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High temperature study of FT-IR and Raman scattering spectra of vacuum deposited CuPc thin films

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Abstract

In this work we present the polarized and nonpolarized Raman spectra of copper phthalocyanine CuPc layers deposited on (001)Si and borosilicate glass substrates. These spectra are compared with FT-IR spectra of CuPc molecules in KBr pellets and thin layers of CuPc on (001)Si substrates obtained by thermal evaporation method. The observed Raman and FT-IR bands are assigned to definite phonon modes on the basis of their symmetry and comparison with the frequencies predicted by lattice dynamical calculations (LDC). The films of CuPc grown on Si substrate show very good out-of-plane ordering and have X-ray rocking widths of around 0.03°. For layers grown at different temperatures of substrate, we found a change of the molecular out-of-plane tilt angle, as obtained from Raman scattering. Observed feature is accompanied by a change of the out-of-plane lattice parameter.

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Keywords: Copper phthalocyanine (CuPc); Thin films; FT-IR spectra; Raman spectra

1. Introduction

The metallophthalocyanines are the most promising materials for future molecular devices such as organic light emitting diodes (OLEDs), solar cells, organic field-effect transistors, molecular gas sensors, memories, optoelectronic device and semiconductive junctions as well. Phthalocyanines (Pc) represent a large family of heterocyclic conjugated molecules with high chemical and thermal stability [1,2]. Recently, the thin films of phthalocyanines have been studied extensively due to their potential properties as electronic or optoelectronic materials and possible application for fabricating functional low dimensional structures on solid surfaces. Copper phthalocyanines (CuPc) present also a special interest due to their low cost and potentially high photoelectronic properties. Copper phthalocyanine is a semiconducting molecular crystal possessing several polymorphic forms which

determine the energy state, the band gap and the anisotropy of electrical conductivity. Until now, nine polymorph structures of CuPc have been observed [2–5].

In the case of CuPc thin films, the knowledge of the surface morphology and the preferred orientation of the crystallites are essential for their successful applications.

In order to examine the molecular arrangement and crystallites orientation, vacuum-deposited films were prepared on amorphous or crystalline substrates [4–7]. Some of the experimentally observed phenomena, such as high photoconductivity, considerable changes in the conductivity under gas adsorption, thermal dependent conductivity in charge-coupled devices (Meyer–Neldel rule) were not explained. Due to this reason, in spite of their remarkable properties the copper phthalocyanine is promising material for a wide application in the multilayer microelectronics and nonlinear optics [8]. It is reasonable to expect that the understanding of the complicated processes in their electronic structure will accelerate their application. The most important elements of OLED are emissive, hole

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and electron transporting layers. One of the most commonly used materials as the transparent hole transporting layer is the copper phthalocyanine (CuPc).

The copper phthalocyanine (CuPc) layers are employed as hole transporting materials also in photovoltaic cells and thin film transistors [9]. These devices have many advantages such as: high brightness and efficiency, fast response time, broad temperature range and relative low cost in comparison with other technologies. For the intended future applications of these materials it is necessary to have a precise knowledge of the interaction and crystallization mechanisms on substrates and a practical experience of how to achieve certain orientations and morphologies.

Within the analysis of preferred orientation in CuPc layers, polymorphism of crystalline structure CuPc layers plays an important role [2,3]. The differences between them are as follow: (i) the tilt angle of the molecules within the columns and (ii) the mutual arrangement of the columns [10]. The preferred orientation is usually determined by sample preparation conditions such as type of substrate (amorphous or single crystalline), temperature of substrate, deposition rate, and quality of the substrate surface. Depending on the preparation parameters, the phthalocyanine layers have been reported being composed of different polymorphs [11–14] which have different lattice structure and different morphology. Moreover, the structure and morphology of these layers have an essential influence on the properties of the solar cells, thin films field effect transistors or light emitting diodes.

The films deposited on crystalline or amorphous substrates at room temperature are the α -CuPc form but layers deposited on the crystalline substrates heated above 180 °C are the β -CuPc form. Kolesov et al. [15] used the approach based on the analysis of lattice vibrations for the determination of the orientation of β -CuPc thin films. That method is simple, nondestructive and reliable. Nevertheless, it is not useful for the analysis of mixed form films because the crystal structure of these forms are unknown.

The characterization of the preferred orientation and understanding of its dependence on deposition conditions plays an important role for the successful application of CuPc-based thin films in optoelectronic devices. The influences of different deposition conditions on the preferred orientation of CuPc crystallites within films and on the surface morphology were investigated using X-ray diffraction analysis. The morphology of thin-film surfaces also depends decisively on sample preparation conditions. Slowly deposited films exhibit usually rather rough surfaces while high deposition rates reveal smoother surfaces with improved performance [11–15].

In the present work, we demonstrate experimental results concerning temperature study of polarized and nonpolarized Raman scattering spectra of vacuum deposited CuPc films and FT-IR spectra of molecules in KBr and polyethylene (PE) pellets and thin films of CuPc. The observed absorption and Raman bands are assigned to definite phonon modes on

the basis of their symmetry and comparison with the frequencies predicted by lattice dynamical calculations (LDC).

2. Theory

The conductivity of metallophthalocyanine layers deposited on the inorganic substrates is observed mainly along the stacking axis, parallel to the column direction, where the π – π^* interaction of the conjugated orbitals takes place [16]. In the CuPc layers column–column interaction is very weak and layers can exhibit different growth forms, characterized by different angles between the normal to the surface and the stacking axis. A strong influence of the substrate on the growth morphology of CuPc layers is still not well recognized and understood. In particular, both, the chemical nature and the surface geometry of the substrate are important parameters [17–19]. Furthermore, CuPc-inorganic heterostructures have become a very interesting research subject, because of the possibility of exploiting both, the optical sensitivity of an organic material and the transport properties of an inorganic material [20]. In these systems, at the nanoscale range, even interfacial properties become important [21].

The orientation of thin organic films can be determined using the analysis of external crystal modes [15] as well as internal molecular vibrations [17–19]. The number and symmetry of vibrational modes are directly connected with the symmetry of crystal structure.

It is known that the symmetry type and intensity of Raman modes of crystals can be determined by the scattering tensors.

Basova and Kolesov showed [22] that because of the weakness of intermolecular interactions in CuPc crystal the spectra of internal vibrations of crystalline CuPc are very similar to the spectra of the free molecules.

The CuPc is a planar molecule consisting of 57 atoms and possessing D_{4h} point group symmetry (Fig. 1). This planar molecule has the following vibrational representation [23]:

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

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 is out-of-plane vibrations. In the case of B_{1g} modes, the atomic shift is a symmetric relative to the twofold axis C_2 through the central copper atom Cu, and the benzene rings. In the case of B_{2g} modes, the atoms are shifted symmetrically relative to the C_2 axis through the N_α and N_β atoms (Fig. 1) [22].

The symmetry of molecular vibrations can be determined from the analysis of the polarized Raman spectra of the oriented CuPc layers grown on different crystalline substrates. For each type of D_{4h} point symmetry, the terms

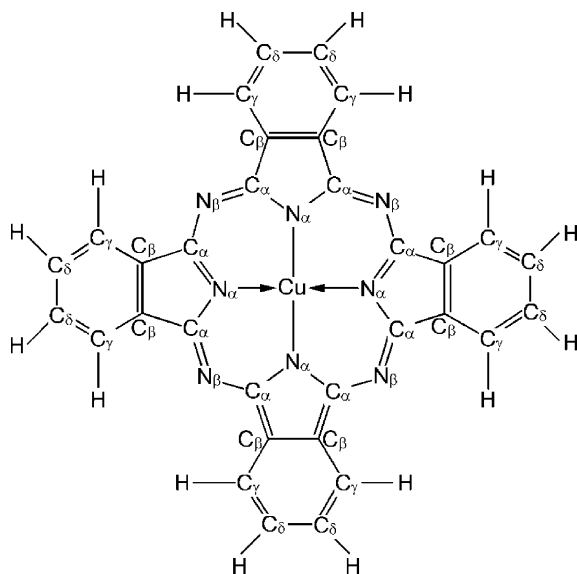


Fig. 1. The molecular structure and atomic notation of CuPc molecule.

of the Raman scattering tensor appear as [19,22]:

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \quad B_{1g} = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$B_{2g} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad E_{g1} = \begin{pmatrix} 0 & 0 & e \\ 0 & a & 0 \\ e & 0 & 0 \end{pmatrix},$$

$$E_{g2} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{pmatrix},$$

The diagonal tensor of A_{1g} type vibration has $\alpha_{xx} = \alpha_{yy} = a$ and $\alpha_{zz} = b$. For planar molecules we can assume that $a > b$ and for calculation we have taken $b = 0$. For the determination of the orientation of molecules in CuPc layers, it is necessary to know the intensity ratio of Raman modes for parallel (VV) and crossed (VH) polarizations (I_{VV}/I_{VH} ratio) for each type of vibration [19,23].

3. Experimental

The copper phthalocyanine (CuPc) layers have been prepared in vacuum chamber at pressure about $p = 2 \times 10^{-4}$ Pa. Purified CuPc powder (99.99% Sigma Aldrich Co.) was loaded into a quartz effusion cell with a nozzle of 3 mm in diameter on the top. The glass (BK7) and n-type (001)Si substrates were located above 10 cm from the source. The substrates (Si and BK7) were first sonicated in acetone, distilled water, isopropanol and finally in distilled water. Next, the substrate were

moved into the deposition chamber ($p < 2 \times 10^{-4}$) where CuPc layers were deposited onto heated substrates. During evaporation the substrates were held at different temperatures at the range from room temperature to 523 K. The deposition rate was 0.2 nm/s.

The FT-IR and Raman scattering studies have been performed in the temperature range 298–523 K and 298–515 K, respectively. The polarized Raman spectra at room temperature were obtained in different scattering geometry: VV, HV, HH and VH. The polarization of the laser light was rotated using a $\lambda/2$ wavelength plate settled on the laser beam path. The CCl_4 liquid was used to check the accuracy and reproducibility of spectra being recorded. The intensities of Raman bands were reduced using Böse–Einstein population factor.

The background line in spectra produced by quasi-elastic wing and the luminescence of some samples was subtracted by linear approximation. The spectra were also corrected for the efficiencies of the monochromator for different wavelengths and polarizations. The peak intensities are used for the quantitative estimation

$$I_{\text{red}} = \left(\frac{\nu}{\nu - \nu_0} \right)^4 [1 - \exp(-h\nu/kT)] I_{\text{obs}}$$

where ν , ν_0 , k and T represent the observed Raman shift, the wavenumber of the excitation source in cm^{-1} , Boltzmann constant and temperature, respectively [24]. The Raman spectra were recorded using the double grating monochromator GDM1000 (Carl-Zeiss Jena) equipped with the photomultiplier EMI 9658 AM (Quantum efficiency of 6% at 700 nm). Excitation was provided by an Argon ion laser (Carl-Zeiss Jena). The laser beam was focused on the sample surface at the incident angle of 36° . The detection was performed in a back-scattering geometry. The spectral resolution was 6 cm^{-1} .

The FT-IR spectra of CuPc samples pelletized with KBr and polyethylene (PE) were studied using the Perkin–Elmer Spectrum series 2000 spectrometer. The spectra were recorded in the spectral range from 600 to 4000 cm^{-1} for CuPc in KBr (3/100 mg) and from 30 to 600 cm^{-1} for CuPc in PE (3/100 mg) with spectral resolution of 4 and 2 cm^{-1} , respectively.

4. Results and discussion

The absorption spectra of CuPc layers usually show absorption characteristics: a Q-band in the range from 600 to 800 nm (2.066–1.56 eV) and a B-band in the range from 300 to 400 nm (4.133–3.099 eV) [25,26]. In the spectral range from 400 to 600 nm (3.099–2.066 eV), the valley of ground-state linear absorption spectrum, reverse saturated absorption (RAS) can occurred [26].

In Fig. 2 we present the UV–VIS absorption spectra of CuPc layer covering the range from 1.05 to 2.80 eV, measured for layer grown on glass substrate at room

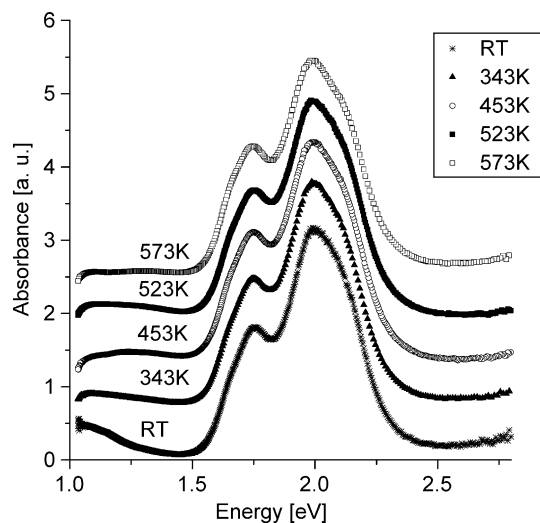


Fig. 2. The absorption spectra of CuPc film grown on glass substrate at room temperature and annealing at different temperatures.

temperature and annealed at different temperatures. The absorption spectra are typical for the molecules of metallophthalocyanines. From Fig. 2, it is seen that the absorption Q-band consists of two bands. One band positioned at 1.990 eV with shoulder at 2.002 eV and another one located at 1.756 eV. These peaks arise from the electronic transitions out of the highest occupied orbital a_{1u} (HOMO) into the lowest unoccupied orbital e_g (LUMO) and belong to $\pi \rightarrow \pi^*$ transition of the π -system consisting of carbon and nitrogen atoms [25, 26]. For the annealing temperatures below 380 K, the intensity of the first peak is larger than that of second one. One has to note, that there is a change in energy gap with annealing temperature and the change of energy gap is related to change of the structure of CuPc thin films from α to β form. The observed values of both absorption peaks and the calculated energy gaps are depicted in Table 1. In the UV–VIS absorption spectra of CuPc layers grown on glass and Si substrates we observe valley of ground-state linear absorption spectrum from 400 to 600 nm, reverse saturated absorption (RAS) can occurred absorption bands at 433 and 350 nm (Fig. 2). Hence, we could expect a pre-resonance Raman effect at 457, 488, or 514 nm.

The nonpolarized Raman spectra of CuPc layers grown onto (001)Si and glass (BK7) substrates measured at room

Table 1

The absorption peak position (Q band) and energy gap of CuPc layers at different temperatures

| Temperature (K) | Q band 1 (eV) | Q band 2 (eV) | E_{gonset} (eV) |
|-----------------|---------------|---------------|--------------------------|
| RT | 1.756 | 2.002 | 1.593 |
| 343 | 1.749 | 1.997 | 1.588 |
| 453 | 1.748 | 1.995 | 1.586 |
| 523 | 1.746 | 1.993 | 1.584 |
| 573 | 1.744 | 1.990 | 1.582 |

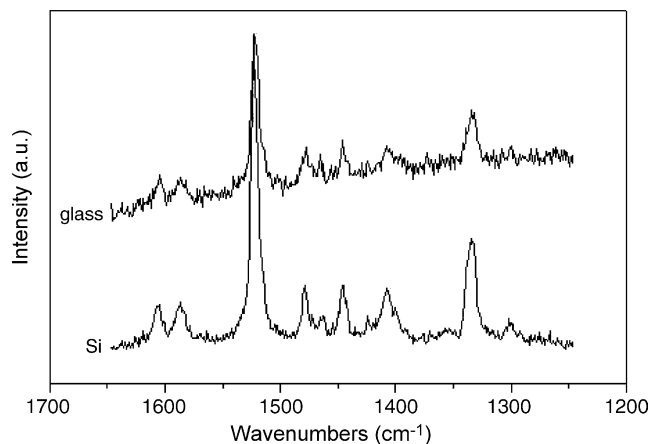


Fig. 3. The nonpolarized Raman spectra of CuPc layers grown onto glass (BK7) and (001)Si substrates measured at room temperature.

temperature (RT) are presented in Fig. 3. The spectra of CuPc grown onto (001)Si recorded at different temperatures are shown in Fig. 4. In the temperature range from RT to 515 K, the Raman bands shift to lower frequencies with the increase of temperature due to anharmonic scattering effect.

The orientation of CuPc molecules in thin layers has been determined by measuring the bands intensity of C–C and C–N bonds in different scattering geometry (VV, VH)

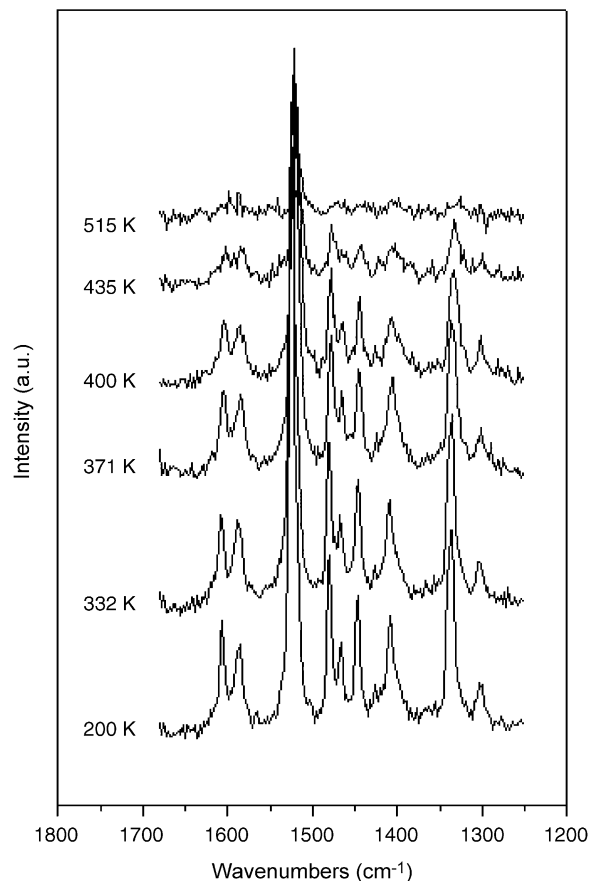


Fig. 4. The nonpolarized Raman spectra of CuPc layers grown onto (001)Si measured at different temperatures.

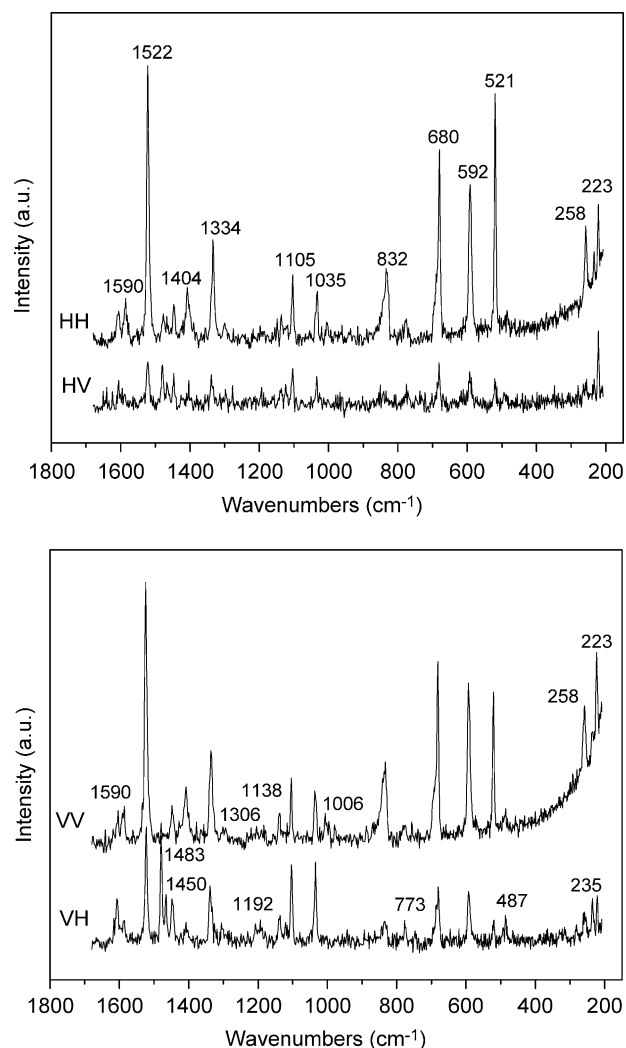


Fig. 5. The polarized Raman spectra of the CuPc layers grown on (001)Si substrate at room temperature for VV, VH, HH and HV polarizations.

(see Fig. 5) and is based on the polarization studies of internal molecular vibrations, using the films of α - and β -copper phthalocyanine [17,18,27,28]. The wavenumbers of Raman modes and their intensities are shown in Table 2.

The Raman spectra of CuPc crystals and CuPc layers grown on crystalline substrates, can be divided on two regions: external (below 200 cm^{-1}) and internal (above 200 cm^{-1}) [15,19]. The symmetry of A_{1g} or B_{2g} modes can be identified by their appearance in the VV, HH, VH or HV polarization spectra, respectively. The lines of B_{2g} symmetry are not observed in the VV scattering geometry but can be recorded in VH scattering geometry because of the orientation of the molecules in the layers. The Raman intensities are proportional to the square of matrix elements [19,22]:

$$I_{VV} = \frac{2}{\pi} \int_0^{\pi/2} k^2 \cos^4 \beta d\varphi = k^2 \cos^4 \beta$$

$$I_{VH} = \frac{2}{\pi} \int_0^{\pi/2} k^2 \sin^2 \varphi \cos^2 \beta \sin^2 \beta d\varphi = \frac{1}{2} k^2 \cos^2 \beta \sin^2 \varphi$$

Table 2

Tentative band assignment of the infrared and Raman bands of copper phthalocyanine

| Theory | FTIR | Raman | Symmetry of vibration |
|--------------------------------|--------|---------|-----------------------|
| Frequency (cm^{-1}) | | | |
| 54 w | 49 s | | |
| 62 vw | 69 s | | |
| 110 vs | 107 s | | |
| 123 w | 124 s | | |
| 160 w | 155 s | | B_{2g} |
| 194 w | 206 s | | |
| 224 vs | | 223 m | |
| 231 w | 230 s | | |
| 238 s | | 235 w | |
| 245 s | 243 w | | |
| 267 w | 262 s | 258 m | |
| 281 s | 284 s | | |
| 308 vs | 304 s | | |
| 390 s | 352 s | | |
| 455 vs | 434 s | | |
| 486 vs | | 487 vw | B_{1g} |
| 504 w | 506 s | 521 vs | |
| 552 vs | 546 s | | |
| 554 vs | 563 s | | |
| 573 s | 573 w | | |
| 574 vs | 579 s | | |
| 595 vs | | 592 s | A_{1g} |
| 644 vs | 637 w | | |
| 684 vs | | 680 s | B_{1g} |
| 733 s | 730 s | | B_{2g} |
| 756 vs | 754 s | | |
| 773 vs | | 773 w | B_{2g} |
| 781 vs | 781 s | | |
| 782 w | | 782 w | B_{1g} |
| 791 vs | | 832 m | A_{1g} |
| 859 s | 856 s | | |
| 876 w | 878 w | | |
| 904 s | 900 s | | |
| 931 vs | 948 w | | |
| 1004 vw | 1002 w | 1006 w | A_{1g} |
| 1018 vw | | 1035 m | B_{1g} |
| 1072 vs | 1068 s | | |
| 1073 w | 1068 s | | |
| 1089 vs | 1089 s | | |
| 1101 vs | 1101 s | | |
| 1107 s | | 1105 m | |
| 1131 vs | 1121 s | | |
| 1135 vs | | 1138 w | B_{2g} |
| 1160 vs | 1166 s | | |
| 1193 s | | 1192 w | |
| 1199 vs | 1201 w | | |
| 1251 vs | 1248 w | | |
| 1278 vs | 1288 s | | |
| 1304 vs | | 1306 vw | |
| 1341 vs | 1334 s | | B_{1g} |
| 1359 vs | 1372 w | | |
| 1386 s | 1384 w | | |
| 1389 vs | | 1404 m | B_{1g} |
| 1435 vs | 1421 s | | A_{1g} |
| 1451 s | | 1450 m | B_{2g} |
| 1472 vs | 1465 s | | B_{2g} |
| 1480 s | | 1483 s | |
| 1507 vs | 1508 s | | |
| 1516 vs | | 1522 vs | A_{1g} |
| 1547 s | 1548 s | | |
| 1563 vs | 1564 s | | |
| 1585 vs | 1587 s | | B_{1g} |

(continued on next page)

Table 2 (continued)

| Theory | FTIR | Raman | Symmetry of vibration |
|---------|--------|--------|-----------------------|
| 1599 vs | | 1590 m | |
| 1600 s | 1609 s | | |
| 1644 vs | 1659 w | | |
| 1655 vs | 1692 w | | |
| 1741 vs | 1726 w | | |
| 1816 vs | 2224 w | | |
| 3051 s | 2924 w | | |
| 3052 s | 3028 w | | |

vs, very strong; s, strong; m, middle; w, weak; vw, very weak.

Table 3

Measured I_{VV}/I_{VH} ratios for A_{1g} and B_{1g} modes in the spectra of CuPc films and calculated angles between the molecule plane and substrate

| Film | Symmetry of vibration | Frequency (cm ⁻¹) | I_{VV}/I_{VH} | Angle (°) |
|------------------------|-----------------------|-------------------------------|-----------------|-----------|
| Rotation 0° β-CuPc | A_{1g} | 592 | 2.872 | 34.85 |
| | B_{1g} | 680 | 2.198 | 43.65 |
| | B_{1g} | 1522 | 2.712 | 36.41 |
| Rotation 90° β-CuPc | A_{1g} | 592 | 1.559 | 52.06 |
| | B_{1g} | 680 | 1.886 | 46.68 |
| | B_{1g} | 1522 | 2.089 | 43.75 |
| Average | | | | 42.89 |

where $k = a$ for A_{1g} modes and $k = c$ for B_{1g} modes. The angle β is a parameter representing the angle between molecule plane and substrate surface. From these equation we obtained:

$$\frac{I_{VV}}{I_{VH}} = 2 \frac{\cos^2 \beta}{\sin^2 \beta}.$$

The measured intensities I_{VV} and I_{VH} for A_{1g} and B_{1g} modes in CuPc layers grown at 475 K on (001)Si substrate

and the β angle calculated from above equation are presented in Table 3.

The absorption spectra of CuPc in KBr films in spectral range from 1800 to 400 cm⁻¹ at different temperatures and from 600 to 30 cm⁻¹ at room temperature are presented in Figs. 6 and 7, respectively. The frequencies of all experimentally observed Raman modes are listed in Table 2 along with the mode frequencies obtained from FT-IR measurements and predicted by LDC calculations. For these calculations a shell model described in detail in [12] has been used. As it can be seen from Table 2 we observe the small differences between LDC theoretical calculations for free molecules and experimental wavenumbers obtained for thin layers deposited on glass and Si substrates. They can be caused by the strain existing in CuPc layer due to difference of thermal expansion coefficients of CuPc layer and substrate [29].

The copper phthalocyanine grows on monocrystalline substrates generally in two polymorphs, the α - and the β -form. In both forms the copper phthalocyanine molecules are arranged in a herringbone pattern and their main difference is the angle of inclination of the molecular plane with respect to the crystallographic ac-plane. In the α -form and β -form this angle is 25–30°, and 45–49°, respectively [15,19,25]. The orientation of the CuPc molecules towards the substrate plane depends on the thickness of the layer, the rate and the temperature of growth, the temperature of substrate and the lattice constant of substrate. For instance, thick layers on gold or glass at room temperature form the α -form with the b-axis perpendicular to the substrate, thus the molecular plane forms an angle of 25–30° with the substrate. In thinner films (<1 μm) deposited on amorphous substrates the b-axis is parallel to the substrate, thus resulting in an angle with the substrate of about 60–65° [25]. For CuPc thin films prepared on (001)Si at high

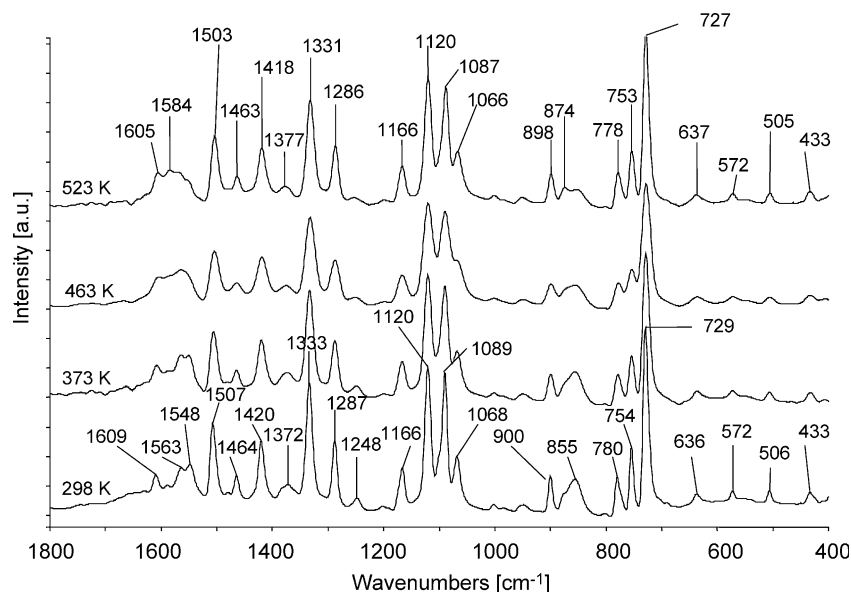


Fig. 6. The IR spectra of CuPc molecules in KBr at different temperatures.

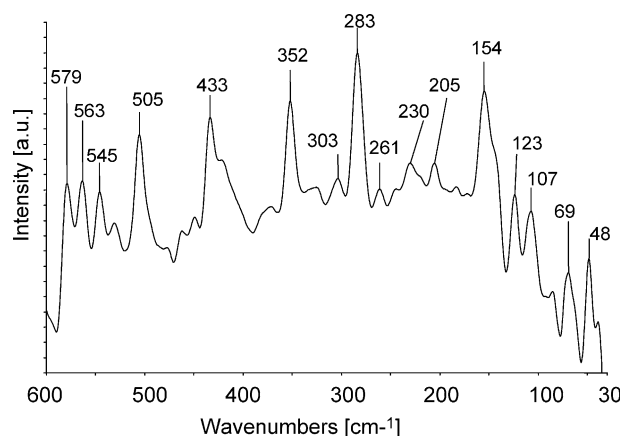


Fig. 7. The IR spectra of CuPc at room temperature in far infrared range.

deposition rates and higher temperature of the substrate develop a preferred orientation with the CuPc molecules approximately at 43° to the surface of the substrate. This value is in good agreement with the value obtained by Basova and Kolesov [19,22].

5. Conclusions

The polarized Raman scattering spectra, UV–VIS absorption spectra and infrared reflectivity measurements (FT-IR) allowed us to determine the complete set of vibrational modes of CuPc crystalline layers. From the studies mentioned above it can be concluded that the sample preparation conditions influence significantly on the preferred orientation of CuPc crystallites within thin films, while the roughness of the thin film surfaces remains approximately the same. The deposition rate and temperature of substrates have a strong influence on the preferred growth of CuPc crystallites. In several opto-electronic applications of CuPc layers such as light-emitting devices or solar cells, the electrical conductivity should be optimized in the perpendicular film direction but in field effect transistors in the parallel direction. CuPc thin films prepared on (001)Si at high deposition rates and higher temperature of the substrate develop a preferred orientation with the CuPc molecules approximately at 43° to the surface of the substrate. The expected enhancement of the electrical conductivity through these layers will increase the performance of several types of applications.

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