Improved stability of organic light-emitting diode with aluminum cathodes prepared by ion beam assisted deposition

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Abstract
We have fabricated highly stable organic electroluminescent devices based on spin-coated poly-p-phenylene-vynylene (PPV) thin films. The electrical properties of aluminum cathode, prepared by ion beam assisted deposition, on PPV have been investigated and compared to those by thermal evaporation. Although energetic particles of Al assisted by Ar+ ion may damage the organic material, I–V–L characteristics are improved by applying thin Al buffer layer. In addition, a dense Al cathode inhibits the permeation of H2O and O2 into PPV film through pinhole defects, and thus retards dark spot growth. It may be deduced from highly packed structure of Al cathode with an increase in the contact area between Al and PPV that reduce the contact resistance. In conclusion, the lifetime of organic light-emitting device (OLED) has been extended effectively by dense Al film through ion beam assisted deposition process.

1. Introduction
In recent years, organic light-emitting device (OLED) have attracted increasing attention due to their potential advantages in low power, emissive, flexible, and cost-competitive flat panel displays [1–3]. However, its limited lifetime that arises from the exposure to oxygen, moisture and high electric fields still remains to be solved for the practical applications [4,5]. The pronounced morphological change observed in a debased OLED is the delamination of the cathode material that appears as dark spot [6]. Researchers revealed that the dark spot had a domelike structure, ‘bubbles’, filled with gases (mostly oxygen) presumably evolved during electrochemical and photoelectrochemical processes in the presence of water [7]. Some recent articles revealed that the bubbles originated from pinholes of metallic electrode in the presence of atmospheric humidity. Gases stimulated by significant heating during the device operation form these bubbles, and then cause cathode delamination at metal/organic material interface. Therefore, humidity and heat evolution are primary reasons in bubble formation [8,9].

One of the most important factors limiting the durability of OLED is the degradation of electron injecting contact. In OLED, metal cathode layer is commonly deposited by thermal evaporation to minimize the damage of organic materials. In case of energetic process like sputtering, energetic atoms and ions are incident onto the organic surface and transfer their energy to the surrounding organic molecules. The interactions between ions and solids can cause substantial damages to organic material and result in degraded device performance [10]. In the other aspect, metal cathode layers formed by energetic process are known to have better adhesion to the substrate than those deposited by thermal evaporation. Suzuki et al. reported that the lifetime of their OLEDs prepared by sputtering increased due to the improvement of Al/organic contacts [11].
However, the radiation damage effect appears to be more pronounced for devices with a durability of several thousand hours [12,13]. Gu et al. reported that even a 7.5-nm-thick Mg:Ag layer was not sufficient to prevent an underneath organic layer from ion damages upon sputtering deposition of an ITO electrode on the Mg:Ag layer [12].

Although many researchers explored the mechanisms of current transport and carrier injection from the contact [14–18], a definite relationship of damages in organic materials to the device performance had rarely been investigated. Liao et al. reported that the highest occupied state extended towards the Fermi level ($E_F$), implying that a metal-like conducting surface was formed when tris-(8-hydroxyquinoline) aluminum (Alq$_3$) film was irradiated by 100 eV Ar$^+$ ion. Such damaged surface would cause nonradiative quenching in an electroluminescent device when electrons are injected from the cathode to the Alq$_3$ layer, and may result in electrical shorts [10]. Therefore, the damages of organic materials must be minimized during the energetic deposition of metal layer on OLED device to avoid nonradiative quenching.

In the current investigation we developed a dense aluminum cathode along with ion beam assisted deposition (IBAD) process to protect OLED device from the O$_2$ and H$_2$O. It improved the $I$–$V$–$L$ characteristics minimizing Ar$^+$ ion beam damages generating nonradiative quenching sites. It was also found that this highly packed Al structure induced not only the passivation of OLED but also the minimization of joule heating occurred at the Al/PPV contact resulting in the formation of gas bubbles. We have carried out a systematic study of cathode preparation by IBAD to obtain high passivation and $I$–$V$–$L$ improvement.

2. Experiment

Indium tin oxide (ITO) coated glass was used as the substrate for OLEDs and it was approximately 200 nm thick with a sheet resistance of approximately 15 Ω/square. The standard cleaning procedure included the sonication in a detergent, acetone, and isopropyl alcohol successively, and then rinsing in deionized water. After the ITO cleaning, poly-3,4-ethylenedioxythiophene (PEDOT) doped with poly (styrenesulfonate) PSS was spin coated approximately 50 nm thick as a hole transport layer (HTL) and poly-p-phenylene-vinylene (PPV) was spin coated approximately 80 nm thick as an emissive layer on HTL layer successively. LiF layer was deposited 3 nm as an electron injection layer (EIL) with 1 Å/s, and then aluminum cathode was deposited by conventional thermal evaporation method or IBAD process. Ar$^+$ ion energy and current density were 150 eV and 70 μA/cm$^2$, respectively, and Al deposition rate was 1–2 Å/s. The Al cathode depositions by IBAD were made in two different conditions, one with the thermally evaporated Al buffer layer about 300 Å before using IBAD process to avoid PPV damages by Ar$^+$ ion bombardment and another without Al buffer layer.

3. Results and discussion

Fig. 1 shows the SEM and AFM data of Al cathodes deposited by thermal evaporation and IBAD process with Al buffer layer the films. In thermally evaporated Al cathode, islands and voids are very large, and Al cathode deposited by IBAD contains the fine islands and voids that may reduce the permeation of H$_2$O and O$_2$. Energetic Ar$^+$ ions bombard the depositing Al atoms and cause not only the highly packed structure of Al cathode but also the large contact area between Al and PPV due to the high surface adatom mobility.

Fig. 2 shows the optical image of electroluminescence in Al cathodes deposited by thermal evaporation and IBAD process. Dark spots induced by dust particles were formed at the first stage inevitably since the device was fabricated at ordinary laboratory without screening process from the air.

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Fig. 1. The surface morphologies of Al cathodes prepared by (a) thermal evaporation and (b) ion beam assisted deposition with Al buffer layer.
In thermally evaporated Al device, dark spots were growing gradually with time whereas those in ion beam assisted Al device remained almost steady. It was believed that the formation of pinholes by dust particle was minimized due to high surface adatom mobility in ion beam assisted deposition. But the cell degraded due to the edge permeation of H$_2$O and O$_2$ because the device type was a passive matrix with the structure exposed to air at the interface between Al and PPV, and so we failed to show the optical image of electroluminescence only after 3 h due to such debasement.

The thickness of Al buffer layer is adopted as 300 Å because this condition minimize the Ar$^+$ ion induced damages with maintaining highly passivation property. When the buffer layer thickness is 100 Å, the intensity of electroluminescence was reduced by Ar$^+$ ion induced damages, even though that was a little better than case of non-buffer layer device. In the case of 500 Å buffer layer device, the passivation characteristics was reduced, even though electroluminescence was almost same with the non-buffer layer device because of degradation by edge permeation. We also examined the ion beam assisted Al cathode in a active matrix device composed of Al/LiF/Alq3/TPD/ITO with the structure not exposed to air at Al/PPV interface. The device without any passivation layer was operated even after 2000 h in the air.

The current–voltage ($I$–$V$) characteristics of the OLEDs with ion beam assisted Al cathodes were measured and compared with that of a conventional PPV-based device, as shown in Fig. 3. The measurements have been carried out in a glove box filled with argon gas of 99.9999% purity to exclude the permeation effect of H$_2$O and O$_2$ because dark spots formed by the cathode oxidation restrain the current injection. Each device was fabricated as identical as possible from neighboring pieces of the same PPV/PEDOT/ITO substrate. The $I$–$V$ characteristics of the OLEDs with ion beam assisted Al cathode did not differ appreciably from that of the conventional device with thermally evaporated Al cathode. The power-law dependence of the $I$–$V$ was consistent with the pervious work, where it was suggested that current in OLED was limited basically by traps and space charge effects. Antoniades et al. reported that electrons, in contrast to holes, were severely trapped in PPV that resulted in an unbalanced electron and hole transport [18]. Such a severe electron trapping will certainly affect the $I$–$V$ characteristics and efficiency of polymer LEDs. As the forward bias is increased, the electron quasi-Fermi level $E_n$ rises toward the LUMO along with the increased injected electron density. The traps below $E_n$ are filled with the injected electron, resulting in the reduction of available density of empty traps and the increase of electron effective mobility, and the sharp increase of current. So the larger damage by Ar$^+$ ion beam brought about the gradual increase of current indicating the ohmic regime, resulting from the traps below $E_n$ caused by local damage incurred in the ion beam process, as revealed in Fig. 3. In case of Al cathode deposited by IBAD process, many traps raised the ohmic regime through the low bias range, compared to the thermally evaporated one. This can be explained by a distribution of trap-level energies.

Fig. 4 displays the quantum efficiency plot with the increasing current density. At first stage quantum efficiency increased linearly with the current density in all the samples, and then saturated at a certain current density. Below the current density of 20 mA/cm$^2$, the quantum efficiency of a thermally evaporated sample was slightly higher than that
of Al buffer layered IBAD one. It indicated that the PPV was somewhat damaged by Ar\(^+\) ion bombardment. The quantum efficiency became the lowest in IBAD sample without Al buffer layer, due to severe electron trapping in deep trapping sites. When the current density increased above 20 mA/cm\(^2\), the quantum efficiency of thermally evaporated Al device was stabilized to become lower than that of Al buffer layered IBAD one. It might be caused by small contact resistance ensued on the large contact area. At higher current density regime (> 20 mA/cm\(^2\)), thermally evaporated Al device might be also deteriorated by the Joule heating originated from Al/PPV interface contact resistance because the quantum efficiency was decreased slightly, but the Al buffer layered IBAD sample did not show this reduction. The larger the contact area is, the smaller the current density per unit area becomes and minimizes the Joule heating between Al and PPV. At low current density regime (< 20 mA/cm\(^2\)), the quantum efficiency was highest in OLED with thermally evaporated Al cathode because the injected electrons in the IBAD case were trapped in the damages caused by Ar\(^+\) ion beam and did not contribute to the radiative recombination process. Upon increasing the bias the traps were filled with the injected electrons, provoking a strong increase in the number of free electrons that participated in recombination to elevate the device efficiency. On the other hand, the quantum efficiency became very low in the device without buffer layer throughout the whole bias range.

Fig. 3. \(I-V\) plots of OLED devices with Al cathodes deposited by thermal evaporation and ion beam assisted deposition.

Fig. 4. Quantum efficiency vs. current density plot of OLED devices with Al cathodes deposited by thermal evaporation and ion beam assisted deposition.
One way to maximize the quantum efficiency is to keep the ratio of electron and hole currents by moving the recombination zone away from the metal/organic interface. And the preeminent approach to enhance the EL efficiency is to employ the polymeric bilayer structures with different electronegativities, so that the recombination is confined in the heterojunction between two polymers.

The devices with ion beam assisted Al cathodes with buffer layer showed higher current level and luminescence and it indicated lower serial resistance \( R_S \) originated from Al/PPV interface on PPV/PEDOT/ITO substrates. It can be explained from the fact that the contact resistance is inversely proportional to the contact area between Al and PPV. The packed structure in IBAD case has the larger contact area that indicates smaller contact resistance.

Impedance spectroscopy was executed to characterize the contact resistance between Al and PPV. Fig. 5 shows the real part \( \text{Re}(Z) \) and the imaginary part \( \text{Im}(Z) \) of the complex impedance \( Z(u) = \text{Re}(Z) + j\text{Im}(Z) \) of an ITO/PPV/Al which excludes the HTL layer for simple consideration. In the equivalent circuit the depletion layer corresponds to a junction capacitance \( C_J \) and a junction resistance \( R_J \). The contact of PPV with high work function metal ITO is regarded as ohmic, which has negligible impedance in the ideal case [19]. Experimentally, the plots of an OLED device show two semicircles at the low and high-frequency end, arising from the bulk PPV and highly capacitive nature of the Al/ITO interface (Fig. 6).

In this plot the implicit variable is the frequency that increases from right to left (20 Hz–1 MHz). The diameter of semicircles in Fig. 5 represents the contact resistance of Al/PPV [20]. It was smaller for ion beam assisted Al device in comparison with thermally evaporated Al device. Since the contact area between Al and PPV is inversely proportional to the contact resistance, the contact resistance is less in IBAD case. Buffered IBAD device may have a larger contact area even though thermally evaporated Al film is deposited to 30 nm prior to \( \text{Ar}^+ \) ion irradiation because the buffered Al film cannot screen the \( \text{Ar}^+ \) ions wholly. So junction resistance of buffered IBAD device is smaller than thermal device. This result coincide with smaller total resistance of ion beam assisted Al device. This result coincide with smaller serial resistance of ion beam assisted Al device in Fig. 5. The low contact resistance reduces a thermal problem caused by joule heating at Al/PPV interface during the device operation. And the constant current test was executed to characterize the lifetime of ion beam assisted, buffered Al device. The current was fixed at 3 mA in a pixel of 3 mm \( \times \) 3 mm area, which indicated 33 mA/cm\(^2\) to observe how the contact area affected the lifetime in a glove box filled with pure Ar gas. Al buffer layered IBAD sample exhibited the highest luminescence among all samples at the same current density without losing high luminescence throughout the whole time range. It was indicative of the larger contact area and the longer lifetime. But ion beam assisted Al device without buffer layer displayed the lowest luminescence due to the damages from the \( \text{Ar}^+ \) ion beam even though it seemed that the device had the largest contact area.

Fig. 7(a)–(c) show the Al gas bubbles of OLEDs arisen during the operation (Fig. 7a). Upon applying the bias the gas bubbles were formed abruptly in thermal evaporated Al device after 3 h (Fig. 7a), whereas ion beam assisted Al device with buffer layer did not have them. Fig. 7(b) represents the Al surface image of the device not operated after heating to 200 °C for 24 h in a humid atmosphere to disclose gas bubbles, whereas any gas bubbles did not formed in a glove box. Fig. 7(c) shows the SEM images of Al gas bubbles, which Al surface is delaminated from the organic materials. It was one of dominant causes that influence the formation of gas bubbles. Therefore the stability of OLED could be enhanced by inhibiting the permeation of moisture and minimizing joule heating.
4. Conclusion

In summary, Al cathode deposited by IBAD has the advantage over that by thermal evaporation such that it became the more packed Al structure that inhibited the permeation of H$_2$O and O$_2$. But IBAD process generated the damage to the cathode due to ion beam bombardment, inducing the lower quantum efficiency. Employing thin Al buffer layer diminished such damage and reduced the contact resistance between Al and PPV, so that led the minimization of OLED’s degradation like gas bubbles. The consequence was that the lifetime of OLED was prolonged with highly passivation effect and less joule heating at Al/PPV interfaces.

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