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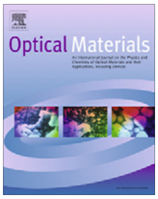

Ultraviolet photodegradation of tris(8-hydroxy-quinolinate) aluminum (Alq_3) thin films studied by electron and laser stimulated desorption

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ABSTRACT

Alq_3 has been the reference material used widely in the fabrication and characterization of efficient OLEDs due to its good properties as electroluminescent and electron transporting layer. Although the inclusion of these devices in commercial displays and lighting devices represents many benefits, the knowledge about the progressive loss of performance and efficiency with time for such devices is still limited. Therefore, it is an incentive to understand the mechanisms of Alq_3 degradation when it is subjected to the influence of various extrinsic factors such as UV radiation. In the present work the degradation processes of Alq_3 thin films as a result of 254 nm UV light irradiation are presented and discussed. The degradation products produced by the action of UV light were evaluated by time-of-flight mass spectrometry using electron stimulated ion desorption and laser desorption ionization techniques. Strong evidence for carboxylic acid formation after photodegradation was observed by the electron desorption technique.

1. Introduction

In 1987 Tang and VanSlyke described the first efficient organic electroluminescent diode employing 8-hydroxyquinoline aluminum (Alq_3) as the luminescent film of the device [1]. Since then, there is abundant literature that shows the use of Alq_3 as electroluminescent or electron transporting layer in Organic Light-Emitting Diodes (OLEDs) with high quantum efficiency and thermal and chemical stability. However, aspects of interest related to the degradation processes induced by intrinsic and extrinsic factors such as sunlight, humidity, temperature and others are still not completely understood. The comprehension of these processes is one of the keys for the full commercial application of this technology.

The incidence of UV light on Alq_3 is an extrinsic effect that may contribute to decrease the lifetime of Alq_3 based-devices. Some studies have estimated the possible degradation mechanisms that lead to the loss of the electroluminescent properties [2–5]. The evolution of a vibrational band at 1697 cm^{-1} in the infrared spectrum of Alq_3 films exposed to UV light suggested the formation of a carbonyl group [2].

In a recent work the degradation of Alq_3 films due to different UV exposures were followed by photoabsorption and photoemission techniques. Comparative studies between exposed and unexposed Alq_3 thin films showed larger degradation processes when Alq_3 is exposed to 254 and 365 nm UV radiation, as observed by total signal intensity of NEXAFS (Near-edge X-ray Absorption Fine Structure) results at the carbon and nitrogen 1s edges [6]. Core level photoemission measurements after 307 nm UV exposure show dramatic changes for nitrogen, oxygen and carbon photoelectric signals [6]. The effects of sunlight radiation on Alq_3 thin films was also investigated using valence and core level spectroscopic techniques [7,8].

Another mechanism reports the catalytic role of water molecules found in the environment, which favor the loss of the 8-hydroxyquinoline ligand (8-Hq) of the molecular structure of Alq_3 and the formation of intermediary compounds [9–11]. 8-Hq develops into a dark-colored, non-emissive polymer compound due to oxidative polymerization. This is an important factor, since many studies are carried out on open atmosphere.

As a part of a systematic study of the influence of extrinsic effects on molecular films used in OLEDs, we employed time-of-flight mass spectrometry coupled to electron stimulated ion desorption (ESID-TOF) and laser desorption ionization (LDI-TOF) techniques in order to raise the knowledge about the Alq_3 degradation mechanisms. To perform this work, 100 nm thin films of Alq_3

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were deposited on silicon substrates and subjected to UV light irradiation at 254 nm for 16 h. Comparative studies were performed between exposed and non-exposed films by ESID and LDI analysis with the aim to produce insight into the degradation mechanisms.

2. Experimental details

Alq_3 samples were produced as films of about 100 nm thick by resistive thermal deposition over silicon substrates with deposition rates of 0.1–0.3 nm/s, in a UNIVEX 300 model LEYBOLD system.

The ESID-TOF measurements were performed in a home-made linear time-of-flight mass spectrometer (TOF-MS) which basic components are an electron gun and a commercial manipulator coupled to an ultra-high vacuum (UHV) chamber at 10^{-9} mbar base pressure. The TOF-MS consists basically of an electrostatic ion extraction system, a collimating electrostatic lens, a 25 cm drift tube and a pair of microchannel plate (MCP) detectors, disposed in a chevron configuration. The electron beam energies range between 5 and 1000 eV and it can be pulsed (pulsed current c.a. 6 nA/cm^2) [12,13]. The samples were fixed onto the *XYZ* manipulator with double sided carbon conductive tapes and submitted to a potential of +1200 V. The pulsed electron beam of 1000 eV energy had a frequency of 80 kHz and a minimal pulse width of 20 ns. The final electron energy results from the potential difference between the sample and the electron gun cathode, in the present work achieving 2200 eV. A pulse generator simultaneously provides a signal to the control grid of the electron gun, thus creating the pulsed electron beam, and a logic start signal to the time-to-digital converter (TDC). The output signal of the detector was processed by standard pulse electronics and used to provide a stop signal to the TDC, which has a time resolution of 1 ns per channel.

The LDI-TOF study was conducted with the aid of a commercial model Biflex III spectrometer manufactured by Bruker. The area illuminated by the N_2 laser pulse was 4.10 cm^2 with a wavelength of 337 nm and pulse width of 3 ns. Ion extraction was made possible by applying a potential of about +30 kV at the metal holder and ion acceleration by a grounded special electrode, grid type, SCOUT model.

The films were exposed during 16 h under ultraviolet commercial lamp at 254 nm wavelength and with 85 mW/cm^2 power density. The distance between the sample and the lamp was 0.5 cm and the irradiation was carried out at room atmosphere. At the end of the irradiation period no more Alq_3 fluorescence emission could be observed. The sample temperature didn't increase during the experiment.

3. Results and discussion

3.1. Electron stimulated ion desorption time-of-flight (ESID-TOF)

Ionic desorption following high energy electron impact can be well understood taking into account the Auger Stimulated Ion Desorption (ASID) mechanism. The Auger mechanism, which dominates for light elements and can be described in a simplified form as a relaxation process following ionization (normal Auger) of a core electron, may produce localized positive holes in valence orbitals, and as a consequence ionic species will desorb due to strong coulombic repulsion. Electron stimulated ion desorption (ESID) studies coupled to time-of-flight mass spectrometry were performed on non-exposed and exposed Alq_3 thin films, covering up to 160 u. For better visualization Fig. 1 shows as-prepared (solid line) and exposed to 254 nm UV light (short-dot line) Alq_3 ESID data, covering two sets of *m/z*: (a) 40–80 and (b) 80–160. The low mass range was also measured but since this region shows no relevant differences between both films, except for peak at *m/z* 31 observed for the exposed film, it will not be presented here. Peaks at *m/z* 31 and 47 may be related to OCH_3^+/CH_2OH^+ and $CH_3O_2^+$, respectively. Some definitions are in order: the total charge of the ions is represented by *q*, the electron charge by *e* and the number of charges on the ions by *z*: $q = ze$, where *m/z* represents the mass-to-charge ratio. In mass spectrometry, masses are generally expressed in u (atomic mass units).

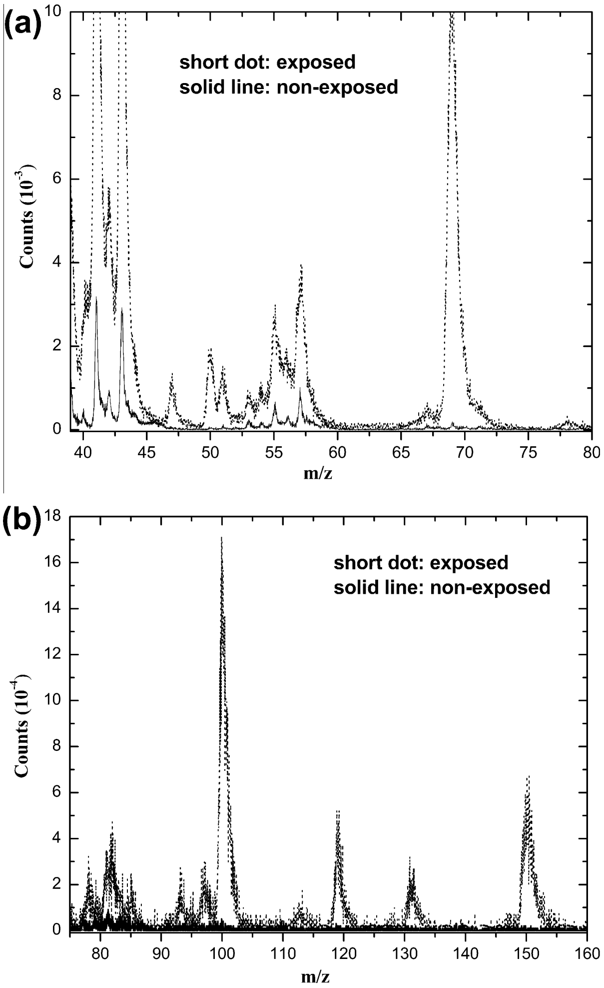

Fig. 1. ESID spectra of Alq_3 film "as-prepared" (solid line) and exposed to 254 nm UV light (short-dot line), covering different *m/z* ranges: (a) 40–80 and (b) 80–160.

The exposed Alq_3 ESID spectrum shows a wealth of peaks as compared to the non-exposed one, especially for heavier fragment ions. Recently experimental and theoretical investigations on the stability of tris(8-hydroxy-quinoline) aluminum (Alq_3) under UV photodegradation pointed out to the most likely degradation products by the analysis of Gibbs free energy calculations and by comparing theoretical and experimental IR spectra [2]. Among the suggested degradation products, the one involving the breaking of Al–O bond was considered unlike, since its theoretical IR spectrum showed poor agreement with experiments. Other suggested products involve keeping the Al–O bond and breaking the phenoxide ring, furnishing theoretical IR spectra that match quite well to the experimental results. As a conclusion the formation of carboxylate groups bound to Al as a result of photodegradation was suggested [2].

Our first step was to check if the fragmentation patterns measured by ESID could corroborate the previous degradation products discussed in the literature. The evolution of a group of ions for *m/z* between 50 and 57 in the spectrum of Alq_3 exposed to UV light shown in Fig. 1a is significant in opposition to their practically