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Magnetic field influence on the molecular alignment of vanadyl phthalocyanine thin films

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Abstract

Thin vanadyl phthalocyanine (VOPc) films with thicknesses ranging between 10 and 100 nm were grown by organic molecular beam deposition (OMBD) in high vacuum on H–Si(1 1 1) and quartz substrates. The influence of a magnetic field (1.3 T) applied during the film growth was investigated by means of variable angle spectroscopic ellipsometry (VASE), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction and atomic force microscopy (AFM). The dielectric function was determined by means of VASE. The VOPc layers were found to be uniaxially anisotropic, i.e. exhibit the same optical constants along two of the Cartesian axes, and different optical constants along the third axis. The values of the dielectric function with in-plane of the substrate are larger compared to those out-of-plane. The in-plane and out-of-plane values of the imaginary part of the dielectric function in the region of the Q-band were used to determine the tilt angle of the molecular plane with respect to the substrate plane. Films deposited without magnetic field have the molecular planes tilted with respect to the substrate plane by about 24°, while those deposited in a magnetic field perpendicular to the substrate, the molecules tend to align their molecular planes with respect to the substrate at ca. 3°. All the samples were found to have a triclinic crystallographic structure. From the comparison between the FTIR spectra of VOPc layers and pellets dispersed in KBr, it can be also deduced that the molecules are lying parallel to the substrate in the case of samples grown in the presence of a magnetic field and slightly tilted in those grown without magnetic field.

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1. Introduction

Organic semiconductors with delocalized π-electrons are considered to be as good candidates for organic-based electronic applications. The electronic structure of the molecules and the layer properties play an important role for the applications. Special attention has been devoted to metal phthalocyanines due to their stability in atmospheric conditions, suitable for organic-based devices [1]. In particular, 3,4,9,10-vanadyl phthalocyanine (VOPc), whose molecular structure is given in Fig. 1a, shows high thermal and chemical stability, good hole conductance, photophysical [2] and interesting nonlinear optical properties [1,3–6], ultrafast Kerr effect [7].

Different crystal structures were observed in VOPc films. The two main polymorphs, which were resolved for the first time by Griffiths [8,9] are shown in Fig. 1b, c. For example, layers deposited on substrates at room temperature have a monoclinic structure (phase-I). A transformation into the triclinic structure (phase-II) takes place during post-annealing above 100 °C or when the substrates are kept above 300 °C during the deposition [10–13]. However, Minami and Asai [2] found that both structures can be formed at room temperature, depending on the evaporation rate, i.e. triclinic—at 0.05 nm/s and monoclinic—at 9 nm/s.

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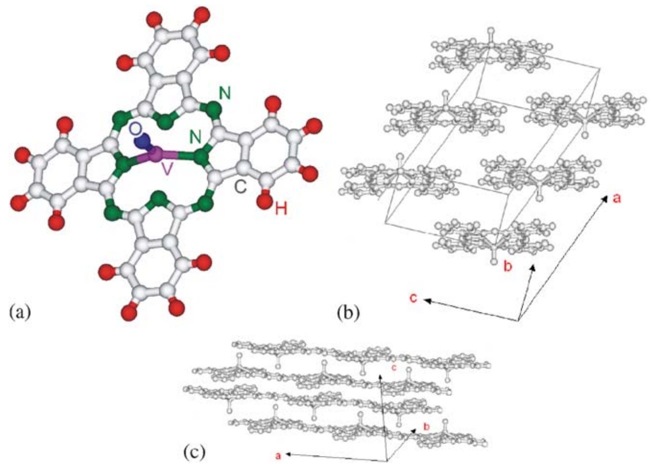

Fig. 1. Molecular structure of 3,4,9,10-vanadyl phthalocyanine (a). With grey colour are marked C atoms, with red—H atoms, with green—n atoms, with blue is marked O atom and with magenta—V atom; the main crystallographic structures known for VOPc: (b) monoclinic, also known as phase-I with $P2_1/c$, $Z = 4$ spatial group; [6,9,13], (c) triclinic, known as phase-II with $P\bar{1}$, $Z = 2$ spatial group [6,9,13].

The monoclinic structure belongs to the $P2_1/c$ space group with the lattice constants: $a = 1.42\,\text{nm}$, $b = 1.31\,\text{nm}$, $c = 1.27\,\text{nm}$ and $\beta = 103.2^\circ$. The triclinic structure belongs to the $P\bar{1}$ space group with lattice constants: $a = 1.20\,\text{nm}$, $b = 1.25\,\text{nm}$, $c = 8.69\,\text{nm}$, $\alpha = 96,04^\circ$, $\beta = 94.8^\circ$ and $\gamma = 68.2^\circ$ [6,9].

Another phase of VOPc has been resolved by means of electron diffraction analysis in experiments with ultrathin films of VOPc grown on KBr and KCl [14]. If the thickness of a film grown in UHV at room temperature does not exceed 10 nm, then the molecules absorbed on these substrates have sufficient energy to form a tetragonal phase.

In addition to substrate temperature and evaporation rate, the structural changes of the films can also be induced by gas exposure [11] and base pressure in the preparation chamber [15], or by applying an external magnetic field during the molecular deposition. Recent investigations on molecules like bianthrone [16–18], *p*-quaterphenyl and copper phthalocyanine (CuPc) [19], demonstrated that a magnetic field can modify the molecular arrangement.

For phthalocyanines in solution the degree of change in the molecular orientation was reported to be proportional to the strength of a magnetic field [20].

When a diamagnetic molecule consisting of benzene or heterocyclic rings moves in a magnetic field with the plane of the aromatic rings oriented perpendicular to the field lines, an electronic current is induced in the ring according to the Lenz rule. This current induces a magnetic dipole opposite to the field direction. The molecule has thus a higher energy which makes this geometrical configuration unstable. Therefore, the aromatic rings tend to align parallel to the field lines of the magnetic field [16–18]. In a magnetic field a molecule acquire an extra energy $E_B = -\vec{m} \cdot \vec{B} = -\chi \cdot B^2/N_A \cdot \mu_0$, where $\vec{m}$ is the induced magnetic dipole moment by the external magnetic field $\vec{B}$, χ the molar magnetic susceptibility tensor, μ_0 the magnetic permeability of vacuum and N_A the Avogadro's number. Due to the anisotropy of diamagnetic susceptibility this energy is depending on the molecular orientation with respect to the magnetic field. Therefore, the molecules tend to align such that its magnetic energy is minimized [20]. The anisotropic diamagnetic susceptibility is the difference between magnetic susceptibilities induced by a magnetic field parallel and perpendicular with respect to the molecular plane [20]. The larger its value the larger the changes in molecular orientation induced by the applied magnetic field. The magnitude of the anisotropic diamagnetic susceptibility was found to be proportional to the number of benzene rings aligned in one plane [18,20–22].

A systematic investigation of several diamagnetic molecules with different amount of benzene rings clearly show this dependence [17,22,23]. The reported anisotropic diamagnetic susceptibility of bianthrone molecules, which has the largest $\Delta\chi$ compared to other diamagnetic molecules like benzene, naphthalene, anthracene, etc. investigated by Mori et al. [17]. Phthalocyanine molecules (Pcs) were reported to have the value of $\Delta\chi$ comparable with bianthrone molecule. This gives a hint to expect comparable changes in molecular orientation of Pcs induced by a magnetic field [22].

Recently, it was shown that also the growth of diamagnetic molecules can be influenced by the presence of a magnetic filed. By means of X-ray diffration (XRD) it was found that the thin films of CuPc grown in a magnetic field oriented parallel to the substrate, consist of higher amount of crystalline domains with the *b*-axis parallel to the magnetic field [19].

In this work, we report changes in the molecular orientation of VOPc thin films induced by a uniform magnetic field. The film properties were characterized by means of spectroscopic ellipsometry (SE), Fourier transform infrared (FTIR) spectroscopy, XRD and atomic force microscopy (AFM).

2. Experimental procedure

VOPc films were prepared by organic molecular beam deposition (OMBD) in high vacuum (HV—8×10^{-7} mbar) on 0.5 mm-thick p-type Si(1 1 1) substrates and 3 mm-thick quartz substrates.

Prior to deposition the Si(1 1 1) substrates were treated by the RCA procedure [24] followed by dipping in a HF(40%) solution for 30 s. Then the substrates were blown dried in nitrogen gas. The quartz substrates were cleaned in an ultrasonic bath using acetone, ethanol and de-ionized water for 10 min each, and then dried with nitrogen gas.

For the deposition of VOPc layers β-phase powder was purchased from Aldrich Chem. Co. The deposition rate was about 0.25–0.3 nm/min. During the film growth the substrates were kept at room temperature. The film

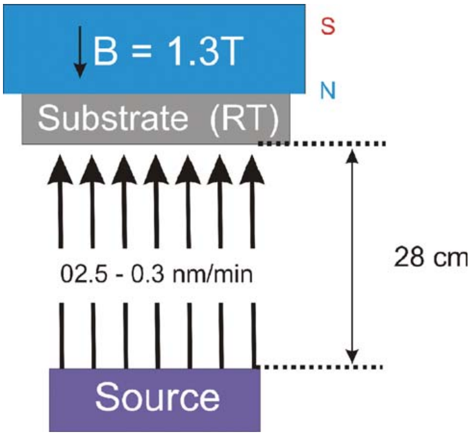

Fig. 2. Schematic configuration of sample growth in magnetic field.

thickness with an accuracy below 10% was measured using a quartz crystal microbalance (QCM). The films with the thickness between 10 and 100 nm were prepared with and without magnetic field.

Fig. 2 shows a sketch of the experimental set-up used for the growth in the magnetic field. The magnetic field induced by a bar magnet with a strength of 1.3 T. The substrates were located 28 cm away from the source to ensure the uniformity of film thickness.

3. Measurement techniques

Absorption measurements of the VOPc layers on quartz substrates were recorded using a double beam spectrometer M40 in UV–Vis in the spectral range between 1.3 and 6.25 eV.

SE measurements were performed using a variable angle spectroscopic ellipsometer (VASE from J.A. Woollam Co., Inc.) equipped with autoretarder and a Xe-lamp source. The SE spectra were recorded in the spectral rage of 0.73–4.5 eV with an energy step of 0.03 eV at incident angles of 50°, 60° and 70°.

Infrared measurements were carried out using a Bruker Fourier transform infrared (FTIR) spectrometer IFS 66. The VOPc thin films on Si(1 1 1) substrates were measured with p- and s-polarized light at 20°, 40° and 60° angles of incidence. The spectral range was between 700 and 1600 $\mathrm{cm^{-1}}$, with spectral resolution of 4 $\mathrm{cm^{-1}}$. Additionally, the transmission measurements at normal incidence were performed on a pellet of VOPc dispersed in a KBr host matrix.

XRD measurements were carried out using a Seifert XRD 3000 PTS diffractometer in Brag–Brentano configuration at grazing incidence and with 1.54 Å of the CuKα line as X-ray source.

The morphology investigations using AFM technique were performed using a APHL-0011 Add LFM device in contact mode.

4. Results and discussion

VOPc has numerous transition bands in the UV–Vis range. The lowest energy transition in the visible range (between 1.45 and 2.0 eV) belongs to the so-called Q-band. This transition is common to all phthalocyanines [11,12]. The absorption spectrum of VOPc layers in the phase-I has the strongest absorption peak at 720 nm (1.7 eV) and a shoulder at 660 nm (1.85 eV) [9,10]. The contribution of phase-II in the spectra is identified with the band at 825 nm (1.45 eV) and a shoulder at about 700 nm (1.8 eV). The line shape of the spectrum in Fig. 3 of a 100 nm thick VOPc film on quartz substrate grown without magnetic field indicates that the layer has the phase-II structure or the so-called “head-to-tail” arrangement [9].

The second important feature of the absorption spectra is located in the UV range at 3.5 eV. This absorption peak is known as B or Soret band. Both bands, Q and B correspond to the π–π^* transitions and their transition dipoles lie in the plane of the molecule [25,26].

The other bands located at 4.64 and 5.56 eV correspond to the L and C bands, respectively [27]. Nahass et al. [26] Edwards and Gouterman [27] reported a shoulder at about 4.25 eV in the spectra of ZnPc thin films and assigned it to the N band. For iron and cobalt phthalocyanines it is thought to involve π–d transitions and for nickel phthalocyanine—d–π^* transition [26,27].

Further experimental investigations of the VOPc films were performed by means of SE. SE measures the changes of the polarization state of polarized light beam after reflection from the surface of a sample. The measured quantities Ψ and Δ are related to the ratio of the Fresnel coefficients:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}, \quad (1)$$

where r_p and r_s are the Fresnel coefficients, Ψ and Δ are SE measured parameters. The analysis of the spectroscopic

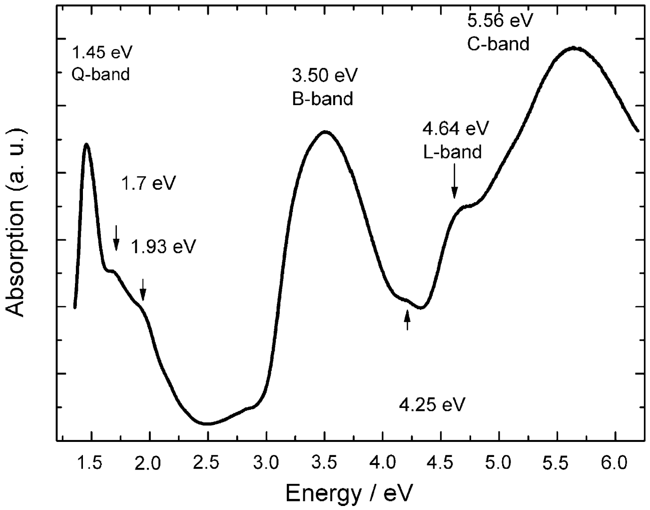

Fig. 3. UV–VIS spectrum of VOPc (100 nm)/quartz substrate.

ellipsometry measurements provides information about the dielectric function, indices of refraction, extinction coefficients, as well as about the layer thickness and roughness.

Another important quantity is the mean squared error (MSE). The MSE is the parameter which is being minimized during the fitting process and is defined as

$$\mathrm{MSE} = \sqrt{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{\mathrm{mod}}-\Psi_i^{\mathrm{exp}}}{\sigma_{\Psi,i}^{\mathrm{exp}}}\right)^2+\left(\frac{\Delta_{\mathrm{i}}^{\mathrm{mod}}-\Delta_{\mathrm{i}}^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}}\right)^2\right]}, \quad (2)$$

where N is the number of experimental points, M is the number of fit parameters and σ the standard deviation for each point.

The number of measured Ψ and Δ pairs is N, and the total number of real valued fit parameters is M. This difference between the model and the experimental data was used to control the quality of the data evaluation. A more detailed description of the basis of ellipsometry and data treatment are given elsewhere [28–30].

For the modelling of the Si(1 1 1) substrate, the Jellison model was considered [31]. Taking into account UV–Vis measurements, the VOPc films are transparent in the range from 0.73 to 1.2 eV. In this range the refraction index can be described by the Cauchy relation

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 + \cdots, \quad (3)$$

where A, B, C are fitting parameters and λ is the wavelength.

The ellipsometric experimental data for this energy range are fitted to determine the thickness and the surface roughness. The surface roughness of the phthalocyanine films was modelled using the effective medium approximation (EMA), i.e. a thin layer consisting of a mixture of 50% films material and 50% voids. This approach yielded an MSE of about 2.0 and a good fit of the experimental data for all samples. For the nontransparent region the experimental data were initially fitted using a point-by-point fitting procedure and subsequently an oscillator model [30].

An isotropic layer is characterized by the same values of the optical constants in all directions. A uniaxial anisotropic layer has the same optical constants along two of the Cartesian axes, and different optical constants along the third one.

For azimuthally rotated sample, the spectra of Ψ and Δ have identical line shape. Thus, it can be concluded that the in-plane optical constants do not depend on the azimuthal angle. This is an indication that the layers are either isotropic or uniaxially anisotropic with out-of-plane optical constants different from the in-plane ones. The data evaluation using a model that considers the VOPc layer to be isotropic presented high MSE values and strong deviations compared to experimental Ψ and Δ data. From this it can be inferred that the VOPc layers are uniaxial anisotropic.

In order to determine the uniaxial dielectric function each film was modelled with two layers: the first layer had the optical dielectric function $\varepsilon_{||}$ and the second $\varepsilon_{\perp}$, where the parallel and perpendicular directions are defined with respect to the substrate plane [30,32]. This method to treat the data was developed by Berreman et al. and is described elsewhere [28–30,32]. The shape of the real part (ε_1) and imaginary part (ε_2) of the dielectric function was simulated using Gaussian oscillators. The thickness and surface roughness previously determined in the transparent region were kept fixed. During the fit procedure, the measured Ψ and Δ of the 100 and 70 nm VOPc/H–Si(1 1 1) samples were coupled in order to reach high accuracy of the optical constant determination.

The ellipsometric parameters Ψ and Δ of VOPc layers and the obtained in-plane and out-of-plane dielectric functions are presented in Fig. 4. The layer thickness and surface roughness are given in Table 1.

In a uniaxial anisotropic layer the absorption in the substrate plane and perpendicular to it is determined by the in-plane and out-of-plane component, respectively, of the extinction coefficient. Recalling that the transition dipole moment of the Q-band lies in the plane of the phtalocyanine skeleton, the tilt angle α of the molecular plane with respect to the substrate plane can be determined by means of the following relation:

$$\frac{I_{\mathrm{oop}}}{I_{\mathrm{ip}}} = \cot\alpha, \quad (4)$$

where I_{oop} and I_{ip} are the areas of the Gaussian oscillator at 1.45 eV in the case of the out-of-plane and in-plane extinction coefficient, respectively.

The value of α was estimated to be $(3\pm1)^\circ$ for the films grown in the presence of an external magnetic field, and $(24\pm1)^\circ$ for those grown in the absence of the magnetic field.

IR spectroscopy was complementary used to check the molecular orientation of VOPc molecules on Si(1 1 1). Previous investigations of IR spectroscopy were done by Pan et al. in polycrystalline VOPc and Hoshi et al. [11,12].

In Fig. 5 the reflectance spectra of films taken in s- and p-polarization and transmission spectra of pellets are shown. Where the vertical scale (R/R_{Si}) of the pictures is the quotient between reflection signal of the VOPc layers and the silicon substrate.

The modes at 734 and 783 cm^{-1} observed in p-polarization (Figs. 5b and d) correspond to the out-of-plane C–H bending modes. They are characteristic for almost all phthalocyanines. The modes at 1078 and 1120 cm^{-1} (Figs. 5a, b) belong to in-plane C–N stretching and C–H bending. The mode observed at 1003 cm^{-1} in the p-polarization and pellet spectra (Figs. 5a, b) can be attributed to the out-of-plane VO stretching mode [11,12].

In the spectra recorded in s-polarization only the in-plane modes are observed. The out-of-plane modes are visible only in the spectra taken in p-polarization and their intensity increases with the incidence angle. From this behaviour it can be deduced that the VOPc molecules have

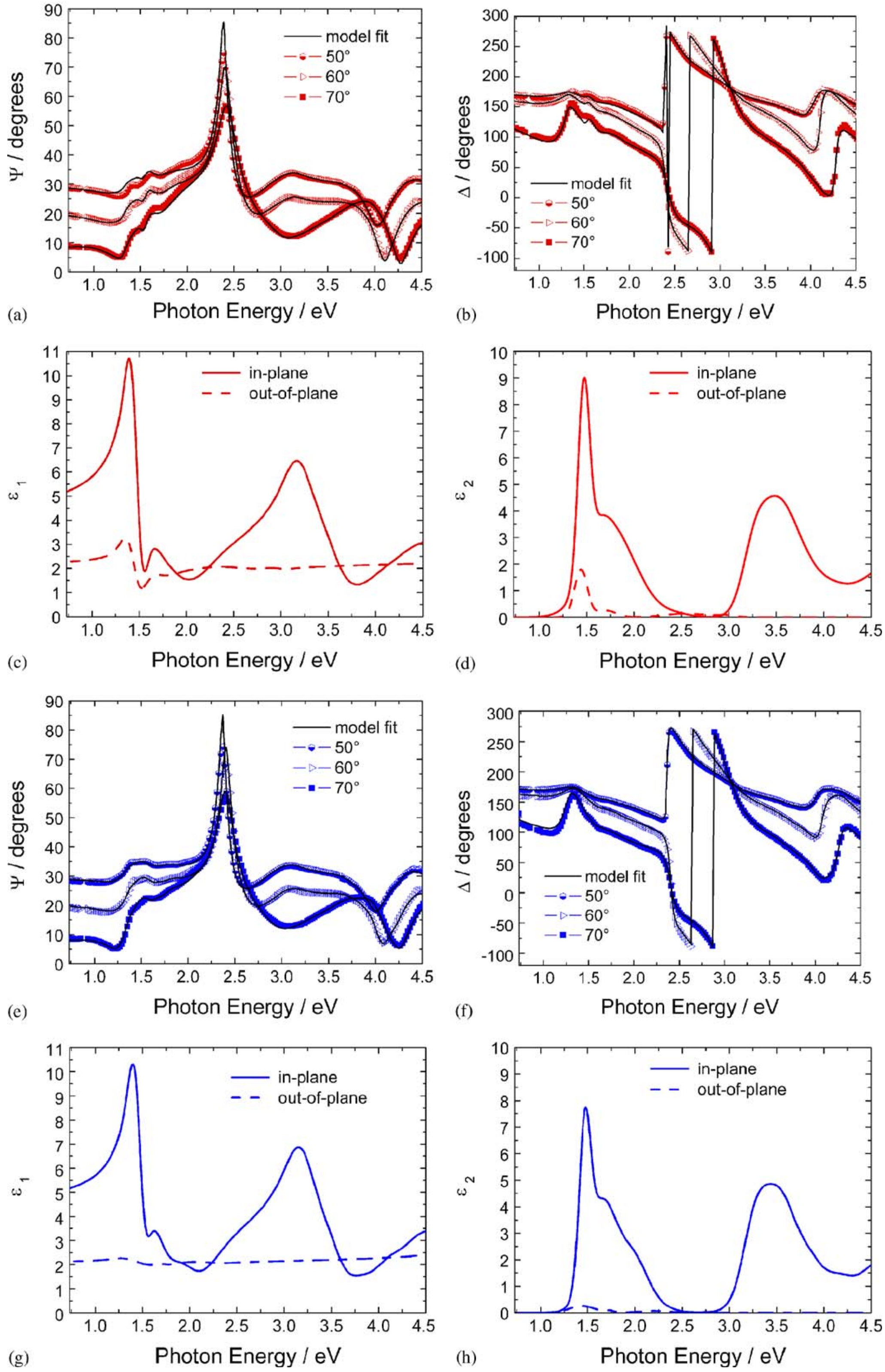

Fig. 4. Ellipsometric parameters of VOPc thin films acquired at 50°, 60°, 70° angles of incidence (a), (e)—Ψ, (b), (f)—Δ, for the films grown without and with magnetic field, respectively; (c), (d)—anisotropic dielectric function, real and imaginary part, respectively, of the layers grown in absence of the magnetic field; (g), (h)—anisotropic dielectric function, real and imaginary part, respectively, of the layers grown in presence of the magnetic field.

Table 1
Thickness and roughness of VOPc thin films grown in and without magnetic field as determined from the fitting of the ellipsometric data along with the corresponding MSE values

Expected thickness (nm)	Thickness (nm)	Roughness (nm)	MSE (a.u.)
100 (in magnetic field)	90.5 ± 0.1	4.7 ± 0.2	6.2
70 (in magnetic field)	74.3 ± 0.1	5.2 ± 0.3	
100 (without magnetic field)	93.5 ± 0.3	3.9 ± 0.3	4.6
70 (without magnetic field)	66.6 ± 0.2	4.9 ± 0.3	

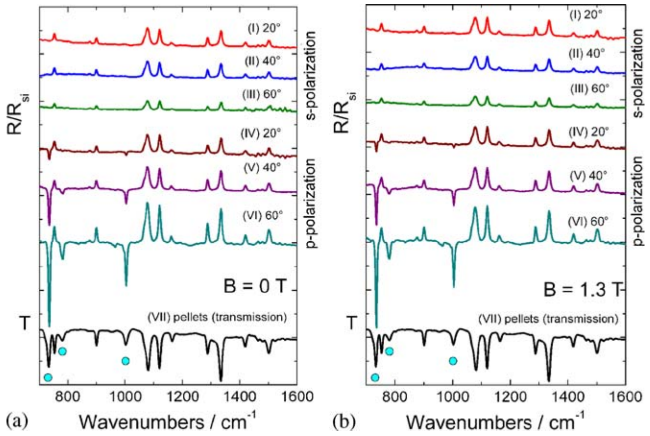

Fig. 5. FTIR reflection spectra of VOPc thin films in s- (I–III) and p-polarization (IV–VI) at: 20° (I, IV), 40° (II, V), 60° (II,VI) angles of incidence for films grown without (a) and in magnetic field (b). For comparison, the IR transmission spectrum of KBr pellets with β-phase VOPc powder at normal incidence is shown in each plot (VII).

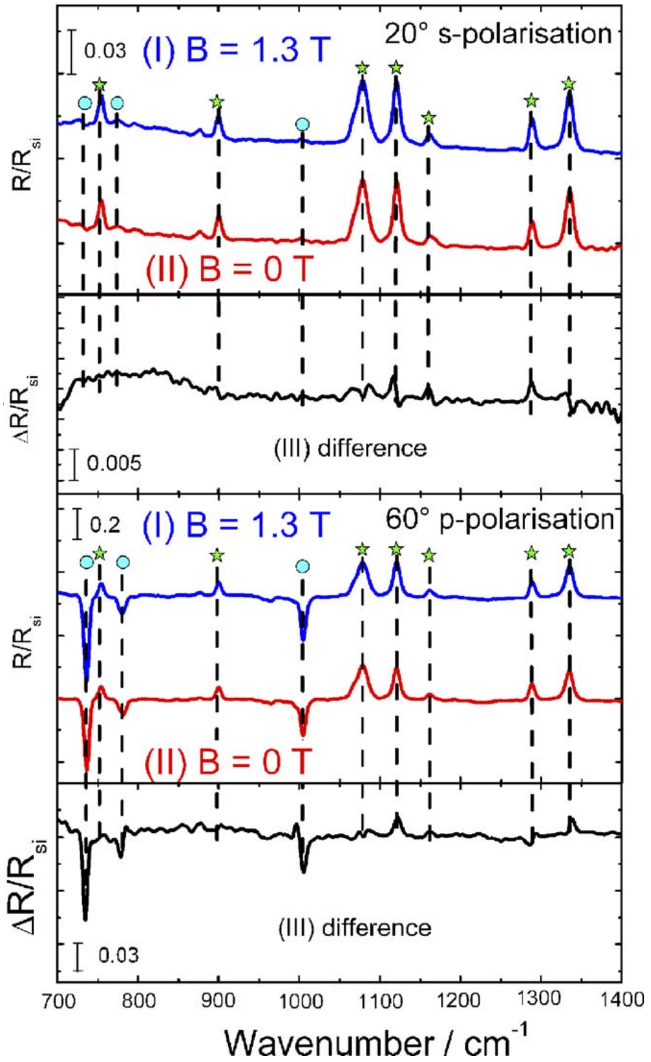

Fig. 6. FTIR reflectance spectra of VOPc thin films in s- and p-polarization: (I)—spectrum of the layer grown in magnetic field; (II) spectrum of the layer grown without magnetic field; (III) difference between spectrum (I) and spectrum (II). The in-plane modes are marked with stars and the out-of-plane modes are marked with circles.

their molecular plane almost parallel with respect to the substrate or slightly tilted.

For a better comparison of the FTIR reflectance spectra recorded for the films grown in magnetic field and without magnetic field, they were normalized with respect to the intensity of the in-plane C–N stretching mode (1078 cm^{-1}) and vertically shifted. The difference spectra ($\Delta R/R_{\mathrm{Si}}$) are then calculated by subtracting the spectrum of the sample grown without from that of the sample grown in magnetic field. In the case of s-polarization the most pronounced difference is observed around the band at 1120 cm^{-1}.

In the reflectance spectrum of the film grown in magnetic field taken in p-polarization the out-of-plane mode at 734 cm^{-1} is more pronounced compared to the film grown without magnetic field (see the difference spectrum (III) in Fig. 6). Thus, it can be concluded that the molecules in the layer grown without magnetic field make a larger average tilt angle with respect to the substrate compared to those in the layer grown in magnetic field (Fig. 6).

The XRD measurements were performed on $\approx$100 nm thick films grown on quartz substrates. The spectrum of the film grown without magnetic field exhibited one peak at $\approx 2\theta = 7.53^\circ$ (Fig. 7). According to Ohta et al. [1] and Pan et al. [11] this peak corresponds to an interstack spacing of 1.17 nm in the phase-II and indicates that VOPc molecules are oriented parallel to the substrate.

The difference between spectra of two films shows an asymmetry, indicating a center of mass shift. This means that the structure of the film is modified by the magnetic field applied during the sample growth. The integral intensity of the peak of VOPc layer grown in magnetic field is with 14% larger compared to that of the film grown without magnetic field. Considering that the peak area is proportional to the number of the grains oriented with their *b*-axis perpendicular to the substrate. It can be concluded that the film grown in magnetic field has more VOPc grains oriented with their *b*-axis nearly perpendicular to the substrate compared to the film grown without magnetic field. In other words, more molecules are oriented with their planes parallel to the substrate plane, in the first case, in good agreement with the ellipsometry and FTIR results.

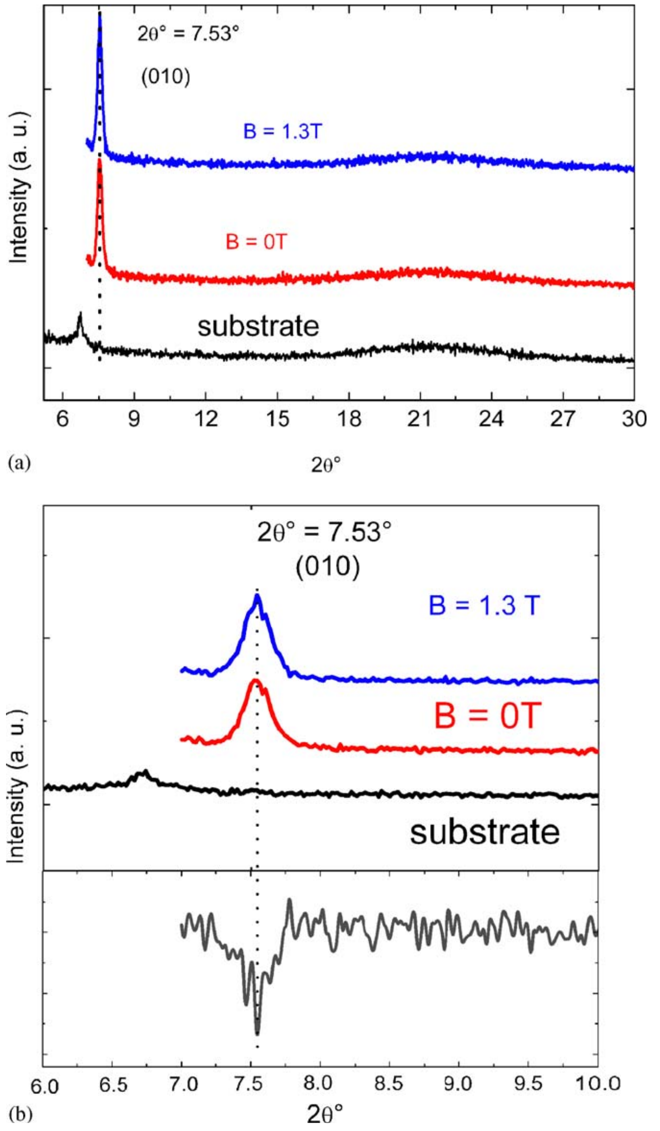

Fig. 7. Comparison of X-ray diffraction spectra of VOPc thin films, from top to bottom: spectra of layers grown in magnetic field, without magnetic field, and bare substrate (a). Diffraction X-ray patterns inset, including the intensity of structures grown in and without magnetic field, (I (B = 0T)–I (B = 1.3 T)), bottom most spectrum (b).

AFM measurements were used to characterize the surface morphology of the films (Fig. 8). The layer consists of well-defined grains showing proportional dependence with film thickness. The values of thickness and roughness obtained from the AFM measurements are in a good agreement with those determined from ellipsometry (compare Tables 1 and 2). The topographic images of 10 and 70 nm thick films grown in absence and presence of magnetic field (Fig. 8) show no significant changes in morphology whether the films are grown in or without magnetic field. The values of thickness and roughness are obtained by the averaging values along different line profiles.

VOPc is a paramagnetic molecule, composed of an aromatic core with the metallic (V) ion located symmetrically off of the core. This indicates its tendency to align in an external magnetic field in such a way that its energy in the field is a minimum. It is likely that the paramagnetic effect is greater than the diamagnetic effect. The magnetic field induces alignment of individual molecules. When the VOPc molecule moves in a magnetic field there are mainly two contributions to the energy given by

- magnetic dipole opposed to the field direction, created by the current induced in the aromatic ring according to the Lenz rule;
- permanent magnetic dipole, that is oriented perpendicular to the molecular plane.

The first contribution tends to align the molecules with their aromatic rings parallel to the field direction. The second contribution tends to orient the molecules with the permanent magnetic moment parallel to the field direction, that means with the aromatic ring planes perpendicular to the field direction.

Our results obtained from ellipsometry, FTIR spectroscopy and XRD indicate that the contribution coming from the permanent dipole moment is stronger and determines the molecular orientation on the substrate.

5. Conclusions

Various experimental techniques: SE, FTIR, XRD and AFM were employed to investigate the influence of the magnetic field on the growth of the VOPc layers on H–Si(1 1 1) and quartz substrates. AFM investigations showed that both films grown in the absence and presence of magnetic field perpendicular to the substrate plane consist of well-defined grains. However, no significant changes in the morphology were observed whether the films were grown in or without magnetic field. XRD measurements revealed that for all deposited films the grains observed with AFM have a crystalline nature. The phase-II structure was identified from the energetical position of the Q and B bands in the UV–Vis spectrum of VOPc film.

All VOPc layers were found to be optically uniaxial anisotropic indicating a preferential molecular orientation with respect to the substrate plane and no preferential azimuthal orientation.

XRD investigations showed that the VOPc films grown in magnetic field have more grains oriented with their *b*-axis nearly perpendicular to the substrate compared to the films grown without magnetic field. This is consistent with a lower tilt angle of the molecular planes with respect to the substrate when the growth takes place in magnetic field observed in FTIR. The SE results showed that samples grown without magnetic field have their molecular tilt angle of $(24 \pm 1)^\circ$ and those grown with magnetic field—ca. $(3 \pm 1)^\circ$.

The magnetic field influences the molecular orientation, i.e. by means of SE and XRD it was shown that molecular

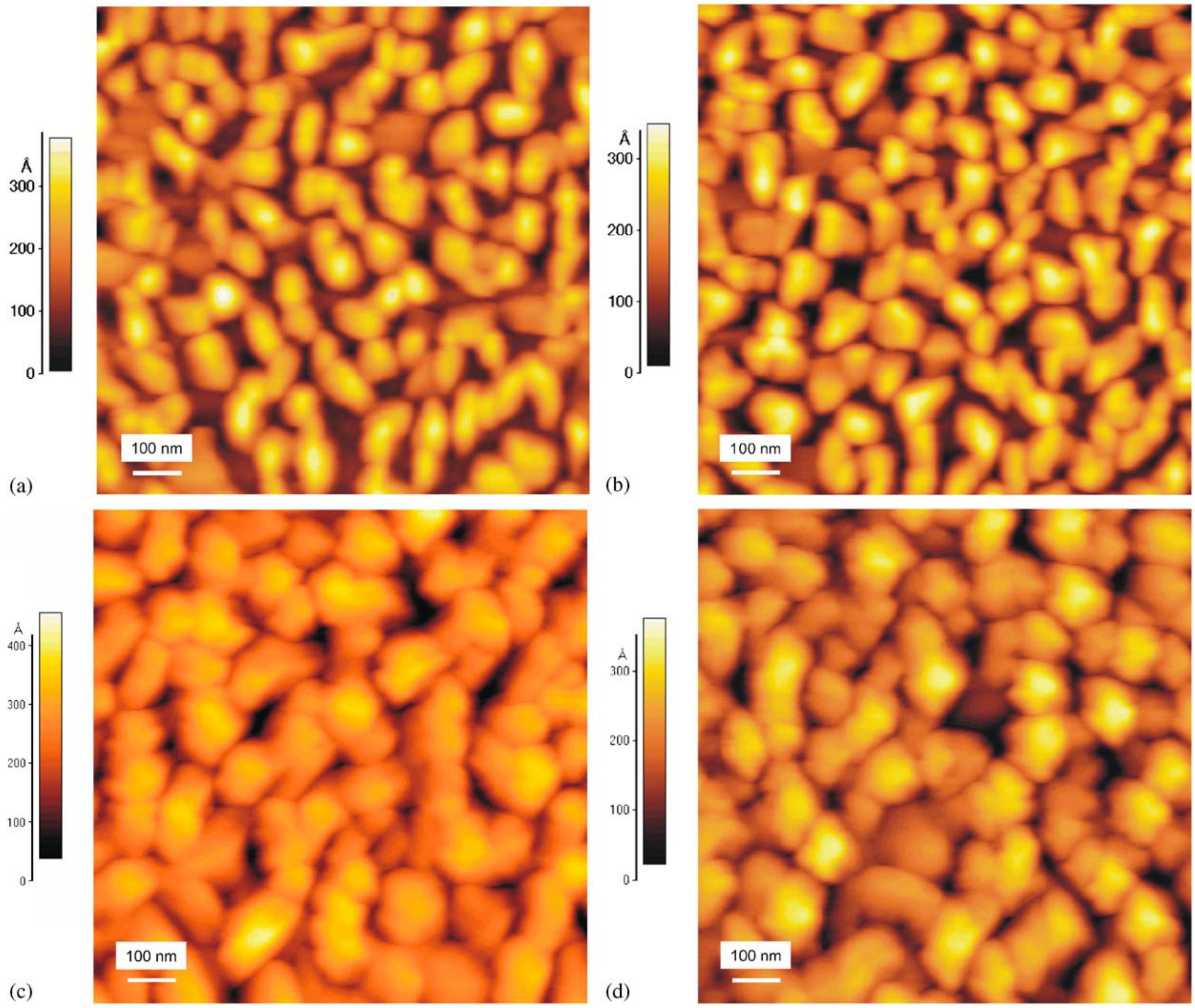

Fig. 8. AFM images of VOPc/H–Si samples: (a), (b) 10 nm, 70 nm grown in magnetic field; (c), (d) 10 nm, 70 nm grown without magnetic field.

Table 2
Thickness and surface roughness of VOPc films on Si(1 1 1) determined by AFM

Expected thickness from QCM (nm)	Thickness (nm)	Roughness (nm)
10 (in magnetic field)	17.5±2.5	4.0±1.5
10 (without magnetic field)	17.5±2.5	4.0±1.5
70 (in magnetic field)	80.0±5.0	5.0±2.5
70 (without magnetic field)	80.0±5.0	5.0±2.5

planes get more parallel to the substrate plane when the growth takes place in magnetic, results confirmed by FTIR.

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