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A nano-indentation study of the reduced elastic modulus of Alq_3 and NPB thin-film used in OLED devices

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ABSTRACT

Two of the commonly-used Organic Light Emitting Diode (OLED) materials tris-(8-hydroxyquinoline) aluminum (Alq_3) and *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)benzidine (NPB) are thermally evaporated as thin-films on two kinds of substrates with different hardness. By using nano-indentation techniques, the reduced elastic modulus of each of the coatings is measured. The data are carefully analysed through the standard Oliver and Pharr method, and the recently developed critical indentation depth method which takes the effect of the substrate more into account.

1. Introduction

Thin-films of organic luminescent molecules have been used in Light Emitting Diodes (LED) for two decades. Applications for lighting and small size displays are said to be approaching the cost and lifetime requirements of the electronics consumer market. Comparing their relatively low power consumption with other rivals such as inorganic LEDs in lighting or backlit liquid crystal devices in flat panel Liquid Crystal Displays (LCDs), the Organic Light Emitting Diode (OLED) distinguishes itself by having the potential to be mechanically flexible. Unlike LCDs and inorganic LEDs, OLEDs or printable polymer LEDs can be fabricated on a plastic substrate to make the device flexible, and amenable to roll-to-roll manufacture. It is therefore essential to understand how this rolling process might mechanically damage the multi-layer structured OLED, and studies towards this aim have appeared in the last 5 years. Most of these studies, however, have focused on what was estimated to be the most brittle layer in the structure – the commonly-used Indium Tin Oxide (ITO) layer as the anode [1,2]. However, study of the elasticity properties of the organic conducting and emissive layers is still rare in literature [3]; to obtain such information from a 100 nm thick thin-film is not a simple task. One method potentially able to perform this task is nano-indentation.

Nano-indentation has been used routinely in the mechanical characterization of thin-films and thin-surface layers in recent years [4]. The technique applies a programmed function of increasing and decreasing load to the surface of interest with an indenter of well-defined shape and continuously measures the indenter displacement. The advantage of this method is that mechanical information, such as elastic modulus, can be obtained through the analysis of the load–displacement behaviour alone with a coating of the material to be tested on a substrate made from different material. This makes it an ideal

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tool for our task. The technique has been used to assess the elastic and plastic properties of micron thick coatings on a range of substrates but there are limitations in measuring the properties of much thinner coatings, particularly when elastic properties are required [5,6]. For coatings of a few hundred nano-metres thickness it has been suggested that extrapolating the properties determined at a range of peak loads or indenter displacements to zero load/depth can be used to determine the coating only properties. With high quality, sharp indenters it is possible to assess coatings down to 100 nm thick by this method [7]. This has been attempted in this study.

2. Experimental

Among all the small molecules used in OLEDs, tris-(8-hydroxyquinoline) aluminum (Alq_3) (Fig. 1a) and *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)benzidine (NPB) (Fig. 1b) are two of the most popular materials. Because of the relatively high stabilities of the structures during operation and good electrical conductivities, they can be found in almost every OLED device structure. Therefore it is reasonable to expect that they would be used in the flexible OLED devices, too. So it is important to understand their elastic characteristic. In order to evaluate the effect of the substrate [8], two different kinds of substrates were used: polyethylene terephthalate (PET) supplied from DuPont Teijin Films and standard silicon wafers. All the substrates were cleaned in an ultrasonic bath with acetone, and then isopropanol for 5 min each. The substrates were then loaded into the Kurt J. Lesker Spectros II Deposition System. The tested materials were deposited under a vacuum of 5×10^{-7} mbar. Finally, the samples with 100 nm of Alq_3, 200 nm of Alq_3 and 200 nm of NPD on three individual PET substrates and samples with 100 nm of Alq_3, 100 nm of NPD on two silicon wafers were prepared, respectively (see Table 1).

The Young's moduli of the samples were measured by standard nano-indentation techniques. For each material nano-indentation tests were performed under open loop, load and displacement control with maximum displacements (h_{max}) from 10 nm to 1000 nm using a Hysitron Triboindenter fitted with a sharp Berkovich diamond indenter (tip end radius ~50 nm). In open loop control the indentation loading and unloading segments were controlled by timed ramps whereas in the other loading schemes feedback loops were used to ensure that the desired peak loads and displacements were achieved. The indentation systems frame stiffness and the diamond tip shape was carefully calibrated with a fused silica test sample, using the standard Oliver and Pharr method [9], before and after measurements with no change in either recorded. Nano-indentation load (P) *vs.* displacement (h) curves were then recorded for each indent and only those where evidence of plastic deformation was observed (i.e. the loading and unloading curves are different) were used in the analysis of Young's modulus by the Oliver and Pharr method [9]. The indenter displacement is in fact made up of two components: the plastic depth of the indent, or contact depth, and the elastic deflection of the surface at the edge of the contact. The relationship between the contact depth (h_c) and the maximum displacement (h_{max}) can be determined from Eq. (1):

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S} \tag{1}$$

where, P_{max} is the maximum loading, and ε is a constant that depends on the shape of the indenter [10]. Empirical studies have shown that for a Berkovich indenter, the typical value of ε is about 0.75. S is the unloading stiffness, which comes from:

$$S = \frac{dP}{dh}\Big|_{h=h_{max}} = mB(h_{max} - h_f)^{m-1} \tag{2}$$

where, m and B are fitting parameters, and h_f is the final displacement after completely unloading.

In this approach, S, the initial slope of the unloading curve, can finally be used to determine the reduced elastic modulus of the sample (effectively from the recovery of the elastic deflection of the surface) based upon the Sneddon flat punch solution [11] and the following equation:

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \tag{3}$$

where, A is the contact area which can be deduced from h_c based upon an accurate knowledge of the tip end shape, and β is a constant also depends on the geometry of the indenter (β = 1.034 for the Berkovich indenter) [10].

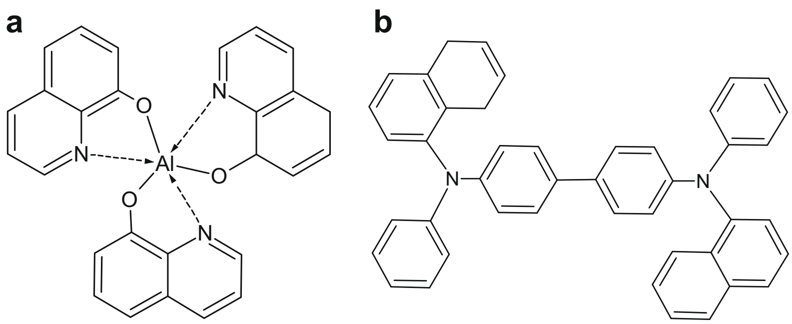

Fig. 1. (a) Structure of tris-(8-hydroxyquinoline) aluminum (Alq_3) and (b) *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)benzidine (NPB).