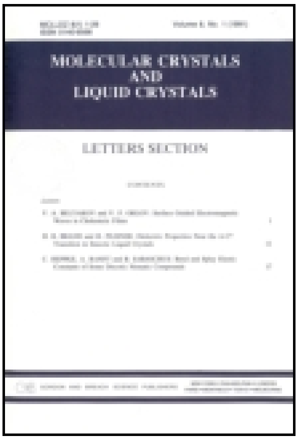

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Fabrication and Properties of Flexible OLEDs on Polyimide-Graphene Composite Film Substrate

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In this work a clear polyimide (PI) film was synthesized by using selected monomers containing multiple CF_3 groups. The polyimide-graphene composite films were made by film coating of mixture of polyamic acid (precursor of polyimide) solution with reduced grapheme oxide. The flexible OLEDs were fabricated by using the polyimide-graphene composite films on which the ITO/Ag/ITO thin films were deposited by roll-to-roll sputter instead of usual ITO-glass and the properties of flexible OLEDs were examined from the viewpoint of flexible substrates.

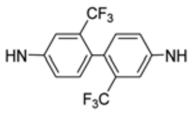
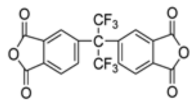
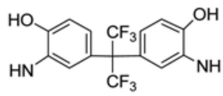
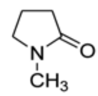
Keywords Graphene; ITO/Ag/ITO; multilayer transparent anode; OLED; polyimide composite film

Introduction

Flexible OLEDs have been studied actively for their potential application to both large size OLED display and decorative lighting [1–3]. The efficiency and life time of flexible OLED are still major problem to overcome compared to the OLED devices based on glass substrate [4]. In this study we made flexible OLEDs based on polyimide-graphene composite film (PGCF) which had high transmittance to visible light, excellent thermal and mechanical property comparable to the rigid glass substrate which could withstand the roll-to-roll sputtering of ITO/Ag/ITO transparent anode and subsequent photolithographic processes. It was also noted that the PGCF flexible substrate could be used directly to fabricate flexible OLEDs without laminating to the glass carrier substrate normally used in the OLED process.

*Address correspondence to L. S. Park, Department of Polymer Science, Kyungpook National University of Daegu, 80 Daehak-ro, Buk-gu, Daegu 702-701, Korea. Tel.: +82-53-950-5627; Fax: +82-53-950-7864. E-mail: lspark@knu.ac.kr

Table 1. Chemical structure of monomers used to synthesize clear poly(amic acid)s

Dianhydride	Diamines	Solvent
 **6FDA** 4,4'-(hexafluoro isopropylidene) diphthalicanhydride	 **TFDB** 2,2'-bis(trifluoromethyl)benzidine  **AH6FP** 2,2-bis(3-amino-4hydroxyphenyl) hexafluoropropane	 **NMP** N-methyl Pyrrolidone

Experimental Details

Preparation of Polyimide-Graphene Composite Films

The monomers used in the synthesis of poly (amic acid) are shown in Table 1 and the synthetic scheme is shown in Fig. 1. The procedure was as following. First aromatic diamines, TFDB 0.54 g (0.85 mmol) and AH6FP 0.11 g (0.15 mmol), were added in the 100 ml three necked flask with 4.34 ml of NMP solvent followed by dropwise addition of aromatic dianhydride 6FDA dissolved in 4.34 ml NMP solvent in the ice bath. The reaction mixture was stirred in the ice bath for 2 hr and then for 2 hr at 35 °C to give poly (amic acid) solution with 15 wt% solid. Second the reduced graphene oxide (rGO) powder was

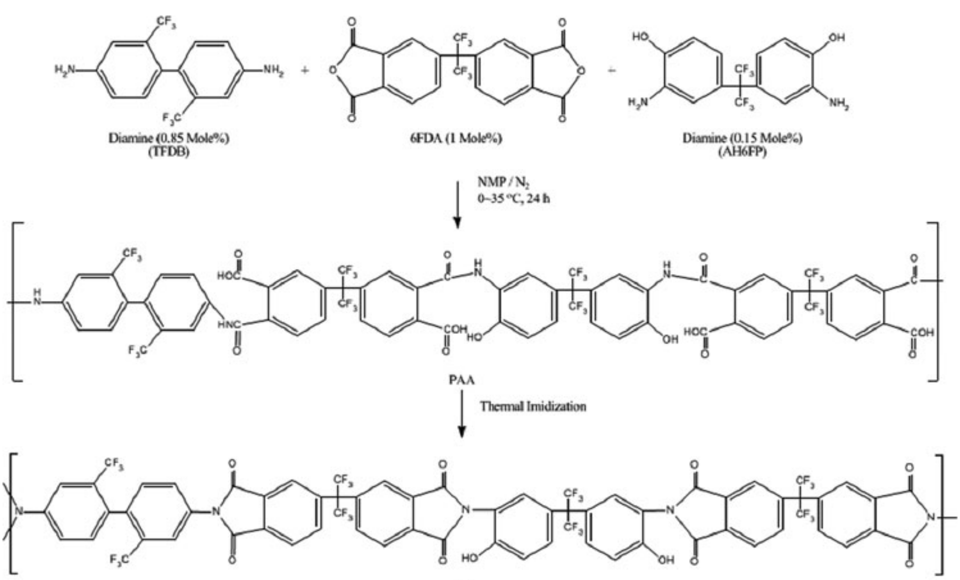


Figure 1. Synthetic scheme of polyimide films by imidization of poly (amic acid) precursor.

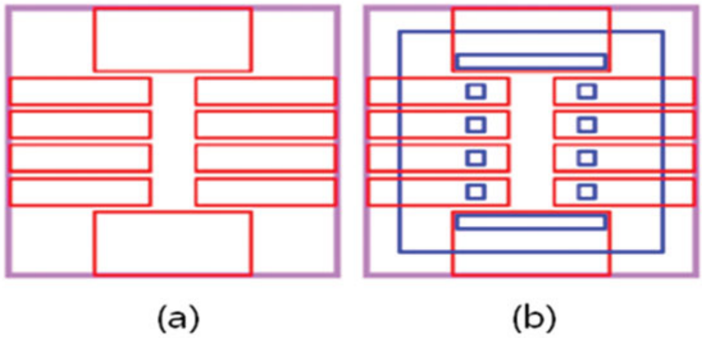


Figure 2. The structure of 8 pixel flexible OLED substrate; (a) after patterning of ITO/Ag/ITO anode layer, (b) after patterning of insulator layer.

mixed with NMP solvent and subjected to sonification for 1hr at room temperature. The poly (amic acid) and rGO in NMP solutions were mixed together and then sonification applied for 1hr. The mixture solution was coated on the glass substrate and then heated to 100 °C to remove solvent followed by heating to 250 °C at rate of 3 °C/min and further heating for 1hr at 250 °C to give PGCF film [5]. The PGCF film was then peeled off the glass substrate by immersing in the hot water bath followed by washing and drying.

ITO/Ag/ITO Thin Film Deposition by Roll-to-Roll Sputter

ITO/Ag/ITO multilayer thin films were deposited on the PGCF films by the sequential RF sputtering (ITO layer) and DC sputtering (Ag layer) utilizing roll-to-roll sputtering system at room temperature [6]. Table 2 lists the detailed deposition conditions for ITO/Ag/ITO

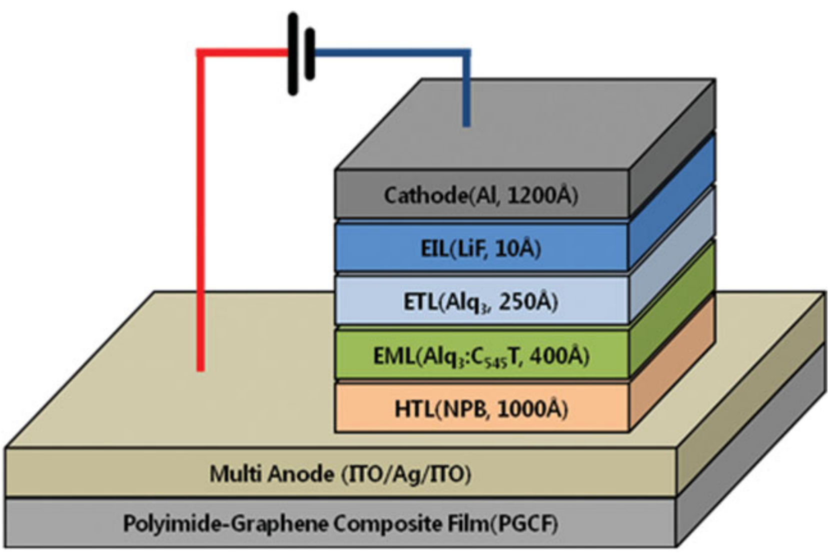


Figure 3. Structure of flexible OLED based on polyimide-graphene composite film.

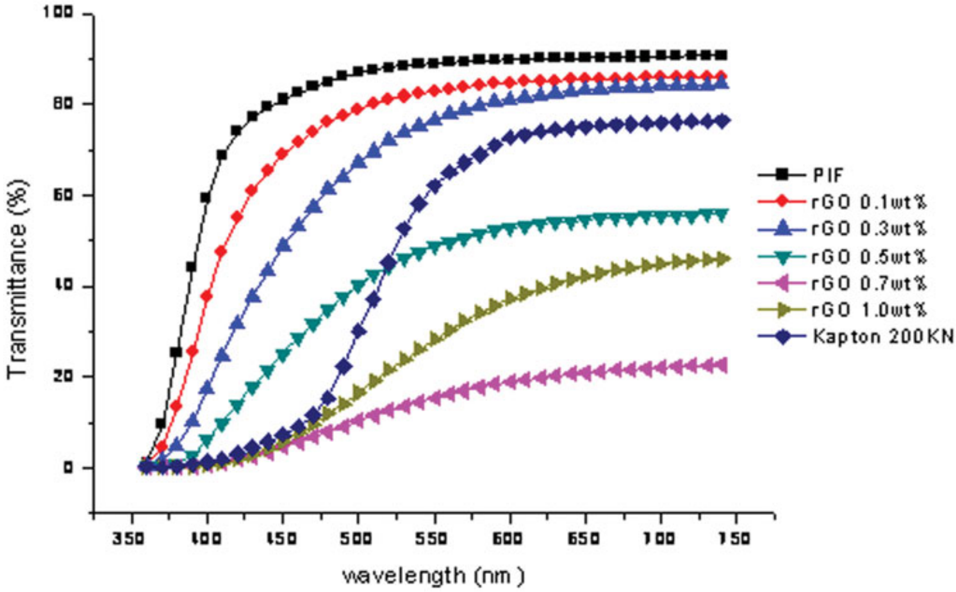


Figure 4. Optical properties of PGCF films.

multilayers on PGCF films. First a bottom ITO layer was deposited to 50 nm thickness with an ITO target containing 5 wt% SnO2. Silver (Ag) thin interlayer was deposited on top of the bottom ITO layer to variable thickness in the range of 15 ∼ 20 nm by using metallic Ag (99.999% purity) target in order to optimize both the sheet resistance and transmittance to visible light of the ITO/Ag/ITO multilayer anode on PGCF film. Subsequently the top

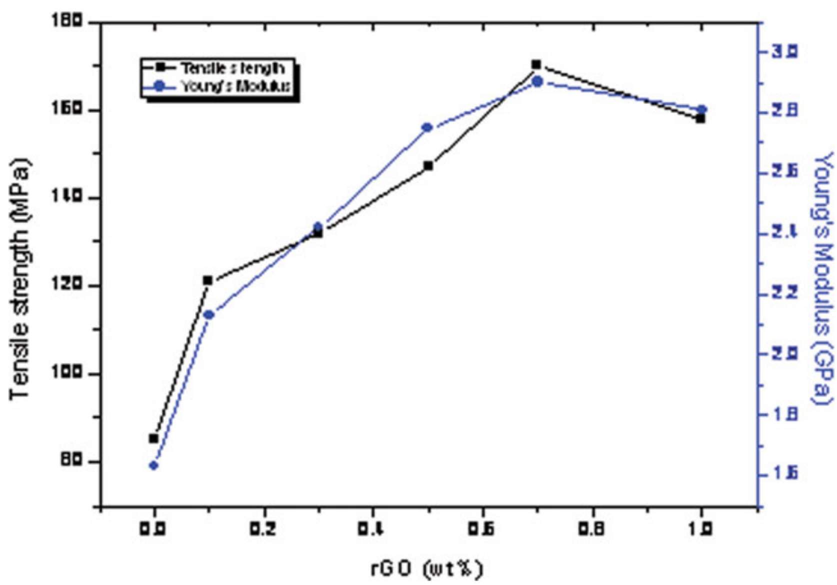


Figure 5. Mechanical properties of PGCF films.

Table 2. Deposition conditions for ITO/Ag/ITO multilayers by roll-to-roll sputtering process

Condition	ITO	Ag	ITO
Power (W)	RF 1400	DC 240	RF 1400
Flow gas rate (sccm)	Ar 30	Ar 20	Ar 30
Base pressure (torr)	1.0×10^{-5}	1.0×10^{-5}	1.0×10^{-5}
Working pressure (torr)	5.0×10^{-3}	3.0×10^{-3}	5.0×10^{-3}

ITO layer was deposited on top of the Ag/ITO layer to 50 nm thickness under the same deposition conditions used for the bottom ITO layer.

Fabrication of Flexible OLEDs and Measurement

For the patterning of ITO/Ag/ITO multilayer anode on PGCF substrates the photolithographic processes have to be modified from the usual ITO glass or ITO film used in the OLED device fabrication. First positive-PR (DS-i1000, Dongjin Chemical Co.) was spin coated stepwise under the condition of 200 rpm (10 sec), 1800 rpm (20 sec) and 2000 rpm (20 sec) followed by soft bake at 90 °C for 3 min. The positive-PR thin film was subjected to UV exposure (MDA-12000, Midas System) at 6 mW/cm2 for 15sec followed by developing in TMAH 2.38 wt% solution (80 sec), D.I. water washing and hard bake at 100 °C for 5 min. The ITO/Ag/ITO multilayer anode was then etched by dipping in an etchant solution (DA-300, Dongjin Chemical Co.) for 10min followed by deionized water washing. After etching of ITO/Ag/ITO anode the remaining positive PR was stripped in an aqueous

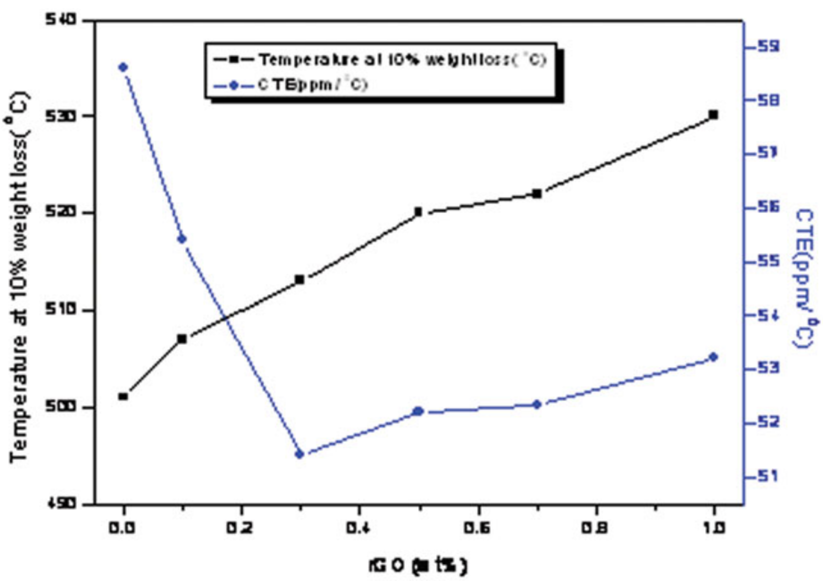


Figure 6. Thermal properties of PGCF films.

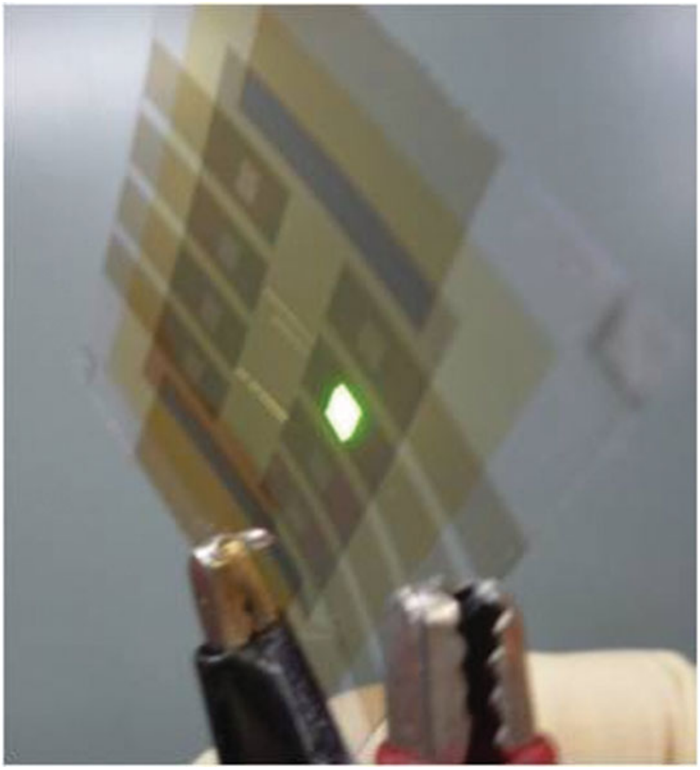


Figure 7. Flexible OLED fabricated on the PGCF film substrate.

alkaline solution (Remover PG, Microchem Co.) by dipping for 5 min followed by D.I. water washing.

After patterning of ITO/Ag/ITO anode the insulator layer was patterned by photolithographic process. Here we used the positive PR (DS-i1000, Dongjin Chemical Co.) used in the ITO/Ag/ITO anode pattering process instead of the normally used polyimide photoresist due to the higher process temperature of the latter photoresist. The back plane of flexible OLED substrate after ITO/Ag/ITO multilayer anode etching and insulator patterning are shown in Figs. 2(a) and (b), respectively.

The fabrication of the flexible OLEDs on the flexible PGCF film after patterning of ITO/Ag/ITO multilayer anode and insulator layer was carried out with the Sunic EL Plus 200, a cluster type OLED panel fabrication system. The flexible OLED on PGCF flexible substrate had configuration of HTL (NPB, 600 Å)/EML (Alq3:NPB, 400 Å)/ETL (ETA, 150 Å)/EIL (LiF, 5 Å)/Cathode (Al, 1200 Å) as shown in Fig. 3.

Results and Discussion

Physical Properties of PGCF Films

As shown Fig. 4 the optical property of the polyimide-graphene composite film (PGCF) was not as good as that of polyimide film without graphene filler (PIF). However, PGCF film with 0.1 wt% of rGO filler exhibited comparable optical property to that of PIF neat film.

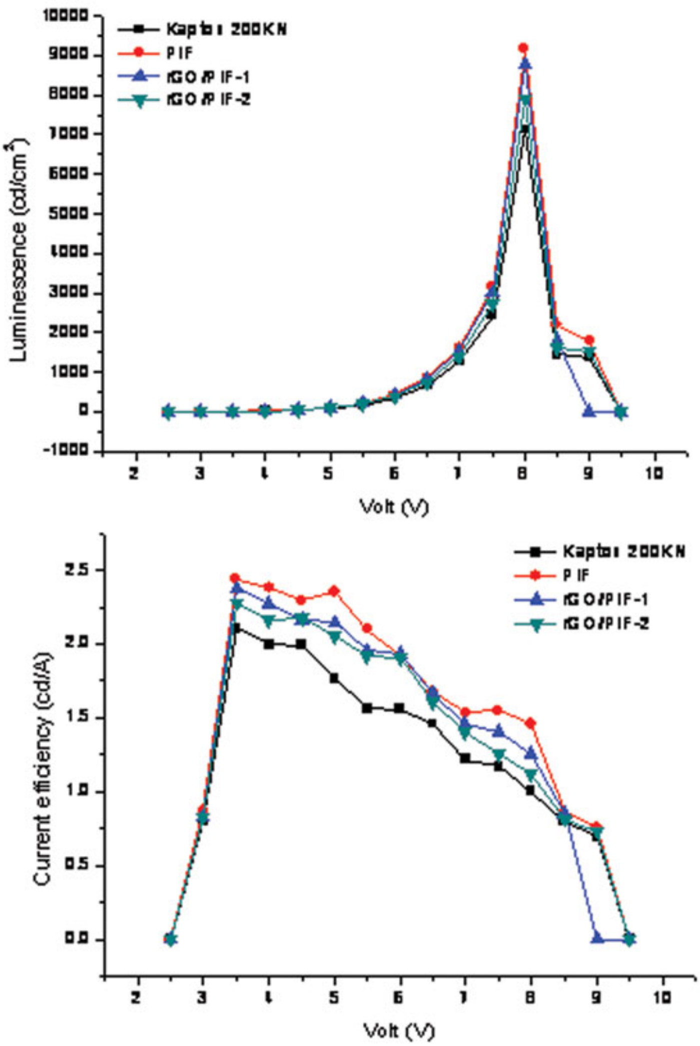


Figure 8. The luminance-voltage (up) and current efficiency-voltage (down) profiles of flexible OLEDs.

The mechanical properties such as tensile strength and Young's modulus of the polyimide-graphene composite films are shown in Fig. 5. As shown in Fig. 5 both the tensile strength and Young's modulus of PGCF films increased almost 200% upto graphene concentration of 0.7 wt%. However the mechanical property was deteriorated at 1.0 wt% of rGO in the PGCF film presumably due to the aggregation of rGO particles in the composite film acting as the crack starting points in the mechanical test.

The thermal properties of the PGCF films are shown in Fig. 6. The composite films with rGO filler exhibited higher temperature at 10% weight loss as measured by TGA and lower coefficient of thermal expansion (CTE) measured by TMA compared to the neat polyimide film (PIF). The CTE value decreased from 58.6 ppm/ °C (PIF neat film) to 51.5 ppm/ °C at 0.3 wt% of rGO filler and then slowly increased when the rGO filler was increased to 1.0wt%. The decrease of the CTE value of PGCF film is a desirable property from the viewpoint of TFT array process in the flexible OLEDs.

Performance of Flexible OLEDs based on Polyimide-Graphene Composite Film

The photograph of the flexible OLED fabricated on the PGCF film substrate is shown in Fig. 7.

The luminance-voltage and current efficiency-voltage profiles of the flexible OLEDs fabricated on the PGCF composite films are shown in Fig. 8 (up) and (down), respectively.

The performance of the flexible OLED based on 0.1wt% rGO composite film exhibited comparable performance to the one based on neat PIF film. However the long time stability and endurance of flexible OLEDs based on PGCF film should be better than the one based on neat PIF film, considering the improved thermal and mechanical properties as shown in Figs. 5 and 6.

Conclusions

The mechanical properties of the GPI films increased up to 0.7 wt% of graphene as reinforcing filler. The performance of the f-OLED especially the one based on PI-rGO-1 substrate exhibited better performance than the one based on commercial polyimide film.

Acknowledgments

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