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L. S. Hung, L. R. Zheng, and M. G. Mason

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Anode modification in organic light-emitting diodes by low-frequency plasma polymerization of CHF_3

L. S. Hung,^{a)} L. R. Zheng,^{b)} and M. G. Mason

Electronic Imaging Products, Eastman Kodak Company, Rochester, New York 14650-2110

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Plasma polymerization of CHF_3 at low frequencies was utilized for anode modification in organic light-emitting diodes. The polymerized fluorocarbon films have a high ionization potential and a relatively low resistivity. The devices with a polymer-coated anode of indium–tin–oxide exhibited enhanced hole injection and superior operational stability. © 2001 American Institute of Physics. [DOI: 10.1063/1.1331639]

In organic light-emitting diodes (OLEDs), anodes are commonly formed of a conductive and transparent oxide. Indium–tin–oxide (ITO) has been widely used as the anode because of its transparency, good conductivity, and high work function. However, a device formed on a bare ITO surface usually shows insufficient hole injection and poor operational stability. The mitigation of these problems has involved interposing an intermediate layer between the ITO and an organic medium and exposing the ITO to a glow discharge in an oxygen ambient.^{1–4} Yang *et al.* reported a polymer light-emitting diode with improved charge carrier injection by using a polyaniline layer between the ITO and an active luminescent layer,¹ whereas it is incompatible to the fabrication of OLEDs because of the process complexity and the nature of spinning coating. VanSlyke *et al.* demonstrated a highly stable organic device formed by using a copper phthalocyanine (CuPc) layer between the ITO anode and a hole transport layer of α -naphthylphenylbiphenyl (NPB) diamine.² The insertion of a CuPc layer generally results in a substantial increase in drive voltage because of a hole injection barrier present at the CuPc–NPB interface. Mason *et al.* and Wu *et al.* disclosed that the ITO contact to the NPB layer could be significantly improved via oxygen plasma or prolonged UV ozone treatments.^{3,4} However, the improvement of operational stability by oxygen plasma is not sufficient, and the effectiveness of the treatment is strongly dependent on processing conditions. In this letter we utilized plasma polymerization at low frequencies to deposit a fluorocarbon thin film on ITO with excellent conformability and sufficient durability. The resulting devices exhibited enhanced-hole injection and superior operational stability.

ITO-coated glass was used as the substrate, and tris-(8-hydroxyquinoline) aluminum (Alq) and NPB were used as the electron transport layer and the hole transport layer, respectively. After a routine cleaning procedure,² the ITO surface was coated with a polymerized fluorocarbon film with a thickness ranging from 0 to 12 nm. A multilayer structure of NPB/Alq/MgAg was deposited on the substrate by resistive

heating with a thickness of 60, 75, and 200 nm for NPB, Alq, and MgAg, respectively. Two control devices were also prepared for comparison, in which one device was formed on a CuPc-coated ITO anode and the other on an O_2 plasma-treated ITO anode without any buffer layer. The fabrication of OLEDs was completed with encapsulation in a dry argon box.

Polymerization was carried out in a parallel plate reactor with CHF_3 using a low-frequency power generator. The reactor was cleaned with oxygen plasma prior to polymerization. An ITO-glass substrate was loaded on the grounded electrode, precleaned by oxygen plasma, and then coated with a polymer film through a shadow mask. Deposition rates were measured on a piece of conductive Si using an ellipsometer. The rate was found to be strongly dependant on the substrate potential in plasma, and could vary from 1 nm/s with the Si on the grounded electrode to 0.25 nm/s with the Si on a piece of glass. The rate 0.25 nm/s was then used to estimate the thickness of the polymerized films grown on ITO glass in all experiments.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface composition of the polymerized films. The atomic ratio of fluorine to carbon was approximately 3:2, and oxygen was the only impurity detected in the film with a concentration of less than 1 at. %. The presence of oxygen was attributed to the reaction of long-lived radicals on the surface of the film with atmospheric oxygen when the film was removed from the reaction chamber. The $\text{C } 1s$ spectra in Fig. 1 were deconvoluted into four peaks, assigned in order of decreasing binding energy to CF_2 , CF_3 , CF , and CF_n .⁵ The relative concentrations of the four fluorocarbon species were found to be in the range of 23–29%.

Ultraviolet photoelectron spectroscopy (UPS) was employed to measure the ionization potential of the films, and a large value of about 9.5 eV was determined. This value has considerable uncertainty because there is no well-defined peak in the UPS valence band spectrum. The intensity slowly decays with decreasing binding energy making it impossible to get an accurate determination of the valence band maximum.

Some properties of the films generated in the low-frequency plasma system were found to be quite similar to the films prepared by rf plasma polymerization reported in the literature.⁶ For instance, the films were highly transparent

^{a)}Also at: Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong; electronic mail: aplshung@city.edu.hk

^{b)}Also at: COSDAF and Dept. of Physics and Material Science, City University of Hong Kong, Hong Kong.

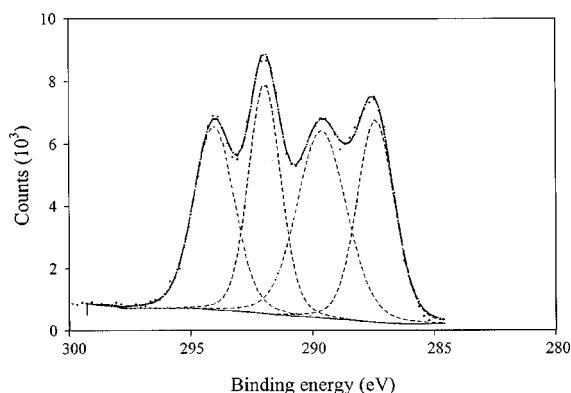


FIG. 1. XPS measurements on a fluorocarbon film grown by plasma polymerization of CHF_3 .

with a refractive index of 1.35–1.39, and exhibited good chemical stability and hydrophobicity.

Rutherford backscattering spectrometry (RBS) was utilized to investigate whether any metallic impurities were present in the films. A polymerized fluorocarbon film was grown on an ultrapure carbon substrate and then analyzed with 2 MeV He^+ ions. In the RBS spectrum of Fig. 2, a fluorine peak is well separated from the substrate, and some counts extend to energies above the front edge of the fluorine signal. The signals at energies greater than 0.93 MeV were blown up by a factor of 20 for clarity. The height ratio of the background to the fluorine peak is less than 1/300, and the background signal is apparently caused by pulse pile up. No counts other than noise signals are observed in the energy range from 1.2 to 2.0 MeV. The results clearly indicate that the concentration of impurities in the film, if any, is below the sensitivity of RBS analysis, that varies from 2×10^{19} atoms/cm² for Al to 8×10^{17} atoms/cm² for Au.⁷

Electrical and optical characterization were carried out on three devices formed on a polymer-coated ITO anode with the overcoating thickness ranging from 2.5 to 10 nm. Current–voltage (I – V) characteristics of the test devices are plotted in Fig. 3, and the results obtained from the control devices are also displayed for comparison. The use of a CuPc layer substantially increased the drive voltage as compared with the device formed on an O_2 plasma-treated ITO anode. The I – V curves of the test devices showed a more rapid

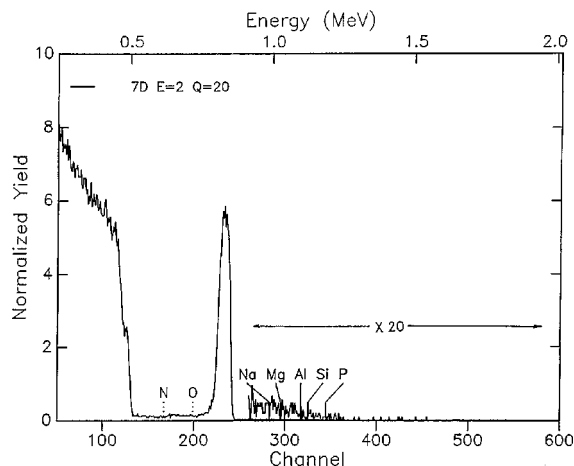


FIG. 2. RBS spectrum of a polymerized fluorocarbon film on a pure carbon substrate.

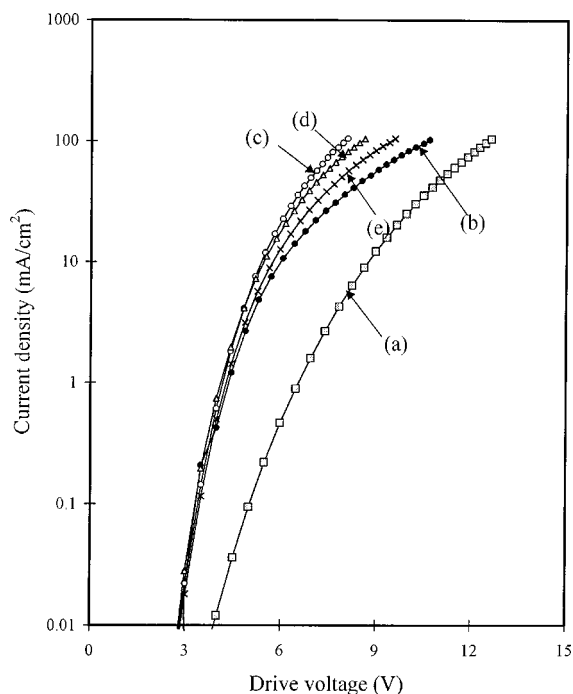


FIG. 3. Current–voltage characteristics of five devices formed on (a) a CuPc-coated ITO anode, (b) an O_2 plasma-treated ITO anode, (c) an ITO anode overlaid with a 2.5 nm thick polymer layer, (d) an ITO anode overlaid with a 5 nm thick polymer layer, and (e) an ITO anode overlaid with a 10 nm thick polymer layer.

increase in current than that of the control devices, and the sharp increase was more pronounced with a 2.5 nm thick polymer layer than that with a thicker layer. The bulk resistivity of the polymer was estimated after attributing the difference in I – V curves to the different thickness of the polymer layers. By subtracting a voltage drop across each polymer layer and taking a resistivity of $1.7 \times 10^7 \Omega \text{ cm}$ into calculation, the I – V curves of the test devices were replotted and found to be almost identical.

When luminance was measured as a function of injected current, the luminance efficiency was determined to be 2.75, 3.03, and 3.32 cd/A for the devices with a 5 nm thick polymer, without a buffer layer, and with a CuPc buffer layer, respectively. It is known in the literature that holes are the major charge carriers in OLEDs, and the luminance efficiency strongly depends on charge balance. Therefore, the reduction in electroluminescence efficiency is attributed to the increase in hole injection by inserting a polymer layer. By plotting luminance as a function of operating voltage, one can readily find that the device on a polymer-coated anode is able to achieve a higher luminance than the control devices operated at the same bias.

The operational stability of the device with a 6 nm thick polymer layer was tested at 40 mA/cm² with a 50% duty cycle, and both forward drive voltage and luminance were continuously monitored. It was found from Fig. 4(a) that the luminance of the device decreased by 28% of the initial brightness after 3000 h, while the control device on an O_2 plasma-treated ITO anode experienced a drop of 53%. In concert with the decrease in luminance, the drive voltage of the test device rose from 6.5 to 6.9 V in Fig. 4(b). The change was much smaller than an increase from 7.6 to 9.1 V measured on the control device. It is of importance to note

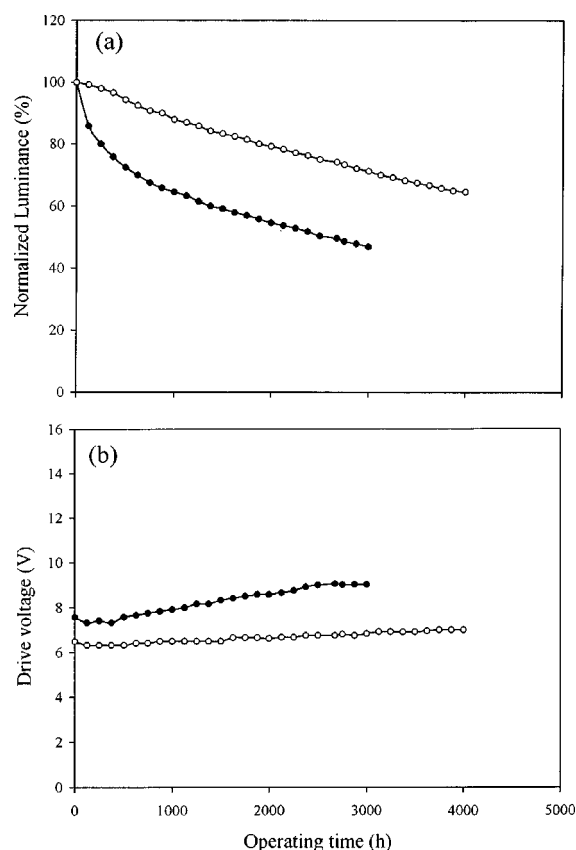


FIG. 4. (a) Normalized luminance and (b) drive voltage as a function of operation time for two devices formed on an O₂ plasma-treated ITO anode (closed circles) and a 6 nm thick polymer-coated ITO anode (open circles).

that the use of a polymer layer on ITO can substantially reduce the initial luminance drop. As shown in Fig. 4(a), the drop in the first 150 h was 1% and 15% measured on the test and control devices, respectively.

The major advantage of using plasma polymerization for anode modification is the process simplicity and the significant improvement of device operational stability. Aziz and co-workers revealed that injection of holes in Alq is the main cause of device degradation, and the improved stability of OLEDs by introducing a buffer layer of CuPc is attributed to slowing down hole transport to the NPB/Alq interface. However, in the present experiments both enhanced hole injection and improved operational stability occurred concurrently, thus implying some mechanisms other than the formation of cationic Alq species are also operating.^{8,9} Adachi *et al.* proposed that the stability is inversely related to the energy barrier of the hole-injecting contact.¹⁰ One may use this argument to explain our results of enhanced stability as no barriers are present to hole injection from the polymer layer to the NPB layer. Lee *et al.* reported indium diffusion from the ITO electrode into an organic multilayer structure after prolonged operation and a substantial reduction in quantum efficiency due to the presence of indium in organic emissive layers.¹¹ The polymer layer on ITO in this work may act as a buffer to impede indium diffusion from the ITO and thus enhance device stability. It is also likely that the ITO surface may be modified under fluorocarbon plasma, thus suppressing ITO surface degradation during device operation.

Plasma polymerized films in rf are insulating with extremely high resistivities.^{12–15} For tetrafluoroethylene poly-

merized by plasma, Vollman and Poll reported dc resistivity values in the range 10^{17} – 10^{18} Ω cm.¹² Because of the high resistivities, the materials are commonly used as dielectrics or corrosion protective coating. However, the films reported in this letter are somewhat conductive with a resistivity substantially lower than that reported in the literature.¹² It is well known that plasma polymerized layers with low resistivities could be formed only from some specific metal containing monomers, such as organogermanium or organometallic compounds.¹³ The relatively low resistivity of the polymer films in this work cannot be attributed to the presence of metallic impurities, as both XPS and RBS measurements revealed no substantial impurities in the films. The conductivity may be associated with the use of low-frequency plasma polymerization, however, the physical origin is not certain at present, and more work is required to clarify this issue.

In summary, plasma polymerization of CHF₃ at low frequencies was utilized for anode modification in OLEDs. The polymerized fluorocarbon films exhibited a relatively low resistivity and a high ionization potential. The devices formed on a polymer-coated ITO anode showed enhanced hole injection and superior operational stability. The improved stability is attributed to the presence of a barrier to impede indium diffusion and/or the modification of ITO in CHF₃ plasma. The resistivities of the films are considerably lower than that reported in the literature although the physical origin is not certain at present. This technique may form a conductive surface over a Teflon substrate for manufacturing new electronic devices.

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