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OPTICAL PROPERTIES AND STABILITY OF BILAYER RUBRENE-ALQ₃ FILMS FABRICATED BY VACUUM DEPOSITION¹

We report on the optical and structural characterization of the two-component vacuum deposited (VD) rubrene (Rub)-Alq₃ films. As is known, Rub-doped OLED active materials demonstrate both promising electroluminescence and transistor characteristics. However, in terms of operational lifetime, the Rub practical application in basic devices has a few drawbacks related to its chemical instability. Our main attention was focused on the role of the Alq₃ coverage and the isomeric transformation of a Rub molecule on its chemical stability in these structures. By monitoring the evolution of PL emission in time, we found that the Rub degradation in Rub-Alq₃ films is slower than that in vacuum-deposited Rub layers. These results demonstrate that the deposition of an Alq₃ layer can be a way to enhance the stability of Rub to the photo-oxidation in optoelectronic devices. The Rub amorphous film crystallization at elevated temperatures in open air was observed for the first time.

Keywords: rubrene, Alq₃, oxidized rubrene, vacuum deposition, thin films, FTIR spectra, photoluminescence.

1. Introduction

In the last decade, the problem of OLED stability and long-term degradation is in the focus of organic semiconductor researches [1–3], since the operational stability of the current generation of such devices is limited by chemical reactions of the molecular components of devices. Recently, various approaches to the stabilization of OLEDs such as the doping of a hole transport layer, introducing a buffer layer at the hole-injecting contact, and using mixed emitting layers of hole- and electron-transporting molecules were applied [4–6]. However, the complex mechanisms of OLED degradation are still to be completely understood. Recently, we have studied the molecular structure, morphology, and photoluminescence (PL)

of Rub layers deposited on freshly cleaved KBr(100) or Au(111) substrates by the vacuum thermal evaporation. Additionally, the two-component vacuum-deposited (VD) Rub-tetracene (Tc) films were studied. Special attention was paid to the susceptibility of films to the oxidation under ambient conditions. It was shown that Rub molecules in VD thin films are subjected to the strong oxidation in open air and, in the bi-layer structure, the deposited Tc layer only slightly enhances the stability of Rub to the photo-oxidation. In continuation of that research, we report on the optical and structural characterization of vacuum-deposited bilayer rubrene-Alq₃ films.

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Alq3 belongs to small organometallic complexes, which generally demonstrate good light emitting properties, but do not have good enough parameters for field effect transistors (FETs), probably because of their amorphous morphology in OLED devices. Alq3 is widely used in these devices due to its high fluorescent efficiency, relatively good electron mobility, and thermal stability [7]. Despite its low environmental stability, rubrene single crystals have demonstrated a high carrier mobility in FET devices [8], so it was assumed that the doping with rubrene could effectively help to maintain both FET and PL performances of OLED materials.

Rub was reported [9] to be used in important Alq3-based OLEDs to improve their operational parameters by reducing the formation of unstable Alq3 cationic species [10]. Since the properties of the organic-organic interface to a great extent affect the performance characteristics of FET and OLED devices, the investigation of the interaction between the two organic components is of importance. In this work, we will focus on the effect of an Alq3 coverage on the VD Rub film stability and the aging rate in a simple model system consisting of a Rub film deposited by the thermal evaporation in vacuum on a fresh-cleaved KBr (111) or glass surface and an Alq3 cover layer deposited on this film in the same deposition environment.

2. Materials and Experimental Methods

2.1. Materials

Rubrene ($C_{42}H_{28}$, 5,6,11,12-tetraphenyltetracene, Rub) and Alq3 (tris (8-hydroxyquinoline) aluminum, $C_{27}H_{18}N_3O_3Al$) of 98% purity were received from Merck and used without further purification. The Rub molecule is an aromatic molecule consisting of a Tc backbone with four additional phenyl groups. A Rub molecule can exist in two different structures known as twisted (D2) and planar (D1) isomers. The planar isomer is more stable in the crystal phase, since it favors the more dense packing of Rub molecules, while the twisted isomer is energetically more favorable for free molecules and those adsorbed on dielectric surfaces [11–12]. The chemical structure of Rub planar and twisted isomers and two possible geometrical isomers of Alq3, meridional (C1 symmetry) and facial (C3 symmetry) forms, are shown in Fig. 1.

2.2. Samples preparation

The thermal vacuum deposition of organic semiconductors is widely used for the fabrication of various organic devices including organic FETs [13–14] and OLEDs [15]. In our experiments, Rub was deposited on a freshly cleaved KBr(100) or glass substrate held at room temperature. In some experiments, Alq3 layers of about 20–40 nm thick were deposited on the Rub surface. The Rub and Alq3 molecules were sublimed from a polycrystalline powder. The deposition was carried out at a pressure of $\sim 5 \times 10^{-6}$ Torr, with a deposition temperature of 120 °C and a deposition rate of 5 Å/min. The substrates were kept at room temperature. The thickness of the deposited Rub layers was controlled with a digital quartz balance monitor and varied from ~ 1 to 150 nm.

2.3. FTIR spectroscopy

FTIR transmission spectra were used to examine the chemical structure and molecular orientation in the VD thin Rub and Rub-Alq3 films. The infrared spectra of the films were measured with a Bruker IFS-88 FTIR spectrometer in the spectral range of 380–4000 cm^{-1} at room temperature and in the temperature range 25–200 °C. The spectra were recorded with 1- cm^{-1} resolution and averaged over 64 scans to obtain the high signal-to-noise ratios. The background spectra were recorded for a bare substrate of the same film. OPUS 4.2 software package was used for the spectral data processing.

2.4. UV-vis spectroscopy measurements

Photoluminescence measurements of the VD Rub and Rub-Alq3 films on KBr or glass substrates were carried out with a LOMO MDR-32 monochromator. The spectral sensitivity of the system was previously calibrated. The samples were irradiated with a Hg lamp through a filter of 365 nm. Origin 6.1 software package was used for the spectral data processing. All measurements were performed at room temperature.

3. Results and Discussion

3.1. FTIR spectra and stability of the VD films

FTIR spectroscopy can be used as a very helpful tool for the investigation of molecular interactions and the recognition of subtle structural changes in solid state compounds due to its high sensitivity and resolution. The vibrational spectra of Rub and Alq3

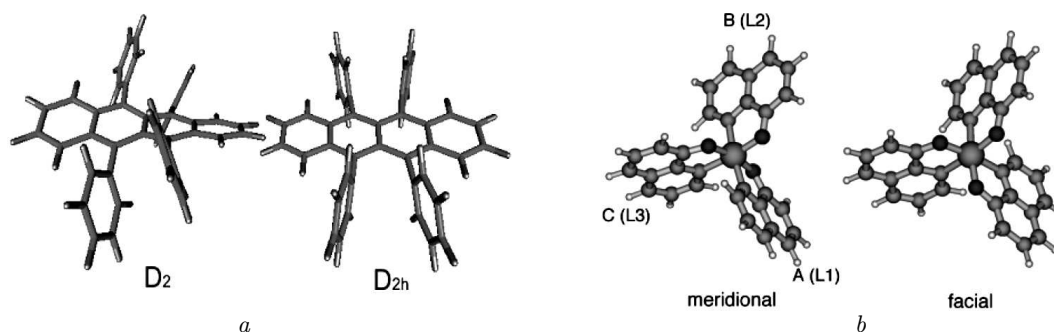


Fig. 1. Molecular structures of Rub D_2 and D_{2h} isomers obtained from the geometry optimization at the BP86/TZVP level (a) and two geometrical isomers of Alq3 (b). Reproduced from [9] and [10], correspondingly

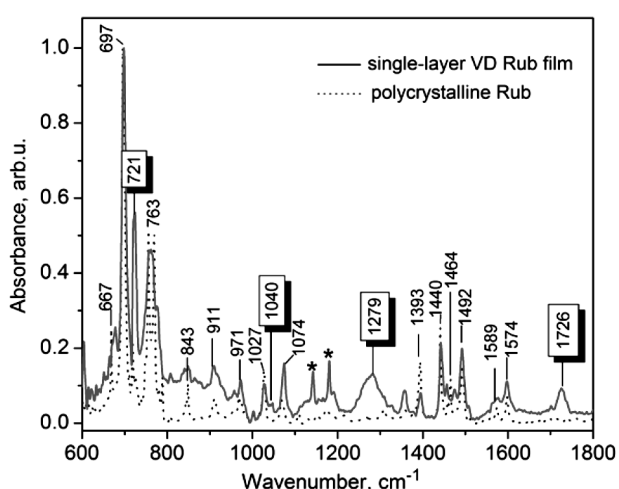


Fig. 2. FTIR absorption spectra of a single-layer VD Rub film as-deposited on KBr (100) surface (solid line) and bulk polycrystalline Rub (dotted line). Framed peak positions are for newly emerged bands due to the Rub film degradation in air. Asterisks indicate the absorption bands originating due to impurity centers in KBr windows

molecules were described elsewhere in our previous papers [16–17], and the assignment of their major absorption bands to characteristic vibrations of Rub and Alq3 functional groups has been reported in various papers using experimental spectra and theoretical calculations [18–20]. In the present paper, we use these assignments for the analysis of the FTIR spectra of our samples.

First, we checked a safe vacuum deposition of single-layer Rub in our experimental environment. The results of comparative FTIR transmission measurements of Rub polycrystalline samples and single-layer Rub VD thin film (with a thickness of about 150 nm), are shown in Fig. 2. As seen from Fig. 2,

in the FTIR spectra of the VD Rub film, all major absorption bands of polycrystalline Rub (the C–H out of plane bending bands centered at 667, 697, and 763 cm^{-1} , bands of out-of-plane CH vibrations centered at 843, 911, 971, 1027, and 1074 cm^{-1} , the middle intensity bands at 1492, 1464, 1440, and 1393 cm^{-1} of the acyl backbone benzene rings C=C stretching vibrations, and the bands at 1589 and 1574 cm^{-1} assigned to phenol ring vibrations [21]) are observed, though most of them in the spectra of the VD film are broaden, which suggests an inhomogeneous local surrounding of the Rub molecules in the VD film due to random positions and orientations of the neighboring Rub molecules, and thus confirms an amorphous structure of the obtained film. Note that the amorphous structure of the fabricated single-layer VD films was also confirmed in our STM studies (not shown here) and reported elsewhere [16]. A similarity between the IR spectra of the VD Rub films and those of a polycrystalline sample implies the lacking of the formation of chemical bonds between Rub molecules and the substrate, confirming the safe vacuum deposition of Rub.

However, it should be noted that the FTIR spectra of as-deposited single layer Rub thin films give evidence of a chemical transformation in the film just after the vacuum deposition. This is confirmed by the emergence of new absorption bands centered at 721, 1040, 1279, and 1726 cm^{-1} . Since Rub is known to easily react with oxygen under the exposure to air with the formation of rubrene peroxide ($\text{C}_{42}\text{H}_{28}\text{O}_2$), we might expect to see new absorption bands of $\nu(\text{O}-\text{O})$ and $\nu(\text{C}-\text{O})$ stretching modes due to the Rub oxidation. In some cases, as with the formation of rubrene endoperoxide, the oxidation of acene will lead to a loss of planarity in the

backbone [22]. This could lead to a distortion of the local force field and the appearance of twisted Rub isomer vibrational modes with frequencies somewhat different from those observed for a planar isomer in the vibrational spectra of a Rub crystal. This may be a cause for the new strong narrow absorption band at 723 cm^{-1} , which could be attributed to a twisted Rub conformer CH wagging mode. In the vibrational spectra of peroxides, the characteristic frequency is due to the $\nu(\text{O-O})$ stretching mode, which gives rise to strongly polarized Raman bands about $900\text{--}700\text{ cm}^{-1}$ [23] being, however, weak in the IR absorption. According to [24], the $\nu(\text{O-O})$ stretching vibration interacts with other skeletal C-O and C-C bonds bending vibrations, and there is an extensive coupling between the $\nu(\text{O-O})$, $\nu(\text{C-O})$, and $\delta(\text{C-O-O})$ modes. In addition, with the oxygen gradual permeation into the amorphous Rub film under the photo-excitation with visible light, a subsequent chemical reaction between O_2 and rubrene pendant phenyl groups may take place with the formation of benzoic acid moieties. This process could be responsible for the observance of the carbonyl stretching mode at 1726 cm^{-1} in the FTIR spectra of the Rub film after the deposition (Fig. 2). So, the changes observed in the FTIR spectra of single-layer Rub-films probably are due to the contribution from $\nu(\text{O-O})$ and $\nu(\text{C-O})$ modes of Rub peroxide and other oxidized Rub moieties, as well as the contribution from twisted Rub isomers. These changes indicate the formation of oxidized species such as Rub endoperoxide within the amorphous Rub film under the exposure for a few minutes under ambient conditions just after the VD deposition. This observation is in compliance with previous findings of other authors [25–27].

Next, we checked the molecular composition of the as-deposited bilayer Rub-Alq3 VD films by using infrared spectroscopy to detect any changes in the absorption spectra of the films after the deposition. In Fig. 3, the room temperature FTIR transmission spectra of the obtained bilayer Rub-Alq3 films are compared with those of individual components – polycrystalline Rub and Alq3. As can be seen from Fig. 3, the FTIR spectrum of the bilayer Rub-Alq3 structure shows all major absorption bands characteristic of both polycrystalline Rub (the bands centered at 697 , 763 , 911 , 971 , 1027 , and 1074 cm^{-1} [21]) and Alq3 (the bands centered at 647 , 748 , 804 , and 825 cm^{-1} related to ring deformation/breathing

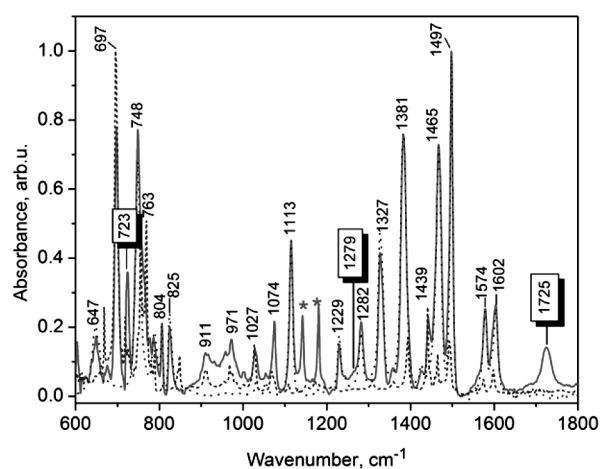


Fig. 3. FTIR absorption spectra of an as-deposited bilayer Rub-Alq3 VD film (solid line), bulk polycrystalline Rub (dashed line), and bulk polycrystalline Alq3 (dotted line). Spectra were normalized by the 647-cm^{-1} Rub absorption. Framed peak positions mark the new $\nu(\text{O-O})$ and $\nu(\text{C-O})$ bands due to the Rub degradation in air. Asterisks indicate the absorption bands originating due to impurity centers in KBr windows

and CH wagging vibrations, the bands at 1113 , 1229 , 1282 , 1327 , and 1381 cm^{-1} characteristic of CH bending vibrations, the bands centered at 1465 and 1497 cm^{-1} that correspond to CC/CN stretching + CH bending vibrations, and the bands at 1579 and 1602 cm^{-1} originating from CC ring stretching vibrations [19, 28]).

This observation implies the lack of the formation of chemical bonds between Rub or Alq3 molecules in the film, and also that no significant changes in either Rub or Alq3 molecular structure occur after the bilayer film deposition. However, just after the deposition, the new bands centered at 1279 and 1725 cm^{-1} are present in the FTIR spectra of the bilayer Rub-Alq3 films. These new bands could be attributed to $\nu(\text{O-O})$ and $\nu(\text{C-O})$ stretching vibrations due to the formation of endoperoxide under the Rub exposure to open air like those observed in the spectra of an as-deposited single layer Rub film. At the same time, there is no sign of Alq3 chemical transformations within a few hours under the vacuum deposition. Considering that the peroxide bands are not observed in the spectra of Rub polycrystalline samples, this suggests that amorphous Rub films are oxidized much faster than polycrystalline ones. These findings well agree with observations of the Rub oxidation by other authors [22, 25, 29].

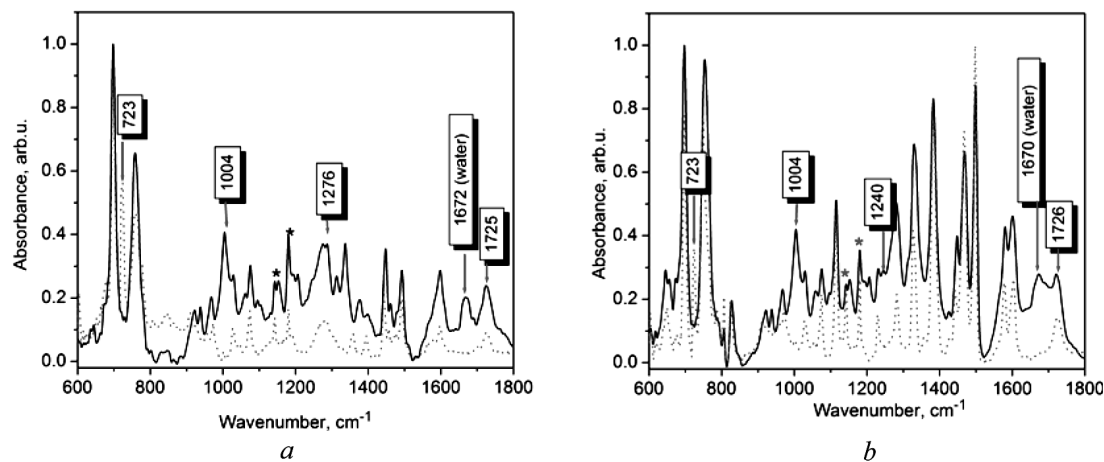


Fig. 4. FTIR absorption spectra of as-deposited (dotted line) and exposed to ambient conditions (solid line) single-layer Rub (a) and bilayer Rub-Alq3 (b) VD films. Spectra were normalized by the 647-cm⁻¹ Rub absorption. Framed peak positions mark $\nu(\text{O-O})$ and $\nu(\text{C-O})$ bands due to the Rub degradation in air, and water adsorption bands. Asterisks mark the absorption bands originating due to impurity centers in KBr windows

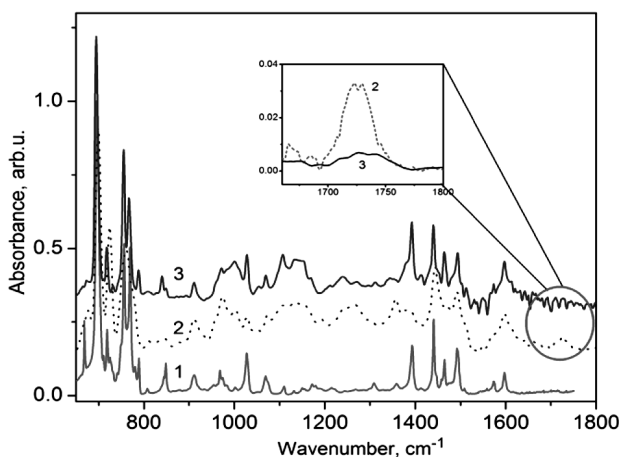


Fig. 5. Thermal treatment effect on the FTIR spectra of single-layer Rub VD film: bulk polycrystalline Rub (1); amorphous VD Rub film (2); amorphous VD Rub film annealed to 180 °C (3). All spectra are normalized by the Rub 647-cm⁻¹ absorption band and shifted vertically against each other for clarity. The inset shows the magnified region of C=O stretching vibrations

In Fig. 4, we compare the FTIR spectra of single-layer Rub and bilayer Rub-Alq3 VD films after their light-exposure in air for 48 hours with those of as-deposited films. In particular, we note the appearance of new absorption bands at 1004, 1240, and 1726 cm⁻¹ in both exposed films after the exposure. We consider that these new bands may be ascribed, correspondingly, to $\nu(\text{O-O})$, $\nu(\text{C-O})$, and

$\nu(\text{C=O})$ vibrations of endoperoxide species formed under the Rub interaction with oxygen under the light-exposure. The band centered at 1670 cm⁻¹ is ascribed to bending vibrations of adsorbed water molecules. As could be seen from Fig. 4, the observed spectra are much similar, and no detectable changes were observed as for the relative intensities of the emerging $\nu(\text{O-O})$, $\nu(\text{C-O})$, and $\nu(\text{C=O})$ bands. We may ascribe this to the chemical oxidation of the very Rub in the bilayer structure, while, from the perspective of molecular structure, the number of degraded Alq3 molecules is not substantial for their detection by FTIR spectroscopy. Therefore, we can conclude that the presence of the Alq3 cover layer has no significant effect on the Rub degradation in the VD films under the impact of ambient environment.

3.2. Thermal treatment effect on Rub VD films

There have been also attempts in several research groups to improve the crystallinity and stability of Rub thin films [22, 25, 30]. Here, we investigated the effect of elevated temperatures on the VD Rub film. Upon the 48-h exposure in air, the oxidized amorphous Rub film, which became colorless, was heated to 180 °C under ambient conditions. The FTIR spectra of a VD Rub film before and after heating are shown in Fig. 5. After the Rub film annealing at elevated temperatures, we observed a pristine orange-

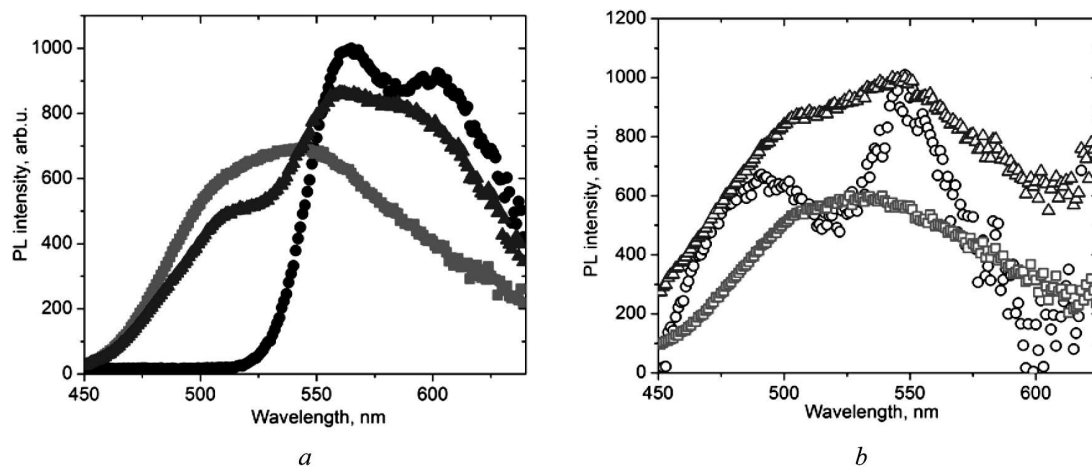


Fig. 6. PL spectra of (a) the as-prepared and (b) light-exposed single layer Rub (circles) and Alq3 (squares), as well as bilayer Rub-Alq3 (triangles) VD films.

red colored film with clearly seen crystalline grain structure. Major differences are also observed in the FTIR spectra of the Rub film after the annealing. The relative intensities of the $\nu(\text{O-O})$ and $\nu(\text{C-O})$ bands at 1004 and 1246 cm^{-1} due to the Rub degradation in air, as well as that of adsorbed water at 1670 cm^{-1} significantly decrease, thus suggesting the decomposition of endoperoxide moieties at high temperature. The bands associated with pristine Rub, such as the bands at $697, 763\text{ cm}^{-1}$, become very narrow, and their relative intensity increases similarly to that observed in the spectra of polycrystalline Rub with the strongly decreased intensity of the band at 723 cm^{-1} characteristic of twisted Rub isomers. Therefore, we could conclude that the changes observed in the FTIR spectra of an amorphous Rub film after the annealing at temperatures $150\text{--}180\text{ }^{\circ}\text{C}$ suggest the formation of pristine non-oxidized Rub. The observed structural changes appeared to be irreversible on the cooling.

3.3. Photoluminescence studies

We monitor the time evolution of the visible PL emission from the two types of fabricated VD films during the exposure under ambient conditions. Earlier, we investigated the influence of the protective layer of tetracene on the degradation rate of the photoluminescent properties of VD Rub films [16]. It was shown that such a layer slows down, but does not completely eliminate, the process. In this work, we checked the Rub degradation behavior in VD

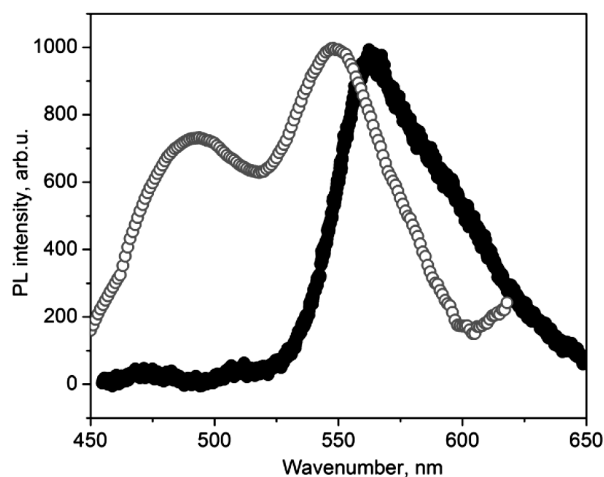


Fig. 7. PL spectra of the VD Rub film light-exposed in air for 1 month before (open circles) and after the thermal treatment (filled circles)

thin layers with Alq₃ as the protective cover. Unlike tetracene, Alq₃ demonstrates the intense photoluminescence. Therefore, the PL spectra of the bilayer structure contain the emission bands from the both layers. In our experiments, the PL was excited with a Hg lamp from the side of the Alq₃ layer, and the PL emission spectra were recorded from the side of the substrate. Therefore, the PL emission from Alq₃ was partially absorbed by the underlying Rub layer in the spectral range of Rub intrinsic absorption.

Figure 6 shows the PL spectra of single-layer VD films of Rub and Alq₃ and a bilayer Rub-Alq₃ VD

film on a glass substrate before and after the light exposure in air.

The PL spectrum from the as-deposited VD Rub film consists of two strong broad emission bands centered at 565 and 610 nm. According to the literature, the 565-nm band corresponds to the M-polarized emission (along the short axis of a rubrene molecule), and the 610-nm band to the L-polarized emission (along the long axis of rubrene) [31].

It can be seen from the comparison of Fig. 6, *a* and *b* that the PL spectra of the VD films exposed to ambient conditions indicate the degradation of Rub both in the single- and bilayer structures. The observed overall decrease in the photoluminescence intensity is accompanied by a change in the shape of the spectrum. A new emission band appears at 485 nm, which is characteristic of oxidized Rub species [31] and indicates the Rub oxidation in the bilayer structure. This was also confirmed by IR spectroscopy, as shown above. It is noteworthy that the band at 485 nm is more pronounced in the absence of a protective layer.

As was reported elsewhere [29], only twisted isomers of Rub molecules react with oxygen, while planar ones do not undergo the oxidation. This was also confirmed for the VD Rub films in our previous paper [16]. The ratio of twisted and planar isomers in the film is determined by the technological features of the preparation of samples, in particular, by the temperature of a substrate [32].

The thermal treatment of the VD Rub film light-exposed for 1 month in open air described in Subsect. 3.2 leads to the restoration of the photoluminescence spectrum of the initial film. The changes observed in the PL spectrum of the VD Rub film after the thermal treatment (Fig. 7) suggest the formation of pristine non-oxidized crystalline Rub. The nature of such a phase transition is not completely clear so far and needs the further investigation.

4. Conclusions

With FTIR spectroscopy, it is shown that Rub or bilayer Rub-Alq3 thin films deposited by the thermal evaporation in vacuum on freshly cleaved single crystalline KBr (100) or glass substrates are of amorphous structure.

Changes in the FTIR spectra of VD Rub and Rub-Alq3 films indicate the formation of oxidized Rub endoperoxide species under the film exposure to light

under ambient conditions. These changes are less obvious for the bi-component films.

The PL degradation kinetics of the deposited Rub and Rub-Alq3 films suggests that the protective Alq3 layers are only slowing down the Rub oxidation process in the films, but do not eliminate it completely. This can be related to the diffusion of oxygen through the Alq3 layer to the rubrene molecules.

The Rub amorphous film crystallization at elevated temperatures in open air is observed for the first time. The changes observed in the FTIR spectrum of an amorphous Rub film after the annealing suggest the crystalline phase formation of pristine non-oxidized Rub that leads to the restoration of the photoluminescence spectrum.

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ОПТИЧНІ ВЛАСТИВОСТІ
І СТАБІЛЬНІСТЬ ДВОШАРОВИХ
ТОНКИХ ПЛІВОК РУБРЕН-ALq3, ОДЕРЖАНИХ
МЕТОДОМ ВАКУУМНОГО НАПОРОШЕННЯ

Резюме

Досліджено оптичні та структурні властивості двокомпонентних плівок рубрен-Alq3, одержаних методом вакуумного напорошення (ВН). Відомо, що доповані рубреном активні матеріали для органічних світлодіодів та транзисторів демонструють покращені електрооптичні та електротранспортні характеристики, але практичному застосуванню таких систем перешкоджає хімічна нестабільність рубрену, що скорочує експлуатаційний термін служби відповідних пристроїв. В роботі досліджено вплив захисного шару Alq3, а також наявності різних ізомерів молекули рубрену на його хімічну стабільність у двошарових тонкопліткових структурах. На основі експериментальних досліджень спектрів ІЧ поглинання та часової еволюції спектрів фотолумінесценції було показано, що процес фотодеградації (утворення перекису) рубрену у плівках рубрен-Alq3 відбувається більш повільно, ніж у тонких шарах самого рубрену. Результати свідчать про те, що нанесення захисного шару Alq3 може бути засобом підвищення хімічної стійкості рубрену до фотоокислення у оптоелектронних приладах. Також нами вперше виявлено процес кристалізації аморфної плівки фотоокисленого рубрену під час її високотемпературного відпалу, який супроводжується відновленням первісної хімічної структури молекули рубрену.