Photoluminescence, optical transmission and reflection of Alq₃ layers obtained by thermal evaporation deposition

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In this paper we present the photoluminescence emission spectra (PL), photoluminescence excitation spectra (PLE), transmission (TS) and reflection (RS) spectra of tris(8-hydroxyquinoline) aluminum(III) (Alq₃) layers grown by thermal evaporation deposition method. All investigated samples exhibit strong luminescence in the wide temperature range from 13 K to room temperature and for different energies of excitation. In our experiments, we have focused on temperature dependence of photoluminescence. The thermal quenching of PL in the measured samples has been found. We have observed also distinct oscillations from reflection and transmission measurements. The energies of thermal activation estimated by means of configuration coordinate diagram and also the layer thickness and refractive index are presented.

Keywords: photoluminescence, transmission, reflection, refractive index, Alq₃.

1. Introduction

Recently, it is observed an enhanced interest in materials of large photoluminescence, great mobility of carriers, high electric conductance, and also low cost and simple technology of their fabrication. These materials may be used as components of optoelectronic devices such as photodetectors, organic LEDs [1], laser diodes, flat and flexible colour displays [2], and photovoltaic cells. One of the complex compounds widely investigated lately from the point of view of their applications, especially in optical devices, is tris(8-hydroxyquinoline) aluminum (III). This material exhibits quite a lot of features similar to inorganic semiconductors.

There are two different ways developing organic light emitting diode (OLED) systems, and each has its advantages and disadvantages. One way is the use of small organic molecules (for example Alq₃) to generate light, the other one focuses on using of polymers (for example PPV) for the same reason [3]. The most important elements of OLEDs are emissive layer and electron or hole transport layers. Alq₃ can act both as a transport layer and fulfil part of the emission because of its relatively good hole carriers mobility compared to other organic compounds. However, the speed of carriers transport is still very slow compared to inorganic semiconductors. Therefore, this layer is very thin, so that the electrons reach the emission layer to meet the holes [3].

For application, it is necessary to make more stable layers which exhibit the higher brightness of light. From the beginning of investigations on the Alq₃, a considerable progress has been achieved but still many effects which take place in that material are not fully understood. For this reason, there is a need for further detailed study on optical properties of Alq₃.

2. Experimental

The molecular structure of Alq₃ discussed in this paper is shown in Fig. 1. Thin films of Alq₃ were prepared by thermal evaporation deposition method from quartz effusion cells on a glass substrate. The process of their preparing...
Photoluminescence, optical transmission, and reflection of Alq3 layers obtained by thermal evaporation deposition

has been carried out under the pressure of about 2×10⁻⁵ Torr and at the temperature of the Alq3 source of ~430 K. For PL and PLE measurements we have used the apparatus which scheme is presented in Fig. 2. This equipment includes a halogen lamp (250 W) for PL and PLE measurements as a source of excitation. The spectral selection was done using two monochromators (SPM2 ZEISS) with a quartz prism. During a measurement of the temperature dependence of luminescence, the samples were enclosed in a helium cryostat in vacuum environment. Both PL and PLE signals were registered by a photomultiplier (R-928 HAMAMATSU) using photon counting system. The output signal from a photodetector was processed and analysed by a personal computer.

Transmission and reflection spectra were measured using a halogen lamp as a source of light with a prism monochromator (SPM2 ZEISS) and silicon photodiode as a detector. Signal from a detector was processed by built-in lockin (EG&G Instruments 7260) analogue to a digital converter. A schematic diagram of the reflection and transmission apparatus is shown in Fig. 3.

3. Theory

The optical system under consideration is a thin homogeneous layer with the complex refractive index \( N = n - ik \) and the film thickness \( d \) on a thick substrate with the refractive index \( n_s \). Figure 4 illustrates the principle of measurement using reflection effect. A portion of the incident light \( I_r \) is reflected on the upper surface of the film, the remainder \( I_t \) penetrates the film. A part of \( I_t \) is absorbed in the film, a part passes through the film and the remainder \( I_r \) is reflected from the lower surface of the film. A part of light reflected from the upper surface interferes with the light reflected from the lower surface and as a result reflection spectrum is characterized by rapid oscillation with the changing wavelength (Fig. 5). Geometry of optical system does not exclude presence of multiple reflection or reflection from the lower surface of the substrate but contribution in the total reflection spectrum originating from these reflections is negligible small. The reflection \( R \) of optical system mentioned earlier is a complex function of \( n, n_s, k, d, \) and \( n_s \). For weakly absorbing dielectric films, when \( n > n_s, n_s > k \) conditions are performed, \( k \) can be approximated by zero. Then, the reflection becomes a function of \( n \) and \( x \) only, where \( x = \exp(-ad) \) and envelopes of the reflection spectrum maxima \( R_M \) and minima \( R_m \) are given by the equation [4]

\[
R_M \cdot R_m = \frac{(ad \pm bcx)^2}{(bd \pm accx)^2} + \frac{gx^2}{(bd \pm accx)^2 (b^3 f \pm 2abdx + a^3 ex^2)}
\]

where

\[
a = n - n_s, \quad b = n + 1, \\
c = n - n_s, \quad d = n + n_s, \\
e = n - n_s^2, \quad f = n + n_s^2, \\
g = 64n_s(n_s - 1)^2n^4.
\]

Analogous equation may be obtained for the transmission envelopes [5]

\[
T_M \cdot T_m = \frac{Ax}{B \pm Cx \pm Dx}
\]

where

\[
A = 16n^2, \\
B = (n + 1)^3(n + n_s^2), \\
C = 2(n_s^2 - 1)(n_s^2 - n_s^2) \cdot (n_s^2 - n_s)^2, \\
D = (n - 1)^3(n - n_s^2).
\]

The procedure for calculation of the refractive index \( n(\lambda) \), extinction coefficient \( k(\lambda) \), and layer thickness from the reflection spectrum is the following [4]. First, it is nec-
necessary to draw the envelopes $R_M$ and $R_m$ illustrated in Fig. 5. The envelopes should be constructed from the tangent points close to the reflection curve, not from the interference extremes \[6,7\]. Usually, they are constructed using cubic spline interpolation through the estimated tangent points or drawn by hand. The envelopes are considered as continuous spectra vs. wavelength and it is possible to read off $R_M(\lambda_i)$ and $R_m(\lambda_i)$ for all the tangent points $\lambda_i$.

The refractive index of the substrate $n_s$ can be calculated from the reflection spectrum in the transparent region, using the relation

$$R_m = \frac{(n_s - 1)^2}{n_s^2 + 1} \Rightarrow n_s = \frac{1 + [R_m(2 - R_m)]^{1/2}}{1 - R_m}. \quad (3)$$

When the tangents points $\lambda_i$ and the corresponding values $R_M(\lambda_i)$ and $R_m(\lambda_i)$ are known, the first approximation refractive index $n_i^0$ and $x_i^0$ can be obtained by numerical solving the system of Eqs. (1) or (2) for all $\lambda_i$. It is recommended to begin the calculation from the transparent region, where for an initial approximation $n_i^0$ is used but for $x_i^0 = 1$. As a wavelength decreases for the initial values $n_i^0$ and $x_i^0$ are used that were obtained from the previous tangent point.

The first approximation for the thickness of the film $d_0$ is an average thickness obtained for both adjacent tangent points from the well-known equation

$$d_0 = \frac{\lambda_i \lambda_{i+1}}{4(n_i^0 n_{i+1} - n_i^0 n_{i-1})}. \quad (4)$$

The letter “$i$” denotes consecutive tangent point.

Basing on the approximated values of the refractive index $n_i^0$ and the average layer thickness $d^0 = \text{mean}(d_i^0)$, the order number of the given tangent point $\lambda_i$ is estimated from the equation

$$m_i = \frac{4n_i^0 d^0}{\lambda_i}. \quad (5)$$

Because the obtained values $m_i$ usually are not integers, they should be rounded to the integer $m_i^{\text{int}}$, even for the minima and odd for the maxima.

The values $m_i^{\text{int}}$, together with the values $n_i^0$ for all $\lambda_i$ are used to calculate next thickness approximation $d_i^1$ from Eq. (5). The average values $d^1 = \text{mean}(d_i^1)$ is a final value of the layer thickness

$$d_i^1 = \frac{m_i^{\text{int}} \lambda_i}{4n_i^0}. \quad (6)$$

Using $d^1$ and $m_i^{\text{int}}$, the final value of the refractive index $n_i$ can be obtained for all $\lambda_i$ from the following equation

$$n_i = \frac{m_i^{\text{int}} \lambda_i}{4d_i^1}. \quad (7)$$

The final value of the extinction coefficient $k_i$ can be determined from $x_i$ by different approaches. One of this method uses previously obtained $x_i^0$ values and the equation

$$x_i^0 = \exp(-ad_i^1) = \exp\left(-\frac{4\pi k_i}{\lambda_i} d_i\right) \Rightarrow k_i. \quad (8)$$

The best results are achieved by calculating the extinction coefficient from Eq. (1) for the upper envelope $R_M$ of the reflection spectrum because the lower envelope $R_m$ is independent of $n$ and $k$ in the transparent region and can generate false values for $k$ in this region.
4. Results and discussion

The reflection and transmission data for 1701-nm Alq₃ layer deposited on a glass substrate are shown in Figs. 5 and 6, respectively. The optical bandgap determined from a transmission spectrum is equal to 2.84 eV. Numerous interference oscillations were obtained for both these spectra. The interference fringes were used to calculate optical constants and layer thickness using a procedure described in the previous section. The results for reflection are presented in Table 1. The refractive index of this layer was also computed using transmission envelopes. Figure 7 shows comparison of a refractive index calculated from the reflection and transmission spectra separately. Good agreement of a refractive index determined from two different measurements is clearly visible.

Figure 8 shows the temperature dependence of the PL spectrum of the Alq₃ sample measured in the temperature range from 13 K to 300 K. These spectra were measured at

Table 1. Results of reflection measurements.

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<tr>
<th>(\lambda) (nm)</th>
<th>(R_M)</th>
<th>(R_m)</th>
<th>(n^0)</th>
<th>(x^0)</th>
<th>(d^0) (nm)</th>
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\(n_s = 1.52\)  \(d^0 = 1741\) nm  \(d^1 = 1701\) nm
the wavelength range from 450 nm to 750 nm. At low temperatures, the higher intensity of PL line is clearly observed. With increasing temperature, the PL intensity decreases. An interesting detail is a very small dependence of the integral intensity of the PL emission in the temperature range of 10–80 K, which was typical for all Alq3 samples. The changes are more clear for above 80 K.

The observed behaviour can be explained by means of a configuration coordinate model which is schematically shown in Fig. 9. The curves $S_0$, $S_1$, and $T$ are adiabatic potentials of the initial and final states of a molecule. The AB transition corresponds to excitation of the electron-hole pair. The BC transition over the barrier $E_1$ corresponds to capture a carrier by a defect. When the temperature increases, the electrons can easily skip to the state $T$ and return with phonon emission to the ground state $S_0$. This behaviour of carriers results in increase in nonradiative recombination and decrease in luminescence. The CD transition is a thermal excitation of carrier over the crossover of the curves $S_0$ and $T$, after which nonradiative recombination takes place (DA transition). $E_2$ is the energy of this thermal excitation. A plot of PL intensity vs. an inverse temperature is shown in Fig. 10. In this figure, the temperature dependence of PL intensity is fitted by the expression [8]

$$I(T) = \frac{I_0}{1 + A \exp\left(-\frac{E_1}{kT}\right) + B \exp\left(-\frac{E_2}{kT}\right)}$$

where $A$ and $B$ are the constants and $E_1$ and $E_2$ are the thermal activation energies. In all investigated samples, $E_1$ was $\sim 74$ meV and $E_2 \sim 19$ meV. We have also observed (see Fig. 11) a small shift of PL spectra with decreasing temperature to a blue range of a spectrum (blueshift).

In Fig. 12, the PLE and PL spectra are presented. Typical mirror symmetry is observed here. As we can see in Fig. 13, for PLE spectra a similar temperature behaviour (thermal quenching) is clearly visible as well. The strong temperature dependence of the PL spectra is attributed to the reduced exciton-phonon interaction with a decreasing temperature. In planar molecules as Alq3, strong coupling exists between the excitons and intermolecular phonon modes. Phonon-enhanced internal conversion provides a nonradiative transition path for excitons, leading to quenching of the integral PL at higher temperatures [9,10].

One of virtues of such kinds of materials are very stable parameters of molecular levels [11]. It is a principal point for their applications.

5. Conclusions

In this paper, we presented photoluminescence emission and photoluminescence excitation spectra of tris(8-hydroxyquinoline) aluminum (III) layers. Our results have shown...
Photoluminescence, optical transmission, and reflection of Alq3 layers obtained by thermal evaporation deposition

**Fig. 11.** Shift of PL peak with changing temperature.

**Fig. 12.** PL and PLE spectra at the temperature of 13 K.

strong luminescence for all the measured samples. It was also observed a strong dependence of PL intensity on temperature, especially, for the temperatures of above 80 K. We have explained the mentioned temperature dependence using configuration coordinate model and we have calculated the energies of thermal activation. We also presented reflection and transmission spectra for the same material and estimated the refractive index and thickness of a layer. The determined layer thickness of the investigated sample is equal to 1701 nm whereas the refractive index is about 1.7 for visible spectral region. Our results for the refractive index value are in good agreement with the other published results obtained with different methods, e.g., ellipsometry spectroscopy [12].

**References**


2.34 eV

13. PL and PLE spectra at the temperature of 13 K.

2.34 eV

180 K

200 K

250 K

300 K

Fig. 13. Photoluminescence excitation spectra of Alq3 at different temperatures.

2.34 eV