Polarized photoluminescence of Alq_3 thin films obtained by the method of oblique-angle deposition

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Abstract. We show that the degree of linear polarization of the photoluminescence of tris-(8-hydroxyquinoline)aluminium (Alq_3) thin film can be increased by about 10 times, using a method of oblique-angle deposition. This is due to greater ordering of molecular alignment in this thin film.

Keywords: tris-(8-hydroxyquionoline) aluminium, photoluminescence, polarization, oblique-angle deposition, thin films

UDC: 535.37, 535.518, 539.2

1. Introduction

Organic light-emitting diodes (OLEDs) are extensively investigated and commercialized. One of the most pressing problems in OLED technology is obtaining diode structures which produce polarized emitted light with a dichroic ratio larger than 40 [1]. Polarized light has a wide range of applications such as anti-glare and 3D displays, encrypted transport, optical communications, stereoscopic projection systems and biomedicine [1–3].

Tris(8-hydroxyquinoline)aluminium(III), which is commonly known as Alq_3, is a material widely used in OLEDs [4]. It has been shown in Ref. [5] that the refractive index of Alq_3 can be reduced from 1.75 to 1.45, when using an oblique-angle deposition and depositing it at 80°. Employing a lower refractive index of Alq_3 layer in an OLED stack can give rise to a 30% increase in the efficiency, if compared to a control device. Nonetheless, no polarized-luminescence properties have been studied for Alq_3. The only exception is Ref. [6] that has reported on obtaining a circularly polarized photoluminescence in Alq_3 films fabricated by a method of glancing-angle deposition.

In the present study, we report the results concerned with fabrication, structural characterization and polarized-luminescence properties of the Alq_3 thin films obtained using a method of oblique-angle deposition on glass substrates.

2. Experimental

Organic Alq_3 layers with the thickness less than 50 nm were thermally deposited in the vacuum 10^{-4} Pa onto two glass substrates placed at the deposition angles (i.e., the angles between the

incoming vapour direction and the normal of substrate) equal to 0° and 80°. Alq_3 powder with the purity higher than 98% was purchased from Tokyo Chemical Industry Co., Ltd. Thickness control during the processing was provided by a quartz-crystal deposition-rate controller.

X-ray diffraction measurements were carried out using a STOE STADI P diffractometer with a linear position-sensitive detector in a transmission Bragg–Brentano geometry (Cu $K_{\alpha 1}$ radiation with the wavelength $\lambda = 0.15406$ nm, a Ge (111) monochromator, the detector-scanning step amounting to 0.480° 2θ, the accumulation time 320 s, the 2θ angle resolution 0.015 deg, and the 2θ range 5–65 deg).

Alq_3 powder was investigated by a standard method of differential thermal analysis (DTA), using a synchronous thermal analyzer Linseis STA PT 1600. Heating was performed in a dynamic argon atmosphere at the rate of 10 K/min from 298 K up to 683 K. A surface morphology of our samples was examined using a SOLVER P47-PRO atomic force microscope (NT-MDT Co., Moscow, Russia).

Room-temperature photoluminescence spectra were measured using a quartz polarizer (Glan–Taylor prism) and a portable fibre-optic spectrometer AvaSpec-ULS2048L-USB2-UA-RS (Avantes BV, Apeldoorn, Netherlands) with the input slit 25 μm, a diffraction grating characterized with 300 lines/mm, and the resolution 1.2 nm. The accumulation time was equal to 200 ms. A rotating polarizer was placed between a source of photoluminescent radiation and a light detector. Detection of light in a spectrometer was carried out with a 2048-pixel CCD detector. Special software for automated computer control of spectrometer apparatus and spectra processing was used. The samples were excited with an M365FP1 fibre-coupled LED (Thorlabs, Inc., Newton, New Jersey, United States). It produced a non-polarized exciting radiation with the wavelength 365 nm, the bandwidth (FWHM) 9 nm and the output LED power 15.5 mW.

3. Results and discussion

Up to now, it has been demonstrated that Alq_3 molecule has two different geometric isomers: meridional (*mer*-) and facial (*fac*-) [7]. To our knowledge, five crystalline phases of Alq_3 have already been observed, which are termed as α, β, γ, δ and ε [7]. In their unit cell, α- and β-phases have two *mer*-Alq_3 molecules, γ-phase two *fac*-Alq_3 molecules, δ-phase four *fac*-Alq_3 molecules and ε-phase three *mer*-Alq_3 molecules [7–9].

X-ray diffraction pattern of the initial Alq_3 powder is shown in Fig. 1. It is worthwhile that the X-ray diffraction analysis of OLED materials, including Alq_3, is rather difficult, because the corresponding crystals are often disordered and 'contaminated' by some other polymorphs.

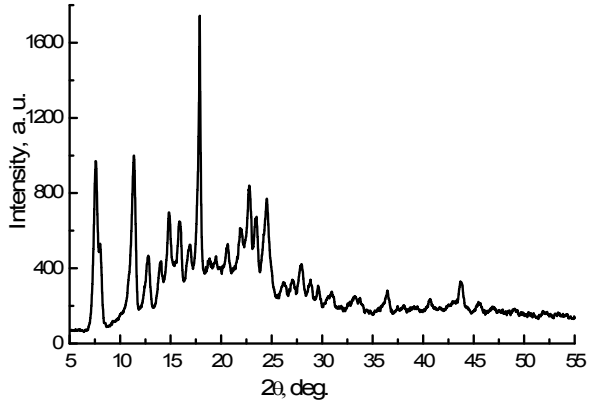

Fig. 1. X-ray diffraction profile obtained for initial Alq_3 powder.

To understand better the thermal factors involved in generation of Alq_3 phases, we have utilized a standard DTA method. A DTA curve for the initial Alq_3 powder (the starting ε-Alq_3 phase) is shown in Fig. 2. Phase transitions resulting from thermal processing of Alq_3 are evident. The temperatures of transformations are equal to 623 K (for the transition from ε-Alq_3 to α-Alq_3) and 662 K (for that from α-Alq_3 to γ-Alq_3).

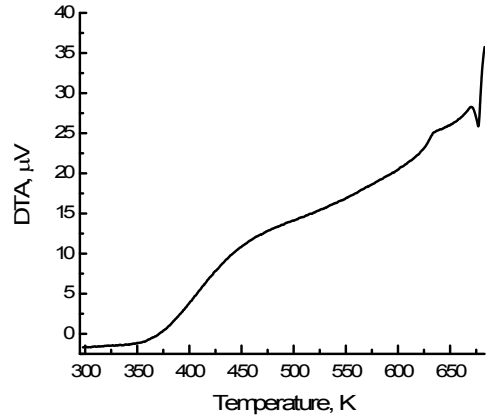

Fig. 2. DTA curve measured for initial Alq_3 powder.

AFM micrographs of the thin Alq_3 films are displayed in Fig. 3. Finally, Fig. 4 presents the room-temperature photoluminescence emission spectrum of Alq_3 powder. This spectrum exhibits a characteristic green emission, with a wide band being observed in the region from approximately 430 nm to 650 nm (see Fig. 4).

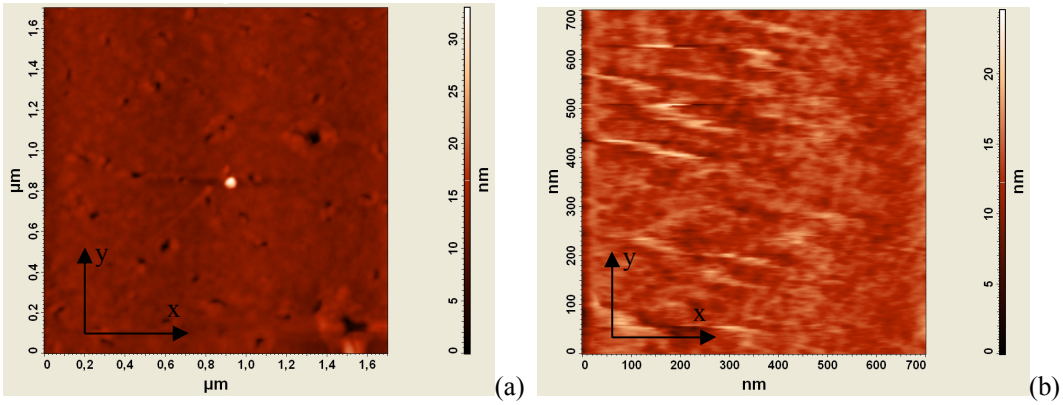

Fig. 3. AFM images of Alq_3 thin films placed on glass substrates, as obtained at the deposition angles 0° (a) and 80° (b).

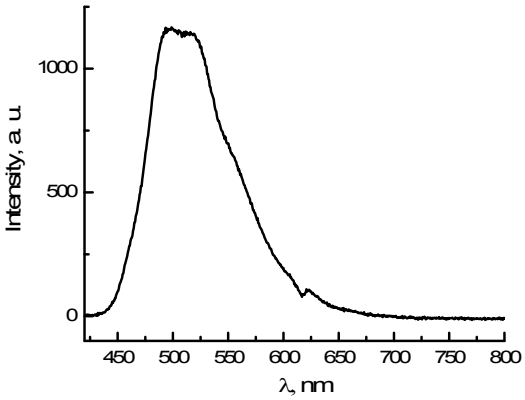

Fig. 4. Room-temperature photoluminescence emission spectra of Alq_3 powder.

When comparing our experimental results obtained by the methods of DTA, X-ray diffraction and luminescence spectroscopy with the literature data [10–15], one can conclude that our powder contains the crystalline phases ε-Alq_3 and α-Alq_3.

The polarized room-temperature photoluminescence emission spectra of thin Alq_3 films are shown in Fig. 5 and Fig. 6. We suppose that a weakly distinguishable peak located at 550 nm is associated with a possible presence of $Alq_3(HCON(CH_3)_2)$ compound in our sample [16].

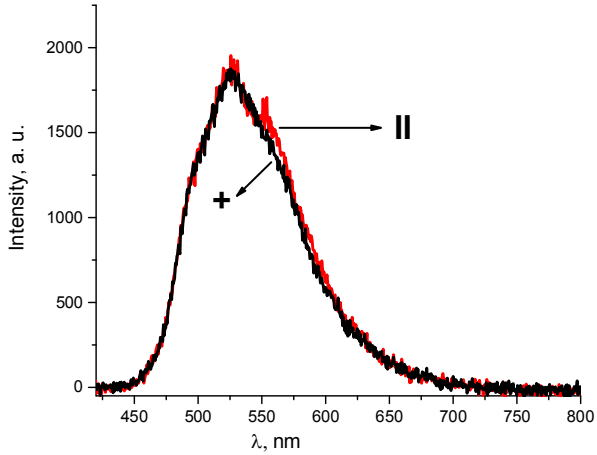

Fig. 5. Room-temperature photoluminescence emission spectra of Alq_3 thin film polarized parallel to X axis (curve ||) and Y axis (curve **+**), as obtained at the deposition angle 0° (see also Fig. 3).

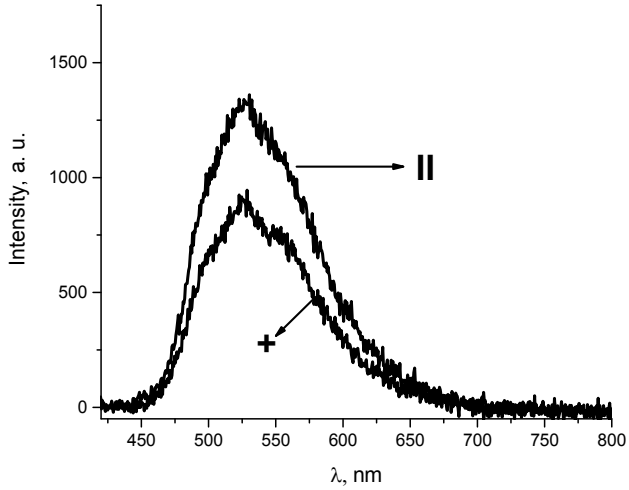

Fig. 6. Room-temperature photoluminescence emission spectra of Alq_3 thin film polarized parallel to X axis (curve ||) and Y axis (curve **+**), as obtained at the deposition angle 80° (see also Fig.3).

Following from the polarized-photoluminescence measurements, we have calculated the degree ρ of linear polarization [17]:

$$\rho = (I_{\parallel} - I_{+})/(I_{\parallel} + I_{+}). \quad (1)$$

Here $I_{\parallel}$ and I_{+} are the luminescence intensities of the perpendicular and parallel components, respectively. Note that correcting coefficients derived from the measurements with non-polarized light sources have been used. Basing on this approach, we have obtained the polarization degrees for the Alq_3 thin films placed on glass substrates. For the case of light wavelength 526 nm, they are equal to $\rho \approx 0.02$ and $\rho \approx 0.19$ respectively for the deposition angles 0° and 80°.

It is known that the Alq_3 molecule has a permanent dipole moment with 4.1 D [18, 19] and there is a lot of these molecules in the unit volume (~ 10^{14} cm^{-3}) [19]. The molecules tend to be oriented with their dipole moments pointing away from the substrate. In the case of Alq_3 films evaporated under 'dark' conditions, many researchers have observed a presence of a giant build-up surface potential, which reaches as large values as +50 V/μm [18–23]. This surface potential disappears after irradiating the film during (or after) its deposition, whenever the irradiating-photon energy exceeds the absorption edge of Alq_3 [20, 22, 24]. A noncentrosymmetric orientation of the molecule is considered as the origin of this potential [20, 23, 25], although the mechanism of acentricity is still unclear. The alignment degree of the molecules is small ($\langle \sin\theta \rangle \sim 0.05$, with θ being the angle between the dipole moment and the plane of layer and $\langle\ \rangle$ denoting thermodynamic average for the molecules over all directions [19]. Therefore, the degree of anisotropy is also low [18, 20]. A very small polarization degree obtained by us at the deposition angle 0° agrees well with these statements.

In the oblique-angle deposition process, the substrates are oriented at an oblique angle with respect to the incident vapour flux. Upon adsorption of the initial vapour species on the substrate and formation of the first islands, self-shadowing of these islands prevents the vapour flux from reaching the shadowed regions, thus leading to an ordered, porous and columnar growth [5, 26] (see Fig. 3b). In our opinion, this can be the reason for a significant increase in the polarization degree for our Alq_3 thin films deposited at the angle 80°.

4. Conclusion

The thin films of Alq_3 are synthesized using the method of thermal vacuum deposition on glass substrates placed at the deposition angles 0° and 80°. The optical and morphological properties of these films are discusssed. It is shown that the thin Alq_3 films obtained by the method of oblique-angle deposition can exhibit a significant polarized luminescence.

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Анотація. *Показано, що ступінь лінійної поляризації фотолюмінесценції тонкої плівки три-(8-гідроксихінолін)алюмінію (Alq3) можна збільшити приблизно в 10 разів, використовуючи метод осадження під деяким кутом до нормалі. Це пов'язано з більшим упорядкуванням молекулярного вирівнювання в цій тонкій плівці.*