Orientation study of iron phthalocyanine (FePc) thin films deposited on silicon substrate investigated by atomic force microscopy and micro-Raman spectroscopy

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Abstract In this article, we present temperature and orientation study of iron phthalocyanine (FePc) thin films with different thickness deposited on silicon substrate. The organic thin films were obtained by the quasi-molecular beam evaporation. The micro-Raman scattering spectra of FePc thin layers were investigated in the spectral range 550–1,800 cm^{-1} using 488-nm excitation wavelength. The Raman scattering and atomic force microscopy studies were performed at room temperature before and after annealing process. Annealing process of thin layers was carried out at 453 K for 6 h. From polarized Raman spectra using surface Raman mapping procedure the information on distribution of polymorphic phases of FePc layers has been carried out. Moreover, the obtained results showed the influence of the annealing process on the ordering of the molecular structure of thin films deposited on silicon substrate. For the very thin layers we did not observe the change of the polymorphic phase but only reordering of the thin layers and change of molecular structure to intermediate phase. Using atomic force microscopy method, we observed arrangement of the thin layers structure connected with the change of roughness of the thin layers after annealing process. The obtained results indicate that the structure of thin layer deposited on silicon substrate is strongly affected by the annealing process.

Introduction

In recent years, there has been a growing interest in organic semiconductor thin layers due to their important role in finding new materials for optoelectronic applications, magnetic materials, and photovoltaic devices. One of them are the thin layers of organic compounds based on metall-ophthalocyanine (MPc) deposited on a solid state substrate using different methods [1, 2]. The metallophthalocyanines have attracted a great deal of attention for a wide variety of applications such as organic light emitting diodes (OLEDs), solar cells, organic field-effect transistors, molecular gas sensors, memories, and optoelectronic devices [3–6]. Metallophthalocyanines represent a large family of heterocyclic conjugated molecules with high chemical and thermal stability [7, 8]. These materials have the advantage of being sufficiently stable, because they can be prepared in thin film form by quasi-molecular beam evaporation method.

Recently, they have been intensively investigated using the optical methods such as absorption ellipsometry, FTIR absorption, Raman spectroscopy, X-ray diffraction (XRD), scanning tunneling microscopy (STM), and atomic force microscopy (AFM) [9–14].

The core structure of the metallophthalocyanine is formed by four isoindole units endowing the molecule with two-dimensional conjugated π electron system. Metallophthalocyanines can occur in many different polymorphic forms connected with different crystalline structure. The most popular is metastable α form and stable β form [15, 16]. In both forms, the molecules are arranged in a herringbone pattern. Their main difference is the angle of inclination of the molecular plane with respect to the crystallographic ac-plane. In the α and β-form, this angle is equal to 25°–35° and 40°–49°, respectively [17].

The characterization of the preferred orientation and understanding of its dependence on deposition conditions plays an important role for the successful applications of FePc-based thin films in optoelectronic devices. The

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influence of different deposition conditions on both, the preferred orientation of FePc crystallites within films and surface morphology was investigated using X-ray diffraction method [18]. The morphology of thin film surface depends also decisively on sample preparation conditions. Slowly deposited films exhibit usually rather rough surfaces, while high deposition rates cause smoother surfaces with improved performance [19, 20]. Notably, chemical nature of the metallophthalocyanine, as well as substrate's geometry and temperature play a very important role. The influence of the substrate of that kind and its temperature on the growth of FePc layers still is not well recognized and understood.

Also, very important is heating and cooling process of organic thin layers, which in many cases lead to the changes in polymorphic forms and arrangement of structure. In most cases, the molecules of MPc, where: M = Cu, Zn, Mg, Ni, Fe, and Co, take the form of the flat molecules with D_{4h} symmetry [21]. The heating process changes the polymorphic form and physical properties of the investigated material. The obtained results for ZnPc thin layers deposited on silicon and glass substrates have been already reported in our previous article [22].

In this study, we present investigations of the orientation and temperature dependencies of Raman spectra for very thin FePc layers. The main aim of our study was to determine the molecular orientation and distribution of the polymorphic phase of iron phthalocyanine thin film deposited on n-type silicon substrate and temperature behavior of FePc associated with the possible change of molecular symmetry at high temperatures. The revealed changes are discussed in terms of the annealing process.

Experimental

Thin film preparation

The iron phthalocyanine layers have been prepared at room temperature from Knudsen cell (quasi-molecular beam evaporation) in vacuum chamber at pressure of about $p = 2 \times 10^{-4}$ Pa. Purified FePc ($C_{32}H_{16}FeN_8$) powder (Sigma-Aldrich Co.) was loaded into a quartz effusion cell with a nozzle of 3 mm in diameter on the top. The n-type (001)Si substrates were located 10 cm away from the source of MPc which before loaded into vacuum chamber were sonicated in acetone, distilled water, isopropanol, and finally in distilled water. During evaporation process the substrates were held at room temperature. The deposition rate was 0.2 nm s^{-1}. We obtained thin FePc layers of a thickness of 79, 230, and 250 nm. The last sample has been used in temperature study.

Characterization of thin films

The Raman scattering spectra of FePc layers were investigated in the spectral range of 550–1,800 cm^{-1}. The nonpolarized and two types of polarized (for VV and VH scattering geometry) Raman spectra were recorded in the back-scattering geometry using inVia Renishaw micro-Raman system. As an excitation light, we used the blue line of argon laser operating at 488 nm. The same laser as a source of exciting light was used to study Raman surface mapping. The laser beam was tightly focused on the sample surface through a Leica 50× LWD microscope objective (LWD—long working distance) with numerical aperture (NA) equals to 0.5 leading to a laser beam diameter about 2 μm. To determine orientation of the FePc thin layer the polarized (VV and VH) Raman spectra were recorded. To prevent any damages of the sample an excitation power was fixed at 5 mW. Because, all measurements were recorded in back-scattering geometry we could neglect the angle dependence of reflection coefficients of thin layer and substrate for different polarizations of the incident light. The position of the microscope objective with respect to the thin layer was piezoelectrically controlled during surface mapping (XY position). The reference position (level 0) was assumed for the laser spot focused on the surface of sample. The obtained Raman maps of surface of the thin layer covered an area 20 × 20 μm with the step of 2 μm.

Temperature measurements were performed using Lincam THMS 600 temperature stage connected with temperature controller TMS 94 operating with an accuracy of ±0.1 K. The micro-Raman spectroscopy study has been performed in the temperature range from 300 to 480 K. During temperature study, to obtain thermodynamic stability the investigated sample was stabilized at the selected temperature by 20 min.

The AFM observations were performed using Innova SPM (Veeco, USA) system. Tapping mode height images were recorded using Si (p-doped) cantilevers with spring constant ranging from 20 to 80 Nm^{-1} and resonant frequency of 250–300 kHz. All measurements were performed at room temperature.

Results and discussion

It has been revealed that the orientation of thin FePc layers relatively to the surface of the substrate can be determined using the analysis of external and internal molecular vibrational modes connected with symmetry of FePc molecule. At room temperature, FePc is the planar molecule and possesses D_{4h} point group symmetry. The determination of molecular orientation of thin layer from Raman scattering studies was based on the analysis of external

molecular vibration. The molecular orientation of thin film is connected with the elements of matrix of scattering tensors for individual type of vibrations.
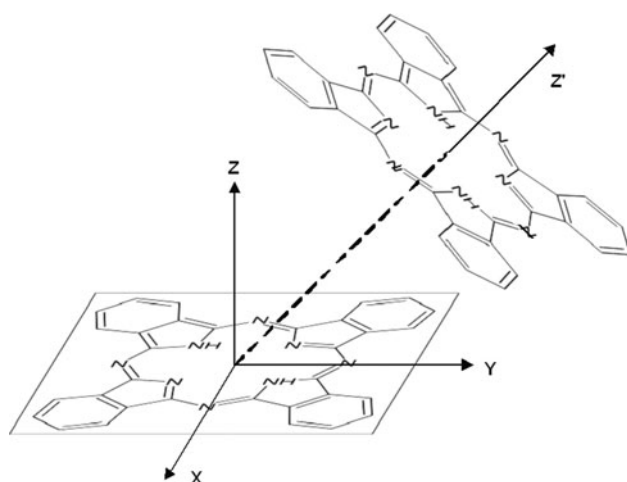
The method permitting to determine orientation of the phthalocyanine thin films deposited on the substrate was proposed by Basova et al. [23].

The vibrations of the FePc planar molecules which consist of 57 atoms and possessing D_{4h} point group symmetry has been described in our previous article for CuPc, MgPc, and ZnPc can be classified into following irreducible representation (taking into account only internal vibrations) [22–24]:

$$\Gamma_{vib} = 14A_{1g} + 13A_{2g} + 14B_{1g} + 14B_{2g} + 13E_g + 6A_{1u} \\ + 8A_{2u} + 7B_{1u} + 7B_{2u} + 28E_u \tag{1}$$

where A_{1g}, B_{1g}, B_{2g}, and E_g modes are Raman-active. The nondegenerate A_{1g}, B_{1g}, and B_{2g} modes are in-plane vibrations, and double degenerate E_g are the out-of-plane vibrations.
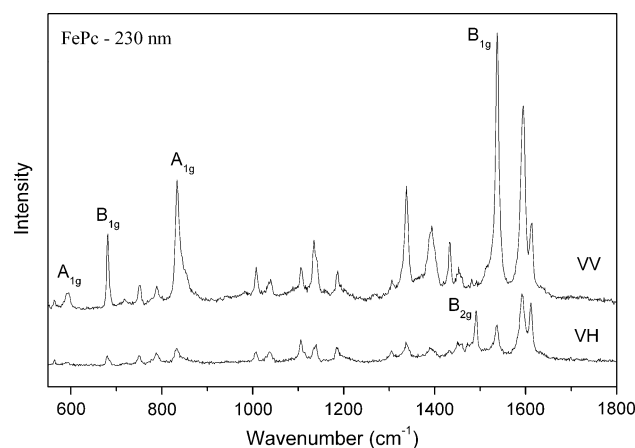
To estimate the molecular orientation (α- and β-form), it is necessary to know the I_{VV}/I_{VH} ratio of symmetry types vibrations (A_{1g}, B_{1g}), where I_{VV} and I_{VH} are Raman intensities obtained for vertical and horizontal polarization of scattering light, respectively. The angle between molecule and substrate is calculated from the ratio intensities (I_{VV}/I_{VH}) for A_{1g} and B_{1g} Raman modes obtained from Raman spectra. The orientation of the phthalocyanine molecules with respect to the substrate is presented in Fig. 1. This figure shows the scheme of suggested orientation with respect to the substrate surface. The axes z and z' coincide with C_4 axes of FePc molecule. Molecular orientation is described as an inclination angle of the molecule plane (planar macrocycle) with respect to the

substrate plane (Fig. 1). In this configuration, the molecular z'-axis does not coincides with the normal to the surface (z-axis). Detailed information concerning the designation of the orientation of the metallophthalocyanine thin layers using polarized Raman spectra have been already reported in our previous articles [22, 24]. The molecular orientation of FePc thin films was examined for two thicknesses of the thin layers equal to 79 and 230 nm. The sample with the thickness of about 250 nm was used for temperature study performed in temperature range 300–480 K.

Figure 2 presents polarized (VV and VH) Raman spectra of FePc thin layer (230 nm) obtained for 488 nm excitation wavelength before annealing process. Assuming that FePc possesses D_{4h} point group symmetry we observe in Raman spectra active modes of the symmetry A_{1g} at 595 cm^{-1} (benzene ring deformation), B_{1g} at 681 cm^{-1} (macrocycle breathing), B_{1g} at 1,536 cm^{-1}, and B_{2g} at 1,491 cm^{-1} (pyrrole stretch). As it is seen from this figure, all Raman bands associated with vibrations of C–N–C bridge bonds, also with vibrations of central atom of phthalocyanine molecule (Fe) connected with nitrogen atoms are recorded in Raman spectra. The position of the most intense band at 1,536 cm^{-1} is closely linked to metal ion adapted to phthalocyanine molecule. This band is characterized by the displacement of C–N–C bridge bonds of the phthalocyanine macrocycle. So it can be useful as a marker for distinguishing a different metallophthalocyanine thin film. In our previous study, we recorded this band at 1,544 cm^{-1} for CoPc; 1,525 cm^{-1} for CuPc; 1,509 cm^{-1} for ZnPc, and 1,499 cm^{-1} for MgPc thin layers [24]. As it is known, the change of energy of this band is connected with the mass of the substituted metal atom in phthalocyanine molecule, metal ion size and cavity diameter of phthalocyanine [21]. For heavy atoms adopted in central position of phthalocyanine molecule we observe a nonplanarity of the molecule and change of symmetry from D_{4h} to lower symmetry—C_{4v} (e.g., SnPc, PbPc) [25].
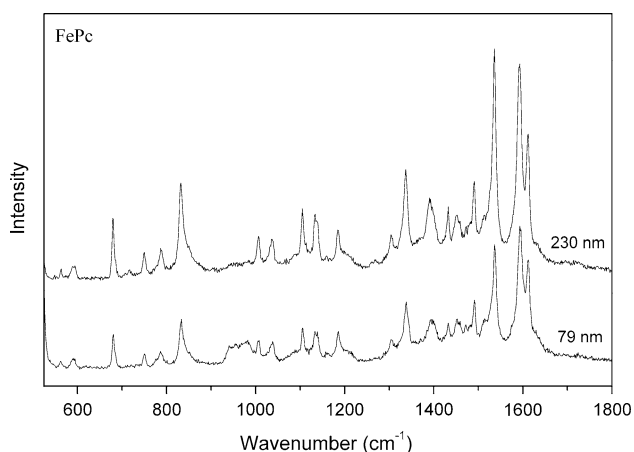

Fig. 1 The orientation of the phthalocyanine molecule with respect to the substrate (x, y, z), z' axis coincides with C_4 axis of FePc molecule

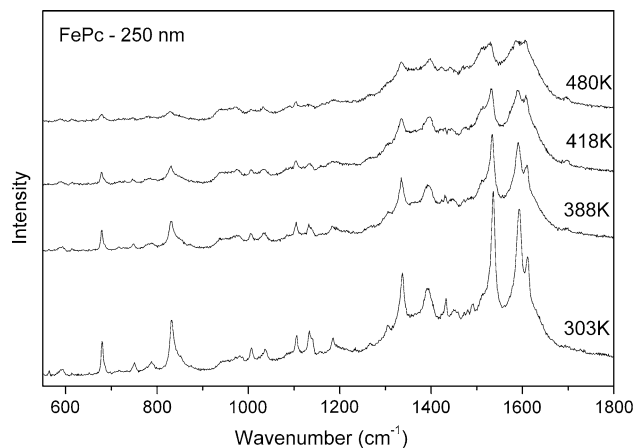Fig. 2 Polarized Raman spectra (VV and VH) of FePc thin layer

As it is seen from Fig. 2, the intensity of this band in VH polarization is about four times smaller than in VV polarization. The I_{VV}/I_{VH} ratio of B_{1g} mode allows us to estimate the angle between molecule and substrate. Thus, it gives information concerning determination of molecular orientation and polymorphic form.

Figure 3 shows nonpolarized Raman spectra for FePc thin layers recorded (under the same experimental conditions) before annealing procedure for two different thicknesses (79 and 230 nm). As it is seen from this figure, we observe the change of intensity of Raman bands for different samples. These spectra differ only in intensity for the samples with different thickness of the deposited layer. This means that the layers do not differ in polymorphic form. Generally, we do not observe any relative changes of the intensity for samples with different thickness.

The Raman spectra obtained for FePc thin layer (250 nm) deposited on silicon substrate recorded at different temperatures during heating process (300–480 K) are presented in Fig. 4 (for temperature: 303, 388, 418, and 480 K). In order to obtain information connected with the change of spectral parameters of selected Raman bands, special fitting procedure was performed. Before fitting procedure, all Raman spectra recorded at different temperatures have been normalized using Böse factor calculated for corresponding temperature. The integral intensity and band position of selected Raman-active modes were determined using the Lorentzian line shape fitting by SpectraCalc software. As it can be seen from this figure, we observe slight change of above mentioned band's position, also their width. Moreover, while growing the temperature, we observe overlapping of bands located in the spectral range 1,450–1,700 cm^{-1}. At about 480 K, we observe one broad band, which is probably connected with the change of polymorphic phase of the thin layer deposited on silicon surface.
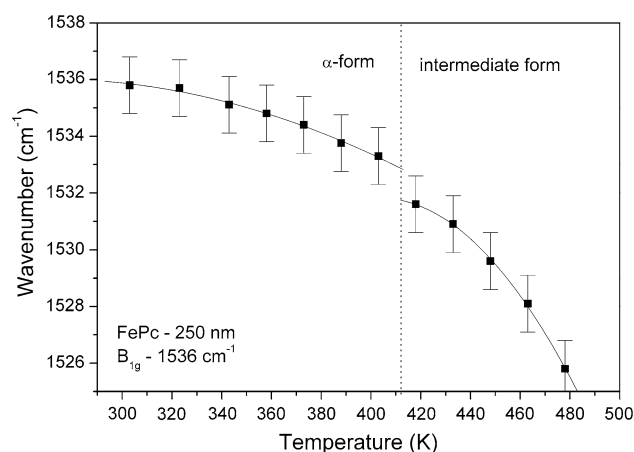

Fig. 4 The Raman spectra of FePc thin layer (250 nm) obtained at different temperature

Figure 5 presents peak position of the B_{1g} Raman band at 1,537 cm^{-1}, associated with C–N–C bridge bond, as a function of temperature while heating procedure. As it is seen from Fig. 5, we observe a discontinuity of the wavenumber of the analyzed band at temperature about 410 K. We can distinguish two areas of the changes. One of them in the temperature range from 300 to 410 K and second one in the range from 410 to 480 K. Because, we observed monotonic change of wavenumber in the large temperature range (300–480 K) the observed discontinuity seems to be very evident. In order to determine the angle between molecule and substrate, we also recorded for each temperature polarized Raman spectra (for VV and VH polarization). Figure 6 presents the angle between molecule and substrate as a function of temperature while heating procedure, obtained from polarized Raman spectra. Above 410 K (see Fig. 6), we observe the change of polymorphic phase of molecule to intermediate form (between α- and β-phase). It means that the change of peak

Fig. 3 Raman spectra of FePc thin layers for different thickness of the layer (79 and 230 nm) and powder sample

Fig. 5 The temperature dependence of wavenumber of 1,536 cm^{-1} Raman band of FePc thin layer (250 nm thickness)
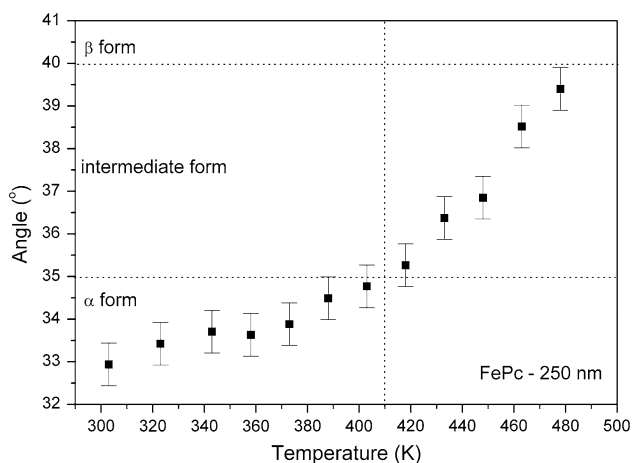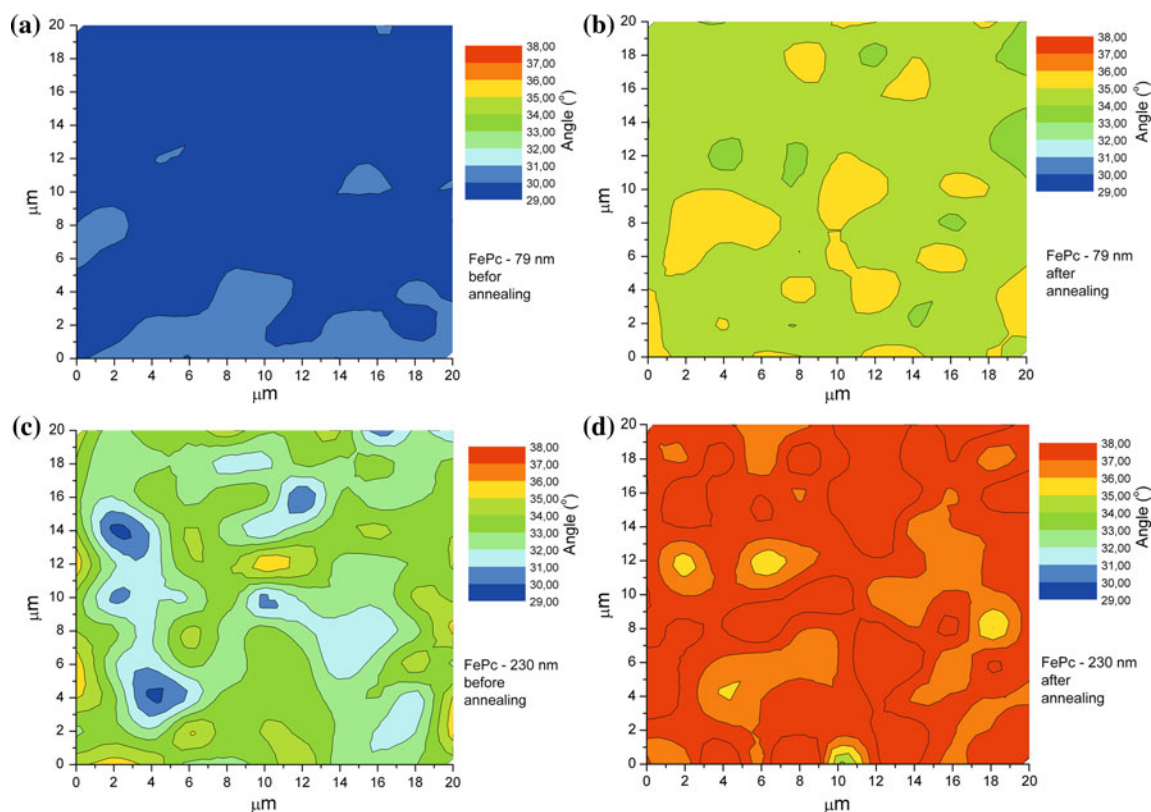
Fig. 6 The angle between molecule of FePc and substrate as a function of temperature

position of Raman band at 410 K is caused by change of molecule orientation (in our case to intermediate phase).

Very important thing is the impact of pollution and especially in the case of contamination by oxygen during the deposition process of the thin layer. The interaction between oxygen and phthalocyanine was described as a weak charge transfer equilibrium producing oxidized phthalocyanine species. It is known, that the α-phase of

MPc adsorbs a larger amount of the oxygen than the β-phase. Since, with increasing annealing temperature and time of the annealing process, the amount of β-MPc phase increases. Consequently, the subsequent exposure of these thin films to air leads to decrease of the oxygen content.

The performed surface Raman mapping measurements allowed us to obtain information concerning distribution of polymorphic form of FePc thin layer before and after annealing procedure at 473 K by 6 h in vacuum under pressure $p = 2 \times 10^{-6}$ Pa. Surface Raman mapping was performed for samples with different thickness: 79 and 230 nm. Using Raman mapping (obtained for VV and VH scattering geometry) carried out for B_{1g} mode at 1,536 cm^{-1} we were able to estimate the map (distribution) of angles between molecules and substrate. In Fig. 7a, we present the map of the angles between molecular plane and substrate estimated from polarized Raman spectra for FePc thin layer (79 nm) before annealing process. As it can be seen from Fig. 7a, we observe small change of the angle between molecules and substrate (in the range of 29°–31°). However, the dominant value of the angle is about 30°. This result gives information on the homogeneity of the investigated material and the presence of an α-form of thin layer. After annealing process (see Fig. 7b), we observe increase of the angle between molecules and substrate. The average value of


Fig. 7 Maps of angles between molecule of FePc (79 and 230 nm) and substrate estimated from polarized Raman spectra: before—**a**, **c** and after—**b**, **d** annealing procedure

the angle is about 34°. We observe the same phase of FePc thin films as before annealing process. In the case of very thin layer, we do not observe the change of polymorphic phase. The same measurements have been performed for FePc thin layer with thickness of 230 nm (Fig. 7c, d). As it can be seen from these figures annealing process leads to the ordering of structure. We recorded an increase of homogeneity of the thin films caused by an increase of structure rearrangement. As a result of heating process, we observe an increase of average angle between the molecule and the substrate from 33° to 37°. However, there has not been change in poly-morphic form to β-form (stable form). We observe only change to intermediate form.

In our previous studies, we reported change of poly-morphic form from α to β form as a result of annealing process for ZnPc, MgPc, CuPc, and CoPc thin layers deposited on silicon substrate using vacuum deposition method. However, in these cases, the thickness of the deposited layer was about 400 nm. As it is known, from our earlier study the increase of thickness leads to a change of

the angle between molecule and substrate due to increasing of the layer–layer interaction and decreasing of the inter-action process between layer and substrate [24]. The annealing process in most cases is leading to the formation of stable form of molecules (standing molecules). This effect is not observed in the case of ultrathin films, for which the dominant form of the molecules is parallel ori-entation (laying molecules). However, in most cases for FePc thin layers, the annealing process leads to intermediate form. In some cases, dominant form of molecular orienta-tion is parallel orientation. It is connected with different growth modes observed on various substrates, for example polycrystalline and crystalline substrate. This feature can be explained in terms of different molecule–substrate and molecule–molecule interactions. If the molecule–substrate interaction is stronger than the molecule–molecule inter-action, the adsorption of the molecule occurs in a lying geometry (the molecular plane is parallel to the substrate surface). In particular, this was shown for materials with relatively strong intermolecular interactions, such as
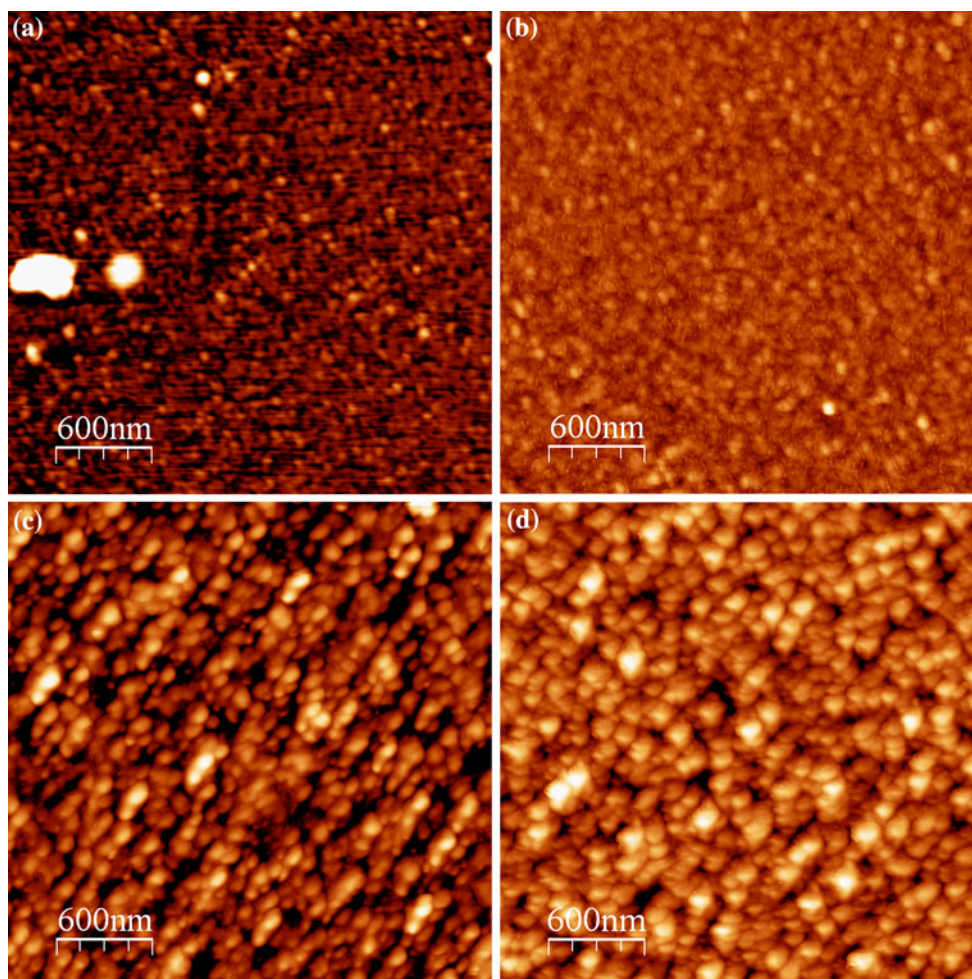
Fig. 8 The AFM image of FePc (79 and 230 nm) thin layer obtained before—a, c and after—b, d annealing process

unsubstituted phthalocyanines. For the various growth processes, the strength of molecule–substrate and molecule–molecule interactions is a crucial parameter which can be changed by different chemical substitutions. The metal–substrate interaction is particularly crucial for the first few layers of the molecules on the metal substrate, whereas for higher coverages the molecule–substrate interaction becomes negligible. Thus, in some cases are observed for ultra thin layer using different evaporation method form of lying molecules. The geometry changes from lying for the first layers via disordered to standing molecules for thicker films. This behavior can be observed for example for alkyl-substituted metal phthalocyanines thin layers deposited on single crystalline Au (100) surface [26].
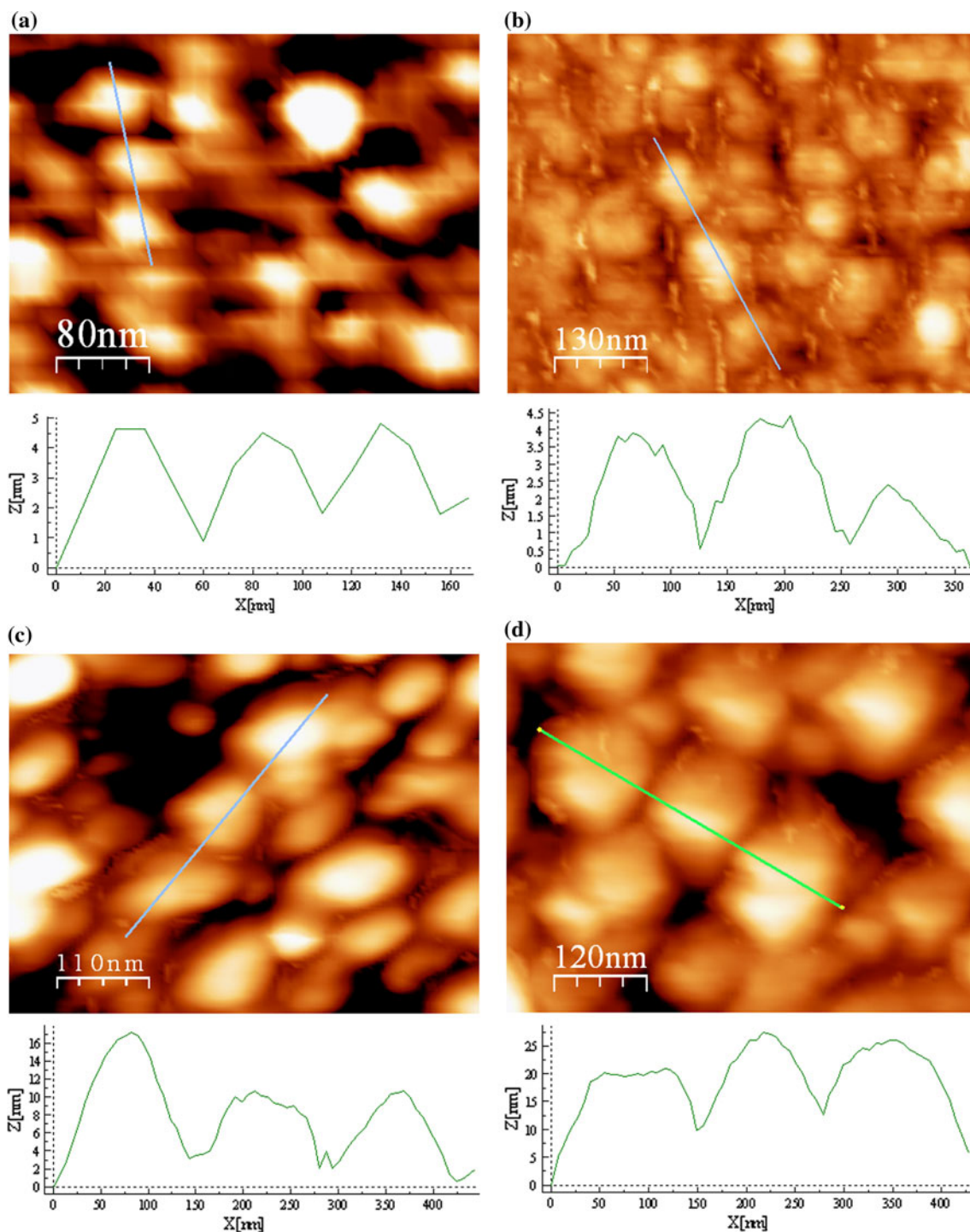
Fig. 9 The line profile of the AFM image of FePc (79 and 230 nm) thin layer obtained before—**a**, **c** and after—**b**, **d** annealing process

To compare results obtained from Raman measurements, we performed AFM studies before and after annealing process for FePc thin layers with thickness of 79 and 230 nm. The analysis was carried out for AFM images using WSxM 5.0 software [27]. The obtained results for a sample of the thickness of 79 nm before and after annealing process are presented in Fig. 8a and b, respectively. In order to analyze the structure of a thin layer (before and after annealing process), we used two parameters estimated from AFM image, root mean square (RMS) roughness, and average grain size. The RMS roughness was estimated as 2.36 and 1.04 nm before and after annealing, respectively. The average grain size was equal to 40.54 before and 55.48 nm after annealing process. It means that we observe homogenous morphology with well-defined globular structures. This may be evidenced that the most of the molecules are distributed uniformly. The same analysis we performed for a sample of the thickness of 230 nm (Fig. 8c, d). In this case, RMS roughness was estimated as 8.16 and 7.81 nm before and after annealing process, respectively. The average grain size was about 72.03 and 100.77 nm. As it can be seen from Fig. 9c, we observe network of distributed of FePc grains. Figure 9a–d shows line profile of the AFM image obtained for different thicknesses of the thin layer before and after annealing process. After annealing process, we obtain more homogenous structure, where grains (with larger diameter) form aggregates and flake-like structure (slightly lower RMS roughness parameter after annealing process). Similar behavior can be observed in the case of thin films deposited at different temperatures of the substrate [28, 29]. The variation of RMS roughness and the grain size is smaller at lower temperature but these are significantly higher in case of higher deposition temperatures. In our study, we observe similar behavior for different thickness of the thin film (deposited at room temperature) and annealing process in higher temperature.

The obtained results showed that the stability of thin layer depends on the experimental conditions such as: the type of substrate, temperature of substrate under preparation, thickness of thin films, and annealing process. It has been also revealed that the polymorphic phase, temperature stability, symmetry of molecules, and preferred arrangement of FePc thin layer is closely related to their physical (optical, electrical) properties. The annealing process is leading to the formation of intermediate form (between α and β form) and rearrangement of the molecular structure. In our investigations, we did not observe either the change of symmetry of molecules and the change of polymorphic phase to stable form, β-form. This feature is probably caused by interaction between FePc molecule and substrate, which is significantly higher in comparison with molecule–molecule interaction.

Conclusions

In this article, we performed the high temperature and orientation study of FePc thin layers deposited on silicon substrate using AFM and micro-Raman scattering spectroscopy. It has been shown, that the atomic force microscopy and micro-Raman scattering method are very useful methods to investigate both, molecular orientation and symmetry of FePc molecules deposited on solid state substrate. It has been revealed that the polymorphic phase, temperature stability, symmetry of molecules, and preferred arrangement of MPc thin layer is highly related to their physical (optical, electrical) properties. The temperature dependencies of spectral parameters of FePc thin layer such as wavenumber of Raman bands revealed discontinuity at high temperature (in the vicinity of 410 K). This effect is probably connected with the change of molecular form from less stable α-form to intermediate phase. The orientation of the FePc thin layers with different thickness deposited on silicon substrate has been also estimated using polarized Raman spectra (Raman mapping). We obtained information concerning the distribution of polymorphic phase of FePc molecule. It was found that annealing process strongly affects the structural organization and homogeneity of the organic thin layers.

References

1. Ji ZG, Wong KW, Tse PK, Kwok RWM, Lau WM (2002) Thin Solid Films 402(1–2):79
2. Albouy PA (1994) J Phys Chem 98(34):8543
3. Hanack M (1998) Turk J Chem 22:13
4. Kerp HR, Van Faassen EE (2000) Chem Phys Lett 332:5
5. Carpi F, De Rossi D (2006) Opt Laser Technol 38:292
6. Tang CW, Slyke SAV (1987) Appl Phys Lett 51:913
7. Simon J, Andre JJ (1985) Molecular semiconductors. Springer-Verlag, Berlin
8. Erk P (1997) Proceedings of 17th European crystal meeting, 24–28 August. AIP Press, Lisbon
9. Brożek-Płuska B, Jarota A, Kurczewski K, Abramczyk H (2009) J Mol Struct 338:924
10. Brożek-Płuska B, Szymczyk I, Abramczyk H (2005) J Mol Struct 481:744

11. Debe M, Kam K (1990) Thin Solid Films 186:289
12. Saijo H, Kobayashi T, Uyeda N (1977) J Cryst Growth 40:118
13. Berger O, Fisher WJ, Adolphi B, Tierbach S (2000) J Mat Sci Mater Electron 11:331
14. Zanfolim AZ, Volpati D, Olivati CA, Job AE, Constantino CJL (2010) J Phys Chem C 114:12290
15. Sharp JH, Abkowitz M (1973) J Phys Chem 77:477
16. Assour JM (1965) J Phys Chem 69:2295
17. Kolesov BA, Basova TV (1997) Thin Solid Films 304:166
18. Miller CW, Sharoni A, Liu G, Colesniuc CN, Fruhberger B, Schuller IK (2005) Phys Rev B 72:104113
19. Debe M, Kam K (1990) Thin Solid Films 186:289
20. Saijo H, Kobayashi T, Uyeda N (1977) J Cryst Growth 40:118
21. Tackley DR, Dent G, Smith WE (2001) Phys Chem Chem Phys 3:1419
22. Szybowicz M, Runka T, Drozdowski M, Bała W, Grodzicki A, Piszczek P, Bratkowski A (2004) J Mol Struct 704:107
23. Basova T, Kolesov B (2000) J Struct Chem 41:770
24. Szybowicz M, Bała W, Fabisiak K, Paprocki K, Drozdowski M (2011) J Mater Sci 46:6589. doi:10.1007/s10853-011-5607-4
25. Liu Z, Zhang X, Zhang Y, Jiang J (2007) Spectrochimica Acta Part A 67:1232
26. Peisert H, Biswas I, Zhang L, Knupfer M, Hanack M, Dini D, Batchelor D, Chasse T (2006) Surf Sci 600:4024
27. Horcas I, Fernández R, Gómez-Rodríguez JM, Colchero J, Gómez-Herrero J, Baro AM (2007) Rev Sci Instrum 78:013705
28. Karan S, Mallik B (2008) Phys Chem Chem Phys 10:6751
29. Gredig T, Gentry KP, Colesniuc CN, Schuller IK (2010) J Mater Sci 45:5032. doi:10.1007/s10853-010-4319-5