane used (wire type).

moment, it needs to be empathized that the molded-by-capillary action method is a simple way to construct nano thick tubule or wire structures. Because, in this new method, there is no need to use either chemical or electrochemical polymerization procedure to fill the template pores [10–11]. Controlling the viscosity of glue solution and selecting template can produces fine structure of conducting polymer from nano wire to micro tubule shape. In this procedure, the glue

polymer was playing two important roles simultaneously; joining ITO substrate and template membrane, and forming the tubule itself.

Field emission current was measured from the tubule of 1.2 μm diameter on which Au was plated chemically. The plating method have been published elsewhere [12]. Emission current density acquired from the Au plated tubule is shown in Figure 3 as a function of applied field strength. The emission current starts to increase at *eletric field (E)*. 1.8 V/μm up to 21 μA/cm^2 at *eletric field (E)*. 2.5 V/μm. The plot shows small current peaks even below the 1.5 V/μm. This is not clearly understood right now. What we wonder is gold nano particles formed during the chemical plating procedure involved in theses emissions. Au nano particle of various sizes are observed in SEM image of the Au plated sample (not shown). Inset of the same figure shows that current vs. 1/V plot has a linear relationship and this emission follows the Fowler-Nordheim mechanism. The same tubular structures were sputtered with Au to enhance electrical conductivity. About 25 nm thick Au film was sputtered from Au/Pd target onto the

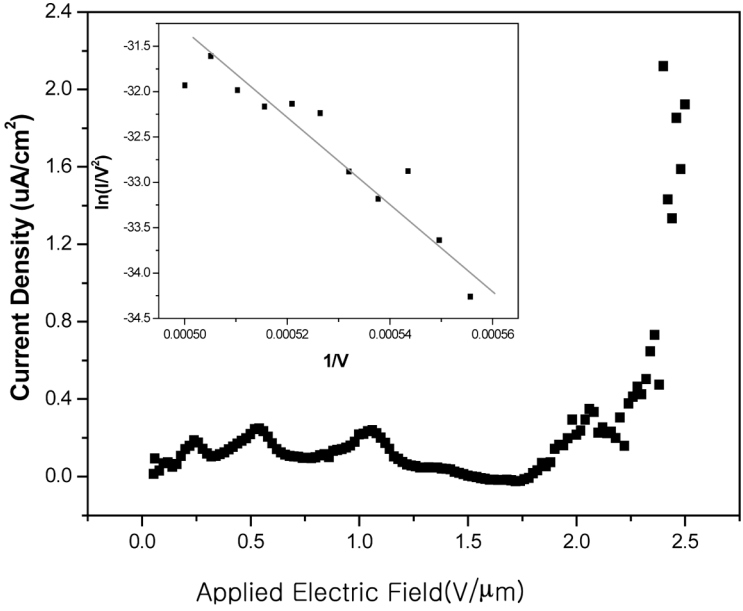
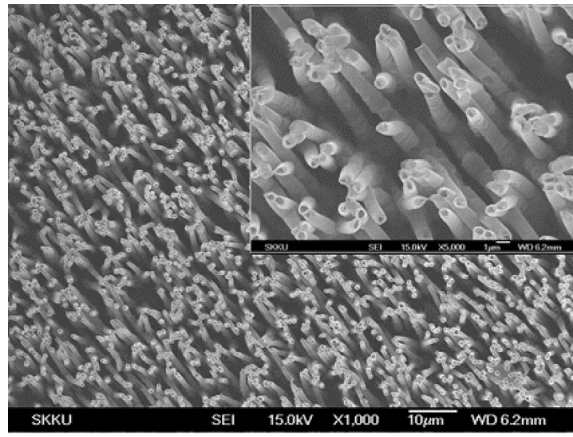
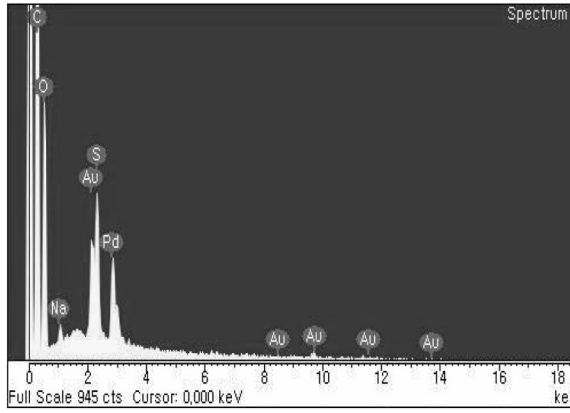


FIGURE 3 Emission current density is plotted as a function of applied electric field: using PEDOT/PSS/PVA composite emitter electrode was plated with Au chemically. The diameter of the tubules is 1.2 μm. The linear plot in inset implies the emission follows the F-N mechanism.

polymer tubule structure. The Au sputtered structure was observed by SAM and EDAX. Figure 4(a) shows the tubule structure keeping its regularity even after Au deposition. In this image, no Au particles are observed and looked quite similar to the one in the (a). This is quite different from the one Au plated chemically. The EDAX analysis taken from several places of the tubule structure confirms the existence of Au in Figure 4(b). Field emission properties of the tubule array were examined before and after the Au deposition. The results are in Figure 5. Before deposition of Au, the emission current was hardly



(a)



(b)

FIGURE 4 (a) SEM image of the Au sputtered micro tubule of 1.2 μm diameter, (b) EDAX data shows Au is covering the structure.

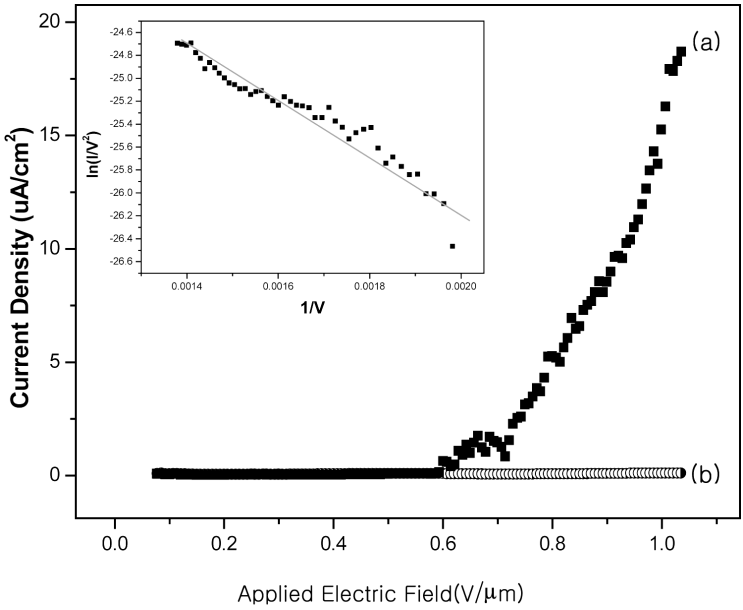


FIGURE 5 Current density is plotted against the applied electric field: (a) obtained from the electrode with Au sputtered, (b) no current density is observed from the electrode without Au sputtering. Both are of 1.2 μm diameter tubular structures.

measured as (a) of the figure. But Au treated cathode show nice increase in emission current. The increase in emission current starts at *elecric field (E)*. 0.58 V/μm which is the lowest value we ever measured and reached up to the current density of 18.7 $\mu A/cm^2$ at 1.2 V/μm as illustrated in (b) of the same figure. The inset also shows that this emission is giving a linear relation in F-N plot and follows the Fowler-Nordheim mechanism [13]. The only difference between plating and sputtering methods is the metal shape deposited on the polymer; chemical reduction of $AuCl_3$ produces $\sim 10^2$ nm range particles on the surface, but sputtering produces smoothly covered surface as shown in Figure 4(a). This coating may be reducing the resistance of the polymer structure and lowering the emission threshold.

The numbers in emission current density and turn-on voltage from our experimental results looks somewhat different compared to those from other reports of conducting polymer based emitters [14–16]. We presume that the main reasons for superior results are caused by the followings. First of all, compared to other doped with chemical film like as polypyrrole, polyaniline, metal such as gold used has a

relatively high conductivity that may decrease the turn-on voltage. Secondly commercial polycarbonate membrane has a relatively low pore density (usually $10^5 \sim 10^8$ pores/cm^2; $10^9 \sim 10^{11}$ pores/cm^2 for aluminum oxide membrane) that may increase the emission current density. The low pore density leads the standing tubules are able to be independent form one another. This regular space interval between tubules enhances the structural factor effect of the emitting electrodes [17]. As compared with the conventional methods, we believe, this molded-by-capillary action method is a better process for mass production.

CONCLUDING REMARKS

Molded-by-capillary action method, a simple way of fabricating polymer structure from nano wire to micro tubule, was introduced in this study. The emission property of the micro tubule electrode array was enhanced by metal deposition on the polymer structures. Au sputtering improves field emission effect by lowering the threshold voltage up to *eletric field (E)*. 0.58 V/μm while chemically plated one allowed only *electric field (E)*. 1.8 V/μm. Sputtered film of 25 nm Au on the polymer electrode contributes to the great enhancement in emission threshold because it lessens electrical resistance of the polymer electrodes. We could control the shape of emitters by varying membrane specification and viscosity of the molding materials. This Molded-by-capillary action method is found to be an ease way of fabrication of polymer micro structures. Au sputtering was efficient to produce emission property and superior compared to the others composite making method. The current density of field emission reached to 18.7 μA/cm^2 at 1.2 V/μm. This result shows the possibility of application of the cathode tip as an active emission electrode for a field emission display.

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