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Photoluminescence in Semiconductor Structures Based on Butyl-Substituted Erbium Phthalocyanine Complexes

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Abstract—The study is concerned with the luminescence properties of ensembles of semiconductor structures containing organic phthalocyanine molecules with erbium ions as complexing agents. The photoluminescence spectra of the structures of the type of erbium monophthalocyanine, bisphthalocyanine, and triphthalocyanine are recorded. The photoluminescence peaks are detected at the wavelengths 888, 760, and 708 nm (and photon energies 1.4, 1.6, and 1.75 eV) corresponding to electronic transitions within the organic complexes. It is found that, when a metal complexing agent is introduced into the molecular structure of the ligand, the 708 nm luminescence peak becomes unobservable. It is shown that, in the bisphthalocyanine samples, the photoluminescence signal corresponding to transitions from the $4F_{9/2}$ level of erbium ions is enhanced.

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1. INTRODUCTION

Organic semiconductor structures find expanding applications in the problems of present-day microelectronics [1]. In particular, it is known that structures composed of large protein molecules feature a rather high mobility of electrons [2]. The basic advantage of organic materials is the simplicity of their production from the derivatives of organic compounds widely occurring in nature. The technologies of synthesizing organic molecules do not require large expenditures of energy or complex instrumentations, such as are used, e.g., in molecular beam epitaxy, gas phase epitaxy, hydride epitaxy, photolithography, or anisotropic chemical etching [3, 4]. It should be also noted that many organic structures exhibiting semiconductor properties occur in nature in a ready form [5]. For example, the structures of magnesium porphyrinates reveal themselves as chlorophyll molecules in the cells of any plants, and erythrocytes in blood corpuscles of mammals are the compound of porphyrin with an iron atom.

Phthalocyanine is a synthetic analogue of porphyrin. The basic feature of phthalocyanines is their stability to thermal decomposition [2].

To the advantages of organic structures can be added their selective optical properties that can be varied by modifying the structure of molecules during synthesis [6, 7]. In [8–10], it was shown that phthalocyanine molecules exhibit three peaks of absorption of optical radiation in the visible and ultraviolet spectral regions and can show two distinguishable photoluminescence (PL) peaks in the range between 900 and 1100 nm.

Current achievements in the chemistry of phthalocyanines make it possible to synthesize three-dimensional-structured organic molecules, in which one complexing atom is bound with two organic ligands [11]. The purpose of this study is to obtain and analyze the spectral dependences of the PL signal from semiconductor structures based on erbium monophthalocyanine, bisphthalocyanine, and triphthalocyanine in the visible spectral region.

2. EXPERIMENTAL

Molecular structures based on free ligands (metal-free monophthalocyanine) with butyl peripheral substitutes were produced by boiling dibutylphthalodinitrile in *n*-pentanol in the presence of metal sodium [12]. The butyl-substituted structures of erbium monophthalocyanine and lutetium monophthalocyanine were synthesized in argon atmosphere in 3–4 h by boiling stoichiometric amounts of metal-free phthalocyanine ligands and the corresponding rare-earth acetates in ortho-dichlorobenzene (DCB) in the presence of 1.8-diazabicyclo[5,4,0]undecene-7 (DBU). The sandwich-like structures of butyl-substituted erbium bisphthalocyanine and triphthalocyanine were produced in cetyl alcohol [13].

The prepared molecular complexes were deposited on quartz substrates by centrifuging (spin-coating). The
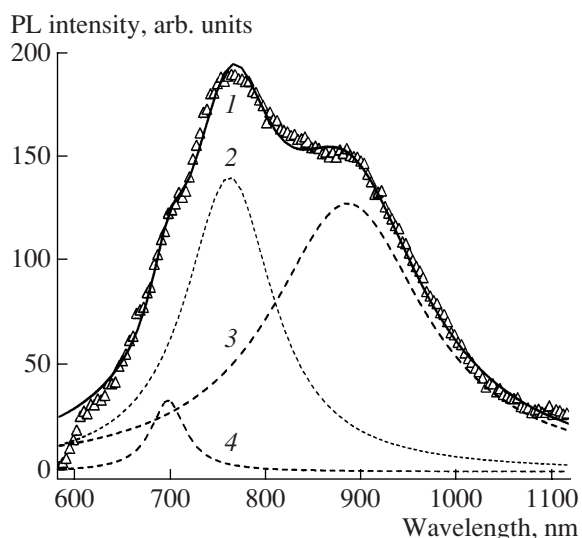
Fig. 1. The photoluminescence spectrum of butyl-substituted monophthalocyanine, as (symbols) observed experimentally and (*1*) fitted with (*2–4*) three Lorentzian contours.
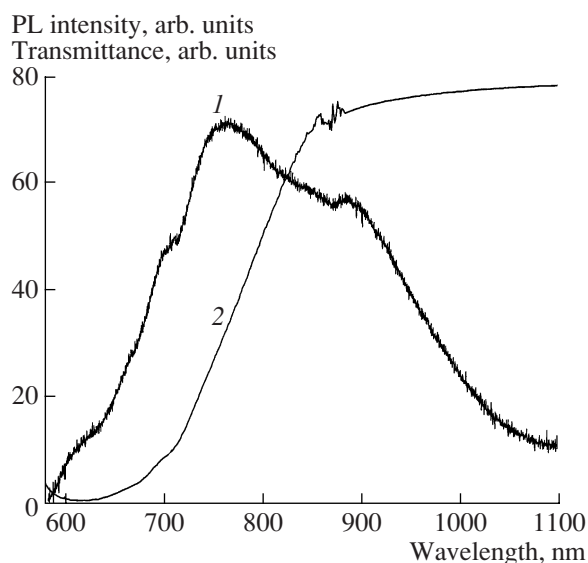

Fig. 2. Spectra of (*1*) the photoluminescence and (*2*) transmittance of semiconductor structures based on metal-free butyl-substituted monophthalocyanine.

thickness of the sample produced in such manner was 50 μm.

The PL signal of phthalocyanine molecules was excited by radiation of a nitrogen laser operating at the wavelength λ = 337 nm with the pulse duration 10 ns. The PL spectra were recorded using a monochromator equipped with a cooled CCD cell.

To record the transmittance spectra, we used a Hitachi-330 spectrophotometer. The wavelength resolution was 1 nm.

3. RESULTS AND DISCUSSION

The PL spectrum of the structures composed of free ligands (metal-free monophthalocyanine) is represented by a broad band with three distinguishable peaks at the wavelengths 888, 760, and 708 nm corresponding to the photon energies 1.4, 1.6, and 1.75 eV (Fig. 1). Approximation of the experimental curve with three Lorentzian bands allows us to establish that the peak at 880 nm makes the major contribution to the observed PL band in the red region, whereas the PL peak at 760 nm is maximal in spectral intensity. Pakhomov et al. [14] recorded the PL spectra that consisted of two peaks at 980 and 1100 nm. It was also shown that, in phthalocyanine molecular structures deposited on sapphire substrates, structural and compositional variations in the samples are liable to influence the spectral position of the PL peaks. In the PL spectra recorded in this study, the intermediate-intensity peak at 888 nm can be attributed to the molecular luminescence ($S_1' - S_0$) or to the formation of the excimer state [14].

The peak at 760 nm may appear due to emission from the first singlet exciton state [14]. The PL peak

observed at the wavelength 708 nm can be due to excitonic transitions from one molecular orbital to another inside the molecule itself, similar to the PL at interband transitions in crystalline semiconductors. In order to gain a deeper insight into the origin of the high-energy peak at 1.75 eV (708 nm), we carried out a comparative analysis of the spectral dependences of the transmittance and PL intensity in butyl-substituted monophthalocyanine samples. The experimental results are shown in Fig. 2. For convenient comparison, the PL spectra and the transmittance spectra are shown together (Fig. 2).

The drastic decrease in the transmitted intensity in the short-wavelength part of the spectra of butyl-substituted monophthalocyanine complexes corresponds to the electronic transitions between the highest occupied molecular orbital (HOMO) b_1 and the lowest unoccupied molecular orbital (LUMO) e_3 of the phthalocyanine ligand, in which the orbitals b_1 and e_3 are predominantly localized at the α-isoindole carbon atoms [15]. In publications, this absorption line is referred to as the *Q* band; its spectral position in monophthalocyanine molecules corresponds to 690 nm [8, 15]. In the spectra of the structures under study, the transmitted intensity steadily decreases even starting from 850 nm.

The decrease in the transmittance in the spectral range from 850 to 620 nm suggests that the absorption of electromagnetic radiation may involve contributions of two processes, specifically, the formation of molecular excitons in the first singlet state and the transitions between the HOMOs and LUMOs. The transitions between the HOMOs and LUMOs are responsible for the PL peak around 706 nm. From the relationship between the PL signal intensities, we can conclude that the major contribution to the absorption of electromagnetic
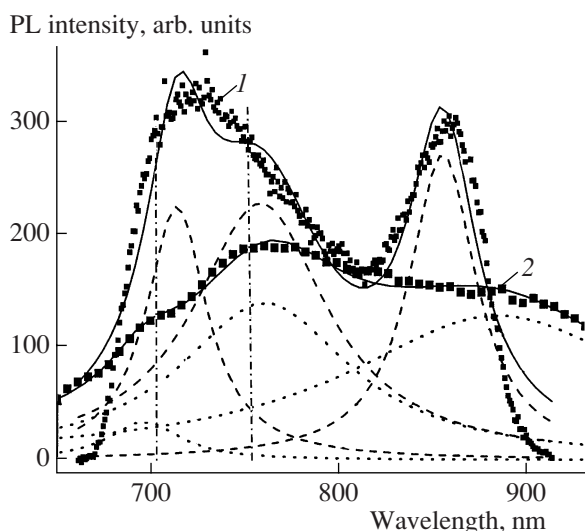
PL intensity, arb. units

Fig. 3. Photoluminescence spectra of the metal-free monophthalocyanine sample at the temperatures $T =$ (1) 4 and (2) 300 K. Dashed and dotted curves show the Lorentzian components obtained by decomposing spectra 1 and 2, respectively; solid curve refers to the sums of the Lorentzian components.
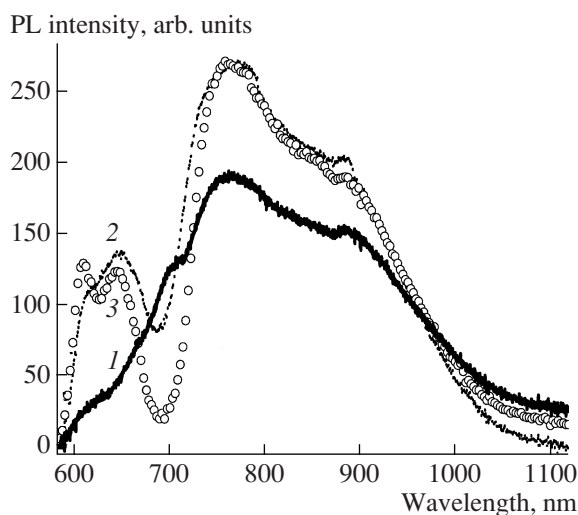
PL intensity, arb. units

Fig. 4. Photoluminescence spectra of semiconductor structures based on butyl-substituted phthalocyanine complexes. Curves 1, 2, and 3 refer to metal-free monophthalocyanine, erbium monophthalocyanine, and lutetium monophthalocyanine, respectively.

radiation in the visible wavelength region is made by the exciton states formed in phthalocyanine molecules.

As temperature is decreased to 4 K, the PL signal intensities at the wavelengths 708 and 760 nm increase by factors of 2.4 and 1.5, respectively (Fig. 3). In this case, the PL peak corresponding to the exciton states slightly shifts, from 760 nm at $T = 300$ K to 752 nm at liquid-helium temperature; at the same time, the spectral position of the PL peak corresponding to transitions between the molecular orbitals remains unchanged. A noticeable shift to shorter wavelengths is observed for the long-wavelength peak characterizing the excimer state; with decreasing temperature, the signal intensity at 850 nm becomes twice as high. It should also be noted that, with decreasing temperature in the cell with the sample, the PL signal intensity corresponding to the short-wavelength peaks remains virtually unchanged.

When erbium ions or lutecium ions as complexing agents are incorporated into phthalocyanine molecules, an extra peak at 660 nm (1.87 eV) appears in the PL spectra (Fig. 4); this peak corresponds to transitions from the $4F_{9/2}$ level in lanthanide ions [16]. The PL spectra of the lutecium monophthalocyanine structures also exhibit an extra peak observable at 606 nm (2.04 eV). The lack of extrema in the high-energy region of the PL spectra of metal-free phthalocyanine allows us to relate the high-energy PL lines exactly to the lanthanide atoms. It should be noted that the line corresponding to the HOMO $\longrightarrow$ LUMO transitions is lacking in the PL spectra of the compounds containing complexing agents.

When studying the sandwich-like structures of bisphthalocyanine and triphthalocyanine instead of the planar monophthalocyanine structure, we observe dramatic degradation of the PL signals corresponding to the exciton states of the molecules as such (Fig. 5). From the spectral dependences of the PL intensity (Fig. 5), it can be seen that the intensities of the peaks at 888 and 760 nm (1.4 and 1.6 eV) become, correspondingly, 1.8 and 2.24 times lower (Fig. 5, curve 2). However, the intensity of the peak produced by electronic transitions between the energy levels of erbium ions (1.87 eV) becomes 1.4 times higher.
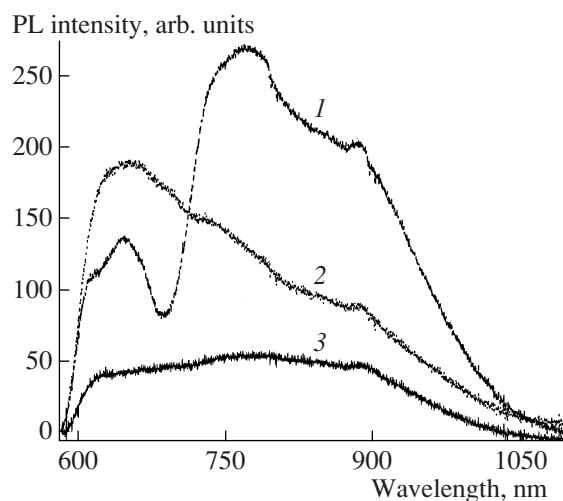
PL intensity, arb. units

Fig. 5. Photoluminescence spectra of semiconductor structures based on butyl-substituted phthalocyanine complexes containing erbium. Curves 1, 2, and 3 refer to monophthalocyanine, bisphthalocyanine, and triphthalocyanine, respectively.

In the erbium triphthalocyanine samples, we observe all three peaks, at 1.4, 1.6, and 1.87 eV, with the identical intensities. However, in such complex sandwich-like structures as triphthalocyanine, the magnitudes of intensities of the PL peaks are 3, 4, and 5 times lower than those in the PL spectra of the planar monophthalocyanine structure.

The butyl complexes in the molecular structure of all three types of organic molecules rule out the possibility that alkyl peripheral substitutes affect the observed luminescence properties.

It should be also noted that there is no peak at 708 nm (1.75 eV) in the PL spectra of the sandwich-like structures of erbium bisphthalocyanine and triphthalocyanine, as well as in the case of incorporation of a complexing agent. This allows us to conclude that the coordination bonds formed in organic ligands inhibit the HOMO ⟶ LUMO transitions.

4. CONCLUSIONS

In this study, the PL spectra of disordered semiconductor structures based on butyl-substituted phthalocyanine complexes containing erbium ions and lutecium ions as complexing agents are recorded and analyzed. The study has allowed the observation of the PL signal at the wavelengths 888, 760, and 708 nm (the photon energies 1.4, 1.6, and 1.75 eV). The signal is due to electronic transitions within the organic complexes themselves, and upon the incorporation of a metal complexing agent, the PL peak at 708 nm is not unobserved.

It is established that, as the molecular complexes are made more complicated, the intensity of PL signals corresponding to electronic transitions in the molecules becomes three times lower. At the same time, in the bisphthalocyanine structures, an increase in the intensity is observed for the 660 nm PL signal produced by erbium ions.

From the above experimental results, it is concluded that the coordination bonds in the molecules of organic ligands are responsible for the quenching of the PL signal at 706 nm.

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