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Enhanced luminescence properties of hybrid Alq_3/ZnO (organic/inorganic) composite films

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ABSTRACT

Pristine tris-(8-hydroxyquionoline)aluminum(Alq_3) and (Alq_3/ZnO hybrid) composites containing different weight percentages (5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%) of ZnO in Alq_3 were synthesized and coated on to a glass substrate using the dip coating method. The optimum concentration of ZnO in Alq_3 films to get the best luminescence yield has been identified. XRD pattern reveals the amorphous nature of pure Alq_3 film. The Alq_3 films containing different weight percentages of ZnO show the presence of crystalline ZnO in Alq_3/ZnO composite films. The FTIR spectrum confirms the formation of quinoline with absorption in the region 600 – 800 cm^{-1}. The hybrid Alq_3/ZnO composite films indicate the presence of Zn – O vibration band along with the corresponding Alq_3 band. The band gap (HOMO–LUMO) of Alq_3 film was calculated using absorption spectra and it is 2.87 eV for pristine films while it is 3.26 eV, 3.21 eV, 3.14 eV, 3.10 eV, 3.13 eV and 3.20 eV for the composite films containing 5–50 wt% of ZnO. The photoluminescence (PL) spectra of Alq_3 films show a maximum PL intensity at 514 nm when excited at 390 nm. The ZnO incorporated composite films (Alq_3/ZnO) exhibit an emission in 485 nm and 514 nm. The composite films containing 30 wt% of ZnO exhibit maximum luminescence yield.

1. Introduction

The electroluminescent devices based on organometallic semiconductor complexes are promising materials for high potential display applications from small area telecom devices to large area displays due to their high luminance, low fabrication costs and the ability to tune the emission wavelength. Organic light emitting diodes (OLEDs) assume importance in display technologies and lighting applications. An efficient organic electroluminescent (EL) device was first reported by Tang and Van Slyke [1,2] using tris (8-hydroxyquinoline)aluminum (Alq_3). Generally, metal quinolates are standard organic small molecules which are used to fabricate optoelectronic devices (OFET, OLEDs and OPVs). Alq_3 is a metal chelate that is commonly used as an electron transport layer and photoemitting layer in OLEDs. The absorption and emission in Alq_3 may happen due to transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbit (LUMO) [3]. OLEDs based on Alq_3 are quite sensitive to environment and photooxidation. This may lead to reduced stability and reduced luminescence efficiency of the devices [4–6]. One of the important factors for device fabrication is stability, balance charge carriers and encapsulation. Usually some of the organic electroluminescent materials have imbalances in charge carrier injection. When these charge carriers pass through emissive layer, they fail to recombine with the opposite charges, resulting in reduced light emission in the emissive layer and induce the Ohmic loss [7].

Hybrid (organic/inorganic) composite materials offer high mechanical strength, chemical resistance, thermal stability, electrical and optical properties [8,9]. The combinations of organic – inorganic hybrid materials result in better transport properties of charge carriers. It provides high potential to improve the capability of the device [10]. Coe et al. [11] reported an organic/inorganic hybrid device (organic polymers and II–IV semiconductor) to generate high external quantum luminescence (0.4) and intense luminescence (2000 cd/m^2). In the present work of preparing a composite containing Alq_3, we have selected zinc oxide (ZnO) due to its high oxygen vacancies and interstitial defects. It is expected that the incorporation of ZnO would improve the charge mobility and stability in ambient atmosphere [12]. Zhang et al. [13] reported that dispersion of ZnO nanorods in fluorescent dye doped polymer nanocomposites has enhanced the hole current density with a balanced current injection.

In this work Alq_3 in pure form and Alq_3 incorporating different weight percentages (5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt% and

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50 wt%) of ZnO (hybrid Alq_3/ZnO composite) were synthesized. These were coated on to a glass substrate using the dip coating method to obtain a thin film for possible OLED applications. The Alq_3 films exhibit enhanced luminescence intensity with the addition of ZnO particles. This paper reports the result obtained on films of Alq_3/ZnO composite and their optimization.

2. Experimental

Alq_3 and ZnO have been synthesized by the precipitation method as reported elsewhere [14,15]. The chemical reaction for the synthesis of Alq_3

$$C_9H_7NO + Al^{3+} + OH^- \rightarrow C_{27}H_{18}AlN_3O_3\downarrow + H_2O$$

Alq_3 and Alq_3/ZnO composite films were coated using the dip coating method. The as-prepared Alq_3 and ZnO (5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%) were dissolved in 100 ml ethanol (C_2H_5OH) with addition of four drops (~0.2 ml) of con. HCl. The solution was continuously stirred at 70 °C for an hour. Alq_3/ZnO films were coated on to a glass substrate at a withdrawal speed of 15 cm/min. The film after each coating (each layer) was dried in an atmosphere of air and was treated at 150 °C for five minutes. Totally 10 layers have been coated. Finally the 10 layer films were annealed for an hour at 150 °C. Thickness of the film was calculated using ellipsometry. The 10 layer film was estimated to be of 220 nm thickness. X-ray diffraction (XRD) analysis was performed using PANalytical XPERT-PRO X-ray diffractometer with Cu K_α incident beam (λ=0.1540 nm). FTIR spectra have been recorded using a Perkin-Elmer Spectrum BX-II spectrometer in the range of 400–4000 cm^{-1}. Surface morphology of Alq_3 and Alq_3/ZnO film was investigated using Tescan VEGA-3 LMU scanning electron microscope. The absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrophotometer in the range of 200 – 1100 nm. Photoluminescence studies were carried out using a Perkin-Elmer LS 55 luminescence spectrometer in the region 200 – 900 nm at room temperature.

3. Results and discussion

XRD patterns of pure Alq_3 film and ZnO incorporated composite (Alq_3/ZnO) films are shown in Fig. 1. The small organic molecule (Alq_3) on the glass substrate exhibits amorphous nature [16] as seen from Fig. 1a. The composite film containing 5–50 wt% of ZnO reveals crystalline nature (Fig. 1(b – g)). XRD pattern yields a single peak indicating incorporation of ZnO in Alq_3 in a preferential manner. The Alq_3/ZnO composite films yield a sharp single diffraction peak at 2θ=31.8°. The observed diffraction peak corresponds to ZnO along (1 0 0) (JCPDS card no. 36-1451) [17]. This confirms the presence of crystalline ZnO in Alq_3/ZnO hybrid composite material. The increase in intensity with increased concentration of ZnO is probably due to the addition of mass. The absence of peaks corresponding to Alq_3 indicates that the matrix does not show any change in its structural arrangement as a result of ZnO addition. The XRD pattern of 50 wt% Alq_3/ZnO composite film shows one more low intensity diffraction peak. It exhibits the presence of crystalline ZnO with diffraction peaks at 2θ=31.8°and 66.3°. The observed diffraction peaks of ZnO along with the orientation planes (1 0 0) and (2 0 0) (JCPDS card no. 36-1451). The XRD results indicate that the ZnO particles are incorporated in to Alq_3 with preferential orientation along the '*a*' axis [18].

The FTIR spectra of thin films of pure Alq_3 and hybrid Alq_3/ZnO composite are shown in Fig. 2. A broad band observed around 3414 cm^{-1} is due to characteristic OH stretching vibration. The band at 3047 cm^{-1} is attributed to stretching vibration of C–H bond in the Alq_3 aromatic ring. The band at 1601 cm^{-1} is assigned to stretching vibration of C═C bond. The prominent bands at 1582, 1491 and 1425 cm^{-1} are due to conjugate action of aromatic rings in the Alq_3 molecule. The characteristic bands at 1370–1250 cm^{-1} indicate the presence of aromatic amine resonance (C–N–C bond) [14,19]. The bands in the region 600–800 cm^{-1} are attributed to the vibrations of quinoline and Al ions. The composite films (Fig. 2b, c) exhibit the presence of new stretching vibration bands at 420 cm^{-1} and 460 cm^{-1}. These bands reveal the incorporation of ZnO in the composite films as shown in the inset of Fig. 2(top right). The composite films indicate the presence of metal oxides (Zn–O) along with the corresponding vibration of quinoline and Al ion. Xia Lu et al. [20] reported the vibration band of Zn–O in the region 400–500 cm^{-1}. The presence of ZnO and quinoline were observed in all the composites films. The incorporation of ZnO molecule in Alq_3/ZnO composite films has been confirmed through both FTIR and XRD studies.

Fig. 3 shows the surface morphology of pure and ZnO incorporated Alq_3 composite films recorded at an accelerating potential of

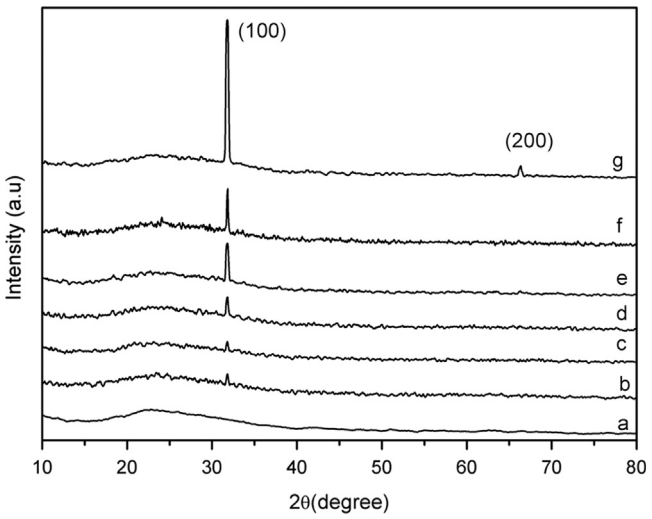

Fig. 1. XRD patterns of pure Alq_3 and Alq_3/ZnO composite films: (a) pure Alq_3 containing, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%, (e) 30 wt%, (f) 40 wt%, and (g) 50 wt% of ZnO.

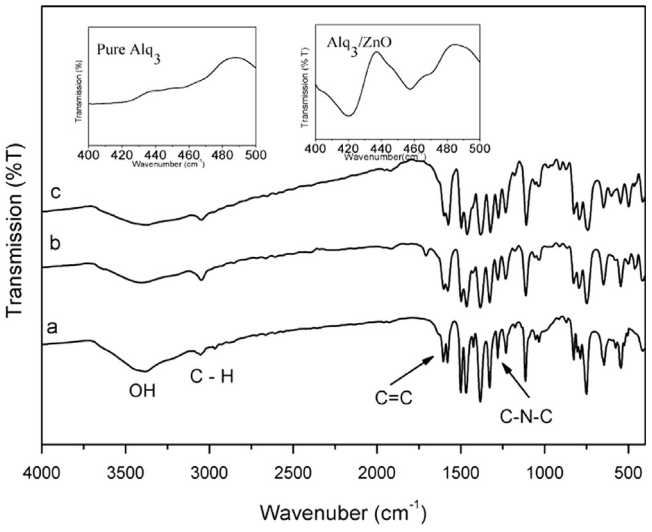

Fig. 2. FTIR spectra of pure Alq_3 and Alq_3/ZnO composite films: (a) pure Alq_3, (b) 30 wt% Alq_3/ZnO, and (c) 50 wt% Alq_3/ZnO. Inset: Pure Alq_3 (left top) and Alq_3/ZnO (right top), in the range of 400–500 cm^{-1}.