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CRYSTALLINE STRUCTURE AND POLYMORPHISM IN POWDERS AND THIN FILMS OF DIBENZOTETRAAZA[14]ANNULENE

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The increasing interest in dibenzotetraaza[14]annulene (TAA) is motivated by the demonstrated perspectives for using this organic semiconductor in actively progressive now spintronics and in other fields of electronics. This work is the first study on polymorphism, which may occur in powder and in thin TAA films. The results of this study showed that the initial TAA powder synthesized by chemical methods are both now known polymorphic forms of TAA which were registered at Cambridge Crystallographic Data Centre as GAGVAL and GAGVAL01. It was also found that at the condensation of thin films G-form initially formed while after increasing the film thickness the G01-form will forms also and a continuous films have twophases and contain both known polymorphs — G and G01. The *X*-ray diffraction pattern indicated also that crystallites in thin TAA films show a strong preffered orientation (texture) with the (100) plane (for G-polymorph) and (002) plane (for G01-polymorph) parallel to the surface of the substrate.

Keywords: organic semiconductors, thin films, dibenzotetraaza[14]annulene, polymorphism.

КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА И ПОЛИМОРФИЗМ В ПОРОШКЕ И В ТОНКИХ ПЛЕНКАХ ДИБЕНЗОТЕТРААЗА[14]АННУЛЕНА

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Увеличение интереса к дибензотетрааза[14]аннулену (ТАА) обусловлено перспективами использования этого органического полупроводника в активно развивающейся сейчас спинтронике, а также и в других областях электроники. Данная работа является первым исследованием, касающимся полиморфизма, который может иметь место в кристаллах ТАА как в порошкообразном виде, так и в его тонких пленках. Установлено, что в порошкообразном веществе ТАА, синтезированном химическими методами, присутствовали обе известные полиморфные формы ТАА, зарегистрированные в Кембриджском центре кристаллоструктурных данных под шифрами GAGVAL и GAGVAL01 (G и G01). Обнаружено, что при конденсации тонких пленок ТАА вначале преимущественно образуются кристаллиты G-формы. По мере увеличения толщины пленки образуется и G01-форма, а сплошная пленка является двухфазной, т. е. содержит оба известных полиморфа. Рентгенодифракционным методом установлено, что пленки ТАА обладали преимущественной ориентацией кристаллитов (текстурой) плоскостью (100), параллельной подложке для G-формы, и, соответственно, плоскостью (002) для G01-формы.

Ключевые слова: органические полупроводники, тонкие пленки, дибензотетрааза[14]аннулен, полиморфизм.

КРИСТАЛІЧНА СТРУКТУРА ТА ПОЛІМОРФІЗМ В ПОРОШКУ І ТОНКИХПЛІВКАХ ДИБЕНЗОТЕТРААЗА[14]АНУЛЕНУ

В. Г. Удовицький

Зростання інтересу до дибензотетрааза[14]анулену (ТАА) обумовлено перспективами використання цього органічного напівпровідника в спінтроніці, яка зараз активно розвивається, а також і в інших областях електроніки. Ця робота є першим дослідженням, що стосується поліморфізму, який може мати місце в кристалах ТАА як в порошкоподібному стані, так і в його тонких плівках. Виявлено, що в порошкоподібній речовині ТАА, синтезованій хімічними методами, були присутні обидві відомі поліморфні форми ТАА, зареєстровані в Кембриджському центрі кристалострукгурних даних під шифрами GAGVAL та GAGVAL01 (G і G01). Встановлено, що при конденсації тонких плівок ТАА спочатку переважно утворюються кристаліти G-форми. Зі зростанням товщини плівки утворюється також і G01-форма, а суцільна плівка є двохфазною, тобто містить обидва відомі поліморфи. Рентгенодифракційним методом встановлено, що плівки ТАА мали переважну орієнтацію кристалітів (текстуру) площиною (100), паралельною до підкладки для G-форми, і, відповідно, площиною (002) для G01-форми.

Ключові слова: органічні напівпровідники, тонкі плівки, дибензотетрааза[14]анулен, поліморфізм.

INTRODUCTION

At the present time there is a great interest for development of molecular (organic) electronics (ME), based on using of various organic molecular materials for creating electronic devices. ME is now often referred to as the next-generation electronics that will enable to implement a number of significant advantages over the traditional electronics based on the using of inorganic materials, the main of which is Si. The main advantages of organic materials and electronic devices based on it are: solubility in many solvents, the possibility for a relatively simple and inexpensive manufacture of flexible elements on the large area, opportunities for obtaining materials with desired electronic properties by purposeful synthesis or physicochemical modification of already synthesized materials, environmental friendliness etc. [1, 2].

One of the main problem which influence on the successful development of the ME is the creation and comprehensive study of molecular materials with the desired properties (semiconductors, conductors, dielectrics). During creation of the active functional elements of ME (diodes, transistors, sensors, a variety optoelectronic devices and so on) the mobility of current carriers is the most important properties of used molecular organic semiconductors.

Organic semiconductors (OS) are now divided into two large groups. The first of them is OS with high molecular weight (polymer, i. e., forming a long chain polymer). The second one is OS with low molecular weight, which based on the individual molecules (often called as a «small molecule organic semiconductors»), and can contain from tens to hundreds of atoms [3]. Now the majority of experiments have been performed with polymeric OS and they are much better investigated than OS based on the individual molecules [4]. A large number of different polymeric OS have been synthesized and investigated, so as a result the impressive results about mobility of carriers in them have been achieved. In the work [5], for example in polymeric OS based on modified fragments polypyrrole the mobility of holes with value about 12 $cm^2 V^{-1} s^{-1}$ have been achieved. This carrier mobility is already comparable to the mobility of carriers in amorphous silicon films

(13 $cm^2 V^{-1} s^{-1}$), which is now becoming more widely used in electronics, in particular, for creating thin-film transistors [6].

The molecules with different atomic composition and molecular structure which can form a solids, including thin films with different crystal structure are synthesized and used at the creation of organic semiconductors. Special interest of researchers cause the low-molecular organic semiconductors based on the molecules with macrocyclic structure, for instance such as phthalocyanine (Pc, Fig. 1) and dihydrodibenzotetraaza[14]annulene (TAA, Fig. 2).
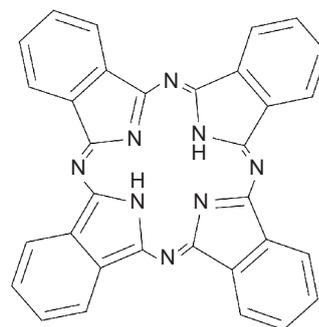
Fig. 1. Phthalocyanine
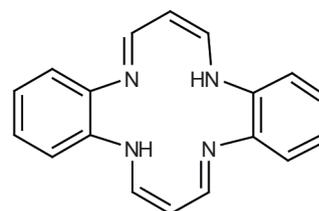
Fig. 2. Dihydrodibenzotetraaza[14]annulene

Due to the nature of its molecular structure and the existence in closed macrocyclic structures the so-called macrocyclic effect, the OS have a high thermal and chemical stability, π-conjugated electronic system as well as good sensitivity of electrical properties for various parameters of chemical and physical nature. This provides wide opportunities of their application for creation of various micro- and nanoelectronic devices, where they are used usually as thin films that can be deposited by various methods.

A characteristic feature of the molecular crystals, especially in the thin film state is the polymorphism, i.e. the existence at least two (and often more) different crystalline phases formed by molecules of the same substance in the solid [7]. This is due to the weak intermolecular forces (Van der Waals forces) that exist

between the individual molecules in a molecular crystal, from which a crystal is formed. The phenomenon of polymorphism in thin films of molecular crystals appears more frequently than in the crystals obtained by different other methods, in particular during crystallization of mono- or polycrystals from the solution. The stable or quasi-stable coexistence of several polymorphic phases is possible in thin films. This is due to significant influence of the substrate on the process of film condensation and the formation of crystalline phases in it [8]. The treatment after condensation of thin films significantly influences on the phase composition of films [9]. At the same time, it was repeatedly found that the phase composition of the films (polymorphism) has a significant effect on their different physicochemical properties, in particular on the movement of charge carriers in them [10], which will determine the main characteristics of the electronic devices that are based on these films.

The phenomenon of polymorphism and its influence on the properties of devices based on phthalocyanine films and its metal complexes have been studied for a long time and it is now well known about close relationship between the phase composition of the films and characteristics of the devices based on them [11–16]. Until recently the TAA (Fig. 2) and materials based on it have been studied and used mainly in chemistry, medicine and pharmacology, however, in the last few years the study about application of this OS in engineering and electronics has intensified significantly. Chemical gas sensors, thin film transistors, compact discs etc. based on TAA have already been created. Questions concerning the properties and using of substances and materials based on TAA was highlighted in our review [17], but now there is a new interesting publications relating to the study of magnetic properties and applications of such materials for spin filters creation [18–21]. The search that aimed for creating new compounds based on TAA molecules is continuing also [22]. This opens new perspectives for using this OS in actively progressive now spin electronics and in other fields of electronics. However, the question about the polymorphic composition of the TAA films currently remains practically not studied. It should be noted that in publications relating

to the development and research of various devices based on TAA and its metal complexes, in particular, field-effect transistors [23], gas sensors [24, 25], compact discs [26], spin filters [18–21] the phenomenon of polymorphism in TAA and its derivatives and its influence on the characteristics of the devices were not analyzed also.

The aim of this work is a review of available scientific publications relating to crystal structure, in particular, polymorphic composition of TAA films and some of its derivatives as well as presentation of author's own experimental results on subject.

A REVIEW OF INFORMATION RELATING TO THE TAA CRYSTAL STRUCTURE AND SOME OF ITS DERIVATIVES IN THE ORIGINAL (POWDERED) STATE

For unsubstituted metal-free ligand of TAA ($C_{18}H_{16}N_4$) according to the data from Cambridge Crystallographic Data Centre, it is known two polymorphous modifications with monoclinic lattice. They are registered in the database as — «GAGVAL» (is briefly denoted by G) and «GAGVAL 01» (is denoted by G01). The main structural parameters of TAA and some of its derivatives obtained by different authors from the XRD results are given in Table 1. The TAA crystals that were grown by the slow sublimation of substances in vacuum have a polymorphic G form [27]. The samples crystallized from a solution of the substance in xylene have a polymorphic G01 form [28]. The question about the thermodynamic range of stability for each of these forms and their interconversion are still unclear. However, we can assume that both these forms are stable enough under normal conditions, because the authors [27, 28] have performed *X*-ray investigation of samples at room temperatures and atmospheric pressure. Noteworthy, there is marked difference in the unit cell parameters between polymorphic G and G01 forms (Fig. 3) along with a very small difference of their volumes (the volume of the G-shape cell is greater than the volume of the G01-shape cell approximately by 1.5 %). Ni(II)TAA and Co(II)TAA metal complexes have the same monoclinic crystal lattice as the

Table 1

The structural parameters of TAA and some of its derivatives, taken from the literature

№	Composition	Crystal system	Parameters of unit cell, Å a, b, c	Angles, deg. α, β, γ	Molecular formula	Ref.
1	TAA «GAGVAL»	monoclinic	9,096 10,648 14,915	90 95,93 90	$C_{18}H_{16}N_4$	[27]
2	TAA «GAGVAL 01»	monoclinic	14,926 5,2342 19,570	90 112,195 90	$C_{18}H_{16}N_4$	[28]
3	Ni(II) TAA	monoclinic	19,456 5,228 14,368	90 112,28 90	$Ni(C_{18}H_{16}N_4)$	[29]
4	Co(II) TAA	monoclinic	19,52 5,228 14,84	90 112,46 90	$Co(C_{18}H_{16}N_4)$	[29]
5	Co(III) TAA CN	orthorhombic	6,986 14,662 15,537	90 90 90	$C_{19}H_{14}N_5Co$	[30]
6	Ni(II) TAA I$_2$	orthorhombic	20,245 13,416 6,418	90 90 90	$Ni(C_{18}H_{14}N_4)I_2$	[31]
7	Pd(II) TAA I$_2$	orthorhombic	20,452 13,430 6,499	90 90 90	$Pd(C_{18}H_{14}N_4)I_2$	[31]

form G   form G01
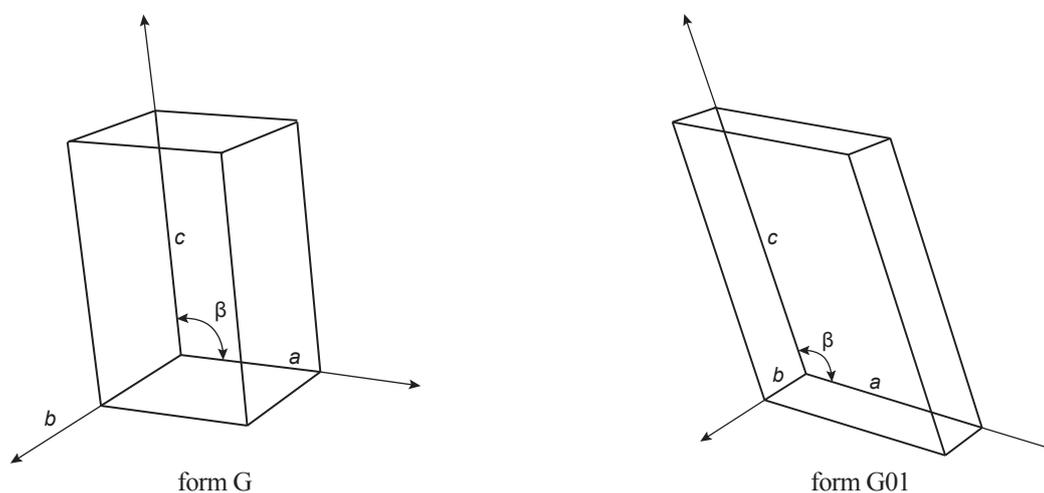
Fig. 3. Unit cells of G and G01 polymorphic forms of TAA

G and G01 polymorphous modifications [29] and, although their crystals were grown by sublimation in a vacuum they were isomorphic to the obtained by crystallization from solution G01 TAA form. Derivatives of TAA metal complexes (Co(III)TAACN [30], Ni(II)TAAI$_2$ and Pd(II)TAAI$_2$ [31]) which obtained by introduction of CN-group ion coordinated with Co(III) or by iodination of molecules on their periphery form a crystal lattice with rhombic symmetry. This is due to changing of steric conditions for dense packing of modified molecules in the lattice and it correlates well with results how iodine influences on the NiPc crystal structure [32].

OPTICAL AND X-RAY DIFFRACTION STUDIES OF TAA IN THE INITIAL POWDERY STATE

The original TAA powder which is then used for thermal evaporation and deposition of thin films have been synthesized at the Department of Organic Chemistry of V. N. Karazin Kharkiv National University by Prof. Orlov V. D. and Prof. Kolos N.N. according to known chemical methods [33, 34]. The synthesized TAA material was further purified by recrystallization in organic solvents and its UV spectra are well correlate with data from literature. At the optical microscope study of the obtained TAA powder we have observed the presence of crystals in two distinctive forms – plates with the rhomboid forms and bricks with elongated shape. The micrograph of one of the observed in optical microscope fragments is shown in Fig.4.
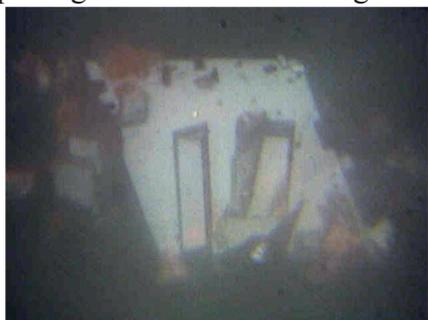
Fig. 4. Micrograph of TAA crystals in the original powder

Phase composition of initial powder and films of TAA was determined using *X*-Ray diffraction studies. The diffraction pattern of initial TAA powder is shown in Fig. 5. The XRD measurements were performed with help of DRON-3M diffractometer in continuous recording mode and with help of SIEMENS diffractometer in
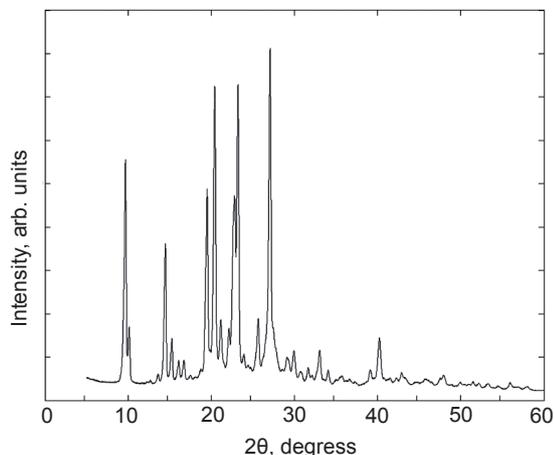
Fig. 5. Diffraction pattern obtained from initial TAA powder, CuKα-radiation

discrete mode with a scanning step of 0.01 deg. with CuKα-radiation.

For accurate identification of diffraction pattern the computer calculation of the diffraction peaks parameters (angle, 2θ, relative intensity I, and the corresponding interplanar spacing, d_{hkl}) for the two polymorphic TAA forms («GAGVAL» and «GAGVAL 01») was performed (see Tab. 1). The calculation showed that in the angles range 2θ < 60° for each of the polymorphic modifications more than 400 of permitted reflections exist. The results of this calculation for a number of the strongest reflexes are given in Tab. 2.

The analysis of the powder diffraction pattern using the data from Table 2 confirmed the presence of both polymorphic modifications in the initial powder. Confirmation of this is in particular that G-polymorphic form characterized by the presence of two closely located diffraction reflexes at 2θ = 9.768 degrees (relative intensity — 50.2 %) and 2θ = 10.217 degrees (27.5 %), while G01-polymorphic form in this angular range has only one reflex at 2θ = 9.755 degrees (100 %). At the same time, G01-polymorphic form has the reflexes of reflection in the diffraction pattern in 2θ angular range from 15 to 16 degrees, but G-form in this angular range has no reflexes.

X-RAY STUDIES OF TAA THIN FILMS

The TAA thin films were prepared by thermal sublimation and condensation of the substance of the OS in a vacuum (at pressure ~10⁻² Pa) with help of VUP-5M setup. Resistive effusion type evaporators have been used. Mandatory requirement for obtaining qualitative films that do not have visible inclusions was very slow temperature rise of the evaporator, which was achieved by fine adjustment of power supplied to the evaporator. The film thickness was regulated by weight of sublimed substance or duration of the period of open shutter position. Monitoring the thickness of thin films was carried out by a quartz resonator and additionally determined by their optical transparency. As substrates for deposition of films we used standard microelectronic substrates such as polished glass ceramic, alumina ceramic, optical glass and the KBr, LiF, NaCl plates (for spectroscopic measurements). The substrate was

Table 2

The results of computer calculation of XRD reflections for TAA (CuK$_\alpha$–radiation)

G-form						G01-form					
h	*k*	*l*	2θ, deg.	*I*, %	*d$_{hkl}$*, Å	*h*	*k*	*l*	2θ, deg.	*I*, %	*d$_{hkl}$*, Å
1	0	0	9,768	50,2	9,047	0	0	2	9,755	100	9,060
0	1	1	10,217	27,5	8,650	2	0	0	12,801	9,2	6,910
1	1	1	14,575	37,9	6,072	–2	0	2	12,835	6,7	6,891
1	0	2	16,203	5,0	5,466	2	0	1	15,341	42,7	5,771
–1	1	2	16,839	7,7	5,261	–2	0	3	15,398	36,8	5,750
2	0	0	19,608	24,1	4,524	0	1	1	17,623	8,4	5,028
–1	2	1	19,936	4,5	4,450	2	0	2	18,851	5,5	4,704
0	2	2	20,517	100	4,325	–2	0	4	18,921	7,1	4,686
–1	2	2	22,222	12,5	3,997	1	1	1	19,391	6,1	4,574
2	1	1	22,706	14,4	3,913	0	0	4	19,581	51,4	4,530
1	1	3	22,923	18,3	3,876	2	1	0	21,278	50,4	4,172
1	2	2	23,304	74,3	3,814	–2	1	2	21,299	48,8	4,168
–1	2	3	25,764	8,2	3,455	2	1	1	22,920	72,5	3,877
1	0	4	26,884	9,9	3,314	–2	1	3	22,959	72,8	3,870
1	2	3	27,173	83,0	3,279	–3	1	1	24,785	8,5	3,589
–1	3	2	29,145	4,3	3,061	2	1	2	25,439	7,3	3,498
–2	0	4	29,500	5,2	3,025	–2	1	4	25,492	7,9	3,491
1	3	2	29,993	7,1	2,977	3	1	0	25,742	5,4	3,458
1	2	4	31,782	3,1	2,813	4	0	0	25,765	11,1	3,455
1	3	3	33,144	11,9	2,701	–3	1	3	25,781	52,7	3,453
1	4	1	35,823	3,5	2,505	–4	0	4	25,835	11,5	3,446
3	2	3	40,298	6,9	2,236	2	0	4	27,294	5,7	3,265
–4	0	2	40,440	3,8	2,229	–2	0	6	27,377	5,4	3,255
–1	2	6	40,493	4,5	2,226	3	1	1	27,575	58,9	3,232
–4	1	3	43,032	3,0	2,100	–3	1	4	27,637	18,5	3,225
2	4	5	51,575	3,2	1,771	3	1	2	30,138	8,0	2,963
						–3	1	5	30,218	23,0	2,955

arranged normally to the molecular flow. In all processes the substrate is not specifically heated and substrates temperature was $T_S \sim 25$ °C and the increasing in their temperature due to radiation heat from the evaporator and molecular flow does not exceed more than 30 °C.

The diffraction pattern of the TAA film with a thickness about ~400 nm which condensed on a non-heated polished substrate from glass ceramic is shown in Fig. 6. As we can see from diffraction pattern the TAA film that condensed on an amorphous substrate without any oriented

sublayer has quite perfect crystallographic texture, i. e. the preferred orientation of particular crystal planes relative to the film substrate. The presence of only two strong peaks in its diffraction pattern (peak 1 at $2\theta \sim 9.77°$ and peak 2 at $2\theta \sim 19.61°$) is evidence about it. The ratio $\sin\theta_2 / \sin\theta_1$ for these peaks is equal two and it is reasonable to suppose that these reflexes are first and second order reflections from one system planes of crystal. The ratio of the intensities of these reflexes also confirmed this conclusion. Table 2 shows that these peaks can be either reflections from (100) and (200) planes of G-modification, or (002) and (004) of G01 — modification of TAA. For refinement the question of which of the polymorphic TAA forms (G or G01) belongs to these peaks, the diffraction pattern was recorded in the continuous recording mode with a minimum speed of movement of the detector (1/32 deg./min). This slow registration of XRD pattern allowed to detect a significant modification of the profiles of these peaks and the appearance of noticeable asymmetry of the peaks recorded for thicker films. It was manifested for both peaks recorded from textured films, but for second order reflection peak this feature was more pronounced. The profiles of X-Ray diffraction peaks that recorded in the range of angles $2\theta \sim 19$–20 deg. for films with various thicknesses and for initial TAA powder are shown in Fig. 7.
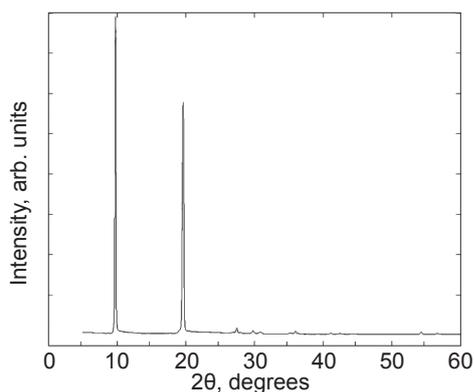
Fig. 6. Diffraction pattern obtained from TAA thin film, CuKα-radiation

As can be seen from fig. 7 the profile of X-ray diffraction peak that recorded from the thinnest investigated film (100nm) is sufficiently symmetrical, but with increasing of film thickness in it from the side of smaller angles the pronounced asymmetry appears and the maximum of peak slightly shifts also to smaller 2θ angles.
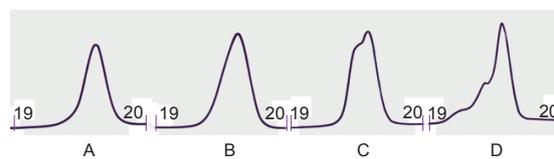
Fig. 7. The profiles of X-Ray diffraction peaks that recorded in the range of angles $2\theta \sim 19$–20 deg. for films with various thicknesses and initial TAA powder (A — 100 nm, B — 400 nm, C — 1500 nm, D — initial powder)

The observed changes in the profiles of the peaks with increasing the film thickness and in fact its separation in thicker films into 2 close peaks are well explained by the following. Since the initial TAA powder as shown above is two-phase (it contains both polymorphs of TAA — G and G01), therefore we can see the total peak on the diffraction pattern of powder, which is the result of superposition closely spaced peaks and instrumental unresolved peaks from (200) planes of G-modifications ($2\theta = 19.608°$) and (004) planes of G01-modifications ($2\theta = 19.581°$).

It is assumed that during film condensation from steam flow a certain way primarily only one of the polymorphic modifications oriented relative to the surface of the substrate is formed initially. Therefore, the observed X-ray reflections peak from the thinnest of the investigated films is most symmetrical (Fig. 7A). Upon further condensation in the final stage of continuous film formation when there is an overgrowing of «channels» and «filling» of voids and subsequent growth of a continuous layer the conditions of condensation and the crystal growth change significantly.

This can lead to the randomly oriented crystallites formation with already existing modification as well as other polymorphous modification. Another polymorphic modification makes new X-ray reflection peaks which are slightly displaced relative to the peaks of the already existing phase. This is manifested in experimentally observed shift of angular position of the total peak and in occurrence of its asymmetry (Fig. 7 B, C).

Since at increasing of thickness of film the top of a joint peak shifted towards smaller angles and on the same side the asymmetry appears this leads to the supposition that in the first stage of film condensation the G-modification mainly forms (it gives a primary peak at $2\theta = 19.608°$) and at later stages of condensation the

G01-TAA modification will also forms (it adds two closely located peak at $2\theta = 19.581°$ and $2\theta = 19.391°$). In thicker films the randomly oriented crystallites also possible form giving new weak peaks at other angles 2θ.

The reason that the G-polymorphic modification of TAA mainly formed at the initial stage of film condensation can be explained on the basis of thermodynamic approach in the following way. In any mechanism of condensation of thin films the first step in the crystal formation is nucleus formation with crystalline phase. It is clear from total energy considerations that the nucleus formation with new phase is more difficult than with a large change in free energy it is associated. Therefore the nucleus of crystal will arise and increase till to critical size more easily with shape and modification (in case of polymorphic modification) for which the difference between free energies of crystal and initial phase will be minimum. This postulate follows from the thermodynamic theory of nucleation, which is based on the idea that the critical nucleus must have minimum free energy.

The volumes of the unit cells of G and G01 — polymorphic TAA modifications (V_G and V_{G01}) differ very slightly, ($V_G = 1436.0$ Å³, $V_{G01} = 1415.632$ Å³, i. e. $V_{G01} \approx 0.986\ V_G$). However, the total area of all unit cells surfaces of these polymorphic forms differ significantly ($S_G \approx 781.22$ Å², $S_{G01} \approx 899.08$ Å², i. e. $S_{G01} \approx 1.151\ S_G$). This is clearly seen from the comparison of the geometric dimensions of unit cell parameters of the considered polymorphic TAA modifications (see Fig. 3). This peculiarity plays a decisive role in the fact that at the initial stage of condensation, i.e. when on the free surface of the substrate the nucleus of crystalline phase begins to appear the nucleus of G-modification mainly forms and grows to a critical size. It is energetically more efficient at this stage.

However, the process of nucleation is probabilistic. If at the initial stage of condensation the formation of G-modifications is energetically more favorable (and hence more probable) in the subsequent stages of condensation many factors influencing on the formation change significantly. Therefore, the occurrence of such conditions in local areas of substrate is possible because it is energetically more favorable and probable for formation of G01-modification and consequently it will be formed in the film, that we have observed in this study.

CONCLUSION

Polymorphism and texture may significantly affect on the electronic properties of thin films of organic semiconductors in organic electronic devices. Therefore, it is important to study the crystal structure and phase composition of thin films and determine the conditions for film deposition and as a result one or another crystal structure and polymorphic form will be formed. This work is the first study on polymorphism, which may occur in powder and in thin TAA films. The results of this study showed that the initial TAA powder synthesized by chemical methods are both now known polymorphic forms of TAA which were registered at Cambridge Crystallographic Data Centre as GAGVAL and GAGVAL01 (denoted by G and G01). It was also found that at the condensation of thin films G-form initially formed while after increasing the film thickness the G01-form will forms also and a continuous films have two-phases and contain both known polymorphs — G and G01. The X-ray diffraction pattern indicated also that crystallites in thin TAA films show a strong preferred orientation (texture) with the (100) plane (for G-polymorph) and (002) plane (for G01-polymorph) parallel to the surface of the substrate. This texture was observed in all thin TAA films, which were deposited on various non-heated polished substrates without any oriented sublayer – glass ceramic, alumina ceramic and optical glass.

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