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Applied Surface Science 252 (2006) 2328–2333

applied surface science
www.elsevier.com/locate/apsusc

Photoluminescence spectroscopy study on tris (8-hydroxyquinoline) aluminum film

Y.F. Xu, H.J. Zhang, H.Y. Li, S.N. Bao, P. He [*]

Department of Physics, Zhejiang University, Hangzhou 310027, China

Received 20 February 2005; received in revised form 6 April 2005; accepted 6 April 2005
Available online 27 April 2005

Abstract

In situ photoluminescence spectroscopy (PL) measurements of tris(8-hydroxyquinoline) aluminum (Alq_3) film were carried out. Upon deposition of Alq_3 on the glass substrate, the PL intensity changes dramatically, while the peak position of Alq_3 emission shows a sharp red-shift from 524 nm at the initial deposition of Alq_3, and tends to a saturation value of 536 nm for the film thickness range from 2 to 500 nm. This red-shift is associated with the change from the 2D to 3D exciton state with increasing Alq_3 film thickness. Temperature dependent PL spectra of Alq_3 films showed, besides the changes in the PL intensity, clearly a blue-shift of Alq_3 emission about 9 nm for the film annealing up to 150 °C, while no any shift of Alq_3 emission was observed for the film annealing below 130 °C. Both changes in PL intensity, and especially in the peak position of Alq_3 emission were attributed to crystallization (thermal) effect of Alq_3 film upon annealing.

PACS: 78.66.Qn; 78.55.Kz; 81.40.Tv

Keywords: Tris(8-hydroxyquinoline) aluminum; Thin film; Photoluminescence; Thermal treatment

1. Introduction

Since its efficient luminescence and relative stability has been demonstrated by Tang et al. in organic light emitting diodes (OLEDs) [1,2], Tris(8-hydroxyquinoline) aluminum (Alq_3) is commonly used as the electron transport/emitting layer in OLEDs. Recently, much effort has been made on the device optimization, such as high luminescence efficiency, operation stability and color tuning [3–6]. The variation of morphology, molecular packing of Alq_3 thin film caused by elevated temperature have been demonstrated to be crucial factors in the stability and efficiency of OLEDs based on Alq_3 [7–9]. Higginson et al. reported that the annealed (more crystalline) Alq_3 thin film has greater stability to hydrolysis than the freshly sublimed one [7]. Kwong et al. demonstrated that the luminance efficiency and stability of the OLED devices with Alq_3 deposited at 100 °C were improved [8]. Trace amount of water in

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[*] Corresponding author. Tel.: +86 571 87953256;
fax: +86 571 87951328.
E-mail address: phypmhe@dial.zju.edu.cn (P. He).

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doi:10.1016/j.apsusc.2005.04.005

Alq_3 film could react with Alq_3 to form 8-Hq, and 8-Hq was facilitated by oxygen to yield a dark, non-emissive polymer, which can acutely reduce the intensity of photoluminescence and electroluminescence [9].

Contrary to the effort made in the application of Alq_3 based devices, the understanding of intrinsic properties of Alq_3 thin film is limited [7–11]. In this paper, we report in situ photoluminescence (PL) spectroscopy measurements of Alq_3 film. The results clearly show thickness dependence and effects of annealing on both the PL intensity and peak position of Alq_3 emission.

2. Experimental

The experiments were performed in a high-vacuum (HV) multilayer growth system with a base pressure less than 5×10^{-8} Torr. The system were equipped with a few organic and metal thermal evaporators, a sample holder with heater, and an optical fiber for outputting the optical signals from vacuum for PL measurements. The source light of Neoark DPS-5004 diode laser (405 nm, 35 mW) for PL measurements was directly delivered through a glass window to the sample. The PL spectra were collected with the USB2000 fiber optical spectrometer (Ocean Optics Inc.).

Thin films of Alq_3 were prepared by thermal evaporation of Alq_3 onto a glass substrate (slide). The glass substrate was firstly cleaned by conventional chemical method, and followed by heating to remove any contaminations in the HV chamber. Alq_3 powder was purified by preheating at about 150 °C, and deposited from a resistance-heating (tantalum boat) evaporator at a temperature of about 180 °C. The deposition rate was about $1 \sim 2$ nm/min. The substrate was held at room temperature. The thickness of Alq_3 film was monitored with quartz oscillator. The temperature dependence of PL spectra of Alq_3 film was measured with a temperature gradient of about 1 K/min in heating (cooling), and the sample temperature was monitored by NiCr/NiAl thermocouple.

3. Results and discussions

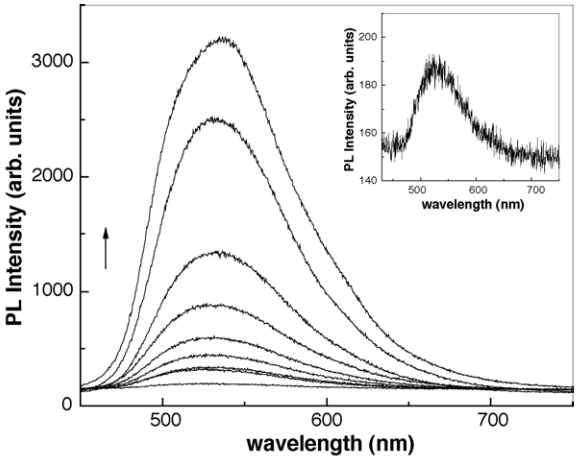

Fig. 1. PL spectra for Alq_3 film of different thickness collected with a laser source of wavelength 405 nm. Along the arrow direction, the thicknesses in turn are 2, 8, 12, 16, 22, 50, 100, 200 and 500 nm. The inset shows the PL spectrum of a 1 nm thick Alq_3 film.

Fig. 1 shows typical PL spectra of the Alq_3 film at room temperature. It shows clearly from the inset of Fig. 1 that there is a visible PL peak at about 524 nm with the Alq_3 film thickness of about 1 nm, approximately one molecular monolayer. Obviously, the PL intensity of the Alq_3 film increases with film thickness, and the position of the Alq_3 emission peak has a slight red-shift. The thickness dependences of the PL intensity and peak position are displayed in Fig. 2. With the Alq_3 film thickness increasing from 2 to 500 nm, the PL intensity showed an increase by a factor of 20 and the peak position shifts from about 524 to 536 nm.

As shown in Fig. 2a, the PL intensity of the Alq_3 emission increases sharply at the initial deposition of Alq_3, and tends to a saturated value with the Alq_3 film in the high thickness range. The increase of the PL intensity with thickness of the film is due to the fact that more molecules are involved in photoluminescence with thicker film. When the thickness of the film (in the high thickness range) reaches to a certain point, the PL intensity should approach a saturated value since the penetration of the excitation laser source into the Alq_3 film (bulk) should be limited. However, the PL intensity increases with the film thickness continuously and it showed a rate deference, as indicated by the arrow in Fig. 2a, i.e., the increasing rate is lower at the initial deposition of Alq_3 than that at the late stage. This low increasing rate at the initial deposition of Alq_3 could be related to the high probability of nonradiative decay caused by interaction of excitons with substrate [12].