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Comparative Analysis of Light Absorption Spectra in Lutetium Diphthalocyanine Films Depending on the Substrate

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Films of lutetium diphthalocyanine were created on various substrates by vacuum deposition. The light absorption spectra and surface resistances in the obtained films were measured. A comparative analysis of the light absorption spectra and resistances of various lutetium diphthalocyanine films was carried out. The effect of substrates on the light absorption spectra in lutetium diphthalocyanine films was determined. The results obtained can be used to consider the possible creation of a gas sensor based on lutetium diphthalocyanine films on organic and inorganic substrates.

Keywords: lutetium diphthalocyanine, films, glass, polyvinylchloride, absorption spectrum, PVC, LuPc2.

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Introduction

Scientific and practical advances in micro- and nanoelectronics based on inorganic semiconductors, such as silicon, gallium arsenide, and boron nitride, have stimulated research in organic semiconductors [1–4] as well. Organic semiconductors (or, in other words, molecular semiconductors) have attracted the attention of researchers due to their chemical and thermal resistance, high processability, low cost, and weak (or completely lacking) toxicity during fabrication, operation, and disposal. Metal phthalocyanines are a particular example of molecular semiconductors. In addition to the above properties, metal phthalocyanines possess semiconducting properties and are capable of forming thin crystalline, polycrystalline, and amorphous films. These properties make it possible to use metal phthalocyanines to create gas sensors, solar cells, and other optoelectronic devices [5–8]. To change optical and electrophysical properties, metal phthalocyanines are modified by various elements; for example, hydrogen atoms in benzene rings are replaced by halogen atoms (fluorine, chlorine, etc.) or complexing agent atoms are replaced by various transition metals and lanthanides [9]. The creation of double- and triple-decked lanthanide phthalocyanines, where lanthanides, such as the trivalent positively charged lutetium ion, are used as the complexing agent, can also be regarded as modification. Lanthanide complexes, in particular lutetium complexes, during their synthesis allow to create monophthalocyanines, diphthalocyanines and lutetium triphthalocyanines. It is important to note that the number of excited states of lutetium diphthalocyanine molecules increases compared to lutetium monophthalocyanine due to ligand interactions. Note also the practical effect that consists in the weaker ability of lutetium diphthalocyanine molecules to form dimers in comparison with lutetium monophthalocyanine molecules. In the present study, samples of the organic semiconductor lutetium diphthalocyanine were produced by vacuum sputtering on different substrates and examined.

Both inorganic materials (silicate glass) and organic substances (pure polyvinyl chloride and heat-treated polyvinyl chloride) were used as substrates. In addition to dividing substrates into organic and inorganic, they can be distinguished by their structure. The substrates may have a crystalline structure, an amorphous structure, or combinations thereof. The structure of the inorganic silicate glass substrate is amorphous. Polymers, which include polyvinyl chloride, exist in two phase states: crystalline and amorphous. At present, all amorphous polymers exist in three physical states: glassy, highly elastic, and viscous. The transition from the glassy state to the highly elastic one occurs at glass transition temperature T_C. The glass transition temperature for pure polyvinyl chloride is $T_C = 80^\circ$C. Both amorphous and crystalline regions are present in real polyvinyl chloride. In this case, crystalline regions dominate over amorphous regions at temperatures below the glass transition temperature. Both crystalline and amorphous structures may dominate in a pure polyvinyl chloride substrate at room temperature.

A polyvinyl chloride+polyacetylene copolymer (heat-treated polyvinyl chloride) was obtained by heating pure polyvinyl chloride to 195°C. Polymers are characterized by a phase transition from a crystalline state to an amorphous one at melting temperature T_m. Depending on the number of vinyl chloride molecules, the melting point for polyvinyl chloride varies within the 150−195°C range. Since the heat treatment temperature is within the melting point, the obtained polyvinyl chloride+polyacetylene copolymer (PVC-PAC) is dominated by an amorphous phase. Therefore, the PVC-PAC copolymer substrate can be classified as a substrate with a predominantly amorphous structure. Thus, three substrates were obtained on which lutetium diphthalocyanine molecules were deposited. The first substrate was inorganic silicate glass with an amorphous structure. The second substrate consisted of organic pure polyvinyl chloride with both crystalline and amorphous structures. The third substrate was obtained by heat treatment of pure polyvinyl chloride and was an organic PVC-PAC copolymer (PVC-PAC organic semiconductor) with a largely amorphous structure.

The surface of substrates made of materials with a crystalline-amorphous structure (in the present case, this is the pure polyvinyl chloride substrate) is inhomogeneous. The surface of substrates made of materials with an amorphous structure (in the present case, silicate glass and organic semiconductor PVC-PAC) is homogeneous, and the structure of the sputtered layer of diphthalocyanine molecules is close to ideal [10,11]. Thus, the surfaces of amorphous and crystalline-amorphous substrates exert a strong influence on the concentration, size, shape, and orientation (location) of lutetium diphthalocyanine crystallites.

Lutetium diphthalocyanine films have valuable properties such as chemical resistance, heat resistance up to 500°C, good processability, no toxicity, significant photoabsorption, electrochromism, and semiconducting properties [12]. Trivalent lutetium ions, which serve as a complexing agent of diphthalocyanine molecules, have good photoluminescent and magnetic properties. All metals with a charge greater than two tend to coordinate. Therefore, various gases such as O_2, NO, NO_2, CO, and NH_3 adsorb well on the surface of phthalocyanine molecules with lanthanide ions being a complexing agent. Lanthanide phthalocyanines readily bind gas molecules on the surface, inducing a marked change in electrical conductivity and optical properties. The change of electrophysical and optical properties of lanthanide phthalocyanines upon adsorption of gases makes it possible to create chemical gas sensors on their basis. The structure of metal phthalocyanine films is influenced by the following deposition parameters: evaporator temperature, substrate temperature, film growth rate, and substrate material. In the present work, the absorption spectra of lutetium diphthalocyanine were studied as a function of substrate material and evaporator temperature at a fixed substrate temperature of 50°C. The aim of the present study was to examine the effect of substrates on the light absorption spectra of lutetium diphthalocyanine and, consequently, the interactions between inorganic and organic substrate molecules and lutetium diphthalocyanine molecules of the film.

Experimental

Among the main practically important properties of unsubstituted metal phthalocyanines, including mono- and diphthalocyanines of lanthanides, are their high thermal stability and ability to sublimate in vacuum without decomposition. This property enables the preparation of thin films of metal phthalocyanines by physical vapor deposition (PVD). For practical applications such as gas sensors, metal phthalocyanine films are more technologically advanced than single crystals.

Thermal vacuum sputtering by PVD was used to obtain lutetium diphthalocyanine films. Powder (in the form of needle-shaped crystals) of green-colored lutetium diphthalocyanine in a molybdenum evaporator was used as the starting material, and silicate glass, pure (original) polyvinyl chloride (PVC), and heat-treated polyvinyl chloride (PVC-PAC) were used as the target (substrate). The chemical formula of lutetium diphthalocyanine can be written in the general form $Lu(C_{32}H_{16}N_8)_2$, the formula of silicate glass is $Na_2O{\cdot}CaO{\cdot}6SiO_2$, the formula of pure polyvinyl chloride will be written as $(C_2H_3C_l)_n$, where $n = 1200$ for PVC grade S-7058M, and the formula of heat-treated PVC (conjugated PVC-PAC copolymer) obtained by heating PVC grade S-7058M can be written as $(C_2H_3C_l)_n{+}(C_2H_2)_m$, where n is the degree of polymerization of PVC ($n = 1200$ for S-7058M) and m is the number of conjugated double carbon-carbon bonds ($2m$ is the number of conjugated π-electrons in the conjugation system) that varies, depending on temperature and time of heat treatment, in the range from 5 to 15. A more brief and informative variant of the chemical formula of lutetium diphthalocyanine with designations of charges at the positively charged trivalent lutetium ion and two negatively charged ligands is $[Pc^{2-}Lu^{3+}Pc^{1-}]^{0-}$, where Pc denotes a phthalocyanine molecule without the complexing agent as a ligand. The most compact form of the formula without designations of electric charges is $LuPc_2$, where the lower index 2 denotes the presence of two Pc ligands. The $[Pc^{2-}Lu^{3+}Pc^{1-}]^{0-}$ notation for lutetium diphthalocyanine indicates that molecules are in their neutral form. A lutetium diphthalocyanine molecule in the neutral form has one unpaired electron in molecular orbital $2a_2$. Molecular orbital $2a_2$ of lutetium diphthalocyanine lies between the HOMO and LUMO molecular orbitals, where HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital.

Each of the phthalocyanine Pc (or metal-free phthalocyanine) ligands has $19\,\pi$-electrons in its macrocycle. The two isolated Pc ligands carry $38\,\pi$-electrons in their macrocycles. In total, there are 37 delocalized π-electrons in a lutetium diphthalocyanine molecule in the neutral form within two macrocycles. Lutetium diphthalocyanine molecules in the film create molecular crystallites due to the Van der Waals interaction at a close distance. Easily polarizable lutetium diphthalocyanine molecules are bound together by dispersive attractive forces and short-range repulsive forces. The dispersive attraction force between $LuPc_2$ molecules can be written as a function of distance as

$$F_{\text{disp}} = -(C/R^7), \tag{1}$$

where F_{disp} is the force of dispersive attraction of interacting molecules $LuPc_2$, C is a coefficient depending on the electron polarizability and ionization potentials of the interacting molecules, and R is the distance between the interacting molecules. The short-range repulsive force between $LuPc_2$ molecules can be written as a function of distance as

$$F_{\text{rep}} = (A/R^{13}), \quad (2)$$

where F_{rep} is the repulsive force of interacting molecules $LuPc_2$, A is an empirical coefficient, and R is the distance between interacting molecules.

Long-range Coulomb forces act between Lu^{3+} ions of different lutetium diphthalocyanine molecules. The force of Coulomb interaction between molecules $LuPc_2$ can be written as a function of distance as

$$F_{\text{K}l} = (kq^2)/R^2, \quad (3)$$

where $F_{\text{K}l}$ is the force of Coulomb interaction of lutetium ions, q is the charge of a positively charged trivalent lutetium ion, and k is a coefficient of proportionality.

Thus, the interaction of lutetium diphthalocyanine molecules in the film is due to Van der Waals forces along the c axis at distances smaller than 0.3 nm and to Coulomb forces at distances on the order of 0.38 nm (for the α-modification) or 0.48 nm (for the β-modification of $LuPc_2$). The distance between lutetium diphthalocyanine molecules nominally located in plane ab is 1 nm; therefore, van der Waals forces along axes a and b can be neglected.

A lutetium ion is positioned almost symmetrically between two diphthalocyanine ligands Pc^{2-} and Pc^{1-}. A lutetium ion forms covalent and coordination bonds with the four nearest pyrrole nitrogen atoms of ligand Pc^{2-} and with the four nearest pyrrole nitrogen atoms of ligand Pc^{1-}. Metal phthalocyanine and metal diphthalocyanine molecules can form several (5–8) coordination bonds. A Lu^{3+} lutetium ion forms one covalent bond with one nitrogen (N) atom of ligand Pc^{2-} and one covalent bond with one N atom of ligand Pc^{1-}. A lutetium ion forms three coordination bonds with ligand Pc^{2-} and three coordination bonds with ligand Pc^{1-}. A total of two covalent and six coordination bonds are formed between one lutetium ion Lu^{3+} and ligands Pc^{1-} and Pc^{2-} in a lutetium diphthalocyanine molecule. Covalent bonds are formed by the exchange mechanism, and coordination bonds are formed by the acceptor-donor mechanism. In lutetium diphthalocyanine, Lu^{3+} ions act as acceptors, and ligands Pc^{2-} and Pc^{1-} are donors for a lutetium ion. In the process of ligand-to-ligand interaction, ligand Pc^{2-} is the donor and ligand Pc^{1-} is the acceptor due to charge transfer between the ligands [1]. This ligand interaction leads to the emergence of additional peaks in the absorption spectra of lutetium diphthalocyanine films.

During heating of $LuPc_2$ powder to 480°C for 30 min, sublimation and deposition (condensation) of lutetium diphthalocyanine molecules on various substrates occurred. To find the optimum sublimation temperature, lutetium diphthalocyanine powder was processed at temperatures of 350, 405, 415, and 480°C for 30 min. This heating resulted in sublimation of lutetium diphthalocyanine molecules and their deposition (adsorption) on the surface of inorganic and organic substrates. As a result, a series of β-form lutetium diphthalocyanine crystalline films with impurity concentrations below $10^{16}\,\text{cm}^{-3}$ were obtained. The thickness of lutetium diphthalocyanine films obtained by heating the $LuPc_2$ powder to a temperature of 480°C was about 200 nm. Absorption spectra of lutetium diphthalocyanine films were measured with an Option Optics 2000 spectrometer with a dynamic range of 300–1100 nm. A tungsten lamp with a power of 10 mW was used as a radiation source. Lutetium diphthalocyanine films on substrates were fabricated using a VUP-5 vacuum unit.

Results and discussion

The presence of a delocalized conjugated π-system in lutetium diphthalocyanine molecules leads to intense absorption of radiation in the 350–1000 nm optical range. Absorption spectra were measured for $LuPc_2$ lutetium diphthalocyanine LuPc films on a silicate glass substrate at a temperature of 23°C (Fig. 1). Analyzing the spectra in Fig. 1, we see that the main light absorption peaks characteristic of lutetium diphthalocyanine molecules are not observed at a $LuPc_2$ powder heating temperature of 350°C. Therefore, it can be assumed that no sublimation occurs when the powder is heated to 350°C and, therefore, virtually no lutetium diphthalocyanine molecules are deposited on silicate glass. When the heating temperature is increased to 405°C, a Q-band absorption band appears, the peak of which corresponds to a wavelength of 668 nm. At the same time, light absorption bands BV and B are not observed in the absorption spectrum. Upon further heating to a temperature of 415°C, three main absorption peaks appear in the absorption spectrum of lutetium diphthalocyanine in the optical range of 350–1000 nm. The Q-band absorption peak corresponds to a wavelength of 667 nm, the BV-band absorption peak corresponds to a wavelength of 462 nm, and the B-band absorption peak corresponds to a wavelength of 350 nm. Absorbance D for Q-, BV-, and B-band light absorption is negligible and lies in the 0.11–0.2 range. The $LuPc_2$ film obtained by heating the evaporator to 415°C is denoted as sample 1.

A film of lutetium diphthalocyanine on a silicate glass substrate obtained by processing $LuPc_2$ powder at 480°C for 30 min is denoted as sample 2. The light absorption spectrum in sample 2 at a measurement temperature of 23°C is shown in Fig. 2. Analyzing the spectrum in Fig. 2, one can see that four absorption peaks and associated absorption bands Q, BV, B, and RV are found in sample 2. The Q-band peak corresponds to a wavelength of 667 nm ($E_{\text{Q}} = 1.86\,\text{eV}$), the BV- band peak corresponds to a wavelength of 464 nm ($E_{\text{BV}} = 2.67\,\text{eV}$), the B-band peak corresponds to a wavelength of 352 nm ($E_{\text{B}} = 3.52\,\text{eV}$), and the RV-band peak corresponds to a wavelength of

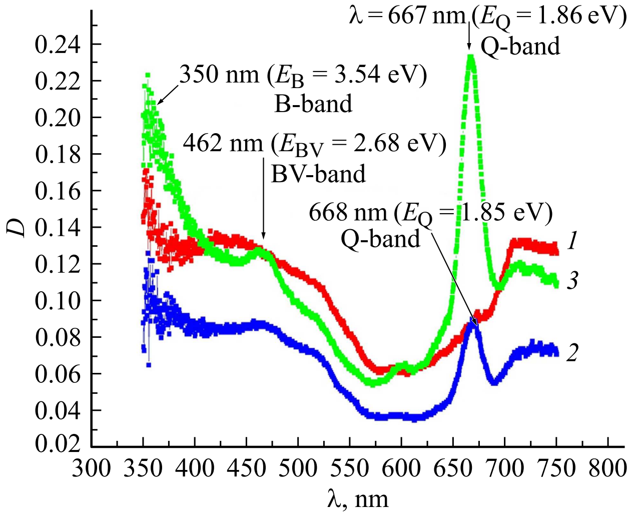

Figure 1. Light absorption spectra of $LuPc_2$ films on a silicate glass substrate at powder heating temperatures$LuPc_2$: 350 (*1*), 405 (*2*), 415°C (*3*).

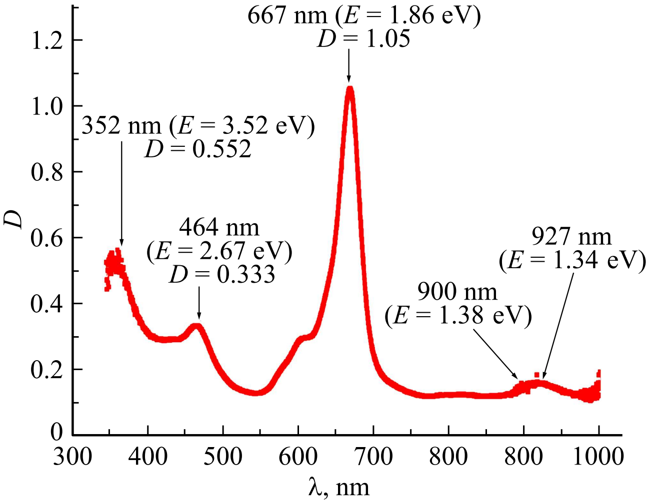

Figure 2. Light absorption spectrum of the $LuPc_2$ film on a silicate glass substrate (sample 2).

920 nm (E_{RV} = 1.35 eV). Absorbance *D* of the Q-band peak is 1.05. The half-width of the Q-band peak is 40 nm. The absorbances of the BV- and B-band peaks are 0.33 and 0.55, respectively. The absorbance of the Q-band peak of the absorption spectrum for sample 2 is six times the *D* value of sample 1. The absorbance of the BV-band peak of the absorption spectrum for sample 2 is three times the *D* value of sample 1. The absorbance of the B-band peak of the absorption spectrum for sample 2 is 2.5 times higher than *D* of sample 1. This marked increase in light absorption in sample 2 compared to sample 1 makes it possible to use sample 2 for a more in-depth study of the optical properties. Heating of $LuPc_2$ powder to temperatures greater than 480°C generally leads to degradation of lutetium diphthalocynanine molecules, so we can consider a heating temperature of 480°C as the optimal temperature for sublimation of $LuPc_2$.

The film of lutetium diphthalocyanine produced on a pure S-7058M polyvinyl chloride substrate in the course of sublimation of $LuPc_2$ powder processed at 480°C for 30 min is denoted as sample 3. The film of lutetium diphthalocyanine produced on an S-7058M heat-treated polyvinyl chloride substrate in the course of sublimation of $LuPc_2$ powder processed at 480°C for 30 min is denoted as sample 4. The light absorption spectra of samples 2, 3, and 4 obtained at a measurement temperature of 23°C are shown in Fig. 3. Analyzing the absorption spectra of lutetium diphthalocyanine films on different substrates in Fig. 3, one sees that five well-defined absorption peaks are found in samples 2, 3, and 4. Four light absorption peaks correspond to absorption bands Q, B, BV, and RV, and the fifth absorption peak is vibrational companion VS of the Q band.

For sample 3, the Q-band light absorption peak corresponds to a wavelength of 667 nm ($E_Q = 1.86$ eV), the BV-band absorption peak corresponds to a wavelength of 464 nm ($E_{BV} = 2.67$ eV), the B-band absorption peak corresponds to a wavelength of 365 nm ($E_B = 3.4$ eV), and the RV-band absorption peak corresponds to a wavelength of 921 nm ($E_{RV} = 1.35$ eV). The peak of vibrational satellite VS corresponds to a wavelength of 604 nm ($E_{VS} = 2.05$ eV). The absorbances of light absorption bands Q, D, B, and RV are 2.27, 0.86, 1.13, and 0.26, respectively. The half-widths of the Q-band, B-band, BV-band, and RV-band are 46, 31, 20, and 53 nm, respectively.

For sample 4, unlike samples 2 and 3, the Q-band peak is not pronounced. The absorbance of this peak remains the same in the 666–676 nm range, and it can be said that the peak is a plateau in absorbance or a broadened peak. If we take the wavelength corresponding to the middle of the peak, then the Q-band absorption peak of sample 4 corresponds tentatively to a wavelength of 667 nm ($E = 1.86$ eV). The peak of the BV absorption band corresponds to a wavelength of 469 nm ($E = 2.64$ eV), the peak of the B absorption band corresponds to a wavelength of 365 nm ($E = 3.4$ eV), and the peak of the RV absorption band corresponds to a wavelength of 923 nm ($E = 1.34$ eV). Absorbances *D* of the light absorption peaks of bands Q, BV, B, and RV were 2.01, 1.23, 1.12, and 0.46, respectively. The half-widths of bands Q, B, BV, and RV are 65, 36, 19, and 45 nm, respectively.

In samples 2–4, the presence of a single peak with a wavelength of 667 nm in the Q absorption bands indicates a decrease in the symmetry of a lutetium diphthalocyanine molecule compared to the symmetry of a molecule of phthalocyanine H_2Pc. Phthalocyanine molecules have symmetry D_{4V}. Lutetium diphthalocyanine molecules are characterized by symmetry C_{4V}, which corresponds to a square-pyramidal spatial structure. The molecular orbitals of a lutetium diphthalocyanine molecule with symmetry C_{4V} are characterized by symmetry a_1, a_2, b_1, b_2, e_1, and e_3.

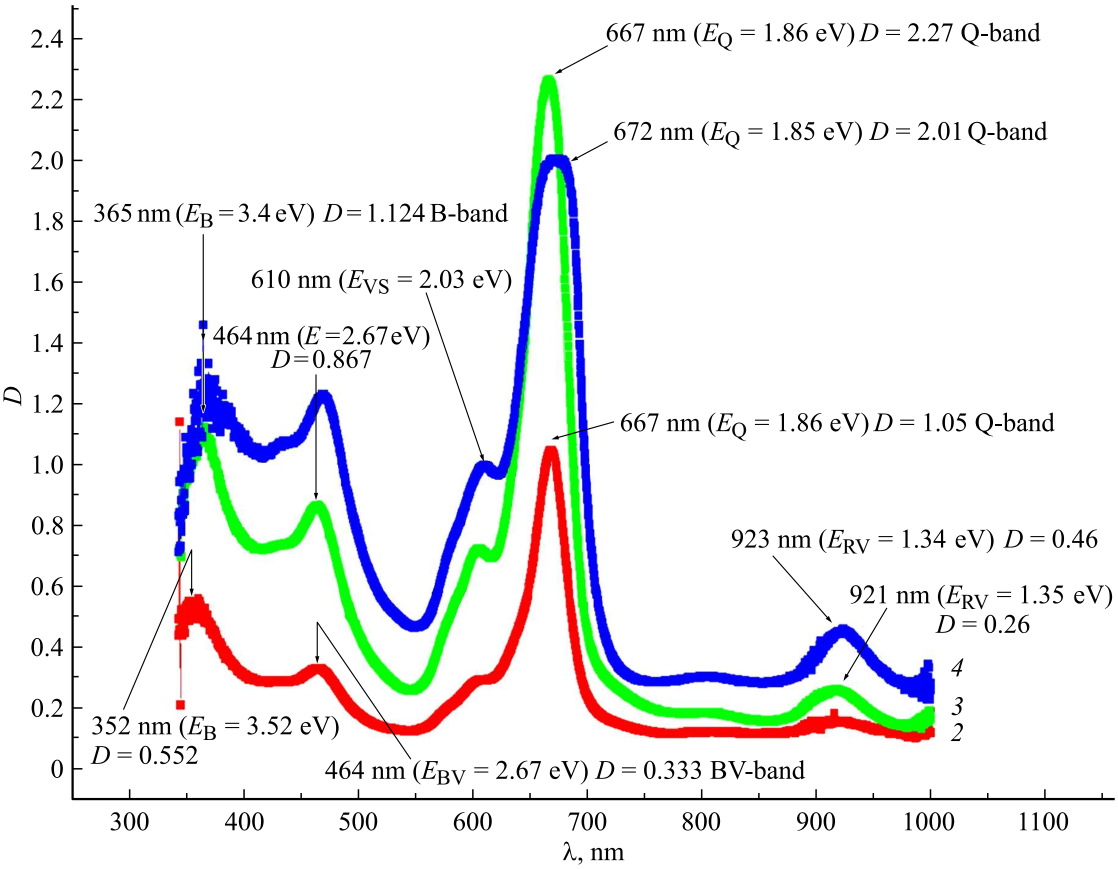

Figure 3. Light absorption spectra of $LuPc_2$ films: *2* — $LuPc_2$ on a silicate glass substrate (sample 2), *3* — $LuPc_2$ on a pure PVC substrate (sample 3), and *4* — $LuPc_2$ on a heat-treated PVC substrate (sample 4).

Light absorption in the Q band with a peak at 667 nm occurs at conjugated carbon–carbon double bonds of benzene rings ($n = 13$) and conjugated nitrogen–carbon double bonds ($n = 6$) of each Pc ligand. Here, n is the number of conjugated double bonds C=C and C=N. In total, there are 37 π-electrons contributing to the light absorption process in two macrocycles of a lutetium diphthalocyanine molecule. The absorption peaks with wavelengths of 667 nm (Q band) in $LuPc_2$ samples 2–4 correspond to the electronic transition from HOMO $2b_1$ to LUMO $6e_3$ (electronic transitions $\pi - \pi^*$). For these samples, the $E_{\text{HOMO-LUMO}}$ (E_Q) energy intervals between the HOMO ground state and the LUMO excited state are 1.86 eV. This electronic transition occurs between the singlet ground state S_0 and the first singlet excited state S_1. Let us consider the main differences in the absorption parameters of samples 2–4 in the Q-band range. The absorbance of the Q-band absorption peak for sample 3 is 2.2 times greater than that of sample 2. The absorbance of the Q-band absorption peak for sample 4 is 1.9 times greater than that of sample 2. We thus can conclude that the light absorption intensity of the Q-band peak in the lutetium diphthalocyanine film on a PVC-PAC copolymer and pure PVC substrates is $1.9 - 2.2$ times higher than the light absorption intensity in the $LuPc_2$ film on a silicate glass substrate. The wavelengths of Q-band peaks for samples 2–4 are the same: 667 nm ($E_{\text{HOMO-LUMO}} = 1.86$ eV). The half-width of the Q band for samples 3 and 4 is 9 and 28 nm larger than that of sample 2, respectively. It can be concluded that light absorption in the $LuPc_2$ film on PVC and PVC-PAC substrates shows broadening of the Q band compared to the $LuPc_2$ film on silicate glass.

The increase in half-width of the Q band is caused by a stronger interaction of lutetium diphthalocyanine molecules with substrate molecules as well as with each other. In the process of film sputtering, most lutetium diphthalocyanine molecules are deposited on the PVC surface, while a smaller fraction diffuses into the PVC or PVC-PAC matrix volume. At the interface of $LuPc_2$ and PVC film, the interaction between $LuPc_2$ molecules and C_2H_3Cl molecules in PVC macromolecules is due to Van der Waals forces. Diffusing into the PVC volume, $LuPc_2$ molecules interact with C_2H_3Cl molecules due to van der Waals forces, while positively charged ions Lu^{3+} in $LuPc_2$ molecules and partially ionized Cl atoms in C_2H_3Cl interact due to Coulomb forces. This, in turn, enhances the interaction between $LuPc_2$ molecules and substrate molecules. This interaction of $LuPc_2$ molecules under illumination of a lutetium diphthalocyanine film causes electronic transitions from molecular orbital HOMO $2b_1$ to higher vibrational levels of orbital LUMO $6e_3$.

The absorption peaks (B band) in samples 2–4 $LuPc_2$ with wavelengths of 352 and 365 nm correspond to two electronic transitions: from orbital $4a_1$ HOMO-1 to orbital $6e_1$ LUMO+1 and from orbital $4b_2$ to orbital $6e_3$ LUMO (electronic transitions $\pi-\pi^*$). For sample 2, energy interval E_{B1} of the $4a_1 \to 6e_1$ transition is 3.52 eV. For samples 3 and 4, energy interval E_{B2} of the $4b_2 \to 6e_3$ transition is 3.4 eV. The electronic transition in the B-band interval occurs between the singlet ground state S_0 and the second singlet excited state S_2. Let us consider the main differences in the absorption parameters of samples 2–4 in the B-band range. The absorbance of the B-band absorption peak for sample 3 is 3.2 times greater than that of sample 2. The absorbance of the B-band absorption peak for sample 4 is 3.4 times greater than that of sample 2. Thus, the light absorption of the B-band peak in the lutetium diphthalocyanine film on a PVC-PAC copolymer and pure PVC substrates is $3.2-3.4$ times higher than that in the $LuPc_2$ film on a silicate glass substrate. The wavelengths of B-band peaks of samples 3 and 4 match and are equal to 365 nm ($E_{B2} = 3.4$ eV). The wavelength of the B-band peak of sample 2, which is 352 nm ($E_{B1} = 3.52$ eV), is 13 nm shorter than the corresponding wavelength for samples 3 and 4. Thus, electronic transition $4a_1 \to 6e_1$ in the B band with energy $E_{B1} = 3.52$ eV occurs in the film of lutetium diphthalocyanine on a silicate glass substrate upon light absorption, and electronic transition $4b_2 \to 6e_3$ in the B band with energy $E_{B2} = 3.4$ eV proceeds in the film of lutetium diphthalocyanine on pure PVC and PVC-PAC substrates upon light absorption. The energy difference between the $4b_2 \to 6e_3$ (B1) and $4a_1 \to 6e_1$ (B2) transitions is 0.12 eV. Thus, the B-band transition energy is lower for $LuPc_2$ films on organic polymer substrates compared to inorganic amorphous substrates. The half-width of light absorption in the B band is 31 nm for sample 3 and 36 nm for samples 2 and 4; i.e., the peak is broadened only by 5 nm.

Note that a characteristic difference between the spectra of lutetium diphthalocyanine and lutetium monophthalocyanine is the emergence of additional absorption bands BV and RV due to the interaction of ligands Pc^{2-} and Pc^{1-}. In other words, the molecular orbitals of lutetium diphthalocyanine are formed by cleavage of molecular ligands Pc^{2-} and Pc^{1-} as a result of their interaction. Note that the BV band is characteristic of the neutral form of a lutetium diphthalocyanine molecule $[Pc^{2-}Lu^{3+}Pc^{1-}]^{0-}$.

The absorption peaks (BV band) in $LuPc_2$ samples 2–4 with wavelengths of 464 and 469 nm correspond to the electronic transition from degenerate orbital $5e_1$ to $2a_2$ SOMO (electronic transitions $\pi-\pi^*$). For samples 2 and 3, the energy of the E_{BV} electronic transition between orbitals $5e_1$ and $2a_2$ is 2.67 eV, and the energy for sample 4 is 2.64 eV. Let us consider the main differences in the absorption parameters of samples 2–4 in the BV-band range. Absorbance D of the absorption peak of the BV band for sample 3 is 2.6 times greater than that of sample 2. Absorbance D of the absorption peak of the BV band for sample 4 is 3.7 times greater than that of sample 2. Therefore, it can be concluded that the light absorption of the BV band in the lutetium diphthalocyanine film on substrates based on an organic semiconductor material (PVC-PAC) and pure PVC is $2.6-3.7$ times higher than the light absorption in the $LuPc_2$ film on a silicate glass substrate.

A small bathochromic shift of 5 nm is observed for sample 4 compared to samples 2 and 3. It follows that energy interval E_{BV} for sample 4 decreases by 0.03 eV compared to samples 2 and 3. It can be assumed that the E_{BV} energy of the $5e_1 \to 2a_2$ electronic transition for the lutetium diphthalocyanine film on a PVC-PAC organic semiconductor substrate is slightly reduced compared to energy E_{BV} for $LuPc_2$ films on pure PVC and silicate glass substrates due to a weak bathochromic effect. The half-width of the BV absorption band for samples 2–4 lies in the range of $18-20$ nm. This suggests that a change in the nature of the substrate does not contribute to broadening of the BV band in the light absorption spectrum of $LuPc_2$ molecules. It can also be inferred that the interaction of lutetium diphthalocyanine molecules via Van der Waals forces with vinyl chloride molecules in a PVC macromolecule and the Coulomb interaction of lutetium ions with partially ionized chlorine atoms do not lead to a marked change in the interaction between ligands Pc^{1-} and Pc^{2-}.

The absorption peaks (RV band) with wavelengths of 920, 921, and 923 nm in $LuPc_2$ samples 2, 3, and 4, respectively, correspond to the electronic transition from molecular orbital $2a_2$ (SOMO) to $6e_3$ (LUMO) (electronic transitions $\pi-\pi^*$). For samples 2–4, energy E_{RV} of the electron transition between the SOMO→ LUMO orbitals is $1.34-1.35$ eV. Let us consider the main differences in the absorption parameters of samples 2–4 in the RV-band range. Absorbance D of the absorption peak of the RV band for sample 3 is 1.6 times greater than that of sample 2. Absorbance D of the absorption peak of the RV band for sample 4 is 2.9 times greater than that of sample 2. Therefore, it can be concluded that the RV-band light absorption in the lutetium diphthalocyanine film on substrates based on pure PVC and an organic semiconductor material (PVC-PAC) is $1.6-2$ times higher than the light absorption in the $LuPc_2$ film on a silicate glass substrate. The half-width of the RV band for samples 2, 3, and 4 is 50, 53, and 45 nm, respectively. Compared to the half-width of the spectrum of sample 2, the half-width of the RV band for sample 3 is 3 nm greater, while the half-width of sample 4 is 5 nm smaller. It can be concluded that a change in the nature of the substrate has almost no effect on broadening of the RV band in the light absorption spectrum of $LuPc_2$ molecules.

Surface resistivity R_S at 23°C was also measured for samples 2–4. For surface resistivity measurements, silver contacts were sputtered on all samples. For sample 2 ($LuPc_2$ film on a silicate glass substrate), surface resistivity R_S was $4 \cdot 10^7\,\Omega$. For samples 3 ($LuPc_2$ on a pure PVC substrate) and 4 ($LuPc_2$ film on a PVC+PAC substrate), resistance R_S

was $3 \cdot 10^8$ and $8 \cdot 10^7\,\Omega$, respectively. It can be seen that the substrates do not affect significantly the surface resistivity of lutetium diphthalocyanine films. Note that in the process of measuring the surface resistivity of sample 2 (silicate glass substrate), the lutetium diphthalocyanine film was removed partially due to the application of contacts of the teraohmmeter when the resistance measurements were carried out without silver contacts. This is indicative of poor adhesion between a lutetium diphthalocyanine film and a silicate glass substrate or insufficient cleaning of the glass surface before sputtering. For samples 3 and 4, the $LuPc_2$ film on PVC and PVC-PAC substrates remained intact, indicating fine adhesion. Thus, to create gas sensors based on lutetium diphthalocyanine sputtered on inorganic and boundary substrates, it is necessary to take into account the nature of interaction between lutetium diphthalocyanine molecules and substrate molecules, as well as their adhesive properties.

Conclusion

The influence of organic and inorganic substrates on the light absorption spectra of lutetium diphthalocyanine films has been studied. The absorption of light in lutetium diphthalocyanine molecules in $LuPc_2$ films on organic substrates was found to be higher than that in $LuPc_2$ films on an inorganic substrate. The effect of substrates on electronic transitions in diphthalocyanine molecules and the half-width of light absorption spectra in $LuPc_2$ molecules was revealed.

The following conclusions have been made as a result of this research.

1. The $E_{\text{HOMO-LUMO}}$ energy gap value of the Q band of lutetium diphthalocyanine molecules is $E_Q = 1.86\,\text{eV}$ and is independent of the substrate nature. This can be explained by the fact that energy gap $E_{\text{HOMO-LUMO}}$ of lutetium diphthalocyanine molecules does not change when lutetium diphthalocyanine molecules interact with silicate glass molecules, vinyl chloride molecules in pure polyvinyl chloride macromolecules, and double conjugated carbon–carbon bonds in PVC-PAC.

2. The electronic transition energies for absorption peaks of the B band of diphthalocyanine molecules depend on the substrate type. In the case of an inorganic silicate glass substrate, transition $4a_1 \to 6e_1$ with energy $E_{B1} = 3.52\,\text{eV}$ occurs in lutetium diphthalocyanine molecules; in the case of organic PVC and PVC-PAC substrates, transition $4b_2 \to 6e_3$ with energy $E_{B2} = 3.4\,\text{eV}$ is typical. It can be concluded that the energy of $\pi-\pi^*$ B-band electronic transitions in lutetium diphthalocyanine films on organic substrates is 0.12 eV lower than the energy of $\pi-\pi^*$ transitions in $LuPc_2$ molecules on inorganic substrates.

3. The electronic transition energies for absorption peaks of the BV band of diphthalocyanine molecules on different substrates differ slightly. For sample 4, the energy of transition $\pi-\pi^*$ $E_{BV} = 2.64\,\text{eV}$, which is just 0.03 eV lower than $E_{BV} = 2.67\,\text{eV}$ in samples 2 and 3. Electronic transitions $\pi-\pi^*$ typical of the BV-band light absorption spectra of diphthalocyanine molecules are practically independent of the nature of the substrate.

4. The electronic transition energies for absorption peaks of the RV band of diphthalocyanine molecules on different substrates reveal almost no variation. For sample 4, energy E_{RV} of the $\pi-\pi^*$ transition is 1.34 eV, while in samples 2 and 3, $E_{RV} = 1.35\,\text{eV}$. Electronic transitions $\pi-\pi^*$ typical of the RV-band light absorption spectra of diphthalocyanine molecules are independent of the nature of the substrate.

5. The half-width of the Q band of the light absorption spectrum in a lutetium diphthalocyanine film depends on the nature of the substrate. The Q band of the light absorption spectrum in a lutetium diphthalocyanine film on organic substrates is broader than the one on inorganic substrates. The half-width of the Q band of the absorption spectrum of lutetium diphthalocyanine molecules on a silicate glass substrate is minimal and equal to 37 nm, and the half-width of the Q band of $LuPc_2$ on a PVC-PAC substrate is maximal and equal to 65 nm. This fact can be explained by stronger van der Waals and Coulomb interactions of lutetium diphthalocyanine molecules and vinyl chloride molecules in PVC and PVC-PAC macromolecules compared to the interaction of $LuPc_2$ molecules with silicate glass molecules.

6. The half-width of the B band of the light absorption spectrum in a lutetium diphthalocyanine film is practically independent of the nature of the substrate. This half-width for lutetium diphthalocyanine molecules on a pure PVC substrate is minimal and equal to 31 nm, while the B-band half-width for $LuPc_2$ molecules on silicate glass and PVC-PAC substrates is maximal and equal to 36 nm.

7. The half-width of the BV band of light absorption in a lutetium diphthalocyanine film is practically independent of the nature of the substrate. The half-width of the BV band of absorption spectra of lutetium diphthalocyanine molecules on organic and inorganic substrates varies in the range of 18–20 nm.

8. The half-width of the RV band of the light absorption spectrum of a lutetium diphthalocyanine film depends on the nature of the substrate. This half-width is 50 nm on a silicate glass substrate, 53 nm on a pure PVC substrate, and 45 nm on a pure PVC+PAC substrate.

Thus, summarizing finally the results of studies into the light absorption spectra of lutetium diphthalocyanine films on different substrates, we can state the following.

1. The energy of electronic transitions typical of the peaks of Q, BV, and RV absorption bands in lutetium diphthalocyanine films does not depend on the substrate nature. The energy of electronic transitions typical of the peaks of B-band absorption spectra in lutetium diphthalocyanine films on organic substrates is lower than the energy of transitions on the inorganic substrate.

2. The half-widths of B and BV light absorption bands in lutetium diphthalocyanine films do not depend on the nature of the substrate. The half-widths of Q and RV

light absorption bands in lutetium diphthalocyanine films depend on the nature of the substrate. For example, the maximum increase in the half-width of the Q band is 28 nm for a lutetium diphthalocyanine film on a PVC substrate compared to a silicate glass substrate.

3. The $\pi-\pi^*$ electronic transition energies of the B band of the light absorption spectrum in lutetium diphthalocyanine films are smaller on organic PVC and PVC+PAC substrates compared to the transition energies on an inorganic silicate glass substrate. The half-width of the Q band of light absorption in lutetium diphthalocyanine films on a PVC substrate is greater than the corresponding half-width on a silicate glass substrate.

4. Gas sensors based on lutetium diphthalocyanine can be produced on both organic and inorganic substrates by exploiting changes in the intensity of the Q band of the light absorption spectrum. The use of the Q band specifically is due to two factors: the Q band has the highest intensity and the $E_{\text{HOMO-LUMO}}$ energy gap value of the Q band of a lutetium diphthalocyanine film is independent of the nature of the substrate.

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