Influence of Thermal Annealing on The Structural Properties of Vanadyl Phthalocyanine Thin Films: A Comparative Study

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Abstract- This paper presents a comparative study on Vanadyl Phthalocyanine (VOPc) thin films deposited by thermal evaporation and spin coating techniques. The samples were prepared on cleaned glass substrates and annealed at various temperatures ranging form 95^oC to 155^oC. To obtain the morphological and structural properties of VOPc thin films, X-ray diffraction (XRD) technique and atomic force microscopy (AFM) have been implied. The AFM topographic images show a very slight difference in the thermally grown films, before and after annealing, however best results are achieved for the spin-cast film annealed at 125^oC. The XRD spectra show no existence of the sharp peaks, suggesting the material to be amorphous. The humps in the XRD patterns indicate the presence of some crystallites.

Keywords- Annealing, optical properties, thin films, Vanadyl phthalocyanine.

I. Introduction

In recent years the phthalocyanines have acquired significant interest among organic semiconductors, due to their chemical and thermal stability [1],[2]. Phthalocyanines are found in different phases i.e. α-, β- and γ-phases [3]. Metal-substituted and metal free phthalocyanines are readily used as active layer in several applications such as gas sensors [4], photocapacitive and photoresistive detectors [5], OTFTs [6], colour filters [7] and organic laser materials [8]. Metal phthalocyanine complexes, occuring mostly as colouring materials, have been explored regarding their properties as pigments for printing inks, coatings, paints and plastics [9]. To explore the potentially interesting properties of the material, structural and morphological characterization is thus considered as a prerequisite for deep insight knowledge of the material. These structural properties mostly depend on the deposition technique, the heat-treatment temperature and the conditions during film deposition. Annealing process is a broadly employed method to enhance the quality of the crystal and exploit structural defects in the material. During thermal annealing, the morphology and structural properties of the material change. For semiconductor devices like light emitting diodes the structural properties are very important, therefore, it is essential to investigate how thermal annealing process affects these properties [10]. The effect of thermal annealing process on the surface morphology and structural properties of cobalt phthalocyanine, tin phthalocyanine [11],[12] have been studied. Ye *et al.* have investigated the effect of different annealing temperatures on the structural and optical properties of fluorinated copper phthalocyanine/α-sexithiophene heterojunction thin films [13]. Vanadyl phthalocyanine (VOPc) is a macrocyclic green color compound whose structural properties under different annealing temperatures are rare exploited, however structural and spectroscopic characterization of VOPc thin films fabricated by vacuum deposition has been carried out [14]. In the present work, thin films of VOPc have been fabricated on glass substrates by vacuum deposition and solution processing techniques. A detailed study on the effects of post fabrication thermal annealing on the surface morphology and structural properties has been performed by atomic force microscopy (AFM) and X-ray diffraction. Hence, the purpose of our work is to find the optimal temperature for which the film produces best structural properties.

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II. Experimental

The molecular structure of vanadyl phthalocyanine is given in $Fig.1$. VOPc was purchased from Sigma Aldrich and was used as obtained without further purification. Prior to the deposition of VOPc thin films, the substrates were thoroughly cleaned by immersing them in detergent for 15 min and subsequently putting them in the solution of acetone and ethanol sequentially. Finally, the cleaned glass substrates were blown with dry nitrogen. The pressure during deposition process was upheld at $10^{-5}mbar$. The VOPc films were sublimed on carefully cleaned glass substrates at room temperature. The thickness of the deposited VOPc films and the rate of deposition was maintained at $150nm$ and $0.1-0.2nm/s$ respectively, using FTM5 quartz-crystal thickness monitor. For the solution processed films, the VOPc was dissolved in chloroform to yield $30mg/ml$ solution. Thin films of VOPc were formed on the cleaned glass substrates by spin coating and thermal evaporation techniques. One thermally deposited film and one spin coated film are selected before any further temperature treatment and are referred as pristine film. The pristine samples were taken as a reference in comparative experiments. The rest of the thin films were subjected to thermal annealing treatment for $20min$ at different temperatures (ranging from 95^oC to 155^oC). Atomic force microscopic (AFM) images

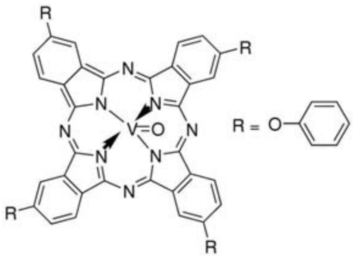

Fig. 1: Molecular structure of VOPc.

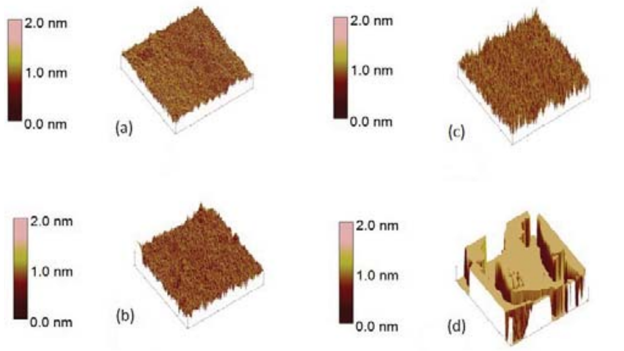

Fig. 2: 3-D AFM topographic images of VOPc thin films spin coated on glass substrates; scan size is 5 $\mu m \times 5$ μm: (a) pristine and annealed at (b) 95^oC, (c) 125^oC and (d) 155^oC.

were measured in tapping mode using Digital Instruments Veeco $D3000$ microscope. The X-ray diffractograms were recorded using a Siemen $D5000$ diffractometer. The radiation was monochromatized Cu-K_α beam of average wavelength 0.154056 nm.

III. Results and discussion

The influence of thermal annealing on the morphology of solution-processed thin films of Vanadyl Phthalocyanine prepared on glass substrates, is depicted in $Fig.2$.

The films were annealed at three different temperatures i.e. 95^oC, 125^oC and 155^oC. It can be observed from the figure that the morphology of the pristine film shows a smooth and uniform surface without any distinct features. The root mean square (rms) roughness of the pristine film and the samples undergone thermal treatment, at different temperatures for a period of 20 minutes, equals 0.286 nm, 0.369 nm and 0.5 nm respectively. The best results can be seen for the film annealed at 125^oC.

The VOPc thin films, after being thermally annealed, show relatively rough and non-uniform surface, suggesting the formation of interpenetrating molecular network of VOPc. Upon annealing of the film at temperature equal to 155^oC and above, deterioration feature is observed due to degradation of the film. From the application point of view, the higher efficiency devices are obtained from the film of greater roughness [15].

$Fig.$ 3 shows 5 μm $\times$ 5 μm AFM topographic images of thermally evaporated thin films of VOPc. The rms roughness

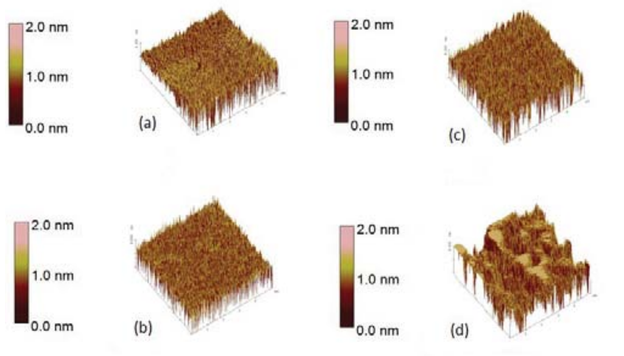

Fig. 3: 3-D AFM topographic images of VOPc thin films thermally deposited on glass substrates; scan size is 5 $\mu m \times 5$ μm: (a) pristine and annealed at (b) 95^oC, (c) 125^oC and (d) 155^oC.

of the pristine film is 0.803 nm while thermally treated thin films at temperatures of 95^oC, 125^oC and $155oC$ exhibit the roughness of 0.915 nm, 1.192 nm and 2.175 nm, respectively. The obtained roughness values of the thermally evaporated thin films reveal a very slight difference in the surface roughness of the pristine film and films undergone thermal annealing. The AFM 3-D height images do not exhibit significant change induced by thermal annealing in the structure of the pristine and thermally annealed films. Part of the film annealed at 155^oC appears to evaporate as in the case of spin-cast annealed films.

A comparative study from the results obtained for the spin-cast films and thermally evaporated films demonstrates that surface roughness and non-uniformity in the solution processed films increase upon thermal annealing whereas the thermally deposited films show almost no difference in the surface morphology before and after thermal treatment. Another significant finding is that the thermally deposited films are coarser and rougher than the spin coated films making them more suitable for high efficiency dependent applications.

The X-ray diffractograms of solution processed VOPc thin films before and after undergoing various annealing temperatures of 95^oC, 125^oC and 155^oC are presented in $Fig.4$ whereas $Fig.5$ depicts the XRD spectra of thermally evaporated VOPc thin films (pristine and annealed). The films show almost no change in the X-ray diffraction patterns. It can be deduced from broad diffraction maxima displayed in the XRD spectrum that no crystal structure is present, due to low X-ray intensities [16]. The diffractograms exhibit broad humps which indicates that the material used as an active layer is amorphous [17]. The absence of any significant peak in pristine and annealed samples reveals that the films lack crystalline quality and are predominantly amorphous in nature.

The close look at the XRD patterns of the spin-coated and thermally deposited thin films of Vanadyl Phthalocyanine suggests that humps contained in the X-ray diffractograms of thermally evaporated films have a little higher and narrower as compared to the solution processed thin films.

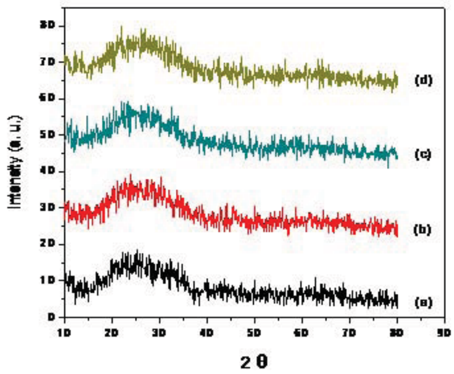

Fig. 4: X-ray diffraction patterns of VOPc thin films spin coated on glass substrates: (a) pristine and annealed at (b) 95^oC, (c) 125^oC and (d) 155^oC.

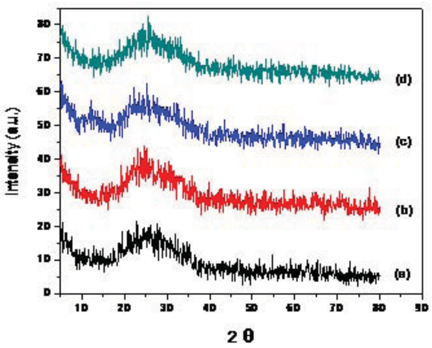

Fig. 5: X-ray diffraction patterns of VOPc thin films thermally deposited on glass substrates: (a) pristine and annealed at (b) 95^oC, (c) 125^oC and (d) 155^oC.

IV. Conclusions

By comparing the AFM and XRD results of both thermally deposited and solution processed films, we can draw the following conclusions. By analyzing the the AFM topographic images, we found that there is a significant influence of annealing on the surface morphology of spin coated films as compared to the films deposited by thermally evaporation. The spin-cast film annealed at the temperature 125^oC showed a rough and non-uniform surface due to the increased number of absorption sites. The surface roughness of thermally deposited thin films is much greater as compared to spin coated films, which makes it useful for high efficiency devices. The increase in the temperature beyond 155^oC has disrupted the film formation and a part of the film is evaporated. The existence of the humps in the XRD patterns of both types of fabricated films suggests the presence of a few crystallites.

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References

[1] D. Gu, Qiying Chen, Juping Shu, Xiaodong Tang, Fuxi Gan, Shuyin Shenb, Kai Liu and Huijun Xu, "Optical recording performance of thin films of phthalocyanine compounds," Thin Solid Films vol. 257 pp. 88-93, 1995.
[2] B. W. Bloom A, US Patent, vol. 4, p. 355, 1980.
[3] S. Shihub and R. Gould, "Structure and phase-change phenomena in evaporated thin films of cobalt phthalocyanine," physica status solidi (a), vol. 139, pp. 129-138, 1993.
[4] A. El-Bosaty, et al., "Surface Plasmon-Cobalt Phthalocyanine Sensor for NO2 gas," Egypt. J. Solids, 2006.
[5] M. Shah, Kh. S. Karimov and M H Sayyad, "Organic semiconductor nickel phthalocyanine-based photocapacitive and photoresistive detector," Semicond. Sci. Technol. , vol. 25, pp. 75014-75018, 2010.
[6] L. Li, Qingxin Tang, Hongxiang Li, Wenping Hu, Xiaodi Yang, Zhigang Shuai, Yunqi Liu, and Daoben Zhu, "Organic thin-film transistors of phthalocyanines*," Pure Appl. Chem., vol. 80, pp. 2231-2240, 2008.
[7] Y. D. Kim, Jae Pil Kim, Oh Sang Kwon ands In Hee Cho, "The synthesis and application of thermally stable dyes for ink-jet printed LCD scolor filters," Dyes and Pigments, vol. 81 pp. 45-52, 2009.
[8] F. Carpi, D. De Rossi, "Colours from electroactive polymers: Electrochromic, electroluminescent and laser devices based on organic materials," Optics Laser Technology vol. 38 2006.
[9] B. D. Bezerine, Coordination Compounds of Porphyrins and Phthalocyanines. New York: Wiley, 1981.
[10] W. Li, Yong Pu, Wenqing Fang, Jiangnan Dai, Changda Zheng, Chunlan Mo, Chuanbin Xiong, Fengyi Jiang, "Effect of high-temperature annealing on the structural and optical properties of ZnO films," Thin solid films, vol. 491, pp. 323-327, 2005.
[11] M. M. El-Nahass, Z. El-Gohary, H.S. Soliman, "Structural and optical studies of thermally evaporated CoPc thin lms," Optics Laser Technology vol. 35 pp. 523 - 531, 2003.
[12] M. M. a. S. Y. El-Nahass, "Effect of annealing temperature on the optical properties of thermally evaporated tin phthalocyanine thin films," Applied Surface Science vol. 255 pp. 1631-1636, 2008.
[13] R. Ye, Mamoru Baba, Kohji Ohta and Kazunori Suzuki, "Effects of thermal annealing on structure, morphology and electrical properties of F16CuPc/a6T heterojunction thin films," Solid-State Electronics vol. 54 pp. 710-714, 2010.
[14] Y. L. Pan, Y. J. Wu, L. B. Chen, Y. Y. Zhao, Y. Y. Shen, F. M. Li, S. Y. Shen and D. Y. Huang, "Structure and spectroscopic characterization polycrystalline vanadyl phthalocyanine (VOPc) films fabricated by vacuum deposition," Appl. Phys. A, vol. 66, pp. 569-573, 1998.
[15] G. Li, Visha Shrotriya, Yan Yao and Yang Yang, "Investigation of annealing effects and film thickness dependence of polymer solar cells based on poly(3-hexylthiophene)," J. Appl. Phys., vol. 98, pp. 043704-1, 2005.
[16] A. M. E. Raj, S. G. Victoria,V. B. Jothy, C. Ravidhas, J. Wollschlager, M. Suendorf, M. Neumann, M. Jayachandran, C. Sanjeeviraja, "XRD and XPS caharacterization of mixed valence Mn3O4 hausmannite thin films prepared by chemical spray pyrolysis technique," Applied Surface Science, vol. 256, pp. 2920-2926, 2010.
[17] M. Na and S. W. Rhee, "Electronic characterization of Al/PMMA [poly (methyl methacrylate)]/p-Si and Al/CEP (cyanoethyl pullulan)/p-Si structures," Organic Electronics, vol. 7, pp. 205-212, 2006.