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Rutherford backscattering and secondary ion mass spectrometry investigation of Mg:Ag–tris(8-hydroxy quinoline) aluminum interfaces

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Abstract

The presence or absence of silver diffusion from Mg:Ag cathodes in tris(8-hydroxy quinoline) aluminum (Alq$_3$) type organic light emitting diodes (OLEDs) has been investigated by Rutherford backscattering (RBS) and secondary ion mass spectrometry (SIMS). Comparison of experimental and simulated RBS data indicated a very abrupt Ag–Alq$_3$ interface, consistent with there being no uniform diffusion of silver into the organic layer of the OLED during deposition, i.e. <0.5 at.% Ag in the first 20% of the organic layer. Silver diffusion through the organic layers of an OLED cannot, therefore, be the root cause of common electrical shorting problems. SIMS profiles of the same sample were obtained using O_2^+, O^- and Ar^+ primary ion beams, and in each case different depth profiles were obtained. The variation in the SIMS results is due to ion beam mixing effects, matrix effects and migration of metal ions in an electrostatic field created by a charged surface. It was concluded, therefore, that SIMS is not a suitable technique for studying metal-on-organic interfaces.

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1. Introduction

Organic light emitting diodes (OLEDs) continue to be the focus of intensive research owing to their potential applications in display technology. Since the first report of an efficient device by Tang and VanSlyke [1], considerable progress has been made. The basic small-molecule OLED structure consists of four thin film layers. It includes in sequence a transparent anode, almost exclusively indium tin oxide (ITO), an organic hole transport layer, often N,N-di(napthalene-1-y1)-N,N-diphenyl-benzidine (NPB), an organic electron-transport/electro-luminescent layer, such as tris(8-hydroxy quinoline) aluminum (Alq$_3$), and finally a cathode. A magnesium–silver alloy is frequently used as the

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cathode. Magnesium is a low work function metal that facilitates electron injection, while the silver adds chemical stability and acts to increase the sticking coefficient of magnesium [2]. The metal–organic interfaces within the OLED structure determine the electrical behavior and thus, the device characteristics. As a result, a comprehensive understanding of the nature of the metal–organic interface is critical for the optimization and eventual commercialization of this technology. Specifically, the interaction of the cathode metal with the organic layer and interdiffusion thereof has been discussed as one of the factors limiting OLED performance.

Correspondingly, many investigations of metallic diffusion at metal–organic interfaces have been reported [2–12]. To date, however, there have been few studies of diffusion of magnesium [2–4] on Alq_3 and even fewer for silver [5,6] on Alq_3. Rajagopal and Khan observed diffusion of Mg into Alq_3 by ultraviolet photoemission spectroscopy [2]. He et al. observed interdiffusion and reaction of Mg into Alq_3 by high-resolution electron energy-loss spectroscopy when the sample was heated [3]. Lee et al., on the other hand, observed no substantial diffusion via secondary ion mass spectrometry (SIMS) [4]. Song et al. observed Ag diffusion into Alq_3 again via SIMS [5]. As will be discussed in this paper, however, we believe that SIMS should be used with caution particularly for metal-on-organic interfaces.

In this study we examine the Mg:Ag–Alq_3 interface with SIMS and Rutherford backscattering (RBS). The RBS data, supported by detailed simulations, indicate that uniform silver diffusion does not occur at the silver–Alq_3 interface. Further, we report that SIMS is not a suitable technique for investigating metal-on-organic interfaces.

2. Experiment

The fabrication of the OLEDs used in this study was carried out in a vacuum system with a base pressure of 10^{-9} Torr. The substrates consisted of patterned ITO on glass. The ITO layer was approximately 200 nm thick with a sheet resistance of 10 Ω/sq. The cleaning process of the substrates involved sonication in a commercial detergent followed by a rinse with distilled water, acetone and methanol. The sonicated substrates were then baked at 100 °C for 20 min to remove excess moisture and then subjected to a 20-min UV-ozone treatment to remove any residual organics. Once loaded into the vacuum system, the organic thin films of NPB and Alq_3 were thermally evaporated in sequence at a rate of 0.2 nm/s. The cathode, consisting of a 10:1 Mg:Ag metal alloy, was deposited by co-evaporation of the two metals. The Mg was evaporated at a rate of 0.2 nm/s and Ag at a rate of 0.02 nm/s. The overall structure consisted of ITO/NPB/Alq_3/Mg:Ag with a thickness of 200, 50, 50 and 50 nm, respectively. The thickness of each layer and the rate of evaporation were controlled in situ using a quartz crystal monitor that had been previously calibrated by RBS measurements of deposition on Si substrates in identical geometry. All samples were studied as deposited, i.e. SIMS and RBS were performed on intact cathodes.

Dynamic SIMS depth profiles were obtained using a Cameca IMS-3f ion microprobe. Primary ion beams of O_2^+ and O^- were employed. In both cases, the accelerating voltage was 12.5 kV while the beam currents were 100 and 25 nA for the O_2^+ and O^- primary ion beams, respectively. Positive secondary ions were monitored by mass spectrometry. Profiles were also obtained with a Cameca time-of-flight secondary ion mass spectrometer IV. In this case, an Ar^+ sputtering beam (1 keV energy and 10 nA beam current) followed by a pulsed Ga^+ analyzing beam (25 keV energy and beam current of 2.5 pA) was used. Again, the positive secondary ions were monitored. Depth scales were determined by measuring the SIMS crater depths with a Tencor P-10 profilometer.

RBS spectra of the same sample were obtained using a 0.7 MeV $^4He^+$ beam from a 2.5 MV Van de Graaff accelerator and a surface barrier detector. The incident ion beam angle was 40° and the scattering angle for backscattered particles was 130°. A silicon (bismuth) standard was used to determine the solid angle of the detector. Simulations of the data were obtained using Quark [13], a simulation package for RBS.

3. Results and discussion

The RBS spectrum for the ITO/NPB/Alq$_3$/Mg:Ag device is shown in Fig. 1. The energy of the backscattered ^{4}He$^+$ ions, at a given angle, depends on the energy lost due to the transfer of momentum to a target atom via collision and the energy lost during transmission through the sample material both before and after scattering [14]. Thus, the high-energy edge of the Ag RBS peak corresponds to backscattering from the surface of the cathode and the energy width provides a measure of the depth of a layer. A steep back edge for the silver peak, such as that shown in Fig. 1, indicates an abrupt interface between the silver and the underlying organic layers.

Simulations of this same sample are shown in Fig. 2. Clearly, the simulations are consistent with the RBS data *only when no silver diffusion is included*. This can be seen by a comparison of Fig. 2(A), in which no silver diffusion was assumed, and Fig. 2(B), in which as little as 0.5 at.% Ag diffusion into the first 20% of the organic layer was assumed. Further simulations were done incorporating both more and less Ag diffusion, however the simulation shown in Fig. 2(B) represents the smallest amount of Ag diffusion clearly discernable by comparison. Thus, it provides an approximate upper bound for the amount of Ag that could have diffused, undetected by RBS, into the organic layer.

As demonstrated above, RBS is a powerful technique for the study of heavy element distributions in thin film structures [14]. Durr et al. further demonstrate the capabilities of RBS in a study of Au on diindenoperylene (DIP), wherein RBS was used to monitor the thermal diffusion of Au into the DIP film [15]. On the other hand, it should be noted that it would be much more difficult to extract meaningful quantitative data for lighter element distributions such as Mg, Al and C within the OLED interface currently under investigation and other similar interfaces.

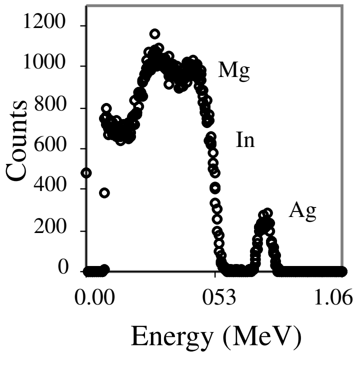

Fig. 1. An RBS spectrum of a 50 nm Mg:Ag/50 nm Alq$_3$/50 nm NPB/ITO OLED device.

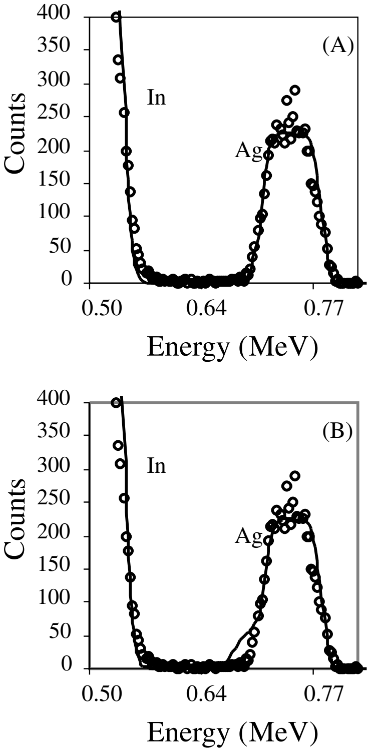

Fig. 2. RBS spectra (○) and simulations (—) of a 50 nm Mg:Ag/50 nm Alq$_3$/50 nm NPB/ITO device assuming (A) no diffusion and (B) 0.5 at.% Ag diffusion in the first 20% of the organic layer.

The SIMS profiles for the same device are shown in Fig. 3. In Fig. 3(A), the SIMS profile using an O_2^+ primary ion beam is shown. The interface between the two organic layers can be seen clearly by the dip in the ^{12}C curve and the drop in the ^{27}Al curve. The ITO substrate is shown by the appearance of the ^{115}In and ^{120}Sn peaks. The ^{107}Ag curve, which extends to the ITO interface, suggests that the silver has diffused into the organic layer;

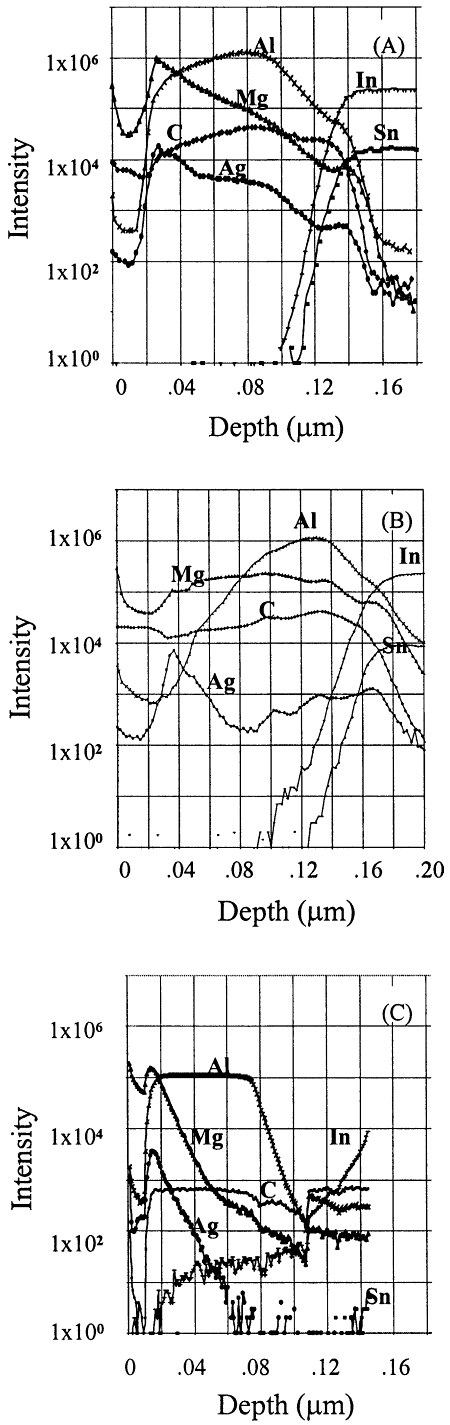

Fig. 3. SIMS profiles of a 50 nm Mg:Ag/50 nm Alq$_3$/50 nm NPB/ITO device obtained using (A) an O_2^+ (B) an O^- and (C) an Ar^+ sputtering and Ga^+ analysis primary ion beam(s).

however, this is inconsistent with the RBS results as well as with other SIMS results. In Fig. 3(B), the SIMS profile using an O^- primary ion beam is shown. In this profile many differences are observed. Most notably is the change in the Ag profile. When using an O^- primary ion beam the Ag peak shifts toward the outer surface of the device and falls off much more rapidly than in the profiles obtained with O_2^+.

Oxygen primary beams are widely used in SIMS studies as it is known that oxygen enhances the secondary ion yield of the more electropositive elements [16]. It is important to consider the effects of oxygen as it will react preferentially with certain layers. Thus, in a multilayer thin film structure, such as an OLED, ion beam mixing can result in altered sputtering rates on either side of an interface. Furthermore, field-induced migration of mobile species can accompany the charging of a surface if the diffusion rate is comparable to the rate of sputtering. Clearly, the organic layers of an OLED are susceptible to charging. In the case of the O_2^+ primary ion beam, positive charge is building up at the surface, and thus any mobile Ag^+ ions will migrate away from the surface and toward the glass substrate. When using an O^- primary ion beam, the mobile Ag^+ ions will tend to migrate toward the negatively charged surface. These effects are clearly seen in Fig. 3(A) and (B). The opposing effects of positive and negative primary oxygen beams has been observed elsewhere for silver sandwiched in metal oxides films as well as for sodium migration in SiO_2 [16,17].

In Fig. 3(C), the SIMS profile using an Ar^+ primary sputtering beam and a Ga^+ analysis beam is shown. For this profile an electron flood gun was also used to compensate for the charging of the surface. Here, it can be seen that the Ag profile is better behaved, as are the Mg, Al and C profiles. Although an improvement in the SIMS profile is observed, the exact location of the Mg:Ag–Alq$_3$ interface remains unclear. This lack of clarity is observed in all of Fig. 3(A)–(C) and is evidenced by (a) the unexpected dips in the Mg and Ag profiles within the first 30–40 nm of the profiles, (b) the position of the Ag and Mg peaks, as well as (c) the tailing of the Ag and Mg profiles into the organic layer. It is likely the result of matrix effects, as there is oxygen in the organic layer, and the result of variations in sputtering rates.

The comparison of the RBS results and simulations with the SIMS data demonstrate clearly that ion beam mixing and matrix effects are a significant problem for SIMS profiling of the Mg:Ag–Alq_3 interface. In fact, the variance among the SIMS profiles acquired with different primary ion beams is even more convincing evidence of the effects of ion beam mixing, i.e. the distortions and shifting of the Ag peak. Therefore, it appears that SIMS is not a suitable technique for the study of metal-on-organic interfaces. Even in the absence of the observed ion beam mixing effects, quantification of the coverages and profiles would require careful calibration of standards in which known profiles of the metals in the appropriate organic layer were used. Without an appropriate standard, we expect the mixing and matrix effects to be a common problem for all metal-on-organic systems. These conclusions indicate that great care must be exercised in interpreting such SIMS data, and call into question the results of some previously published work [5,6] which suggested that metal diffusion was significant. The O_2^+ SIMS profile does, on the other hand, clearly distinguish the Alq_3–NPB interface and may prove useful for the general study of organic–organic interfaces. Further, the organic-on-metal type interface, for example the NPB–ITO interface, is also well behaved for oxygen beam SIMS analysis.

The relevance of the present study to OLED research is that it has been commonly found that during the evaporation of OLEDs using a Mg:Ag cathode, the device suffered from electrical shorting. This was initially attributed to silver diffusion as has been reported in the literature [5,6]. Our present data show that uniform diffusion of silver cannot explain the electrical shorting. This would be consistent with the observation of other groups [7,8] that metal diffusion in organic layers is related to the first ionization energy (IE) of the metal. In the present case silver would not be expected to interact with the organic material as it has a relatively high IE, and correspondingly abrupt interfaces were reported for silver on organic materials other than the one used here. Other explanations of the shorting problems must be advanced and we believe that they are related to edge effects and evaporation conditions leading to incomplete coverage of the inevitable steps between the conducting and insulating areas of the patterned substrates.

4. Summary

In summary, an investigation of the Mg:Ag–Alq_3 interface using SIMS and RBS has been completed. The RBS results and simulations clearly indicated that there was no uniform silver diffusion, i.e. <0.5 at.% Ag into the first 20% of the organic layer. It was also found that SIMS is not a suitable technique for the study of metal-on-organic interfaces. When using an oxygen primary ion beam for SIMS, distortions and shifting of the Ag film due to ion beam mixing and field-induced ion migration are observed. These effects are less severe when using an inert gas as the primary beam, such as Ar^+. However, the metal-on-organic interface remains unclear. SIMS may, on the other hand, prove useful for investigations of organic-organic or organic-on-metal interfaces.

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