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STRUCTURE, MORPHOLOGY, AND PHOTOLUMINESCENCE OF VACUUM DEPOSITED RUBRENE THIN LAYERS

Among organic semiconductors, rubrene ($C_{42}H_{28}$, 5,6,11,12-tetraphenyltetracene, Rub) is extensively studied in recent years, since it exhibits interesting physical properties such as very high charge carrier mobilities in organic field-effect transistors at room temperature. Rub is used as a laser dye and as a fluorescent dopant in other organic light-emitting diodes (OLEDs) to improve the characteristics such as lifetime, stability, color, and brightness. However, there are controversies as to the Rub degradation both in the bulk state and thin layers. So, the better understanding of these phenomena is crucial for improving the performance of organic devices. In this work, we present the results on complex studies of the molecular structure, morphology, and photoluminescence (PL) of Rub layers deposited on freshly cleaved KBr(100) and Au(111) substrates by 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. The chemical structure and molecular ordering in the obtained VD thin organic films were evaluated by FTIR spectroscopy, and the structure of the very first Rub layers on atomically smooth Au(111) surfaces was studied with scanning tunneling microscopy (STM). From the changes in the peaks position and the intensity of room-temperature PL spectra of the films with time, the degradation kinetics of the Rub emission is analyzed.

K e y w o r d s: rubrene, $C_{42}H_{28}$, 5,6,11,12-tetraphenyltetracene, Rub.

1. Introduction

Rub (5,6,11,12-tetraphenyltetracene) has been known since the beginning of the last century, and it is considered a classic example of a material with excellent electroluminescence properties since the 1960s. In recent years, among other polycyclic aromatic hydrocarbons, orthorhombic Rub single crystals were reported to have the highest charge carrier mobility among organic semiconductors, up to $\sim$40 cm^2/Vs, which is comparable to that of amorphous silicon [1–3]. Rub has almost 100% photoluminescence efficiency at room temperature. It was successfully doped into many OLED devices to improve their characteristics such as lifetime, brightness, and stability [4–7]. Despite important semiconducting properties, Rub has some drawbacks hampering its application for the development of optoelectronic devices. It shows a low solubility in common organic solvents, which hampers the use of solution techniques for the deposition of Rub thin films. In addition, it was re-

ported [8–12] that Rub has high reactivity toward molecular oxygen under the light exposure with the formation of an endoperoxide O–O bridge-bond and the resulting loss of planarity and delocalization of the Tc core. It was also established [8, 9] that the optical properties of Rub are strongly affected by the oxidation, and the loss of aromaticity is visually manifested as a change in the color of the Rub solution from its initial bright orange-red color to the almost colorless state.

Regarding the Rub stability in different systems, it was reported that amorphous thin Rub films did completely oxidize and transform into Rub endoperoxide in a few hours under the irradiation with a Xe lamp [8] and in a few minutes under ambient conditions. It was also shown that Rub single crystals oxidize more slowly, and the process is thought to be limited within surface layers [10–12]. Significant changes in the transport parameters due to the oxidation of the Rub single-crystal surface were reported [13]. As shown in [14], the oxidation process is strongly enhanced by the presence of light and involves the bonding of an oxygen molecule to one of the inner benzene rings, with the formation of an endoperoxide O–O bridge-bond and the resulting loss of planarity and delocalization of the Tc core. There have been also attempts in several research groups to improve the crystallinity and stability of Rub thin films. In order to enhance the charge carrier mobility, a pentacene buffer layer was used between Rub and a gate dielectric [15]. Using the pentacene buffer layer, hole mobilities up to 0.6 cm^2/Vs have been found in Rub thin-film devices with the top contact transistor geometry. However, there are controversies as to the Rub degradation both in the bulk state and thin layers. So, the better understanding of these phenomena is crucial for improving the performance of organic devices.

In the present study, we have investigated the structural properties, morphology, and PL emission of Rub thin films deposited on freshly cleaved KBr(100) substrates by thermal evaporation in high vacuum, using a combination of FTIR and photoluminescence (PL) spectroscopy. The morphology of the first near-surface layers of Rub deposited on the atomically flat Au(111) surface was investigated with scanning tunneling microscopy (STM). Special attention was devoted to the stability of Rub molecules in vacuum deposited (VD) thin films. A possibility to

stabilize their properties by using Tc protective layers deposited onto the Rub films was also studied. The VD Rub/Tc bilayer films were fabricated to study the effect of protective Tc layer on the Rub stability in the films.

2. Experimental

2.1. Samples preparation

Thermal vacuum deposition of organic semiconductors is widely used for the fabrication of various organic devices including organic field-effect transistors [16, 17] and OLEDs [18]. The Rub was deposited onto a freshly cleaved KBr(100) substrate held at room temperature. In some experiments, Tc layers ∼20–40 nm thick were deposited onto Rub films. The Rub and Tc molecules were sublimed from a polycrystalline powder. Deposition was carried out at a pressure of ∼5×10^{-6} Torr, with deposition temperatures of about 120 °C and a deposition rate of about 5 Å/min. The substrates were kept at room temperature. Thickness of the deposited Rub layers was controlled by a digital quartz balance monitor and varied from ∼1 to 150 nm.

2.2. FTIR spectroscopy

FTIR transmission spectra were used to examine the chemical structure and molecular orientation in the VD thin Rub layers. Infrared spectra of the films were measured at room temperature with a Bruker IFS-88 FTIR spectrometer in the spectral range of 380–4000 cm^{-1}. 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.

2.3. UV-vis spectroscopy measurements

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

2.4. STM measurements

The structure of Rub films on the atomically flat Au(111) surface was investigated by STM. Gold films (~200 nm thick) deposited in ultra-high vacuum onto freshly cleaved mica wafers were used as substrates. In order to form an atomically flat surface, the gold films were annealed in propane-butane air flame at 550–600 K. The STM tips were mechanically cut from a 0.25 nm Pt/Ir (80:20) wire. Typical imaging conditions were with tunnel currents of 100–170 pA and with a bias voltage of 800 mV. The increase of the bias up to 1 V led to the instability in a tunneling gap due to the polarization and desorption of Rub molecules. All STM-images recorded in the constant-current operation mode were obtained with different samples and tips. The STM measurements were carried out under ambient conditions.

The scanning tunneling spectroscopy mode (STS) was used for the registration of a local current-voltage characteristic to examine the electronic structure. STS-spectra were obtained at a fixed tip-sample distance determined by the imaging parameters (voltage and tunnel current). For the recording of local *I–V* curves, the scan was stopped, and the feedback loop was switched-off. The range of the tunneling voltage ramp was within the limits –1.5 V–+1.5 V.

3. Results and Discussion

3.1. Molecular structure of deposited Rub layers by FTIR spectroscopy

We used FTIR spectroscopy to evaluate the chemical structure and molecular orientation in the VD Rub and Rub/Tc thin films.

Tc and Rub are two prototype fluorescent molecules. The Tc molecule is flat and consists of four elongated *p*-conjugated aromatic benzene-like rings joined sideways along the long molecular axis. Both molecules have the same "fluorescent backbone." But, due to the additional phenyl groups, the backbone of Rub is twisted, whereas it is planar for Tc (see Fig. 1). In Rub, each hydrogen atom of the inner rings has been substituted with an additional phenyl group, which is protruding from the side of the aromatic core almost orthogonally to it. The $sp2$ hybridization of the carbon atoms causes the planarity of the molecules, though the steric hindrance dictates that the substituted phenyl groups in the Rub molecule are flipping out of the plane of the Tc back-
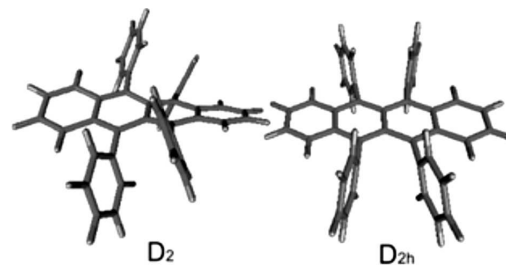

Fig. 1. Geometric structures of Rub D_2 and D_{2h} isomers obtained from the geometry optimization at the BP86/TZVP level [20]

bone. The Rub main polymorph is an orthorhombic crystal [19–20] with the D_{18}^{2h} point group symmetry (while the molecule has the C_{2h} point group symmetry) and has four molecules in the unit cell. Because of the difficulty of growing high-quality single crystals and the existence of multiple polymorphs, the systematic studies of optical and vibrational properties of Rub are very scarce.

In addition, it should be also noted that there are two isomeric structures of Rub reported in the literature [10, 20, 21]: with planar and twisted Tc backbones with predominance of the more stable twisted isomer in Rub solutions and amorphous films. In these two isomers, the Rub molecule symmetry changes from C_{2h} to D_2 (twisted) or D_{2h} (planar); both point groups having centers of inversion. Due to the breaking of the symmetry, some vibrations could be absent in the absorption of polycrystalline Rub. According to the results of DFT molecular simulation of the Rub structure [21], the twisted isomer is energetically more favorable and so more stable as a free molecule and in solution. But as reported in [22], in the crystalline phase, the planar isomer is predominant, since it is stabilized due to the attractive intermolecular interactions between neighboring molecules in the crystalline cell. However, very small difference between the calculated normal vibrational modes of the two Rub isomers makes them of no use for FTIR spectroscopy to distinguish both isomers, though, as suggested in [10], their existence may be revealed in optical spectra.

The literature contains a few studies on the vibrational spectra of thin Rub films or a single crystal [23, 24]. Moreover, there are no comprehensive examples in the literature on the assignment of vibrational spectra of Rub with the use of Raman or infrared spectroscopy.
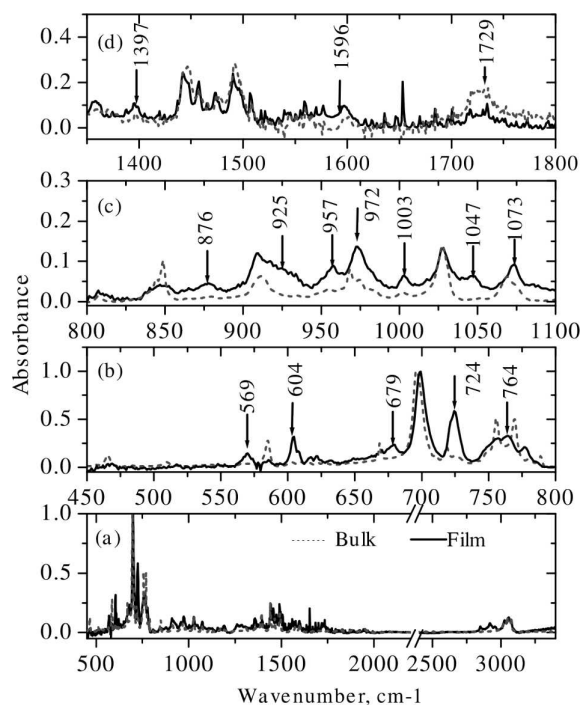
Fig. 2. FTIR transmission spectra of a VD Rub film (solid line) compared to that of polycrystalline Rub (dotted line): full-range spectra (*a*), in expanded selected regions (*b–e*). Arrows indicate new spectral features observed after the deposition

The harmonic vibrational mode frequencies of a planar Rub molecule were determined from *ab initio* calculations, by using the density functional theory and applying the Gaussian98 program [21]. However, it is not easy to assign all the experimental spectral features in the FTIR spectra of Rub polycrystalline samples and VD films to specific intramolecular vibrational modes, since, according to DFT molecular simulations, nearly all of them are of strongly mixed vibrational modes. As a result, the vibrational spectrum of a Rub molecule is very complicated and highly sensitive to minor changes in the molecule structure.

The results of FTIR transmission measurements of Rub bulk polycrystalline samples and VD thin films (with thickness of about 150 nm) are shown in Fig. 2, in which the selected peaks are magnified for clarity. As seen from Fig. 2, in the IR absorption spectra of VD Rub thin films, most bands are broaden, which indicates the inhomogeneous nature of the local surrounding of Rub molecules in a film

due to random positions and orientations of neighboring molecules and confirms an amorphous structure of the VD film. In FTIR spectra of a VD Rub film, as compared to that of polycrystalline Rub, there are also insignificant shifts in positions and intensities of some bands, as well as a number of new absorption bands is observed. Both spectra are seen to be quite different, thus indicating that, at a thickness of about 150 nm, the deposited Rub films show evidence either of impurities or a degradation of the initial compound during the evaporation in vacuum and their further exposure to ambient conditions.

In order to examine more closely the structural changes in the Rub VD films and to distinguish them from that of the bulk crystal, we conducted two types of optical measurements: FTIR and PL spectra measurements (see Section 3.2). In our FTIR transmission measurements, we observed new peaks for the Rub VD thin layers, which are indicated by black arrows in Fig. 2. We used the assignment of FTIR absorption bands (peak position and intensity of fundamental vibration bands) of a Rub molecule based on quantum-chemical calculations [21] as a reference for the analysis of the FTIR spectra of the Rub thin layers.

In general, in the experimental IR spectrum of initial polycrystalline Rub, two groups of bands with substantial intensities can be seen (Fig. 2, *a*). The high-frequency region (3600–2700 cm^{-1}) contains the absorption bands mainly originating from localized symmetric and asymmetric in-plane stretching vibrations of aromatic CH groups [25] in the interval from 3000 to 3100 cm^{-1}: these are the weak absorption bands centered at 3030, 3047, and 3077 cm^{-1}. The bulky phenyl side groups of Rub molecules are very flexible, and their motions are almost uncoupled from the backbone of a molecule. This could result in the additional absorption bands in the region of CH stretching vibrations. The medium frequency region (1700–1000 cm^{-1}) corresponds to in-plane C=C stretching and CH bending vibrations.

Since the Rub molecule is just a derivative of the Tc molecule, it should be possible to categorize some of the vibrational modes of Rub as combinations of modes from the Tc backbone and from individual benzene ring modes. The C=C ring stretching peaks appear between 1430 and 1650 cm^{-1} [25]. In polycrystalline bulk Rub, these are the weak absorption bands centered at 1589 and 1574 cm^{-1} and prob-

ably assigned to phenol ring vibrations, as well as medium-intensity bands from C$\doteq$C stretching vibrations of benzene rings of the Tc backbone at 1492, 1464, 1440, and 1393 cm^{-1}. In the low-frequency region (below 1000 cm^{-1}), the out-of-plane and torsional modes are observed. These are the absorption bands of out-of-plane CH vibrations centered at 848, 968, 1026, and 1069 cm^{-1}. The peaks in the interval from 690 to 900 cm^{-1} (absorption bands centered at 584, 695, 718, 755, and 769 cm^{-1}) arise from the CH out-of-plane bending bands [25].

Since Rub films are known to readily form a peroxide under exposure to open air, we might expect to see new absorption bands of C–O and O–O stretching modes in the spectra of Rub films. In the vibrational spectra of peroxides, the characteristic frequency is due to the v(O–O) stretching mode, which gives rise to strongly polarized Raman bands about 900–700 cm^{-1} [26], being however weak in IR absorption. According to [25], the v(O–O) stretching vibration interacts with other bending vibrations of skeletal C–O and C–C bonds, and there is an extensive coupling between the v(O–O), v(C–O), and δ(C–O–O) modes.

In FTIR spectra of VD Rub films, the most pronounced distinctions in the intensity and line shape are observed for the vibrational modes, which have a contribution from O–O and C–C bending and stretching vibrations. These are the bands at 724, 925, 957, 1003, and 1073 cm^{-1} (Fig. 2, *b, c*). The new weak bands observed at 1397 and 1596 cm^{-1} probably originate from C$\doteq$C stretching vibrations of benzene rings coupled with v(O–O) and v(C–O) modes. These changes in the amorphous VD Rub film spectra indicate the formation of oxidized species such as Rub endoperoxide in a Rub film under its exposure to ambient conditions. This observation is in compliance with the previous findings of other authors (see, e.g., [12–14, 26]).

Our measurements on Rub VD films carried out in some time intervals (each 10 min within 1 h, next two hours, and next 5 days) show no difference in the FTIR spectra, by suggesting that the oxidation processes in the amorphous Rub films during their exposure to ambient conditions occur very rapidly, even without light irradiation, within first several minutes. At the same time, the FTIR spectra of polycrystalline Rub imbedded in the solid KBr matrix do not change with time over a fairly long period of sev-

eral months, by indicating the Rub stability under air-tight conditions. Considering that, according to [8, 21], a planar Rub isomer dominates in polycrystalline Rub, one could suggest that the planar isomer is more stable to the oxidation. On the contrary, a twisted isomer that dominates in Rub solutions and amorphous films is easily oxidized in open air.

We also carried out measurements of FTIR spectra of bilayer Rub/Tc films on KBr(100) surfaces to study the protective action of a Tc layer on a Rub film. The registered FTIR spectra (not shown here) of bilayer VD films obtained by the layer-by-layer deposition of alternating Rub and Tc layers look very similar. Both of them represent an additive sum of the absorption spectra of the initial compounds – Rub and Tc. In addition, the spectral features of Rub in both two-component Rub/Tc films are very similar to those registered for bare Rub VD films. This fact indicates that there is no interaction between the deposited Rub and Tc molecules in the two-component VD films, which consist only of deposited compounds. No changes in the Rub structure were detected, as compared to bare VD Rub films under the influence of Tc molecules, including the absorption bands originating from Rub peroxide. So, the co-deposition of Tc has no significant effect on the Rub stability in such two-component films.

3.2. UV-vis spectroscopy

As was already noted, rapid changes that are observed in the optical properties of the Rub thin films were earlier investigated in detail from the absorption spectra [8–10], and the changes were explained by the Rub oxidation processes [21, 24]. At the same time, changes of the luminescent properties (that are important for practical applications) are still not clearly understood.

We have measured the room-temperature PL emission spectra from the VD Rub thin films deposited on the KBr(100) surface just after the deposition and within several time intervals. Since the spectrum registration time was about 10 min, these time intervals were chosen as a multiple of 10 min. The PL spectra from the as-deposited VD Rub film consists of two strong broad emission bands centered at 565 and 610 nm and a weaker band at 650 nm. Noticeable changes in the PL spectrum begin from the very first scanning sequences. Figure 3 shows a fragment of the
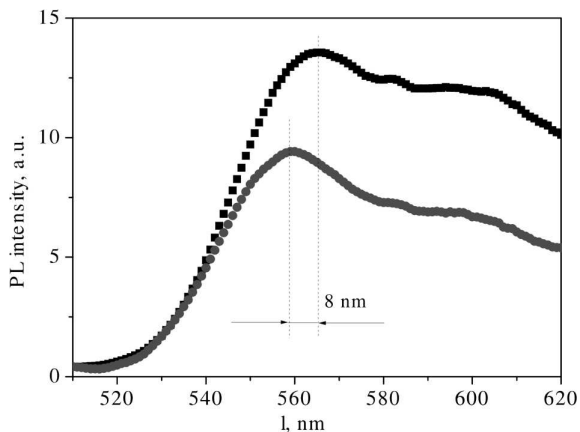
Fig. 3. PL spectra of a VD Rub thin film (100 nm thick): as-deposited (top curve) and measured with a time interval of 28 days (bottom curve)
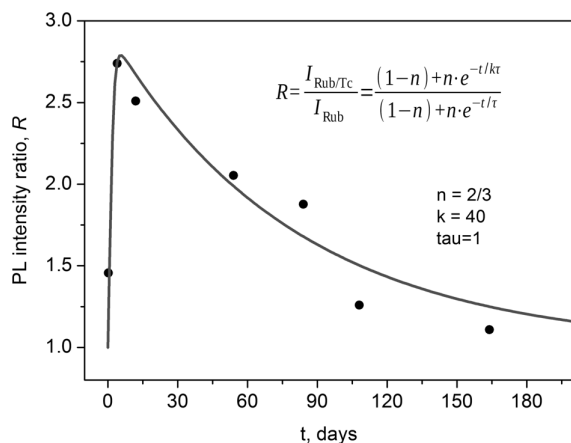

Fig. 4. Time dependence of the PL intensity ratio R of the VD Rub/Tc and bare VD Rub thin films at a wavelength of 560 nm. The solid line shows the fitting results using Eq. (1) with the parameters specified in the inset

PL emission from the VD Rub film and its variation with time. The spectral changes gradually develop with time and are manifested in a blue shift of the PL band maximum and a decrease of the PL intensity. So, according to our results, significant changes in the PL emission from the VD Rub thin films occur over a much longer period of time, as compared to those observed for the absorption spectra.

We have investigated a possibility of preventing the access of oxygen to the Rub molecules using a protective Tc layer. For this purpose, the two-component thin films were fabricated. Over the same deposition cycle, a thin (about 20 nm thick) Tc layer was deposited onto the previously deposited Rub layer of the same thickness. We suggested that the Tc layer would reduce the Rub degradation rate, as compared to the uncoated Rub film. Since the main emission bands of Tc and Rub are located nearly in the same spectral range [27, 28], we firstly measured the Tc emission spectrum under the excitation with a Hg lamp. It appeared that the PL emission from Tc is far less intense. Therefore, the contribution from the Tc emission could be neglected, since it does not affect the accuracy of measurements of the Rub PL spectra. The Rub degradation rate was monitored by changes in the intensity of the 560-nm PL band with time. To evaluate the effectiveness of the protective layer, the ratio R of the PL intensities of Rub films with and without Tc coating

$$R = \frac{I_{\mathrm{Rub/Tc}}}{I_{\mathrm{Rub}}}$$

was taken. The time dependence of the 560-nm PL band intensity ratio R is shown in Fig. 4.

As seen from Fig. 4, the PL intensity ratio R for the thin films of Tc coated and uncoated Rub films increases rapidly over the first 20 days from its initial value close to 1 up to the maximum value of about 2.8, and then it gradually decreases to the initial value over the period of several months.

The following simplest mechanism for the observed PL behavior can be given on the basis of the two-component emission model. We suggest that the PL emission from the VD Rub thin film consists of the PL from twisted Rub isomers, whose PL intensity decays exponentially [9, 10] with a time constant τ; and PL from the planar Rub isomers, whose PL intensity is constant. Then one could suggest that the protective Tc coating increases the time constant by k times. So, the expression for the PL intensity ratio at a time moment t would be

$$R = \frac{I_{\mathrm{Rub/Tc}}}{I_{\mathrm{Rub}}} = \frac{(1-n) + n\,e^{-t/k\tau}}{(1-n) + n\,e^{-t/\tau}}, \qquad (1)$$

where n is a part of twisted Rub isomers.

With the fitting parameters $\tau = 1$, $k = 40$, and $n = 2/3$, Eq. (1) gives good correspondence with experimental results, as shown in Fig. 4. This model is also in good agreement with FTIR spectroscopy results, which prove that a twisted isomer is present in Rub amorphous films.
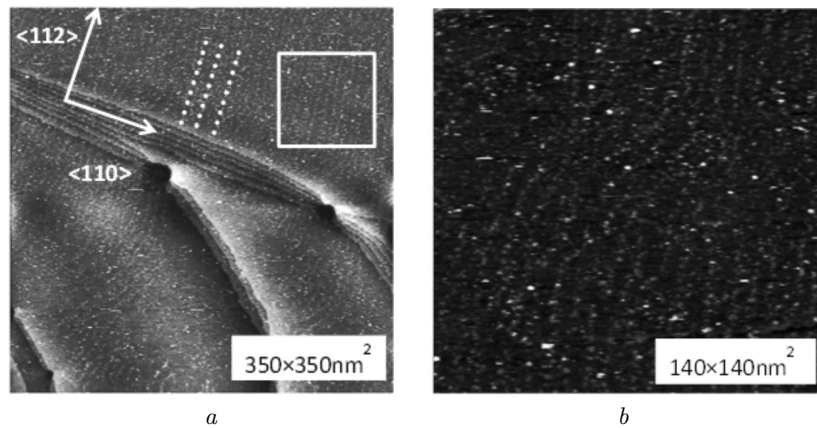
Fig. 5. STM-image of a vacuum deposited ultrathin Rub film on the Au(111) surface ($I_t = 150$ pA, $U_t = 800$ mV)
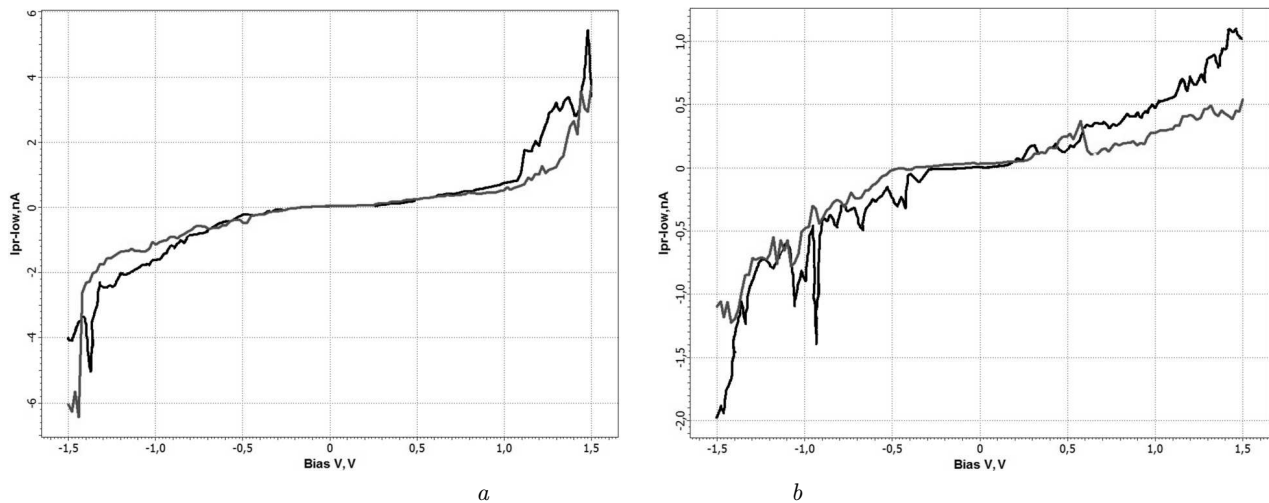

Fig. 6. Local $I - V$ curve of a Rub film measured by STM: near-surface layers (*a*); thick film ($\sim$10 nm) (*b*)

Thus, we have shown that the illumination of VD Rub thin films with light, whose wavelength ia above the Rub band-gap, in the presence of oxygen leads to a gradual decrease of the Rub PL intensity due to the Rub oxidation. It is also shown that the protective Tc layer does somewhat reduce the Rub oxidation rate in two-component Rub/Tc VD thin films, but does not prevent it entirely due to the effective diffusion of oxygen through the Tc layer.

3.3. STM studies

In our STM experiments, wedge-shaped Rub films deposited onto reconstructed Au(111) surfaces were analyzed. The film thickness gradually increased from 1 to 20 nm.

Figure 5 demonstrates the microstructure of the near-surface layers of Rub. For 1–3 monolayer films, the STM-images revealed parallel molecular rows. With increasing the thickness, the row structure disappeared. For thicker films (more than 10 monolayers), the molecular structure was not observed. Since the atomic steps of the Au(111) surface are always parallel to $\langle 110 \rangle$, $\langle 101 \rangle$, or $\langle 011 \rangle$ directions, we adduce that the observed molecular rows are oriented along the $\langle 112 \rangle$ direction. The average height of rows is about 0.2 nm, which is approximately as large as the estimated size of a single molecule.

In the STS-measurements, we recorded the local tunneling current-voltage characteristic $I(V)$. The typical $I–V$ curve of a Rub film is presented in Fig. 6. At voltages below 1.0 V, the $I–V$ curves were symmetric and well reproducible for all film thicknesses. For thick films (Fig. 6, b), a linear behavior of the current sets in above 0.6 V. At higher voltages, the tunneling current becomes unstable due to, probably, the field-stimulated desorption of Rub molecules.

4. Conclusions

With the aid of FTIR spectroscopy, it is shown that VD Rub films are amorphous. It is found that Rub molecules in VD thin films are subjected to the strong oxidation in open air. On the contrary, polycrystalline Rub samples pressed in the KBr matrix show no traces of the oxidation even after months of their storage in open air.

The obtained results on the optical absorption have demonstrated that the deposited Tc layer only slightly enhances the stability of Rub to the photo-oxidation in the amorphous thin films.

The morphology of the first near-surface layers of Rub on the atomically flat Au(111) surface has been investigated by means of STM/STS. It has been revealed that Rub films consist of molecular rows of flat-lying molecules, which are preferentially oriented along the $\langle 112 \rangle$ direction. Thicker Rub films are amorphous.

Our optical and structure investigations for Rub thin film suggest the applicability of Rub organic films in the field of optoelectronic devices only under a protective air-tight cover.

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СТРУКТУРА, МОРФОЛОГІЯ
ТА ФОТОЛЮМІНЕСЦЕНЦІЯ ТОНКИХ ШАРІВ
РУБРЕНУ, НАНЕСЕНИХ У ВАКУУМІ

Р е з ю м е

Рубрен ($C_{42}H_{28}$, 5,6,11,12-tetraphenyltetracene, Rub) активно досліджується в останні роки завдяки його важливим фізичним властивостям, таким як висока рухливість носіїв заряду в органічних польових транзисторах. Рубрен також використовується як лазерний барвник та флуоресцентна домішка в органічних світловипромінюючих діодах для покращання таких характеристик, як час життя, стабільність, колір та яскравість. Проте досі не існує загальної думки щодо стабільності рубрену як у масивному стані, так і у тонких шарах, таким чином, краще розуміння цих властивостей є важливим для покращання характеристик приладів молекулярної електроніки. У даній роботі наведено результати комплексного дослідження молекулярної структури, морфології та фотолюмінесценції шарів Rub, нанесених на підкладки KBr(100) та Au(111) за допомогою термічного випаровування у вакуумі. Крім того, досліджено двокомпонентні плівки рубрен-тетрацен. Головну увагу приділено процесам окислення одержаних зразків в атмосфері. Хімічна структура та орієнтація молекул у досліджуваних зразках вивчались методом ІЧ спектроскопії; структуру перших приповерхневих шарів рубрену на атомно-гладкій поверхні Au(111) досліджено методом сканувальної тунельної мікроскопії. З аналізу часових змін параметрів смуг у спектрах фотолюмінесценції (положення та інтенсивність) досліджено кінетику зміни емісійних властивостей шарів рубрену.