

Organic polymer light-emitting devices

From the standpoint of use in microelectronics and photonics organic materials for a long time of On

shall regard as inefficient, inadequate clean and unstable as the active elements and focused on inorganic matter,

Lamas. In the past 15 years intensive research organizationally photoconductive polymer and electron-hole transport medium led to the development and wide industrial use of new effective

tive light-sensitive materials in the information

GOVERNMENTAL technologies, and currently more than 90% of photo-receptor in copiers and machines and la-

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Beans printers are made of organic polymers [1]. Organic materials reasonably of On-building strategy as certainly promising for microelectronics tronics and photonics.

Sustained high interest are the organic electroluminescent devices (OELU) of two types:

low molecular weight and based on polymers with conjugated governmental double bonds in the main chain. Electronic processes in working OELU include

injection of electrons and holes from the electrodes, transport in layer and recombination with the formation of exciton decay

cides with the emission of a photon. Low molecular

OELU usually obtained by vacuum thermal-

On spraying, and for the manufacture of polymer OELU used a simple method of flushing solution to the center-fugue.

As a basis of low-molecular-OELU naib

Lee is widely used tris (8-gidroksihinolyat) aluminum tion (Alq₃) [2], and for polymer OELU. polyphenylene-

LP [3] or its derivative poly [2-methoxy-5-(2'-geksiloksi ethyl) -1,4-fenilenvinilen]. Flexible polymer

WIDE OELU on a plastic substrate, have an unquestionable advantage over low molecular weight: they are more

sturdy, compact, lightweight and, importantly, more cheap. The use of plastic substrates for in

polymer OELU to realize the principle

new kinds of products: flexible and embossed displays, full-

Stu polymer electronics, protective equipment products

against tampering. However, polymer svetoizlu-

sponding materials have significant shortcomings. Thus,

conjugated polymers, in particular polifenilenvini-

Flax, being reactive systems lose its useful properties when in contact with water vapor and oxygen, especially in the passage of electric passage of electric current. In addition, they are photochemically unstable. Electroluminescence efficiency is often limited due to lack of sufficiently balanced bipolar- tion of electron-hole transport. This is particularly the relative- pertains to a single-layer OELU, in which the electron- hole recombination takes place near one of electrodes (in most cases, the cathode), which leads leads to quenching of excited states in the metal tion surface [4]. Efforts synthesized Immunized elektroluminestsiruyuschie new polymers with close electron and hole mobilities, which is crucial for OELU. Within this problem of priority is the search for poly- mers that do not contain a chain of conjugated bonds, but with electroluminescence is not worse than the conjugate polymers, and with a balanced electron-hole transport, stable to external influences. With this point of view of particular practical interest Some aromatic polyimides with bipolar transport and electroluminescence efficiency. Of this class of polymers as transport and light-emitting materials for single-layer OELU we studied antratsensoderzhaschie polyimides (IPA) [5, 6]. An efficient bipolar transport and good luck- tion relative position of electronic levels in these structures provide a bright electroluminescence OELU based on them. In addition, these polyimides thermo- stable, resistant to oxidation and form excel- WIDE films from solutions. Among the polymers investigated in this class the best elektroluminestsiruyuschie characteristics showed poly- imide structure API1. On the basis of obtained single-layer OELU with a brightness of 600 cd/m² at a voltage of 15 V, state ing from the emitting layer API1 concluded between transparent conductive layer of indium tin oxide (ITO). anode and cathode, deposited from Mg: Ag. Maxi- maximum of the electroluminescence of these devices is observed at 565 nm. Polymer thick film 100,600 nm can be formed in the centrifuge method of irrigation distribution are creating an IPA in chloroform on the surface of ITO / glass at air. Using time-of-flight method was determined that the mobility of electrons and holes in API1 virtually identical: $\mu_e \approx \mu_h = 2.10.5 \text{ cm}^2 / (\text{VS})$ in the electric

electric field $F = 3.105 \text{ V / cm}$ at 291 K . This is an order-of-magnitude higher than that for some other aromatic polyimides not soluble in organic solvents, including aromatic polyimides with a high degree of crystallinity.

IPAs are amorphous semiconductor materials. Temperature and field dependence of the submobility of them, as for most polymers electron transport (except polymers with metallic conduction) [7.11], agrees well with empirical equation Gill (Fig. 1):

$$\mu_h = \mu_0 \exp \left[\left(\frac{E_a}{k} \right) \left(\frac{1}{T_n} - \frac{1}{T_0} \right) \right] \exp \left(-\frac{2R}{\beta} \right)$$

$$E_a = \Delta \cdot \gamma F^{0.5} \quad (1)$$

where E_a : activation energy of mobility; R : average distance between adjacent transport centers; β : constant decline of the wave function of the transport center; Δ : activation energy in zero field; μ_0 and γ : constants, $2 \geq n \geq 1$.

For a typical conductive polymer a hole transport and detection of transport electrons in API1 is a natural interest. In Apparently, the appearance of electron transport in this structure associated with the presence of a phthalide and two phthalimide fragments with almost identical the electron affinity and functioning independently as electronic transport centers because the carbon atom in the tetragonal ring recovering from can be regarded as a "cell". Diphenyl lantratsenovy group, obviously, are hole transportation centers. In the case of manufacturing Beasley GOVERNMENTAL OELU ITO/API1/Alq3/Mg: Ag second monopolar Alq3 layer is introduced between the polymer emitting layers it and the corresponding electrode. This structure improves the balance between the electron and hole injection currents, stimulated electron-hole recombination and retains the generated excitons in light-emitting zone. Brightness OELU based API1 significantly increased in the presence of a second electroluminescence minestsiruyuschego layer. electron-conducting Alq3, so the charges completely recombine directly at the interface API1/Alq3.

Fig. 2 shows the EL spectrum OELU on sulfur polymer API2. As shows the emission spectrum is very wide (as for others gih well-known polymer OELU) due to lateral-

Notice of the vibronic bands and a strong non-homogeneous broadening
tion transitions. In full-color displays individuality
WIDE pixels should play the most at-
saturation red, green or blue color, and as already
emission bands, the more colors can be restored,
produced. The problem is very broad spectral
lines can be solved by the use of OELU
micro-type resonant structures Fabri.Pero
[12]. The real difficulties are not overcome
this complex way connected with the strong dependence
Stu radiation from the angle of the direction of the light-emitting
on the surface of the film OELU with insufficient
homogeneity of polymer films, resulting in no
provided reproducible color elements, and
inability to obtain the maximum saturated
pure red, green, blue colors.

In our paper we propose a way to solve this pro-
lems. It was found that cyanine dyes,
introduced into the polymer matrix with electron-hole
transport, in particular in antratsensoderzhaschy poly-
imide, in certain conditions form associates.
so-called J-aggregates [13]. As an example we mention Shi
optimum utilization of our work cyanine dye
Tel (designated as TSK1):

J-aggregates can be considered as organic
nanocrystals with good nonlinear optical
coefficients on the molecular composition of incumbents
intermediate position between the ordered crystal
crystal structure and the individual molecules
(Fig. 3a). Cyanine nanocrystalline particles ha
terized by intense narrow absorption bands
tion and photoluminescence, the location of bands in the visible
My region of the spectrum depends on the chemical structure
dye.

It was of interest to identify the positive effec-
You influence of J-aggregates in the organic electroluminescence-
technically polymers. A study of thirteen cyanine
dyes belonging to the class of acid-base
dyes that have absorption bands in the range
zone of 550,800 nm. As the matrix were used
antratsensoderzhaschie polyimides, including atoms
sulfur in the main chain, such API2, which is
effective electron and hole conductor
[14.18]. Were fabricated OELU sandwich-type
which represent sections of API2 doped
light-emitting cyanine dyes, between

transparent anode oxides In₂O₃ and SnO₂, and Mg: Ag electrodes (Fig. 3b). Polymer film thickness 100,300 nm were formed on the surface of ITO / glass method of irrigation in the centrifuge from the solution and API2-tsia Ninove dye (15% wt.) in chloroform in the standard-tions. Electrodes Mg: Ag deposited by vacuum Smart spraying at a pressure lower than 5.10.6 mmHg Spectral measurements of electroluminescence OELU based on composites of polymer / cyanine dye Tel (at room temperature in air) is uniquely indicate that there is a link between the generation of electroluminescence, the values of redox potentials and bandgap of the polymer semiconductor (The latter defined as the energy difference between the lower free molecular orbital (LUMO) and the upper occupied molecular orbital (HOMO) of the polymer matrix). Electron work function of Mg is 3.7 eV, electron affinity API2 equal 2.6 eV, and consequently Indeed, there is a barrier (1.1 eV) for injected electrons electrons from the cathode to the polymer, which is significantly higher than barrier for hole injection from the anode (0.7 eV). Obtained results allow us to conclude that the energy band luminescence (ΔE) is defined by redox potentials of doping substances (Measured in ethanol relative to the standard saturated calomel electrode (n.k.e.) [19] potential n.k.e. given as $\phi_{H.K.\text{Э}} = \phi_{B.\text{Э}} + 0.24 \text{ eV}$, where $\phi_{B.\text{Э}} = 4.4 \text{ eV}$. potential hydrogen electrode). Hence $\Delta E = E_{ox} - E_{red} = 2 \text{ eV}$ and the band maximum EL should be performed ratio $\lambda_{max} \approx 612 \text{ nm}$. Experimental value of 617 nm (see Fig. 2) is in good good agreement with this estimate [16]. Bands electron electroluminescence owned 1,084 m \ u1062 TSK1 and polymer matrix, were observed simultaneously at low concentration the concentration of dye in the layer. When the concentration dye intensity of its luminescence became dominant, and in the presence of 15% (wt.) TSK1 radiation tion of API2 generally not observed, since all the energy excitation is absorbed by dye molecules. As The spectra in Fig. 2, band elec-tion TSK1 dye doped in API2 significantly narrower than the band of the pure polymer. Formation of nanocrystalline J-aggregates in TSK1 polymer matrices significantly increases the intensity

Nosta OELU luminescence and thereby substantially improves OELU based composites polymer / nanoparticle compared with isolated components. Nanoparticles introduced into the polymer matrix, modifying the structure of electroactive light emitting layers, increase the injection currents. Note that almost all nanoparticles are traditionally used so far in the polymer system topics as doping additives are inorganic inorganic dielectrics or semiconductors (TiO₂, SiO₂, Al₂O₃, CdSe) [20,22]. In contrast to these materials, J-ar-regattas are organic nanoparticles. Blah Godard, small size, which is many times smaller wavelengths of visible light, they do not cause appreciable scattering in the composite layers. These polymer materials combine the optical characteristics of the organizationally crystals with electronic properties of semiconductive polymers. Were made on OELU basis of API2/J-agregaty TSK1 (J-aggregates) were obtained from solutions of API2 and TSK1 in chloroform through a multiple cycles of heating (60 ° C). cooling. OELU ready-Vili the method as described above for OELU API2/TSK1. In these samples the intense electroluminescence brightness of 100 cd/m². Size J-units are not controlled, but was less than 50 nm. When excited by light samples API2/J-agregaty wavelength $\lambda = 610$ nm, ie in the absorption of J-aggregates, radiates a narrow intense band photofluorescence $\lambda_{max} = 665$ nm, due to the nanocrystalline crystal phase. Spectrum of electroluminescence layer API2/J-agregaty has an intense narrow band with λ_{max} at 675 nm (see Fig. 2). From Fig. 2 it also follows that the width on the electroluminescence band at half strongly narrower, taking values 3,25.10³, 1,20.10³, 0,70.10³ sm.1 for API2, API2/TSK1, API2/J-agregaty respectively.

Explanation of electroluminescence layers API/J-units is hampered by the limited information on redox potentials of these nanoparticles in a polymer matrix Ritz. The only available information relates to photoinduced oxidation of a mixture consisting of tiakarbotsianinovogo dye molecules and their J-aggregates, adsorbed on the surface of the semiconductor [23]. In [23] showed that J-aggregates act as a component which restores the photooxidation of dye molecules, carriers in the mixture, ie ϕ_{ox}

1 / 2 J-aggregates should be higher than ϕ_{ox} 1 / 2 of cyanine dyes. It was noted, but that their oxidation potentials differ not much. Thus, one can assume that the relative positive tion of redox levels of cyanine dyes and J-aggregates in the polymer matrix are close to each other. The energy gap ΔE between the HOMO and LUMO can be estimated from the low-energy decay of the band in absorption of J-aggregates in API2. It was found that ΔE (J-aggregates) \approx 1,49 eV. Hence, the energy E_{red} for J-aggregates localized slightly lower than that of isolated molecules molecules (E_{red} (TSK1) = 3.3 eV). From an examination of energy chart shows that ΔE (API2) > ΔE (TSK1) > ΔE (J-aggregates). In the same manner increases their ϕ_{ox}

1 / 2, Sun-stanovitelye potentials have the reverse order.

It can be concluded that the J-aggregates absorb all excitation energy in the composite.

Kinetic characteristics of the luminescence yayayayayayayayaya (Fig. 4) using rectangular pulses stress duration of 100 microseconds. In the case nomodified-differentiated layer of API2 (d = 100 nm) time delay signal $t_0 \approx 7$ ms (curve 1) (t_0 . the time of flight carriers charge carriers through the polymer layer). Transport properties-Islands vary sharply in the presence of J-aggregates. the film API2/J-agregaty even thickness of 200 nm (curve 2) for-support the signal is not observed. According to the measurements with using time-of-flight mobility method carriers in more than one order of magnitude under-mobility of segments in the case of pure polymer and polymer doped with cyanine dye.

When using other cyanine dyes also received very narrow band electroluminescence tra: for 3,3 '-di (γ -sulfopropil)-9-ethyl-5, 5'-difeniloksakarbotsianinpiridiniya) in the green (λ_{max} = 573 nm), for 3,3 '-di (γ -sulfopropil) -4,5,4', 5'-dibenzo-12-methyl-11, 13 - (β , β -dimetiltrimeti-flax) tiadi-karbotsianinbetaintrietilammoniya) in the IR region (λ_{max} = 780 nm). For green OELU with a brightness of 100 cd/m², current of 10 mA/cm² and the operating voltage of 7 In the quantum efficiency of the light radiated from OELU and effective radiation efficiency of power amounted to \sim 0.3% (1 cd / A) and \sim 0.45 lm / W, respectively.

Thus, we found an efficient electroluminescence nescence in a new class of electroactive organic

skih polymer composites based on J-aggregates of cyanine dyes. Systems allow reproduce the maximum saturated pure colors spectral position of the emitting light can be measured propagate in the visible and near infrared bands in dependence Step on the structure of cyanine dyes. However, nanocomposites ristallicheskaya phase significantly improves the electron-transport characteristics of composite layers. We have also investigated polymer systems, including inorganic semiconductor nanoparticles nick. polyaniline film, dipirovannye nanoparticles mi CdS. Electroluminescence intensity in such system is observed throughout the visible spectral range when applying voltage pulses with amplitude 20 V and a duration of 20 ms. Unlike polymer composites IPAs with J-aggregates in Polyanna Lina containing inorganic nanoparticles, light signal decreases sharply after a few short voltage pulses with an interval of 10 seconds. To ver- o.s to the old values of the signal must be submitted, vat voltage pulse of approximately the same amplitude and duration, but the reverse polarity. It should be noted that large fluctuations of current in the electroluminescence not appreciably affect the kinetics of complex by nature of recombination processes, which leads to dyaschih to radiation. Given the large surface