Optics and Spectroscopy, 2024, Vol. 132, No. 6

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Interaction of ammonia gas with lutetium diphthalocyanine film

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Received June 13, 2024
Revised June 13, 2024
Accepted June 28, 2024

A lutetium diphthalocyanine chromophore film was created on a silicate glass substrate. The light absorption spectra and surface electrical resistance of a lutetium diphthalocyanine film on silicate glass were measured under normal conditions and when exposed to ammonia gas. An analysis of these light absorption spectra in a lutetium diphthalocyanine film was carried out in the absence and under the influence of ammonia gas. The influence of ammonia gas molecules on the Q and B bands of the light absorption spectrum in a lutetium diphthalocyanine film on silicate glass was discovered. The effect of ammonia gas on the electrical conductivity of a lutetium diphthalocyanine film on silicate glass was revealed.

Keywords: lutetium diphthalocyanine, absorption spectra, electrical resistance, ammonia gas.

DOI: 10.61011/EOS.2024.06.59526.6787-24

Introduction

Metal phthalocyanines occupy a prominent place among the known chromophores. Metal phthalocyanines are classified as organic semiconductors, but compared with inorganic semiconductors (Si, AsGa, Ge, SiC) they are little used in microelectronics and optoelectronics. metal phthalocyanines also find minor usage, for example, in gas detectors [1]. Therefore, it is necessary to investigate their optical, photovoltaic and electrophysical properties for potential application in the above-mentioned fields.

Metal phthalocyanines have a set of technologically relevant properties. Metal phthalocyanine films fabricated by the sublimation method are relatively pure with impurity concentration of about $10^{14}-10^{15}\,\mathrm{cm}^{-3}$. The metal phthalocyanine films are successfully deposited by evaporation on inorganic (for example, glass, inorganic semiconductors) and organic (for example, polymers) substrates. Metal phthalocyanines have good thermal stability, chemical and thermal resistance. They have 3 far ultraviolet absorption bands and from 2 to 4 optical and near ultraviolet absorption bands. Optical and electrophysical properties of metal phthalocyanines are attributed to the presence of π-electronic system (conjugated carbon-nitrogen and carbon-carbon double bonds). Various metal (Cu, Zn, Ni, Fe, etc.) and rare-earth (Lu, Er, Dy,etc.) ions may be used in the metal phthalocyanine molecules. Due to the large size, rare-earth ions are outside the ligand plane and are able to form diphthalocyanine and triphthalocyanine complexes. Rare-earth metal diphthalocyanine is a complex formed by two phthalocyanine ligands with a rare-earth metal ion between them. The rare-earth metal ion is bound to the ligands through covalent and coordination bonds (Figure 1).

A lutetium diphthalocyanine film has been fabricated and optical and electrophysical properties have been examined in this study. Chemical formula of the lutetium diphthalocyanine may be written as $Lu(C_{32}H_{16}N_8)_2$ in a general form or as $LuPc_2$ in a short form. Here, symbol Pc denotes a phthalocyanine molecule without a complexing agent as a ligand. On one Pc ligand, there are 20 delocalized π-electrons on the benzene rings and 18 delocalized π-electrons on the macro ring, i.e. a total of 38 delocalized π-electrons in the $LuPc_2$ molecule. Two Pc ligands of the $LuPc_2$ molecule have 76 delocalized π-electrons in the reduced form and 75 delocalized π-electrons in the neutral form. A lutetium diphthalocyanine molecule $LuPc_2$ in the neutral form has one unpaired electron in the molecular orbital 2a and this electron is delocalized

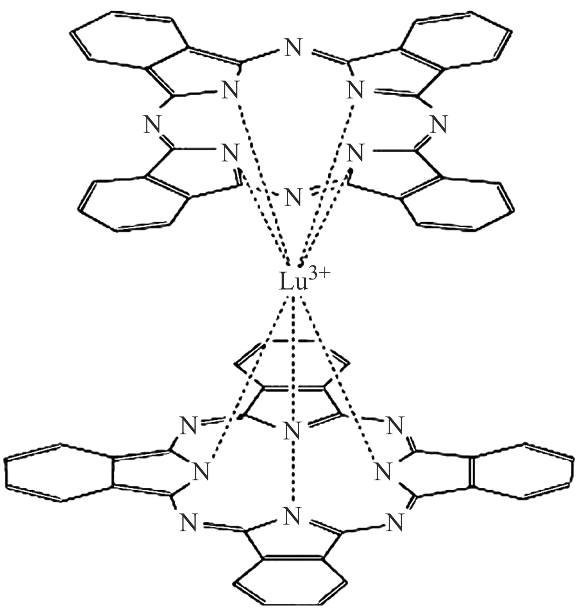

Figure 1. Lutetium diphthalocyanine molecule structure.

on both ligands. The molecular orbital $2a_2$ (SOMO) of lutetium diphthalocyanine is between the HOMO and LUMO molecular orbitals. Here, HOMO is the highest occupied molecular orbital, LUMO is the lowest unoccupied molecular orbital, SOMO is a singly occupied molecular orbital. LUMO-HOMO energy difference defines the energy bandgap width. Energy bandgap inn the diphthalocyanine molecule for the first excited state of the lutetium ion is defined by the electronic transition $2b_1 \rightarrow 6e_3$. In neutral lutetium diphthalocyanine, the Lu^{3+} ions are acceptors, and the Pc^{2-} and Pc^{1-} ligands serve as donors for the lutetium ion. And during interaction between the ligands, the Pc^{1-} ligand serves as the acceptor, the Pc^{2-} ligand is the donor. Interaction between the ligands takes place through the charge transfer between the ligands [2]. Note that the lutetium diphthalocyanine molecules interact in the film due to the Van der Waals forces at a near distance and by the Coulomb forces at a far distance between molecules. Metals with charge more than two, that also include the Lu^{3+} ions, tend to coordinate with the ligands and other molecules [3]. Therefore, various gases, for example, O_2, NH_3, NO, NO_2, CO, CO_2 , etc., are well adsorbed on the surface of the phthalocyanine molecules with the lanthanide ions as a complexing agent and, in particular, on the surface of the lutetium diphthalocyanine molecules [4–6]. Phthalocyanines with lanthanides are able to bind gas molecules on the film surface inducing a significant change in electrical conductivity and light absorption spectra [7–10].

The goal of this study was to investigate the influence of ammonia gas on the light absorption spectra and electrical resistance of the lutetium diphthalocyanine film on the silicate glass substrate.

Experiment

lanthanide phthalocyanines and diphthalocyanines have high thermal stability due to which they are capable of sublimating in vacuum without decomposition [11]. This property allows thin metal phthalocyanine films to be fabricated by the physical vapor-phase deposition method. The lutetium diphthalocyanine films were fabricated by the high-temperature vacuum evaporation method. The thermal evaporation method was used to fabricate the lutetium diphthalocyanine films on the silicate glass substrate at different sublimation temperatures and evaporation times. Lutetium diphthalocyanine film fabricated at a sublimation temperature of $t = 480°C$ and deposition time of 5 min was used to measure the light absorption spectrum and surface resistance. As a result, crystalline β-form lutetium diphthalocyanine film withimpurity concentration not exceeding $N_{\text{imp}} = 10^{15}\,\text{cm}^{-3}$ was fabricated. We designate the lutetium diphthalocyanine film as P480. The silicate glass substrate temperature during deposition was $t = 50°C$.

Lutetium diphthalocyanine films on substrates were fabricated using the VUP-5 vacuum evaporator. Light absorption spectra of the lutetium diphthalocyanine films were measured using the Option Optics 2000 spectrometer with a dynamic range of 300−1100 nm. A 10 mW tungsten lamp with was used as a light source. Surface electrical resistance was measured using the E6-3 teraohmmeter. The lutetium diphthalocyanine film thickness was measured using the ND-MDT scanning atomic-force microscope.

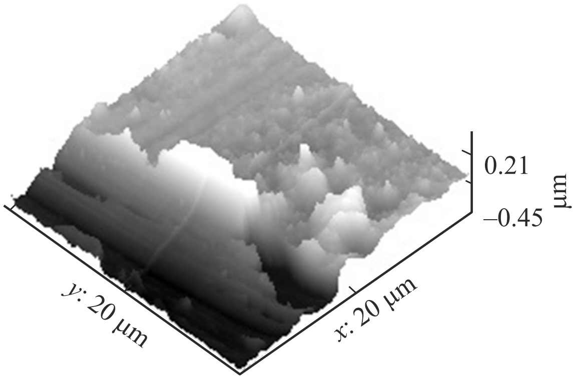

Figure 2. AFM image of the $LuPc_2$ film.

Results and discussion

The impact of various gases on metal phthalocyanines was investigated in [12,13]. This study investigated the impact of ammonia gas on the optical and electrophysical properties of the lutetium diphthalocyanine films. Adsorption of small ammonia molecules takes place on the large surface area of the lutetium diphthalocyanine film due to the Van der Waals forces at near distances and the Coulomb forces at far distances. The NH_3 molecules have donor properties, and the positively charged Lu^{3+} ions exhibit acceptor properties. During interaction between the NH_3 molecules and Lu^{3+} ions, the unshared electron pair NH_3 is transferred to the Lu^{3+} ion in the $LuPc_2$ molecule. This process is driven by the acceptor-donor mechanism, as a result of which a coordination bond between the Lu^{3+} ions and NH_3 molecules is formed. Formation of the $Lu^{3+}-NH_3$ coordination bond may result in the variation of the light absorption spectra and electrical resistance [6].

The NT-MDT scanning atomic-force microscope was used to measure the $LuPc_2$ film thickness (Figure 2). Measurements using the atomic-force microscope (AFM) were performed at $t = 23°C$.

Figure 2 shows that the lutetium diphthalocyanine film thickness is within 200−210 nm.

Localized π-electrons contained in the lutetium diphthalocyanine molecules lead to strong light lutetium in the visible range of 350−1000 nm. For the P480 film, light absorption spectra were measured when the without and with exposure of the film to NH_3 (Figure 3). The absorption spectra were measured on the $LuPc_2$ film at $t = 24°C$.

Analysis of the light absorption spectrum data (Figure 3) suggests that the P480 sample has three absorption

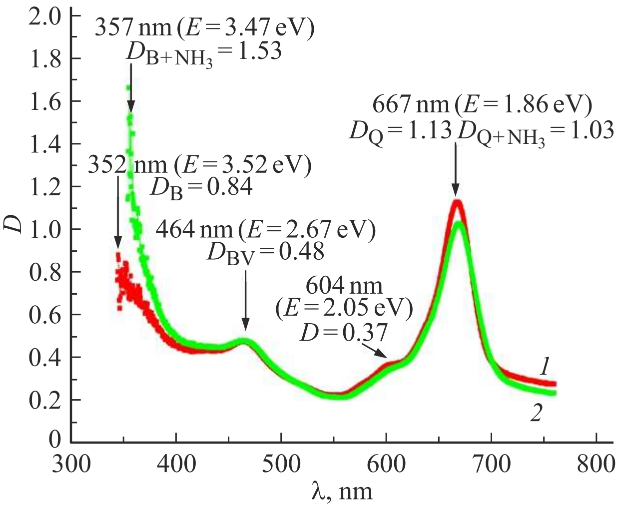

Figure 3. Light absorption spectra of the $LuPc_2$ film on the silicate glass substrate. *1* — red spectrum, $LuPc_2$ film not exposed to ammonia; *2* — green spectrum, $LuPc_2$ film exposed to ammonia.

peaks and the corresponding Q, BV and B absorption bands. For the P480 film, the Q absorption band peak corresponds to $\lambda_m = 667\,\text{nm}$ ($E_Q = 1.86\,\text{eV}$), the BV absorption band peak is at $\lambda_m = 64\,\text{nm}$ ($E_{BV} = 2.67\,\text{eV}$) and, finally, the B absorption band peak corresponds to $\lambda_m = 352\,\text{nm}$ ($E_B = 3.52\,\text{eV}$) without exposure to NH_3 and to $\lambda_m = 357\,\text{nm}$ ($E_B = 3.47\,\text{eV}$) with exposure to NH_3. The absorbance (D) of the Q band peak of the P480 film is equal to $D_Q = 1.13$ without exposure to NH_3 and to $D_{Q+NH_3} = 1.02$ with exposure to NH_3. FWHM of the Q band peaks is $\Delta\lambda = 32\,\text{nm}$, i.e. the Q band is rather narrow, but is larger than FWHM of the $LuPc_2$ Q band in the tetrahydrofurane solution [14]. Absorbances of the BV band peaks of the P480 film without and with exposure to NH_3 almost coincide and are equal to $D_{BV} = 0.48$. The absorbance of the Q band peak of the P480 film is equal to $D_B = 0.84$ without exposure to NH_3 and to $D_{Q+NH_3} = 1.52$ with exposure to NH_3. The absorbance of the Q band peak of absorbance spectrum with exposure to NH_3 decreased by a factor of 1.1 which is equivalent to the result or the $LuPc_2$ film exposed to NO_2 in [6]. The absorbance of the B band peak of the absorption spectrum increased by a factor of 1.8 with exposure to NH_3. As a result of lutetium diphthalocyanine film exposure to ammonia, the Q band peak decreases by a factor of 1.1 the B band peak increases by a factor of 1.8 and the BV band peak remains almost unchanged. FWHM of the Q and BV bands of the light absorption spectra remained almost unchanged after exposure to NH_3.

Light absorption in the Q band with the peak $\lambda_m = 667\,\text{nm}$ occurs on the conjugated carbon–carbon double bonds of the benzene rings($n = 13$) and on the conjugated nitrogen–carbon double bonds ($n = 6$) in the macrocycle of each of the Pc ligands. Here, n is the number of conjugated double bonds C=C and C=N. The absorption peaks with $\lambda_m = 667\,\text{nm}$ (Q band) in the P480 film correspond to the electronic transition from $2b_1$ to LUMO $6e_3$ ($\pi-\pi^*$ electronic transitions). For the P480 film, the energy gap between the ground state of HOMO and excited state of LUMO is equal to $E_{\text{HOMO-LUMO}} = 1.86\,\text{eV}$ (or E_Q). This electronic transition occurs from the singlet ground electronic level S_0 to the stretching levels C=C and C=N of the first singlet excited level S_1. In the neutral lutetium diphthalocyanine molecule, the Q band peak is induced by one excited state caused by the local excitation of the ligands. This type of excitation is identical to the electronic transition HOMO $2b_1 \to$ LUMO $6e_3$ for lutetium monophthalocyanine.

Radiation absorption in the range with the peak $\lambda_m = 464\,\text{nm}$ occurs on the conjugated carbon-carbon double bonds of the benzene rings ($n = 13$), i.e. radiation is absorbed on 26 π-electrons in the $LuPc_2$ molecule. The absorption peak (BV band, $\lambda_m = 464\,\text{nm}$) in the sample spectrum corresponds to the electronic transition from the molecular level $5e_1$ to the level $2a_2$ ($\pi-\pi^*$-transitions) with the energy gap $E_{BV} = 2.67\,\text{eV}$. The presence of the BV band light absorption peak indicates a neutral form of the $[LuPc_2]^0$ molecules in the film. The neutral lutetium diphthalocyanine molecule contains 37 π-electrons. The neutral $[LuPc_2]^0$ molecule contains one unpaired electron that is delocalized on two P_c ligands. This electronic transition $5e_1 \to 2a_2$ occurs from the level $5e_1$ to the level SOMO $2a_2$ ($\pi-\pi^*$-electronic transitions). The electronic transition $5e_1 \to 2a_2$ in the lutetium diphthalocyanine film molecules is induced by the charge transfer between the Pc^{2-} ligand and Pc^{1-} ligand. In other words, the molecular orbital of the BV band of lutetium diphthalocyanine is formed through splitting the molecular orbitals of the Pc^{2-} and Pc^{1-} ligands as a result of their interaction. Absorbance of the BV band for the P480 film without exposure to NH_3 is equal to $D_{BV} = 0.48$, which is 2.4 times lower than for the Q band and 2.1 times lower than for the Q band with exposure to NH_3.

The absorption peak (B band, $\lambda_m = 352\,\text{nm}$) in the lutetium diphthalocyanine film without ammonia exposure corresponds to the electronic transition $4a_1 \to 6e_1$ ($\pi-\pi^*$-transitions) with the energy gap $E_B = 3.52\,\text{eV}$. When exposed to ammonia, the absorption peak (B band, $\lambda_m = 357\,\text{nm}$) in the lutetium diphthalocyanine film corresponds to the electronic transition from the molecular orbital $4a_1$ to a lower vibrational level of the orbital $6e_1$ ($\pi-\pi^*$-transitions) with the energy gap$E_{B+NH_3} = 3.47\,\text{eV}$. The difference between the energy gaps is 0.05 eV. The electronic transitions $4a_1$HOMO-1 $\to 6e_1$LUMO+1 (B band) occur in the ltetium diphthalocyanine molecules due to the radiation absorption on the conjugated carbon-nitrogen double bonds of the pyrrole rings ($n = 6$), i.e., radiation is absorbed on 12 π-electrons in the $LuPc_2$ molecule. Absorbance of the BV band for the P480 film without exposure to NH_3 is equal to $D_B = 0.84$, which is 1.3 times lower than for the Q band and 1.5 times higher than for the

Light absorption spectra parameters of the $LuPc_2$ film with and without exposure to NH_3

Spectral band	Peak wavelength of λ, nm	Peak FWHM $\Delta\lambda$, nm	Peak shift $\delta\lambda$, nm	Electronic transition energy E, eV	Energy level shift ΔE, eV	Absorbance D	D_1/D_2 and D_2/D_1
Film 1. $LuPc_2$ without NH_3							
B band	352	–		3.52	0.05	0.84	
BV band	464	–		2.67		0.48	
Q band	667	32		1.86		1.13	1.1 times
VS — vibrational side sample	604	–		2.05		0.37	
Film2. $LuPc_2$ with NH_3							
B band	357	–	5	3.47		1.53	1.8 times
BV band	464	–		2.67		0.48	
Q band	667	32		1.86		1.03	
VS — vibrational side sample	604	–		2.05		0.37	

Q band with exposure to NH_3. This electronic transition occurs from the singlet ground electronic level S_0 to the stretching levels C=C of the second singlet excited level S_2.

Thus, when the surface of the lutetium diphthalocyanine film is exposed to ammonia molecules, electronic transition takes place from the singlet ground electronic level S_0 to a lower vibrational level C=C of the singlet second excited level S_2. The main light absorption spectra parameters of the lutetium diphthalocyanine film with or without exposure to the ammonia molecules are listed in the table.

Thus, as a result of lutetium diphthalocyanine film exposure to ammonia, the Q band peak decreases by a factor of 1.1 the B band peak increases by a factor of 1.8 and the BV band peak remains almost unchanged. The decrease in the Q band absorbance during ammonia exposure is presumably induced by the reduced probability of electronic transition HOMO $2b_1 \rightarrow$ LUMO $6e_3$ (LUMO occupation reduction). The decrease in the Q band absorbance during ammonia exposure is presumably induced by the increased probability of the electronic transition HOMO-1 $4a_1 \rightarrow$ LUMO+1 $6e_1$ (LUMO+1 occupation increase).

For the P480 sample ($LuPc_2$), the surface electrical resistance R_S was measured at $t = 23°C$ with and without ammonia exposure. For a more accurate measurement of the surface electrical resistance, silver contacts were deposited on the $LuPc_2$ film. For the $LuPc_2$ film on the silicate glass substrate without NH_3 exposure, the surface electrical resistance was equal to $R_S = 2 \cdot 10^4\,\Omega$. For the $LuPc_2$ film on the silicate glass substrate with NH_3 exposure, the surface electrical resistance was equal to $R_S = 11 \cdot 10^5\,\Omega$. It can be seen that the exposure of the $LuPc_2$ film to the NH_3 molecules leads to considerable growth of the surface electrical resistance approximately by a factor of 5.5. Metal phthalocyanine (MPs) films in vacuum are dielectrics. But the electrical conductivity of metal phthalocyanine films in air depends on gases contained in air that show both acceptor and donor properties [15,16]. In air, metal phthalocyanine films start showing semiconductor properties with mainly the *p*-type conductivity.

The *p*-type conductivity may be explained by formation of $[O_{2-}\ MPs^{+}]$ complex compound on the metal phthalocyanine film surface (in our case the O_{2-} atoms coordinate with theLu^{3+} ions). This compound extracts electrons from the volume creating holes in it, thus, leading to formation of the *p*-type conductivity. When the NH_3 molecules having donor properties interact with the lutetium phthalocyanine film, electrons of the lone pair NH_3 are recombined with the molecule holes in the $LuPc_2$ film. As a result of electron and hole recombination, the concentration of holes in the $LuPc_2$ film decreases and, therefore, the electrical resistance increases, in our case by a factor of 5.5. Thus, the increase in the electrical resistance in the lutetium diphthalocyanine film when it is exposed to the ammonia molecules may be used as the gas indicator.

Conclusion

In this study, the lutetium diphthalocyanine film on the silicate glass substrate has been produced and its optical and electrophysical properties have been investigated under the ammonia exposure. Changes in the light absorption spectra and electrical resistance of the lutetium diphthalocyanine film exposed to ammonia have been investigated.

The following conclusions may be made from the investigations of the lutetium diphthalocyanine films on the silicate glass substrate exposed and not exposed to the ammonia molecules.

1. The energy $E_{\text{HOMO-LUMO}}$ of the Q band energy gap of the lutetium diphthalocyanine film is equal to $E_Q = 1.86$ eV and does not vary when the film is exposed to NH_3. Absorbance of the Q band of the light absorption spectrum

decreases by a factor of 1.1 when exposed to NH_3 compared with the absorbance without exposure to NH_3.

2. The electronic transition energy E_B typical for the B band of the lutetium diphthalocyanine film is equal to $E_B = 3.52$ eV and decreases to $E_B = 3.47$ eV when exposed to NH_3. Absorbance of the B band peak of the light absorption spectrum increases by a factor of 1.8 when exposed to NH_3 compared with the absorbance without exposure to NH_3.

3. The surface electrical resistance of the lutetium diphthalocyanine film exposed to ammonia increases by a factor of 5.5.

Thus, the results of the study of optical and electrophysical properties in the lutetium diphthalocyanine films on silicate glass exposed to ammonia gas may be summarized as follows.

1. The energy of $\pi-\pi^*$-electronic transitions typical of the peaks of the Q and BV absorption bands in the lutetium diphthalocyanine films does not vary under the ammonia exposure. The result may be explained by the fact that the energy gap $E_{\text{HOMO-LUMO}}$ and electronic transition $5e_1(\pi) \rightarrow 2a_2(\pi^*)$ do not change when the diphthalocyanine film surface is exposed to ammonia. The energy E_B of the $\pi-\pi^*$-electronic transitions typical of the peaks of the B absorption band is lower by 0.05 eV in the lutetium diphthalocyanine films exposed to ammonia than the energy E_B without exposure to NH_3. The experimental result is presumably caused by the fact that the electronic transition in the $LuPc_2$ molecules exposed to NH_3 occurs from the singlet ground electronic level S_0 to a lower vibrational level C=C of the singlet second excited level S_2.

2. The absorbance of the Q band peak in the $LuPc_2$ film decreases under the ammonia exposure. The result may be explained by creation of a coordination bond between NH_3 molecules and Lu^{3+} ions that induces reduction of the probability of the electronic transition HOMO → LUMO and, consequently, reduction of the LUMO occupation. Absorbance of the B band peak of the $LuPc_2$ film increases significantly (by a factor of 1.8) when exposed to ammonia. The experimental fact may be explained by the increasing probability of the electronic transition HOMO-1 → LUMO+1 as a result of creation of the coordination bond between the NH_3 molecules and hydrogen (H) atoms of the benzene rings of the $LuPc_2$ molecules.

3. Decrease in the Q band peak and increase in the B band peak in the light absorption spectrum when the film is exposed to the ammonia molecules offers the opportunity to use the lutetium diphthalocyanine films as an active substance for gas detectors, for example, through deposition of $LuPc_2$ using the sublimation method on the optical fiber end connected with the remote optical spectrometer.

4. Significant decrease in the electrical resistance of the lutetium diphthalocyanine film exposed to ammonia may be also used for creation of gas detectors through deposition of metal contacts on the $LuPc_2$ film surface to record the electrical resistance variation.

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Translated by E.Ilinskaya