

Copper phthalocyanine nanoparticles and nanoflowers

Santanu Karan, Dhrubajyoti Basak, Biswanath Mallik *

Department of Spectroscopy, Indian Association for the Cultivation of Science, 2A & 2B, Raja S.C. Mullick Road, Jadavpur, Kolkata 700032, India

Received 12 September 2006; in final form 21 November 2006

Available online 15 December 2006

Abstract

Molecular organization of copper phthalocyanine (CuPc) thin films deposited at room temperature (30 °C) on quartz and post annealed gold-coated quartz substrates have been studied. The thin films have been characterized by optical absorption, X-ray diffraction, atomic force microscopy and field emission scanning electron microscopy (FESEM). The FESEM images have shown densely packed nanoparticles and nanoflower like structure for the gold-coated quartz substrates annealed at 500 and 750 °C, respectively. The fractal dimension of the assembly of nanostructures in the films has been estimated from FESEM images. The effect of substrates on the surface morphology, optical properties and the fractal dimension have been discussed.

© 2006 Elsevier B.V. All rights reserved.

1. Introduction

Phthalocyanines belong to a well-studied class of molecules that have a number of wide-ranging applications in fields as diverse as dyes [1], light emitting diodes (LEDs) [2], solar cells [3,4] and field-effect transistors [5]. They exist as a range of derivatives, where the polyaromatic ring (abbreviated Pc for the phthalocyanato anion $C_{32}H_{16}N_8^{2-}$) is most commonly bound to a transition metal (MPc) or hydrogen (H_2Pc) [6]. Metal phthalocyanines (MPcs) are very well known dye pigments having similarity in structure with biological molecules chlorophyll and haemoglobin. These materials have shown many interesting properties, e.g., these are organic semiconductors [7,8], chemically and thermally very stable [9,10], most of these can easily form ordered thin films and exhibit photoconductivity [3,4]; show catalytic activity [11], etc. High vacuum evaporation has become the most widely used technique for the deposition of MPc films [12–17] and attempts have been made to use such films as molecular components in a number of electronic and optoelectronic devices [3,4,18]. The structure, morphology, electronic and optical properties of the films are crucial for their technological applications. For example, a high crystallinity is

known to improve the conducting properties, but smooth amorphous films allow better contacts. It has been reported [19] that ordering and orientation are crucial for the device efficiency. Anisotropic electrical transport properties are often observed in these molecules and they are caused by the preferred orientation of the molecules [19–21]. Recently, molecular orientation of MPcs on various substrates such as conducting polymer [22], glass [14], quartz glass [15], silicon [12], gold [16,17], etc. has been studied for the thin films deposited under various experimental conditions. Such studies have indicated that the orientation of the grains depends on the substrate, the deposition technique, heat-treatment temperatures and condition of substrates during film deposition.

Many electronic and optoelectronic devices rely on the growth of molecular thin films structures on metal electrodes. For the better technological applications of phthalocyanines as organic semiconductors, electronically active organic molecules and components for molecular electronics it is necessary to study, under various experimental conditions, the interactions of these molecules with various electrode materials like gold, silver etc. As among the metal substituted phthalocyanines, copper (II) phthalocyanine (CuPc) has been found to have superior properties [23–25], we started our investigation with this material. In the course of such investigations some interesting results related to the growth of CuPc nanoparticles and nanoflow-

* Corresponding author. Fax: +91 33 2473 2805.

E-mail address: spbm@mahendra.iacs.res.in (B. Mallik).

ers were observed while CuPc was deposited on gold surface by vacuum evaporation method under different annealing conditions. The results are discussed in this letter.

2. Experimental

Gold single crystal with (111) surface orientation was used as a target. Clean gold film surfaces were prepared on the surface of clean quartz plates by D.C. sputtering (7 KV, 10 mA) for 4 min followed by annealing for 1 h at 500 °C and 750 °C under vacuum. The substrates annealed at 500 °C and 750 °C are referred as Au-500 and Au-750, respectively. The CuPc source contained in a molybdenum boat that was resistively heated in the high vacuum chamber. The CuPc powder (β form, dye content $\sim 97\%$, obtained from Aldrich, USA) was used after repeated degassing of the source prior to deposition. Deposition was noted to occur when the chamber pressure could no longer reduce to the base pressure and the current through the boat was kept constant at ~ 20 A. CuPc films were deposited at a chamber pressure of $\sim 10^{-6}$ Torr. The thickness of the deposited CuPc film and the rate of deposition were

maintained at 100 nm and 0.6 Å/s, respectively using a quartz crystal microbalance (Hitech, model DTM-101). The temperature of the substrates during deposition was kept at room temperature (30 °C). The thin films have been characterized by optical absorption, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM). The XRD study of the CuPc films was recorded at a scan rate of 0.05° per sec by using a Seifert XRD 3000P diffractometer with Cu-K α radiation (0.15418 nm). An UV–Vis scanning spectrophotometer (UV-2401 PC, Shimadzu, Japan) was used to record the electronic absorption spectra of the films at room temperature. FESEM (Model: JSM-6700F, JEOL, Japan) was used to record the scanning electron micrograph images of the CuPc thin films. To estimate the surface roughness of the thin films, the contact mode atomic force microscopy (AFM) images were taken using NT-MDT (Solver PRO-M), Moscow, Russia.

3. Results and discussion

The FESEM images of the gold thin films are shown in Fig. 1. Fig. 1a shows the FESEM image of as prepared gold nanoparticles on quartz. The particles are spherical

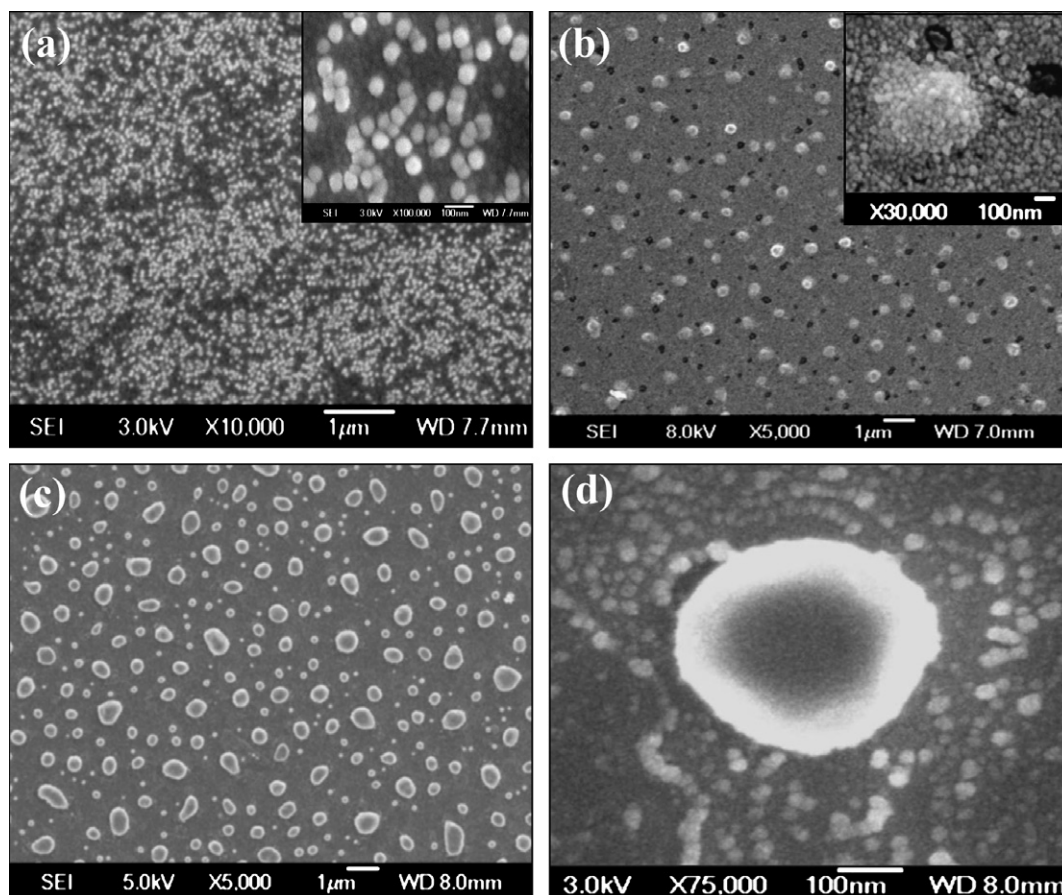


Fig. 1. FESEM images of sputtered gold nanoparticles: (a) as deposited gold on quartz substrate, inset of Fig. (a) shows the same image at a higher magnification, (b) island and porous thin film morphology of Au-500, inset of Fig. (b) shows the individual island and pore at higher magnification, (c) spherical and elliptical clusters of different sizes of gold of Au-750 and (d) shows one large spherical gold cluster surrounded by small gold nanoparticles.

in shape and the average size is 30 nm. There is some bigger cluster (as shown in the inset of Fig. 1a) at the upper surface of the film and the sizes are nearly 50 nm. The FESEM image in Fig. 1b shows the surface morphology of the annealed film at 500 °C. Clearly there are some islands (500 nm) of gold nanoparticles and some pores (150 nm) that are in random order, but the distribution of the islands and pores are almost same throughout the whole surface. The inset of Fig. 1b shows such islands (white spots) and pores (black spots) at higher magnification. The regions between islands and pores are covered by nanoparticles of gold with average size of around 30–40 nm. The FESEM image in Fig. 1c shows the surface morphology of the annealed film at 750 °C. Here some bigger particles of some spherical as well as elliptical shapes are seen with different sizes from 100 to 500 nm. Fig. 1d represents one such spherical particle of size nearly 400 nm surrounded by nano-sized particles having sizes from 10 to 20 nm at higher magnification.

FESEM images of CuPc thin films deposited at room substrate temperature are shown in Fig. 2. The image of CuPc thin film deposited on bare quartz is shown in Fig. 2a, which shows clearly almost uniform distribution

of some nanosized particles of size 25–30 nm. In Fig. 2b the dense packing of CuPc nanoparticles have been found to be deposited on the annealed (at 500 °C) gold-coated quartz substrate at room temperature. The average particle size estimated is nearly 40–60 nm. In Fig. 2c some flower like structure of CuPc on the annealed (at 750 °C) gold-coated quartz substrate at room temperature with different shape and size ranging from 200 nm to 1 μm has been found to be deposited in a regular manner. The residuals position on the film has been found to be covered uniformly by the nanoparticles. Fig. 2d shows one nanoflower of diameter around 850 nm. The flower consists of some nanoribbons of CuPc of diameter nearly 25 nm and few nanometers in length. The structures of such nanoflowers arise due to the interaction of CuPc molecules with annealed gold template (Au-750), which was the same type of surface having spherical and elliptical particles of various sizes. The initial nucleation of CuPc molecules occurs at room substrate temperature on the gold particles and form flower like structure through the process of self-organization.

Fig. 3 shows the X-ray diffraction patterns for CuPc thin films deposited at room temperature on bare quartz, Au-500, Au-750 and the starting β-phase of CuPc powder

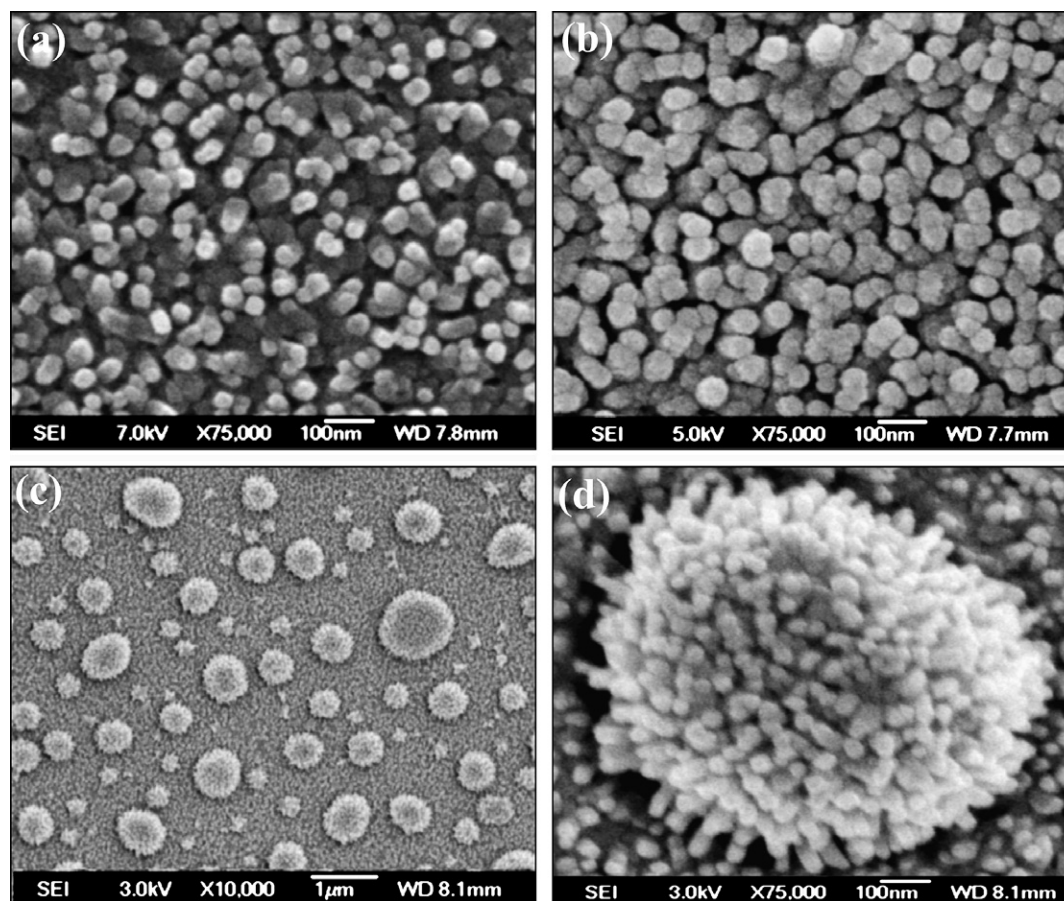


Fig. 2. FESEM images of vacuum deposited CuPc thin films at room temperature. (a) CuPc nanoparticles deposited on quartz, (b) dense and aggregated CuPc nanoparticles deposited on Au-500, (c) arrangement of spherical and elliptical CuPc nanoflowers of different sizes deposited on Au-750 and (d) CuPc nanoflower at higher magnification.

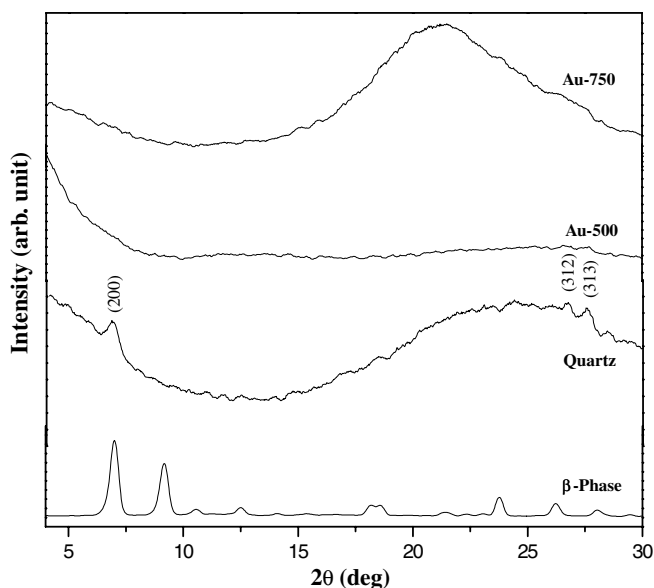


Fig. 3. XRD pattern of CuPc thin films deposited at room temperature on quartz, Au-500, Au-750 and starting β -phase powder of CuPc.

(lower panel). It has been reported that CuPc have three dominant different crystal phases: α -, β -, and χ -phases [14,26]. It can be seen from Fig. 3 that the CuPc thin films formed on Au-500 and Au-750 are totally amorphous and the film deposited on bare quartz shows the indication of α -phase, although the starting CuPc powder was in the β -phase.

Fig. 4a shows the optical absorption spectra of CuPc thin films deposited at room temperature on different substrates. It has been suggested that the UV–Vis spectrum of MPCs originates from the molecular orbitals within the aromatic 18- π electron system and from overlapping orbitals on the central metal [27]. In the near UV region the B-band or Soret band [27,28], representing the $\pi \rightarrow \pi^*$ transition appear with peak position in the range about 329–333 nm depending on the nature of substrate used. The absorption band in the visible region for each sample film known as the Q-band representing the $\pi \rightarrow \pi^*$ transition [28] has a doublet due to Davydov splitting [29]. The position of the absorption peaks including the amount of Davydov splitting for the different sample films are shown in Table 1. From Table 1 and Fig. 4a it is clear that the position and relative intensity of peaks and the amount of Davydov splitting depend on the nature of substrate used. The extent of Davydov splitting is related to the differences in relative orientation of molecules which are close enough to give electronic transitions, namely, interactions between transition dipole moments from adjacent molecules. The amount of Davydov splitting in the case of CuPc films deposited on bare quartz and on Au-500 is almost the same. But the Davydov splitting for CuPc films deposited on Au-750 is appreciably higher. Thus, the change in orientation of the molecules in the CuPc films deposited on Au-750 due to the change in substrate annealing condition is

indicated from the differences in the extent of Davydov splitting. Recently, it has been found that substrate roughness significantly affects the orientation of CuPc molecules. These molecules lie on flat substrates (i.e. the molecular plane is parallel to the film surface) but they stand on rough substrates [16]. Our recorded AFM images for Au-500 and Au-750 surfaces (Fig. 4b and c) have indicated that the roughness of Au-750 is significantly higher than that of Au-500 substrate (rms roughness of Au-500 is 2.1 nm and that of Au-750 is 85.0 nm). Thus, the adsorption of CuPc molecules on Au-750 occurs in a standing/tilted geometry. Annealing of the gold substrate to 500°C caused no essential changes in the adsorption geometry of the CuPc molecules. The high tendency of the self-ordering of phthalocyanine molecules could be one of the main reasons for the anisotropy in film morphology depending on the substrate annealing condition.

The surface structure and surface coverage of CuPc thin film formed on quartz, Au-500 and Au-750 are different and the thin film preparation in this process has a direct relationship with their fractal dimension/structure. The fractal dimension enables us to relate the aggregation of CuPc molecules on quartz and gold surface to a proper kinetic and growth mechanism [30]. Using the FESEM images, the fractal dimension of the assembly of nanostructures (nanoparticles and nanoflowers) in the CuPc films grown on different substrates can be calculated by using the area (S)-perimeter (P) relationship [31,32], which is generally used to estimate the fractal dimension of objects/islands. The perimeter-area relationship for a set of islands can be written as [31,32],

$$P = kS^{D'/2} \quad (1)$$

where, D' is the fractal dimension, the area S is the number of pixels making up a given object, the perimeter P is a count of the number of pixel edges and k is a scaling constant. Self-similarity, or geometric scale-invariance, is expressed by a linear relationship between $\log P$ and $\log S$ over some range of scales.

We have calculated D' for the CuPc thin film surfaces deposited on various substrates by applying the method used for SPM image analysis [32]. Commonly used models for calculating fractal dimensions from SPM images assume the scaling to be equal in the lateral directions on the surface but not necessary the same as in the normal direction [32]. Such surfaces are called self-affine and differ from self-similar surfaces with equal scaling in all three directions. An evaluation of fractal dimension (D') with the area perimeter method uses the fact that the intersection between a plane and a self-affine surface [32] generates self-similar lakes or islands. The evaluated fractal dimension (D') is the fractal dimension of the coastlines and it has a value between one and two; whereas the fractal dimension of the surface = $D' + 1$ [32]. The FESEM images were converted to a digitalized image similar to the approach for SPM image analysis [32]. The area and apparent perimeter, neglecting islands that touch the sides

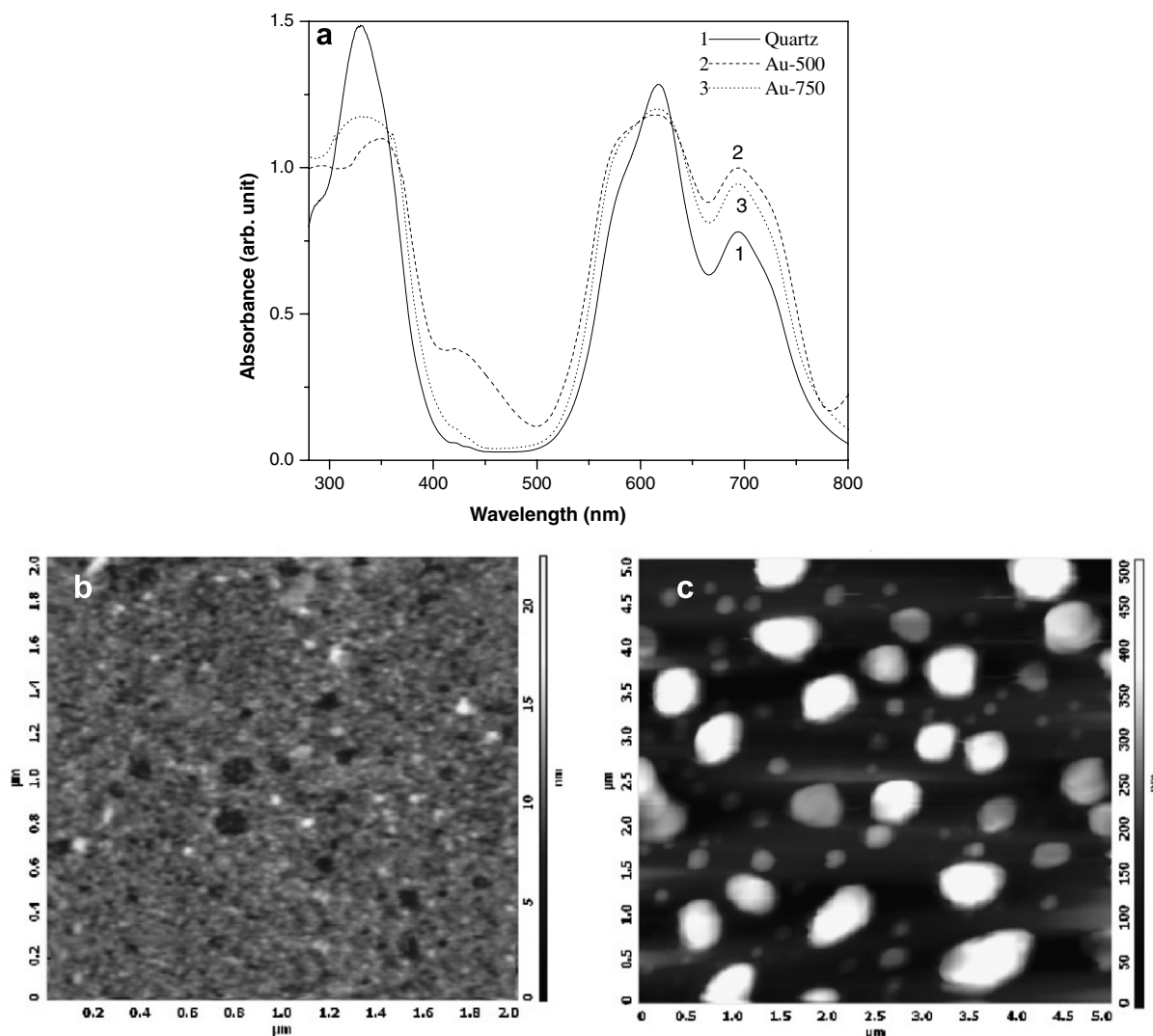


Fig. 4. (a) Optical absorption spectra of CuPc thin films deposited at room temperature on (1) quartz, (2) Au-500 and (3) Au-750. (b) and (c) Contact mode AFM image of gold substrates Au-500 and Au-750 respectively.

Table 1

Positions of absorption peak and Davydov splitting for CuPc thin films deposited on quartz, Au-500 and Au-750

Template used	Positions of absorption peak (nm)				Davydov splitting (cm^{-1})
Quartz	280	329	617	693	1777.16
Au-500	–	347.2	616.8	692.5	1772.31
Au-750	264	333.4	614.6	692.5	1828.78

of the image field, of the independent islands have been calculated throughout the whole image. The slope of the log–log perimeter–area plot for a set of objects gives the value of D' (i.e. $D' = 2 \times \text{slope}$). In Fig. 5a–c, the linear plots of $\log P$ versus $\log S$ are shown on the basis of the analysis of FESEM images corresponding to the CuPc films deposited on quartz, Au-500, and Au-750, respectively. The calculated value of the fractal dimension D' in the cases of CuPc films showing nanoparticles deposited on quartz and Au-500 are nearly the same (1.84 and 1.87, respec-

tively) and for the CuPc film showing nanoflowers (Au-750) it jumps to a smaller value (1.76). Again from Table 1 it is seen that the Davydov splitting for CuPc nanoparticles thin films deposited on quartz and Au-500 are nearly the same and this splitting for the film showing CuPc nanoflowers is different. Thus the results of fractal analysis agree with the result of optical measurements.

The degree of crystal aggregation in organic pigments like CuPc was assessed by Mather [33] using fractal nature of the pigment crystal surfaces. Mather [33] considered that the geometry of the crystal aggregates comprising a particular organic pigment is strongly influenced by the geometry of the pigment crystal and its surface roughness. The fractal dimensions estimated for aggregated β -copper phthalocyanine pigment crystals were less than 2, while for the unaggregated pigment crystals its value was higher than 2 (~ 2.28). According to the work of Mather [33] it follows that the CuPc crystal aggregation on Au-750 is higher compared to that of Au-500 substrate because of enhanced roughness of Au-750 as evidenced by AFM image analysis.

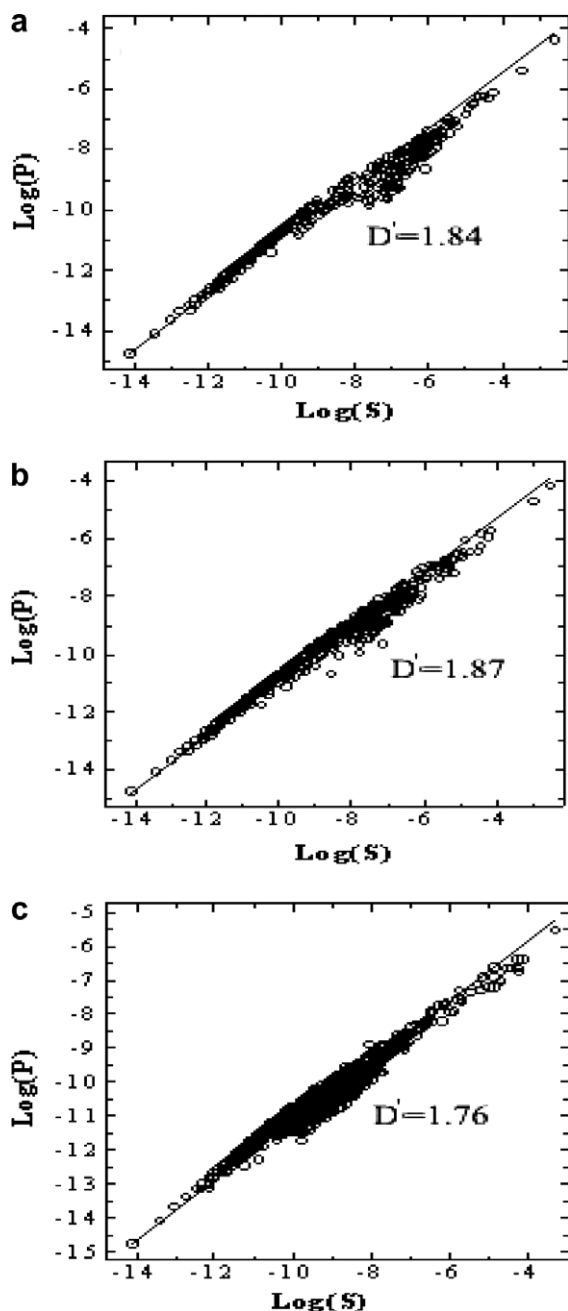


Fig. 5. Variation of $\log(P)$ with $\log(S)$ for CuPc thin films derived from FESEM images: (a) CuPc thin film deposited on quartz, (b) CuPc thin film deposited on Au-500 and (c) some assembly of CuPc nanoflowers deposited on Au-750 at room substrate temperature.

4. Conclusions

In summary, it is clear that for the growth of CuPc film by vacuum evaporation, the surface morphology of the thin film is influenced very strongly by the properties of the gold substrate. In case of quartz and Au-500 substrate, CuPc nanoparticles have been found to be deposited uniformly through the whole surface of the film and for Au-750 CuPc nanoflowers have been grown on film surface. Davydov splitting for CuPc nanoparticles thin films deposited on quartz and Au-500 are nearly same

and this splitting for the film showing CuPc nanoflowers is different. The results of fractal analysis agree with the result of optical measurements. The substrate-effect may extend to structures involving the growth of multilayer heterostructures. The gold template can also be useful as an electrode in an optoelectronic device. The implication of these results for molecular device structures is very important, since it is likely that the templating effect will have a profound influence on the consequential electronic and optical properties of a heterostructures based devices.

References

- [1] C.J.T. Cronshaw, Endeavour 1 (1942) 79.
- [2] J. Blochwitz, M. Pfeiffer, T. Fritz, K. Leo, Appl. Phys. Lett. 73 (1998) 729.
- [3] C.C. Leznoff, A.B.P. Lever, Phthalocyanines, Properties and applications, vol.3, VCH, New York, 1993.
- [4] F. Young, M. Shtein, S.R. Forrest, Nature Mater. 4 (2005) 37.
- [5] D.X. Wang, Y. Tanaka, M. Iizuka, S. Kuniyoshi, S. Kudo, K. Tanaka, Jpn. J. Appl. Phys. 18 (1999) 256.
- [6] N.B. Mc Keown, Phthalocyanine Materials, Cambridge University Press, Cambridge, 1998.
- [7] J. Kaufhold, K. Hauffe, Ber. Bunsenges Phys. Chem. 69 (1965) 168.
- [8] M. Hanack, M. Lang, Adv. Mat. 6 (1994) 819.
- [9] B.J. Prince, B.E. Williamson, R.J. Reeves, J. Lumin. 93 (2001) 293.
- [10] A.O. Ribeiro, J.C. Biazotto, O.A. Serra, J. Non-Cryst. Solids 273 (2000) 198.
- [11] S. Seelan, A.K. Sinha, D. Srinivas, S. Sivasanker, J. Mol. Catal. A: Chem. 157 (2000) 163.
- [12] R. Hiesgen, M. Raebisch, H. Boettcher, D. Meissner, Sol. Energy Mater. Sol. Cells 61 (2000) 73.
- [13] S.F. Alvarado, L. Rossi, P. Mueller, W. Rieß, Synth. Met. 122 (2001) 73.
- [14] E. Jungyoon, S. Kim, E. Lim, K. Lee, D. Cha, B. Friedman, Appl. Surf. Sci. 205 (2003) 274.
- [15] M.M. El-Nahass, Z. El-Gohary, H.S. Soliman, Opt. Laser Technol. 35 (2003) 523.
- [16] I. Biswas, H. Peisert, T. Schwieger, D. Dini, M. Hanack, M. Knupfer, T. Schmidt, T. Chasse, J. Chem. Phys. 122 (2005) 064710.
- [17] H. Peisert et al., Chem. Phys. Lett. 403 (2005) 1.
- [18] W. Kowalsky et al., Phys. Chem. Chem. Phys. 1 (1999) 1719.
- [19] J.R. Ostrick et al., J. Appl. Phys. 81 (1997) 6804.
- [20] W. Michaelis, D. Wohrle, D. Schlettwsin, J. Mater. Res. 19 (2004) 2040.
- [21] S.C. Mathur, N. Ramesh, Chem. Phys. Lett. 37 (1975) 276.
- [22] H. Peisert et al., J. Appl. Phys. 96 (2004) 4009.
- [23] K. Kudo, K. Shimada, K. Marugami, M. Iizuka, S. Kuniyoshi, K. Tanaka, Synth. Met. 102 (1999) 900.
- [24] S.A. Van Slyke, C.H. Chen, C.W. Tang, Appl. Phys. Lett. 69 (1996) 2160.
- [25] J.M. Auerhammer, M. Knupfer, H. Peisert, J. Fink, Surf. Sci. 506 (2002) 333.
- [26] M.K. Debe, K.K. Kam, Thin Solid Films 186 (1990) 289.
- [27] E.A. Ough, J.M. Stillman, K.A.M. Creber, Can. J. Chem. 71 (1993) 1898.
- [28] J. Mack, M.J. Stillman, Inorg. Chem. 40 (2001) 812.
- [29] T.N. Misra, Rev. Pure Appl. Chem. 15 (1965) 39.
- [30] J.S. Ahn, P.T. Hammond, M.F. Rubner, I. Lee, Colloid Surf. A 259 (2005) 45.
- [31] U. Paniveni, V. Krishan, J. Singh, R. Srikanth, Sol. Phys. 231 (2005) 1.
- [32] N. Almqvist, Surf. Sci. 355 (1996) 221.
- [33] R.R. Mather, Dyes Pigments 42 (1999) 103.