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Inhibition of dark spots growth in organic electroluminescent devices

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Abstract

Humidity-induced oxidation has been considered as a major cause for the growth of dark spots in organic electroluminescent devices. In this Letter, we found that a layer of 100 nm thick calcium deposited on top of the magnesium:silver (Mg:Ag) cathode can slow down the growth rate of dark spots. Further experiments verified that calcium not in direct contact with the cathode could not protect the dark spots against growing. This excludes the possibility that the protective function of calcium derives solely from its action as a moisture-resistive agent. In contrast, calcium functions as a sacrificial metal forming a galvanic couple with the magnesium electrode such that calcium would oxidize in preference to the Mg:Ag. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Formation and growth of dark spots is a major degradation cause in organic electroluminescent devices (OELD). This has long been an obstacle for practical applications of OELD. This degradation mechanism has been widely reported since the first high-efficiency OELD was demonstrated by Tang and Van Slyke [1] in 1987. Different causes have been suggested to account for the formation and growth of dark spots. Fujihira et al. [2] reported that the dark spots were caused by interdiffusion of organic layers. Cumpston et al. [3] proposed that the electromigration of cathode was responsible for these non-emissive spots. Lee et al. [4] and Gao et al. [5], respectively, showed that the interdiffusion and crystallization of organic layers might not be necessary factors for the failure of OELD. Most studies today share a common belief that the formation of dark spots and their growth are related to the reaction of the OELD with water or oxygen species [6–10]. Among these studies, the defects related to cathode oxidation are likely the most probable sites for the formation and propagation of dark spots [6–8]. Mg:Ag is often used as a cathode in OELD because of its low work function. Protecting the Mg:Ag cathode against oxygen and moisture is therefore a necessary task.

In the present Letter, we deposited a thin layer of calcium (Ca) directly on top of the Mg:Ag cathode to protect the underlying cathode against oxygen and moisture absorption. The fabricated OELDs were exposed to different relative humidities and the corresponding growth rates of dark spots were monitored. It was found that calcium, being the second highest metal in the electro-

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chemical series (E.C.S.), can protect the Mg:Ag from oxidation.

2. Experimental

Indium tin oxide (ITO) coated glass with a sheet resistance of 50 Ω/□ was used as the anode and substrate for OELD. They were ultrasonically cleaned in a commercial detergent and then rinsed in deionized water. Before depositing the organic layers, the substrate was treated with an oxygen plasma for 1 min with an AC power of 100 W. Double-layer devices were fabricated by sequential high vacuum (10^{-7} mbar) vapor deposition of a hole transport layer (HTL) of 600 Å thick *N*,*N*′-*bis*-(1-naphthyl)-*N*, *N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) and an electron transport layer (ETL) of 600 Å thick *tris*-(8-hydroxyquinoline) aluminum (Alq_3). The Mg:Ag (10:1 by mass) cathode with a thickness of about 2000–3000 Å was then co-evaporated on top of the Alq_3 layer. The deposition rate of the organic layers (both the HTL and ETL) and the cathode was controlled at 2–3 and 10 Å/s, respectively. To study the effect of the Ca over-coating, a device of the same configuration was fabricated but with an additional layer of 1000 Å thick Ca evaporated on top of the Mg:Ag. A third type of device was made with an extra layer of 500 Å NPB or Alq_3 deposited in between the Mg:Ag and Ca. This layer completely isolated both the metals and verifies if any changes of the growth rate of dark spots were due to mechanisms other than the sacrificial protection of Ca. Alq_3 of the same thickness was also prepared on the Mg:Ag for comparison. The configurations of the four types of devices were as follows:

Type A: ITO/NPB/Alq_3 /Mg:Ag (3000 Å),

Type B: ITO/NPB/Alq_3 /Mg:Ag (2000 Å)/Ca (1000 Å),

Type C: ITO/NPB/Alq_3 /Mg:Ag (2000 Å)/NPB or Alq_3 /Ca,

Type D: ITO/NPB/Alq_3 /Mg:Ag (2000 Å)/Alq_3.

For the ease of comparison, the total thickness of the metals in type A and B devices was 3000 Å. The luminance of the devices after deposition was measured with a computer-controlled DC source and a PR 650 SpectroScan. Optical EL images for dark-spot monitoring were taken from time to time with a Leica DMLM fluorescence microscope attached with a charge coupled device camera. All non-encapsulated devices were stored in enclosed containers with different levels of humidity (50%, 70% and 95%) unless taken out for photography. Changes in the diameter of representative dark spots were measured throughout the storage time and the areas of dark spots were counted within a region of 2 mm × 1.5 mm.

3. Results and discussion

The emissive area of all devices was approximately 3.0 mm × 3.3 mm. Current–voltage–luminance (IVB) measurements showed that the luminance of the freshly prepared devices averaged above $550\ \mathrm{cd/m^2}$ at a current density of $20\ \mathrm{mA/cm^2}$ and a voltage of 7.3 V. The characteristics were similar to those in our previous Letter [5] and hence the IVB curves were not plotted here. This implied that the extra films on top of the Mg:Ag do not have any observable influences on the performance of the freshly fabricated devices.

Fig. 1a demonstrates an optical image of a freshly prepared type A device which was connected to a 9 V battery. It can be seen that only a small fraction of the device area was occupied by dark spots. The formation of these dark spots is inevitable. It was claimed that either the presence of residual moisture in the device [9] or reaction of the device with contamination introduced during fabrication [6] played an important role. The sequence of the growth of dark spots in type A devices is shown in Figs. 1b and c. These images correspond to devices which have been stored in an environment with a relative humidity of 50%. In addition to a direct relationship of the growth rate of dark spots with storage time, it is also interesting to note that each dark spot was surrounded by a bright ring. The mechanism of this bright ring formation is still not clear. Localized current due to defects [2,6] or cathode delamination due to crystallization of Alq_3 upon moisture absorption [10] may be possible reasons.

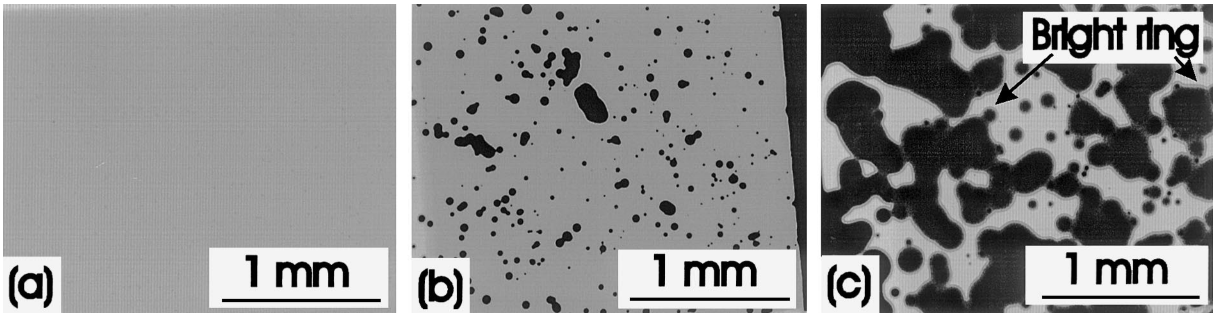

Fig. 1. Optical EL images of: (a) as-prepared type A devices; (b) type A devices after a storage time of 24 h; (c) type A devices after a storage time of 180 h. All devices were stored at a humidity of 50%.

The EL images of type B devices are shown in Fig. 2. The density of the dark spots in the as-evaporated device (Fig. 2a) was comparable to that in type A device (Fig. 1a). Figs. 2b and c indicated that dark-spot area was visibly reduced, compared to the corresponding devices (Figs. 1b and c) without the Ca layer. The relationship between the areal growth rate (G_A) of dark spots and storage time for type A and B devices in different storage humidity ($h = 50\%$, 70% and 95%) is shown in Fig. 3. Since it is difficult to count the number of dark spots at a particular storage time and not all the dark spots were of the same diameter, G_A was obtained from measuring the total areas that were occupied with the dark spots. Therefore, it is not an average areal growth rate of a specific dark spot. At a given storage time, Ca always retards the growth rate of dark spots to some extent. Since the propagation of dark spots is well known to be a humidity-induced and humidity-accelerated process, there is then no doubt that Ca can protect the devices against the moisture effect. The standard electrode potentials of Ca, Mg and Ag are −2.87, −2.34 and +0.8 V respectively [11]. Ag is sufficiently inert and is less likely involved in the oxidation process. Ca, having a more negative potential than Mg in the E.C.S., is anodic with respect to Mg. The Ca then corrodes preferentially when galvanically coupled to the Mg:Ag. In other words, Ca acts as a sacrificial metal and is first consumed resulting in the protection of the Mg:Ag structure.

Fig. 3 shows that the G_A increases linearly with storage time for the device without the Ca layer, or that the radial growth rate (G_R) of dark spots is proportional to the square root of the storage time. This relation suggests that the growth of dark spots is a diffusion-controlled process. However, the situation is different for devices with the Ca layer. The best fitted curve is not linear. Fig. 3

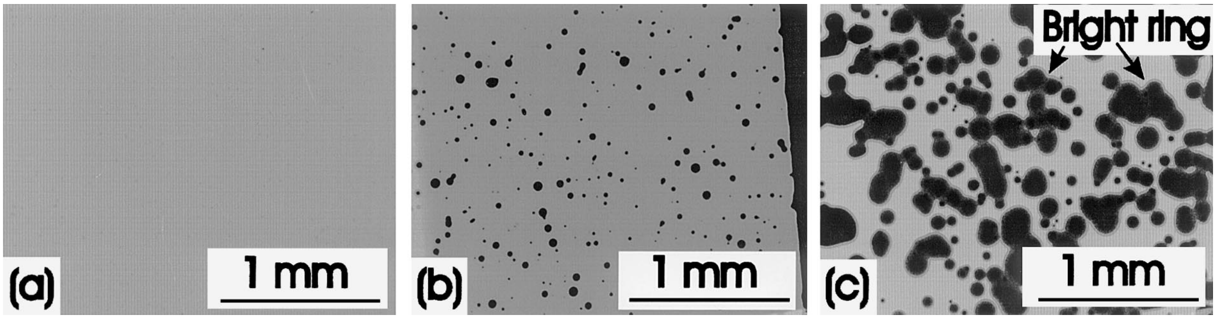

Fig. 2. Optical EL images of: (a) as-prepared type B devices; (b) type B devices after a storage time of 24 h; (c) type B devices after a storage time of 180 h. All devices were stored at a humidity of 50%.

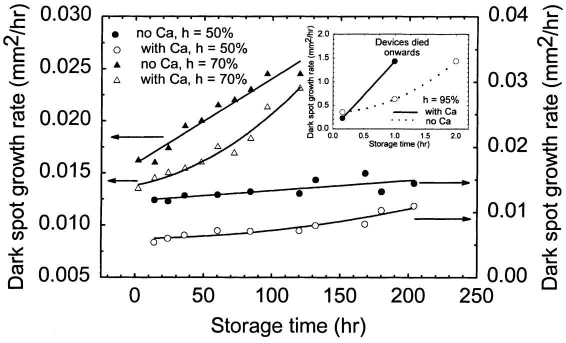

Fig. 3. Areal growth rate of dark sports (G_A) for devices exposed to different humidity ($h = 50\%$, 70% and 95%) as a function of storage time. The inset shows the relationship of growth rate G_A with storage time at a humidity 95%. Open symbols correspond to divices with Ca deposition.

shows that the growth rate of dark spots normally increases slowly at the beginning, followed by a progressive increase at the end of the curves. We suggest that Ca rapidly formed a chemically inert CaO passive film immediately upon exposure to air. This passive film primarily acted as a barrier and hence momentarily protected the Ca against oxidation. Ultimately many corrosive sites were formed on the surface of this sacrificial metal, thus accelerating the oxidation rate until the Ca was completely consumed. Nevertheless, the nonlinear effect was not so apparent for devices stored at 50% humidity. As more than one mechanism may contribute to the growth of dark spots, we suspect the growth rate of dark spots in the above case may be dominated by other factors rather than humidity.

The inhibition of the growth of dark spots for devices with Ca deposition at higher storage humidity ($h = 95\%$) is shown in the inset of Fig. 3. The growth rate of dark spots was at least 2 orders of magnitude higher than that for devices exposed to a humidity of 50%. Nevertheless, Ca still functions as a sacrificial metal.

To further affirm the meritorious role of Ca in OELD, type C devices with an additional Alq_3 in between the Mg:Ag and Ca were fabricated. Type D devices as a reference were also fabricated so as to identify any changes of the amount of dark spots in type C devices that were not due to the extra Alq_3 layer. The fraction of dark spots in devices B, C and D was measured and EL images were taken after a storage time of 24 hours at a relative humidity of 70%. We noted that the size of dark spots in type C and type D devices was indistinguishable (Fig. 4b and c) while the non-emissive areas observed in type C devices (Fig. 4b) were larger than that in the type B devices (Fig. 4a). Accordingly, Ca not in contact is less effective in protecting the OELD against dark spots growing. Hence, it is clear that the protective function of Ca involved in redox reaction is more significant than that as a moisture-barrier layer. We also used NPB instead of Alq_3 as the inter-layer. The situation was even worse as the dark spots grew faster than that in the reference devices (type A). Further pinholes created in the Mg:Ag/NPB interface due to the strong surface tension of NPB may provide an additional path for oxygen and water.

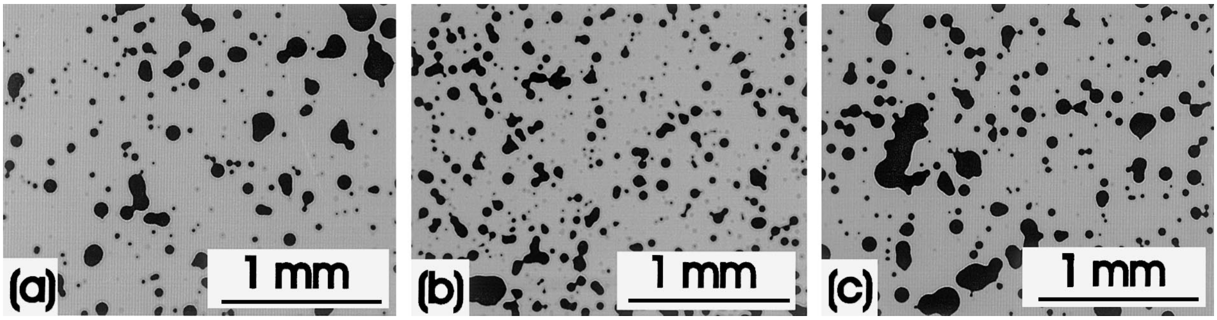

Fig. 4. Optimal EL images of (a) type B devices after a storage time of time of 24 h. All devices were stored at a humidity of 70%. Approximately 10% and 15% of dark spots were counted in a selected area of 1.5 mm × 2 mm for case (a), (b) and (c), respectively.

4. Summary

Growth of dark spots in OELD was inhibited through covering the surface of Mg:Ag with a layer of 1000 Å thick Ca. The presence of Ca did not affect the luminance and efficiency of the devices. With a 500 Å thick NPB or Alq_3 deposited in between the Mg:Ag and Ca, the protective effect of Ca disappeared. Ca is thus considered as a sacrificial metal. When Ca is in contact with Mg, Ca is preferentially oxidized, thus protecting Mg from oxidation. We suppose that utilization of this technique, together with the conventional encapsulation, can further prolong the lifetime of OELD.

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