Semitransparent Cu electrode on a flexible substrate and its application in organic light emitting diodes

Myung-Gyu Kang and L. Jay Guo[a)]
Department of Electrical Engineering and Computer Science, The University of Michigan, 1301 Beal Ave., Ann Arbor, Michigan 48109

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A semitransparent nanomesh Cu electrode on a polyethylene terephthalate (PET) substrate using metal transfer from a polydimethylsiloxane (PDMS) stamp and nanoimprint lithography is reported. A nanoscale dense mesh pattern is replicated by using a high modulus PDMS stamp. It is found that a uniform pressure of 30 psi and a temperature of 100 °C are needed for the transfer of the Cu mesh structure from the PDMS stamp onto the PET substrate. A fabricated semitransparent Cu electrode exhibits high transmittance in the visible range and good electrical conductivity. The authors show that the transmittance is increased by reducing the linewidth of the mesh pattern and an average transmittance of 75% is achieved. An organic light emitting diode on a flexible substrate is fabricated to demonstrate the potential use of a semitransparent Cu electrode as a transparent conducting electrode. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2801873]

I. INTRODUCTION

Organic light emitting diodes[1–3] (OLEDs) are promising for flexible displays because they offer several advantages such as the ease of processing, low cost, light weight, bright self-emission, and wide viewing angle over liquid crystal displays (LCDs) which are built on a rigid and brittle substrate. For the realization of the flexible display using OLEDs, the transparent conducting electrode on a flexible substrate is required. Indium tin oxide (ITO) is the most extensively used material because it offers transparency in the visible range of the electromagnetic spectrum as well as electrical conductivity.[4–7] However, several aspects of ITO are far from optimal for high performance and low cost flexible OLEDs. Because of the limitation in the processing temperature of the flexible substrate, the deposited ITO film shows the electrical conductivity is insufficient for the high performance of the OLED,[4,8,9] which can cause a voltage drop along the addressing line, thus limiting the operation of a large area passive matrix OLED array.[10] It is also known that the migration of indium and oxygen from ITO into organic semiconductors during OLED operation causes device degradation.[11,12] The rough surface of the deposited ITO film and the work function of ITO, ~4.7 eV, limit the efficiency of the hole injection.[13] Moreover, the cost of ITO has risen drastically in recent years due to the limited supply of the indium element. Recently, we proposed using a nanoscale perforated metal mesh structure as a potential replacement for the ITO electrode.[14]

In this work, we report a semitransparent metal (Cu) electrode[14] on the polyethylene terephthalate (PET) substrate fabricated by transfer printing[15] of the nanoscale dense metal mesh which shows high transparency in the visible range, as well as good electrical conductivity, and evaluates its potential as an OLED anode. We also show that the transparency can be increased by reducing the linewidth of the metal mesh. The fabricated semitransparent Cu electrode has advantages over ITO such as no degradation by diffusion of indium and low cost. Moreover, the output efficiency of the OLED can be potentially enhanced by using metal with high work function[13] by preventing waveguiding loss in the ITO layer[16] and by forming a two-dimensional hole array with proper periodicity.[17,18] Metal transferring used in this work is also potentially suitable for the top emitting devices and tandem structure.

II. EXPERIMENT

A. Fabrication of the polydimethylsiloxane stamp and metal transfer

Figure 1 shows the schematic diagram of the fabrication procedure of the polydimethylsiloxane (PDMS) stamp and metal transfer printing. The conventional nanoimprint lithography (NIL) requires high pressure and high temperature when imprinting thermoplastic material, which can cause deformation of the flexible substrate. However, metal transfer from a flexible PDMS stamp does not require such a high pressure and temperature. It is an additive technique that produces metal patterns directly on a plastic substrate, which eliminates the additional processes such as oxygen reactive ion etching for residual layer etching and the lift-off process used in the conventional NIL process as described in our previous work.[14] For metal transfer printing, a resist template with a nanoscale mesh pattern is first fabricated by conventional NIL.[19] The fabrication of the mold with a mesh pattern for NIL can be found in Ref. 14. The mold for NIL consists of two sets of a grating structure which are orthogonally positioned. One has a period of 700 nm, which defines the main part of the semitransparent Cu electrode. The other has a period of 10 μm, which is used to ensure the electrical connectivity of the 700 nm period grating lines. A Nanonex NX 2000 nanoimprinter (Princeton, NJ) was used for the

a)Electronic mail: guo@eecs.umich.edu

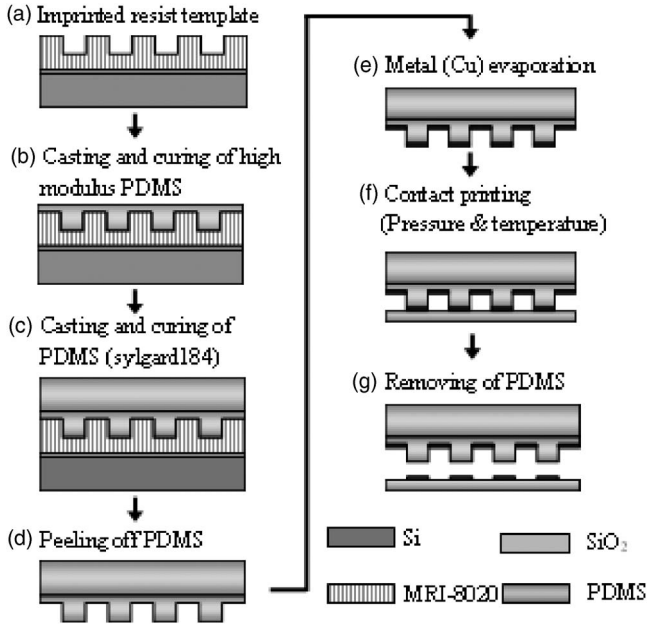

FIG. 1. Schematic diagram of the fabrication procedure of the PDMS stamp and metal transfer printing.

NIL process. NIL is done on MRI-8020 resist (Microresist Technology GmbH) spin coated onto a SiO_2 substrate at a pressure of 600 psi and a temperature of 180 °C for 5 min. After the sample has been cooled and demolded, PDMS is drop casted on the nanoimprinted resist template. For easy generation of the nanoscale mesh pattern, recently developed high modulus PDMS (Ref. 20) was first drop casted and cured at 70 °C for 10 min which gives a 100 μm thick PDMS on the resist. Commercially available PDMS, sylgard 184, is then drop casted and cured at 70 °C for 2 h to support the thin high modulus PDMS for better durability. For this work, two types of PDMS stamps were prepared. One has the mesh pattern with a linewidth of 200 nm and the other with a linewidth of 120 nm. A 40 nm thick Cu and a 3 nm thick Ti are then deposited sequentially on the PDMS stamp by electron-beam evaporation at a rate of 2 Å/s. After a brief O_2 plasma treatment on the PDMS surface on which Cu and Ti were deposited, a Cu layer coated on the PDMS stamp is transferred to the PET substrate as shown in Fig. 1. The O_2 plasma treatment oxidizes the whole Ti layer on Cu which makes adhesion between the metal and PET substrate stronger resulting in a higher fabrication yield. To form intimate contact between the metal layer on the protruded regions of the PDMS stamp and PET substrate, a uniform pressure of 30 psi and temperature of 100 °C for 3 min were applied using a nanoimprinter, NX 2000. It was found that 30 psi was the most effective pressure for the metal transfer. A pressure lower than 30 psi generates a mesh pattern with nonuniformity and a pressure higher than 30 psi causes the metal layer in the recessed region of the PDMS stamp to also transfer to PET because of the shallow depth of the PDMS stamp, 200 nm. The difference in adhesion strength between PDMS/Cu and Cu/PET interfaces determines the success of the metal transfer. Since the PDMS has a low surface energy, the adhesion of Cu to it is poor. The elevated temperature (100 °C) will increase the adhesion ability of the PET substrate by forming a sticky surface. It is also known that heating can reduce the surface energy of the PDMS stamp[15] which was possibly increased by the surface modification of the PDMS during the electron-beam evaporation of the Cu film.[21] Since the metal transfer relies on the intimate contact between the PDMS stamp and PET substrate, the surface roughness of the PET substrate is an important parameter. The initial PET substrate has a rms roughness of about 6 nm with a peak to peak value of 20 nm. The rough surface creates several defects causing a disconnection of the metal mesh pattern, which could limit the proper OLED operation. The surface roughness was significantly reduced by annealing at a temperature lower than the glass transition temperature (Tg) of the PET. A rms roughness of 0.8 nm with a peak to peak value of 2 nm was achieved by annealing PET at 70 °C for 30 min.

B. Fabrication of the OLED using a semitransparent Cu electrode as the anode

The OLED device consists of a semitransparent Cu mesh electrode as the anode, poly(styrenesulfonate)-doped poly(3,4-etylenedioxythiophene) (PEDOT) as the hole transport layer, poly(2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene) as the emissive layer, and LiF/Al as the cathode. Device fabrication details are similar to that in Ref. 14. The only difference was that the PEDOT layer was baked at 60 °C for 4 h in nitrogen purged oven instead of 120 °C because PET has a low Tg, 79 °C.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the perspective view of the fabricated PDMS stamp with a linewidth of 200 and 120 nm, respectively. Figures 2(c) and 2(d) show the top view of the corresponding semitransparent Cu electrode with a linewidth of 200 and 120 nm on the PET substrate. As shown, the dense metal mesh pattern was fabricated. Optical transparency and electrical conductivity are the two most important factors for the transparent electrode. These factors can be quantified experimentally by measuring the transmittance and the sheet resistance, respectively. The parameters for tuning transmittance and sheet resistance in the semitransparent metal structure are the mesh linewidth, the metal thickness, and the periodicity of the grating lines.[14] Here we show that the transmittance can be increased by transferring the metal mesh structure with a reduced linewidth. Figures 3(a) and 3(b) show that the optical transmittance results and photograph of the semitransparent Cu electrode on PET in bent condition, showing the flexibility of the electrode coated substrate. The measured optical transmittance was referenced to the PET substrate. As shown in Fig. 3, the semitransparent Cu electrodes are highly transparent in the visible range. The average transmittances are 61% and 75% for the Cu electrode with a linewidth of 200 and 120 nm, respectively. The results confirm that the transmittance was increased much by decreasing the linewidth of the mesh structure. The associ-

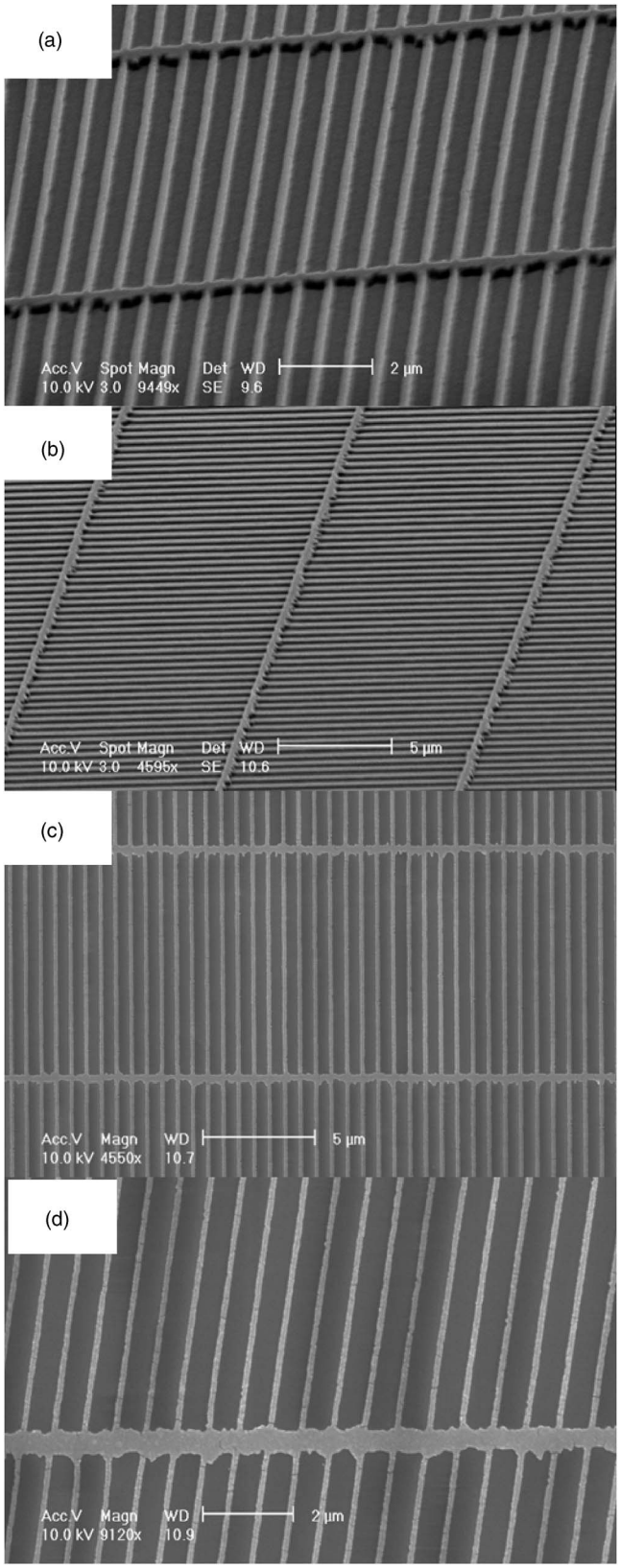

FIG. 2. Perspective view of the fabricated PDMS stamp with a linewidth of (a) 200 and (b) 120 nm and the top view of corresponding semitransparent Cu electrode with a linewidth of (c) 200 and (d) 120 nm on the PET substrate.

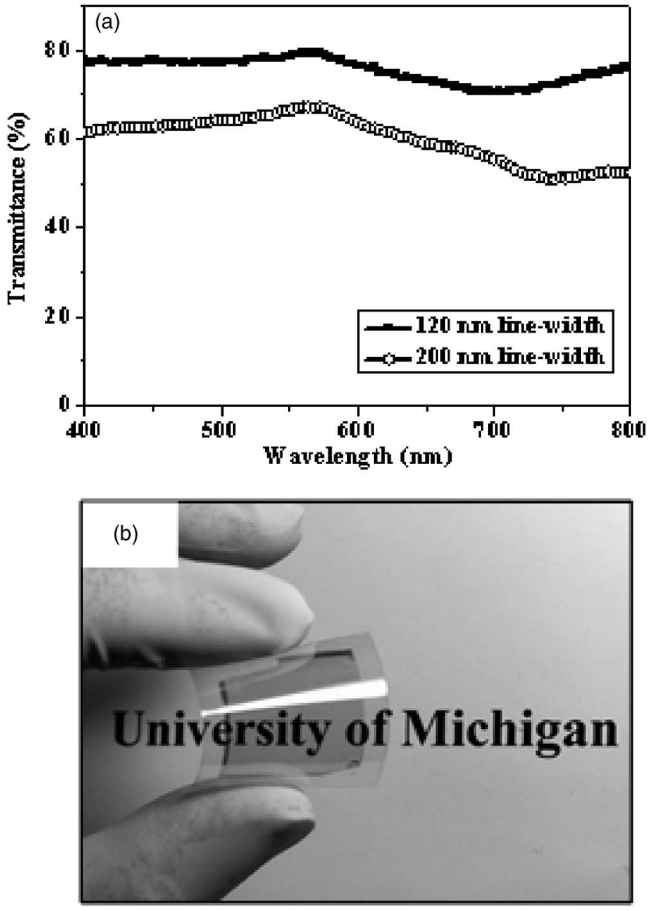

FIG. 3. (a) Optical transmittance and (b) photograph of the semitransparent Cu electrode on PET.

ated sheet resistance is 10 and 14.8 $\Omega/\square$ for a linewidth of 200 and 120 nm, respectively. The increased sheet resistance by reducing the linewidth can be compensated by transferring a thicker metal. For the transparent metal electrode, the linewidth should be narrower for high transmittance which means that the portion of light through the narrow metal line is small. Therefore, there is a small dependence of transmittance on the metal thickness. A simulation on the transmittance versus the metal thickness for a Cu grating with a linewidth of 120 nm shows that the average transmittances in the visible range are 82.4%, 80.4%, 79.4%, 78.7%, and 78.1% for a 20, 40, 60, 80, and 100 nm thick transparent Cu electrode, respectively. For Cu thicker than 40 nm, the average transmittance did not change much because the thick metal can block the light. Therefore, it is expected that increasing the thickness by a factor of 5 can decrease the sheet resistance by the same order but the transmittance by only a slight decrease. It should be noted that the wavelength dependency of the transmittance of the semitransparent Cu electrode on the PET substrate is different from that on the glass substrate.[14] The dip in the transmittance in the case of the PET substrate was redshifted compared with that of the glass substrate but the overall trend of the transmittance is similar. A 2 nm thick Ti layer was used as the adhesion layer for the glass substrate. On the other hand, a 3 nm thick Ti

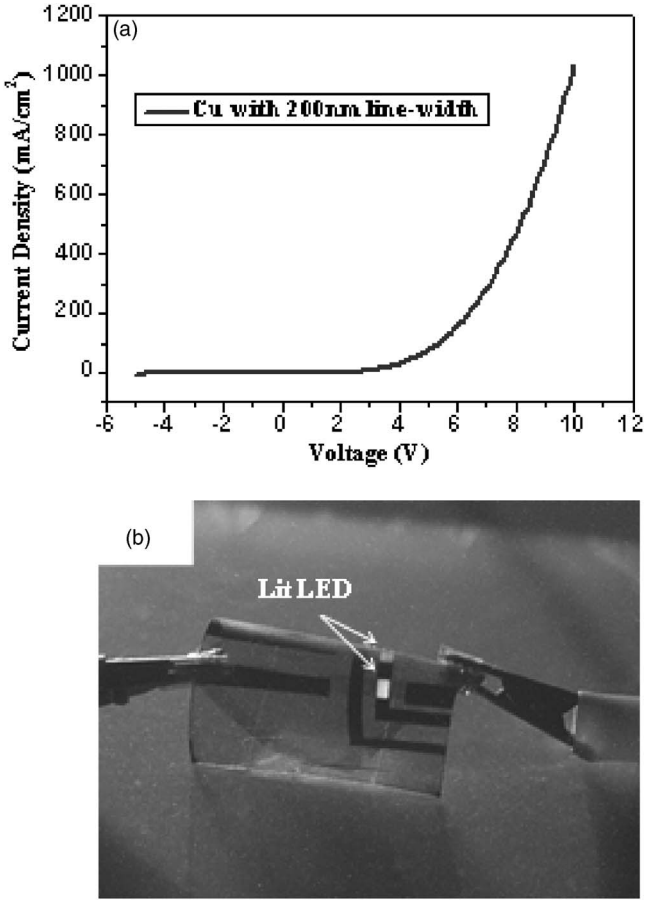

FIG. 4. (a) Current density vs voltage and (b) photograph showing light emission of an OLED made with semitransparent Cu as the transparent anode.

layer was used between the Cu layer and the PET substrate. The wavelength dependence of transmittance is correlated with the plasmon absorption band in the metal which is known to be very sensitive to the refractive index change of the adjacent material. From this result, it could be expected that the transmittance dip can be intentionally changed by adjusting the Ti layer thickness for higher transmittance at the desired wavelength region. Moreover, it would be possible to make the transmittance in the visible range flatter by tuning the refractive index of the adjacent material.

To demonstrate the potential use of a semitransparent Cu electrode as a transparent conducting electrode for optoelectronic devices, a flexible OLED was fabricated using such an electrode as the anode. Cu is well suited for practical flexible display for which light weight and low cost fabrication are essential because it has a similar work function to ITO (~4.7 eV) and is one of the cheapest metals. A semitransparent Cu electrode with a thickness of 40 nm and a linewidth of 200 nm was chosen as the anode in the OLED. Figure 4 shows the current density versus voltage and the photograph showing the light emission of the OLED made with a semitransparent Cu electrode as a transparent anode in bent condition. The junction exhibits good rectifying characteristics. The electrical characteristics of the OLED made with the semitransparent Cu electrode are similar to those in the literature[22] with same organic material and ITO electrode. The turn on voltage is around 5 V and devices have a similar current density at a given bias after the devices are turned on. The quantitative comparison with the device made with the ITO electrode will be reported in the future. Upon optimization, such a semitransparent metal electrode could be used to replace the ITO anode and with an enhanced flexibility on the plastic substrate.[23,24]

IV. CONCLUSION

In this study, a semitransparent Cu electrode on the PET substrate by nanoscale metal transfer printing was demonstrated. The nanoscale dense metal mesh pattern was replicated by using a high modulus PDMS stamp. For the faithful transfer of the metal mesh, it was found that a uniform pressure of 30 psi and an elevated temperature of 100 °C were needed. The fabricated semitransparent Cu electrode showed high transmittance in the visible range and good electrical conductivity. The transparency of such an electrode structure can be increased without sacrificing the overall conductivity by using a narrower and thicker metal film. This characteristic is another advantage over an ITO electrode, in which the sheet resistance has to be compromised to achieve high transmittance. As an application, a flexible OLED was fabricated using a semitransparent Cu electrode as the anode to replace the conventional ITO electrode. The device showed good rectifying characteristic and bright emission upon biasing. Our results indicate that the semitransparent Cu electrode is an attractive and potentially practical solution for low cost flexible display and organic optoelectronic devices such as OLEDs, organic solar cells, photodetector, etc., which require a transparent conducting electrode. The technique presented here could be developed further as a roll-to-roll printing process for high throughput fabrication of metallic nanostructures.

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