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Evolution of optical properties of tris (8-hydroxyquinoline) aluminum (Alq₃) with atmosphere exposure

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ABSTRACT

Tris (8-hydroxyquinoline) aluminum (Alq₃) represents a material of significant interest for electron transport and/or light emitting layer applications in organic light emitting diodes (OLEDs). In spite of advances in Alq₃ based devices, the knowledge and understanding of the optical properties of Alq₃ and its chemical and environmental stability is still limited. With the reports of decreased turn-on voltage and increased efficiency of OLEDs, the issues of lifetime and stability of those devices are attracting increasing attention. The degradation of Alq₃ based OLEDs and dark spots formation and growth have been intensively studied. The studies on degradation of optical properties of Alq₃ itself remain scarce. We have investigated effects of atmosphere exposure to properties of tris (8-hydroxyquinoline) aluminum (Alq₃) thin films by photoluminescence (PL) and absorption measurements. Alq₃ films were evaporated on glass substrates at different temperatures. The influence of annealing to the environmental stability of the films has also been investigated. It has been found that deposition at higher substrate temperature and annealing of the samples deposited at room temperature yields improvement in environmental stability of the films, i.e. less decrease of the PL intensity over time with atmosphere exposure, as well as increased PL intensity. To investigate further effects of the air exposure, films deposited at room temperature were stored for four days in air, nitrogen, and oxygen. No decrease in PL intensity has been found for storage in nitrogen, while decrease for the film stored in oxygen was smaller than that for film stored in air, indicating that both humidity and oxygen play a role in PL intensity decrease in Alq₃ thin films.

Keywords: Tris (8-hydroxyquinoline) aluminum, photoluminescence

1. INTRODUCTION

Tris (8-hydroxyquinoline) aluminum (Alq₃) is a material commonly used as electron transport and/or emitting layer in organic light emitting diodes (OLEDs). While Alq₃ based OLEDs have been extensively studied in terms of performance and stability, studies of the material properties of Alq₃ films have been scarce. It was found recently that Alq₃ crystallizes in different polymorphs.¹⁻⁴ Temperature was found to be a significant parameter which controls the selection of the phases. However, vacuum deposited Alq₃ thin films are amorphous.¹⁻³ Amorphous nature of the films deposited at substrate temperatures in the range from 30°C to 150°C was verified by X-ray diffraction.³ It was found that, for substrate temperature below 125°C, the films consist of small spherical domains whose size increases with temperature.³ For the substrate temperature 150°C, a mosaic of polyhedra was observed, while for substrate temperatures above 150°C desorption process dominates. Amorphous nature of the films results in large distribution of the possible molecular packings. An explanation that the intrinsic disorder in the Alq₃ films may originate in the existence of two stereoisomers has also been proposed.⁵ It was found that partial crystallization occurs in the thin films exposed to atmosphere for several weeks, while no crystallization was found upon exposure to water saturated atmosphere for several hours.⁵

Previous studies of photoluminescence (PL) of Alq₃ films⁶⁻⁸ observed decay of PL signal with atmospheric exposure and proposed likely chemical reactions causing this deterioration. Papadimitrakopoulos *et al.*⁶ have demonstrated that the PL intensity reduces with annealing of Alq₃ film at 175°C, which is slightly above the glass transition temperature of Alq₃. They have found that the annealed films exhibited better environmental stability at the expense of decreased PL intensity. However, if annealing time was 21.5 min, the PL efficiency was increased compared to the sample annealed for

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16.5 min. and slight blue shift can be observed.^{7,8} This was attributed to efficient Rayleigh scattering on crystalline grains for shorter wavelengths.⁸ Qin et al.⁹ have measured PL of Alq₃ films deposited on quartz glass at 77K, 298K, and 438K. They have found that the PL intensity of the film deposited at 438K was higher than that of the film deposited at room temperature (298K). Efficiency of an OLED with Alq₃ deposited at 438K was also significantly higher (0.58 Cd/A compared to 0.2Cd/A) even though current was lower which was attributed to the increased roughness of Alq₃ films at 438K and hence worsened contact area between Alq₃ and the metal cathode.⁹ Increased efficiency and stability of OLEDs using Alq₃ grown at substrate temperature of 140°C has been reported,¹⁰ which was attributed to better crystallinity of the film. This statement was based on the hypothesis that pre-crystallized film would not undergo additional crystallization and hence fewer gaps or pinholes would be created by phase transformation during operation. Changes in the absorption spectrum with exposure to atmosphere were studied previously by Aziz and Narasimhan^{11,12} for samples deposited at room temperature only. To our knowledge, there have been no reports on changes in the absorption spectrum with exposure to atmosphere for either samples deposited at higher substrate temperatures or samples annealed at higher temperatures.

The objective of this work is to study the environmental stability of the Alq₃ thin films. We have studied the evolution of photoluminescence and absorption spectra over time with exposure to air of Alq₃ films. The films have been prepared by thermal evaporation on glass substrates. We have investigated the effects of the deposition temperature, and prepared samples deposited at room temperature and 100°C. We have also investigated the effects of annealing the films deposited at room temperature at 100°C and 150°C. To investigate whether the observed degradation of Alq₃ films is due to moisture or oxygen or their combined effects, we have performed the measurements immediately after deposition, and compared the results with the films which have been stored for five(four) days in vacuum, air, nitrogen, and oxygen. We have found that the films deposited or annealed at higher temperatures exhibit improved environmental stability. The deterioration of the optical properties is most likely due to combined effects of moisture and oxygen, since the films stored in pure oxygen also exhibit degradation, but different from the films stored in air. We have also found that annealing improves the PL intensity.

2. EXPERIMENT

Alq₃ films were deposited by thermal evaporation on quartz or microscope slide glass substrates. Films were made using either high purity Alq₃ from Aldrich Prior evaporation, the substrates have been cleaned, first by rubbing with cotton and acetone, cotton and ethanol, then in ultrasonic bath for 10 minutes in acetone, ethanol, and deionized water, respectively, and blow dried in nitrogen. The films have been evaporated in high vacuum. Pressure during evaporation was of the order 10⁻⁴ Pa. The evaporation rate was 1-2 Å/s. The distance from source to film is about 23 cm to ensure uniformity of film thickness, and the substrate holder is rotating (rotation speed is 7 revolutions per second). The thickness of the films has been controlled using quartz thickness monitor TM 400, Maxtek Inc. The annealing of the annealed samples has been performed in vacuum for one hour. Absorption spectra were measured using Hewlett Packard 8453 UV-Vis spectrometer. Photoluminescence spectra were recorded using Perkin Elmer Instruments LS50B Luminescence Spectrometer for excitation wavelengths 350 nm.

3. RESULTS AND DISCUSSION

Figure 1 depicts the change in the absorption spectra with atmospheric exposure for 100 nm Alq₃ film deposited on unheated substrate. The inset shows enlarged area below the first absorption band. It can be observed that the absorption increases for wavelengths above 400 nm. The intensity of the absorption peak in UV region is decreased. The result for the sample on unheated substrate is in agreement with the result of Aziz and Narasimhan¹¹ who observed that the absorption below 2.5 eV was significantly increased after 3 days of exposure to atmosphere. Figure 2 depicts the change in the absorption spectra with atmospheric exposure for 100 nm Alq₃ film deposited at the substrate temperature of 100°C. It can be observed that the increase in subgap absorption with the atmosphere exposure is smaller for the film deposited at higher substrate temperature. The subgap absorption is increasing with the decreasing substrate temperature, which is also in agreement with the results of Aziz and Narasimhan.¹² However, they have not studied influence of the atmosphere exposure to the absorption spectrum of films deposited at heated substrates. The behavior of the absorption spectra upon atmosphere exposure for the films annealed at 100°C and 150°C is similar to the behavior of the films deposited at 100°C. Two explanations have been proposed in the literature for the existence of subgap absorption: localized gap states due to potential fluctuations^{12,13} and existence of defects.¹³ The facts that purification reduces subgap absorption¹³ and that subgap absorption increases with atmosphere exposure indicate that defect/impurity states play a role in this phenomenon.

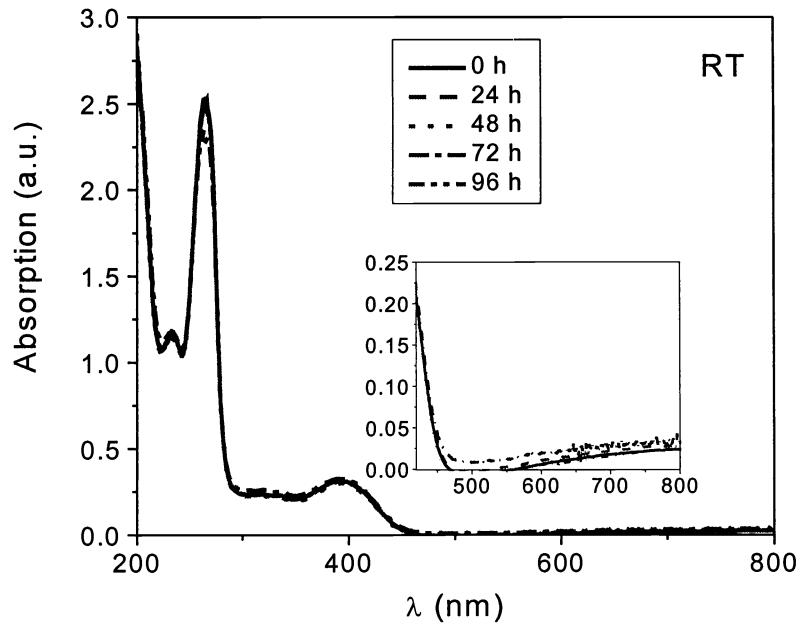


Figure 1 Changes in the absorption spectrum for Alq₃ film deposited on unheated substrate with atmospheric exposure. The inset shows enlarged region below first absorption band.

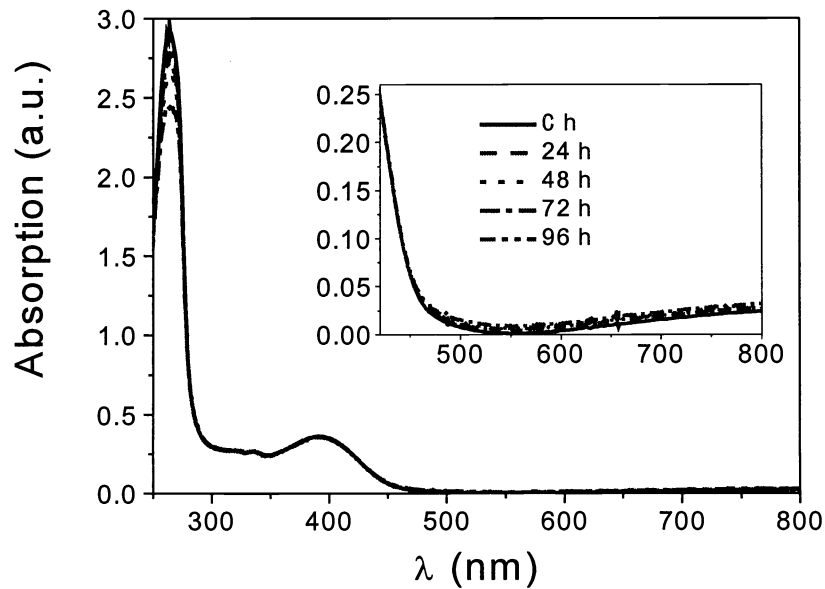


Figure 2 Changes in the absorption spectrum for Alq₃ film deposited on substrate kept at 100°C with atmospheric exposure. The inset shows enlarged region below first absorption band.

Figure 3 shows the PL spectra of a 100 nm thick film of Alq₃ deposited on unheated substrate. Significant drop in the PL efficiency (about 40% reduction) after 96 hours of exposure to atmosphere can be clearly observed. The initial decrease within first 24 hours is the largest, which is in agreement with the results obtained by Yang *et al.*¹⁴ The excitation wavelength is 350 nm. Similar results have been obtained with the excitation wavelength of 300 nm. Since there is no decrease in the absorption at the excitation wavelength, the reduction in PL intensity cannot be attributed to the decrease in excitation light absorbed. The samples deposited at higher substrate temperature and the annealed samples exhibit slower

decay of the PL intensity compared to the sample deposited at unheated substrate. In addition, the annealed samples and the sample deposited at 100°C show increased PL intensity. The best result was obtained for annealing at 150°C. Changes in the PL spectra with atmosphere exposure for the sample annealed at 150°C are shown in Fig. 4.

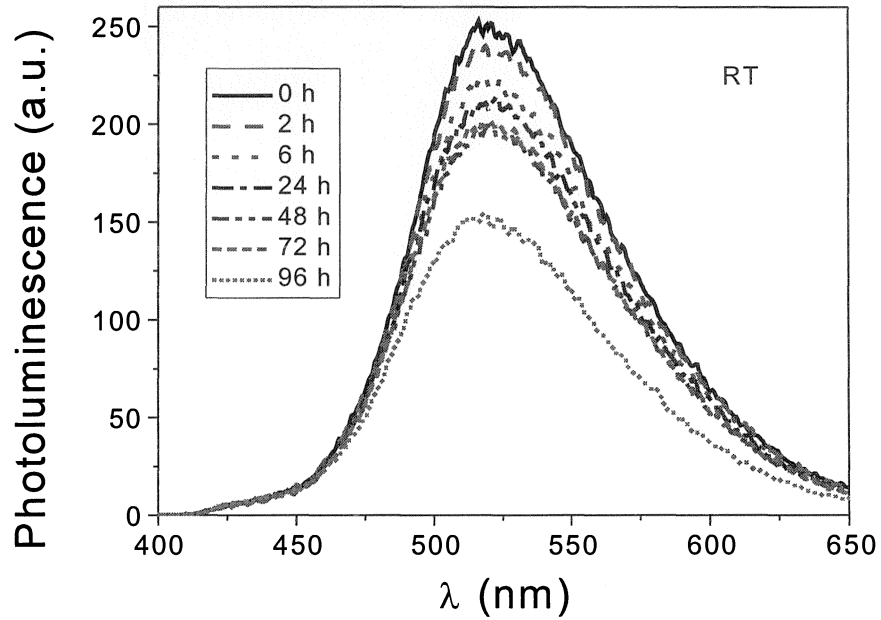


Figure 3 Changes in photoluminescence spectrum for 100 nm thick film of Alq₃ deposited on unheated substrate 0 h-96 h after deposition with an excitation wavelength of 350 nm.

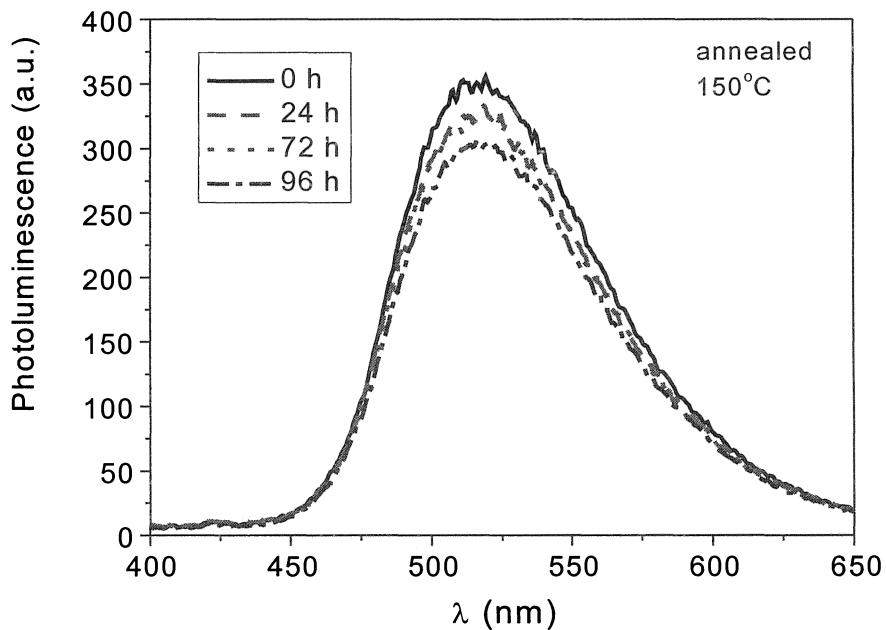


Figure 4 Changes in photoluminescence spectrum for 100 nm Alq₃ film deposited on unheated substrate which was subsequently annealed 150°C 0h-96 h after deposition.

A slight blue shift (~5-10 nm) for the samples deposited at 100°C, as well as for the annealed samples, can be observed. This is in agreement with the result of Higginson *et al.*⁸ who attributed the observed blue shift in annealed samples to more efficient Rayleigh scattering on crystalline grains for shorter wavelengths.⁸ Slight narrowing and blueshift of the PL with the increase of substrate temperature has also been reported by Brinkmann *et al.*³ The increase in PL intensity with higher deposition temperature is in agreement with the results of Qin *et al.*⁹ who found that the PL intensity is higher for the samples deposited at 438K compared to samples deposited at RT. The difference between our results and the results by Qin *et al.*⁹ compared to other results⁶⁻⁸ concerning PL efficiency of Alq₃ films with higher crystallinity is due to difference in annealing conditions by Papadimitrakopoulos *et al.*⁶⁻⁸ The annealing temperature in their study was 175°C, and the longest annealing time in their study was 21.5 min and efficiency is compared to the film annealed for 16.5 min. In both our study and the study of Qin *et al.*⁹ annealing and/or deposition temperature is below the glass transition temperature for Alq₃ films.

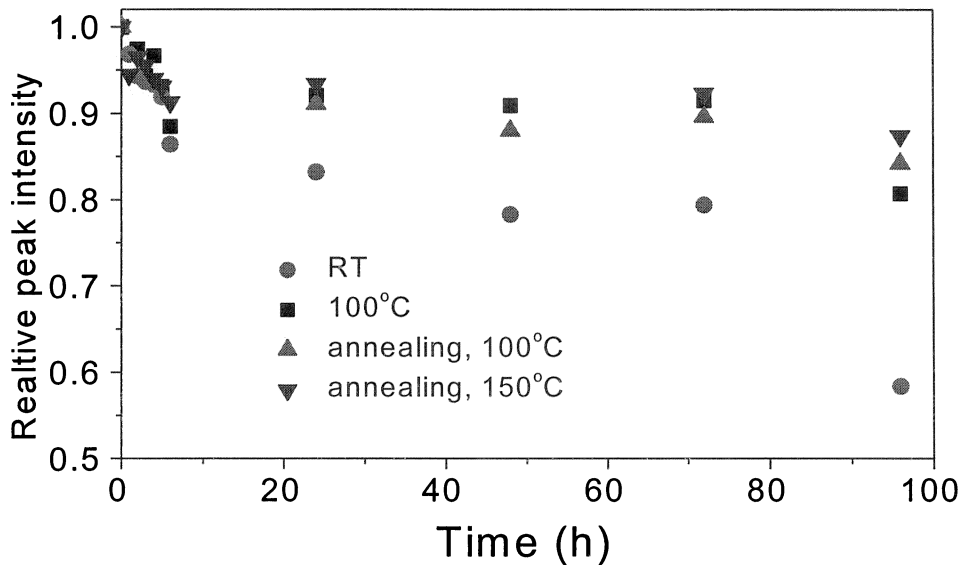


Figure 5 Normalized photoluminescence peak intensity vs. time of exposure to atmosphere for Alq₃ film deposited on unheated substrate (circles), substrate kept at 100°C (squares), film annealed at 100°C (up triangles), and film annealed at 150°C (down triangles).

Figure 5 shows normalized PL peak intensity vs. time of exposure to atmosphere for the samples deposited or annealed at different temperatures. It can be observed that for the as-deposited sample grown on unheated substrate the PL intensity decreases to 58% of its original value after 96 hours of atmospheric exposure, while for the sample annealed at 150°C the PL intensity decreases to 87% of its original value after 96 hours. All samples which are either deposited or annealed at higher temperature exhibit improved environmental stability and the PL intensity above 80% of the original value. Therefore, annealing of the samples significantly improves their environmental stability. The proposed explanation of slower degradation of annealed samples was higher degree of crystallinity.⁶ Material within crystallites is comparatively less accessible to moisture and hence higher crystallinity samples are less susceptible to chemical decomposition due to moisture.⁶ Since it has been established that the samples deposited at temperatures 30°C-150°C are amorphous,³ the explanation of the increased crystallinity is not applicable to the samples studied in this work. Possible explanation for the increased environmental stability deposited or annealed below the glass transition temperature of Alq₃ may be that the differences in the surface morphology for different substrate temperatures^{3,9} influence resistance of the film to the penetration of air and moisture. It has also been found that the nitrogen to carbon (N/C) ratio in Alq₃ films is dependent on the deposition rate.¹⁵ Annealing at 90°C also changed the N/C ratio.¹⁵ It is possible that the deposition at different substrate temperatures or subsequent annealing may also result in differences in the composition of Alq₃ films. Both of these effects, i.e. different degree of crystallinity/different surface morphology and possible difference in N/C ratio, may contribute to observed different change in optical properties with atmospheric exposure for films exposed to higher temperatures. Obtaining optimal performance of the annealed Alq₃ films would clearly require optimization of both annealing temperature and annealing time.

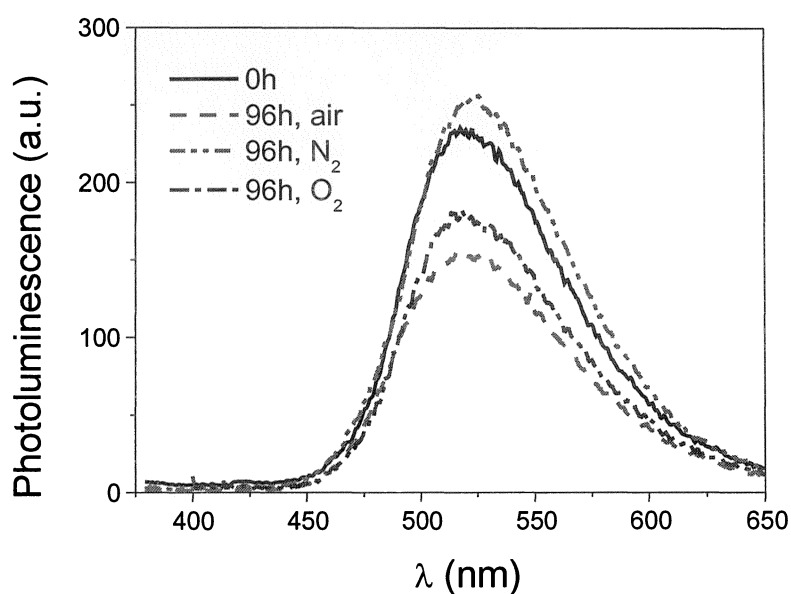


Figure 6 Photoluminescence spectrum for Alq₃ films deposited on unheated substrate immediately after deposition (solid line), after 96 hours in air (dashed line), 96 h in nitrogen (dotted line), and 96 h in oxygen (dash-dot line).

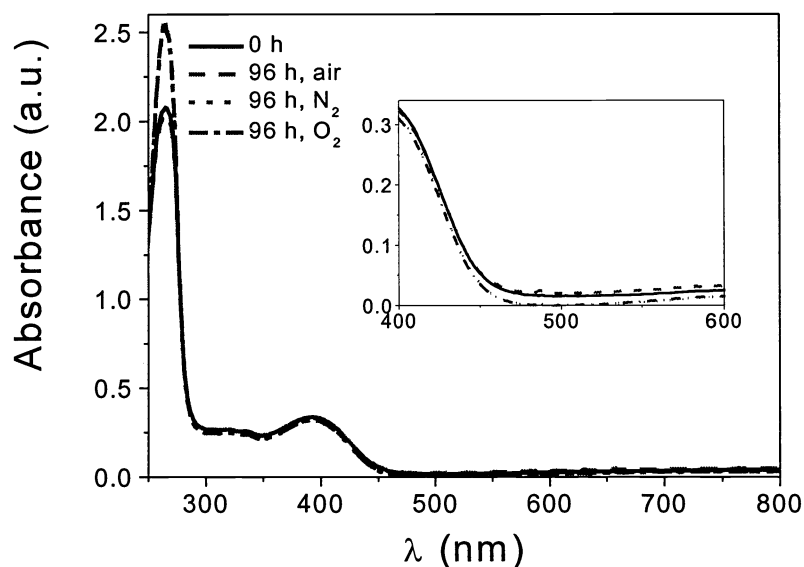


Figure 7 Absorption spectrum for Alq₃ films deposited on unheated substrate immediately after deposition (solid line), after 96 hours in air (dashed line), 96 h in nitrogen (dotted line), and 96 h in oxygen (dash-dot line).

To investigate the influence of air vs. the influence of dry oxygen on the PL spectrum of Alq₃, we have fabricated the 100nm thick Alq₃ films and stored them in vacuum, nitrogen (99.999% purity), oxygen (99.97% purity), and air. Figure 6 shows the PL spectrum of Alq₃ films immediately after deposition, stored in nitrogen for 96 h, stored on oxygen for 96 h, and stored in air for 96 hours, while Fig. 7 shows the corresponding absorption spectra. Sample stored in vacuum was not shown for clarity since it does not show any observable change. All four samples have been prepared during the same deposition process, since four substrates can be placed on the sample holder. It can be observed that there is no decay of the PL intensity for sample stored in nitrogen, while the samples stored in oxygen and air show decrease of the PL intensity.

The decrease in the PL intensity for the sample stored in oxygen is smaller than for the sample stored in air. Samples stored in oxygen and nitrogen show lower subgap absorption than the films stored in air. The obtained result supports the hypothesis that both oxygen and moisture contribute to the degradation of Alq₃ thin films. It has been found that dry oxygen has little effect on I-V characteristics of Alq₃ based devices, while air causes strongly rectifying I-V behavior at significantly reduced currents, attributed to decrease in carrier mobility.¹⁶ However, influence of the dry oxygen on the optical properties of Alq₃ has not been studied previously. We have shown that, while PL intensity of the films stored in dry oxygen decays, the decay is smaller than for the films stored in air which strongly indicates that oxygen alone is not sufficient to explain the degradation of Alq₃ films. This is in agreement with the proposed chemical reactions for Alq₃ degradation,⁶⁻⁸ where 8-hydroxyquinoline is formed in reaction between Alq₃ and water, which is further oxidized into brown, non-emissive polymer (**III**). When thin film of **III** was intentionally inserted in an OLED, no noticeable change in absorption was observed, while PL diminished by 50%.

4. CONCLUSION

To summarize, we have investigated influence of the atmospheric exposure to the Alq₃ films prepared under different conditions (deposited on unheated substrates, substrates kept at 100°C, annealed for 1h at 100°C, and annealed for 1h at 150°C) using photoluminescence (PL) and absorption measurements. We have found that both deposition at higher substrate temperature and the annealing of the samples improve their environmental stability. Annealing of the samples also improves the PL intensity compared to as-deposited samples. After four days of exposure to atmosphere, the PL peak of the film annealed at 150°C is 87% of its initial intensity, compared to 58% for the as-deposited sample. We have also investigated changes in the optical properties of samples kept in different atmospheres: air, nitrogen, and oxygen. As expected, the samples kept in nitrogen did not exhibit any PL decay, while samples kept in oxygen showed smaller decay than the samples kept in air. This indicated that both oxygen and moisture play a role in the degradation of Alq₃.

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