OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 6, No. 7-8, July - August 2012, p. 755 - 760

Structural, optical and electrical characterization of water soluble Copper phthalocyanine based films

AMAN MAHAJAN, ANSHUL KUMAR, MANDEEP SINGH, DINESH PATHAK*, R. K. BEDI
Material Science Research Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar, India

The solution processed molecular semiconductors have attracted much attention due to their potential use for cheaper device manufacture. Among them copper phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid tetrasodium salt (CuTsPc) is an emerging material having potential applications in optoelectronic and gas sensing devices. In the present work, CuTsPc thin films were deposited by drop-cast method on glass and quartz substrate. The absorption spectra of these films show two well defined absorption bands of phthalocyanine molecule, namely, the soret (B) and Q-band. The band gaps calculated from the absorption spectra is found to be lie in 1.55-4.04 eV. X-Ray diffractogram of the films indicate their polycrystalline nature. Atomic force microscope (AFM) investigations of the films show granular grain like morphology. The current-voltage (I-V) studies of the films show the ohmic conduction within the experimental region investigated.

(Received October 10, 2011; accepted July 19, 2012)

Keywords: Thin films, Drop caste technique, Solar energy, Organic electronics, Semiconductors

1. Introduction

Organic semiconductors are extensively studied for their applications in optical and electrical devices such as organic solar cells, organic thin film transistors and organic light emitting diode [1-3]. Phthalocyanine are small organic molecules characterized by their high symmetry, planarity, electron delocalization and are used as an active layer for electronic devices [4-6]. Metallo phthalocyanine (MPcs) are a different class of molecular semiconductor with good thermal and environmental stability, excellent molecular and electronic tunability and also high absorption coefficient [7-10]. Nowadays, the solution processed molecular semiconductors have attracted much attention due to their potential use for low cost device manufacturing. Among them CuTsPc is an emerging material having structure similar to copper phthalocyanine except that polar SO_3Na group is attached to corner benzene ring which make this compound water soluble [11-12]. Recently highly efficient solar cells and gas sensors have been fabricated by using CuTsPc molecule [13]. It has been reported that sulphonated metal phthalocyanine has got enhanced solubility and mobility (1.08 $cm^2v^{-1}s^{-1}$) compared to their non-sulphonated counterpart [14]. In contrast to most solution processed molecular semiconductors, CuTsPc can be deposited from aqueous solution, which simplifies the device fabrication process and makes it potentially more economically as well as ecologically attractive. CuTsPc has also demonstrated potential for more general applications in organic electronics, with new thin film structures being produced for electrode modification as well as template porous and composite structures [15-17]. The electrical, optical, structural and surface morphological studies of several phthalocyanine thin films have been investigated in recent years [18-21], however literature on CuTsPc materials is still scant. In the present work, our particular aspect relates to improving material characterization by determining basic electrical and optical quantities and investigating their dependence on film preparation conditions, structure and morphology. The structural, optical and electrical properties of CuTsPc films prepared by drop cast method are presented in this communication.

2. Experimental

The sulphonated copper phthalocyanine was obtained from Sigma (Aldrich, 85%) and used without further purification. Its molecular structure is shown in Fig 1. Before starting the deposition glass and quartz substrate were cleaned in ultrasonic bath for 10 minute using acetone, followed by rinsing in distilled water. Solution was prepared using deionised water and basic solution (0.1M NH_3, ph11) with the CuTsPc concentration ranging from 5 to 20 mg per ml. The solution was stirred for 24 h at 50^0C and then filtered (0.2 **μ**m filter) before being drop cast in air at ambient conditions. The films were dried for 30 minute in air at room temperature, followed by heating for 15 min at 100^0C under an inert atmosphere to remove any remaining water and ammonia. The structural properties of CuTsPc films were investigated by means of XRD scan taken using CuK_α (wavelength =1.5405 Å) by Bruker diffractometer. The optical studies were carried out on CuTsPc films grown on glass and quartz substrate using absorption data. The absorption spectra of CuTsPc films deposited on glass substrate were measured in the wavelength range 200-800 nm using UV-VIS-160A (Shimadzu) spectrophotometer. The surface morphology of CuTsPc films was studied by atomic force microscope (Nanosurf AFM). The electrical measurements are performed by using a programmable Keithley electrometer (6517A).

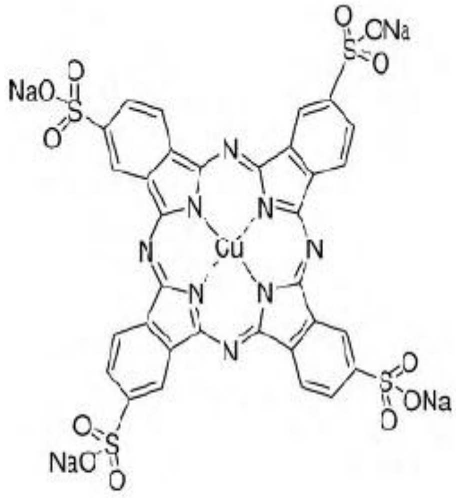

Fig. 1. The chemical structure of sulphonated copper-phthalocyanine (CuTsPc).

3. Results and discussion

3.1 Structural properties

XRD spectra of CuTsPc thin films deposited on glass and quartz substrate is shown in Fig. 2 and 3. CuTsPc films shows X-ray diffraction peaks at diffraction angle 2θ = 4.66^0 and 6.98^0 which is typical feature of α- phase [8]. The most commonly observed phases for CuTsPc are known as alpha and beta polymorphs. The Beta phase commonly arises at high processing temperature. It is important to note here that highly crystalline CuTsPc films are obtained by low cost drop cast method. XRD data of CuTsPc also reveal a higher crystallinity for sample grown on quartz as compared to glass, indicating better crystal perfection of former [22]. The crystallite size is calculated using Scherrer's equation [23]

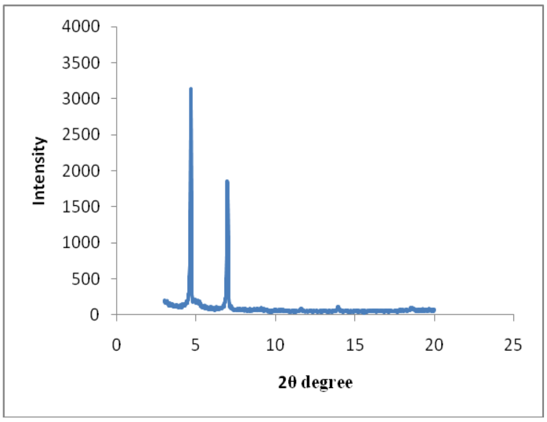

Fig. 2. X-ray diffraction spectra of CuTsPc film deposited on glass substrates.

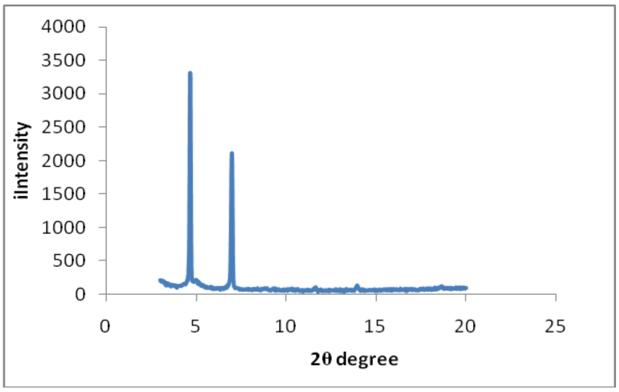

Fig. 3. X-ray diffraction spectra of CuTsPc film deposited on quartz substrates

$$D = k\lambda / \beta\cos\theta \qquad (1)$$

where k is the shape factor of the crystallite which give information about the roundness of the particle [24], λ is the wave length of the X-Rays, β is the full width half maximum (FWHM) in radians, θ is the Brag angle. Shape factor is given by

$$K=4\pi.(\text{area})/(\text{perimeter})^2 \qquad (2)$$

Which is 1 for spherical crystallites and less for others [24]. Depending upon the shape of the crystallites in CuTsPc film deposited on quartz and glass substrate, shape factor is calculated around k= 0.9 and used to determine the crystallite size**.** The crystallite size for samples on quartz and glass is found to be about 110.17 nm and 106.3 nm. The crystallite size of films deposited on glass substrate appears to be somewhat lower than that of films deposited on quartz substrate. This may be due to less strained films grown on quartz substrate as compared to films grown on glass substrate [24].

The surface morphology of CuTsPc films on the glass and quartz substrate was studied using digital multimode operated AFM in tapping mode. AFM investigations of films reveals that films were smooth, dense and have crack free morphology. Fig. 4 and 5 shows 2D and 3D structure of (50×50) **μ**m images of 500 nm thick sample. Investigations point out better uniformity of CuTsPc films on quartz substrate as compared to those of grown on the glass substrate. The surface morphology shows a roughness of about 397.32 nm on quartz which is comparatively more than that of film deposited on glass substrate which shows a roughness of about 289.87 nm. The evolution of rough CuTsPC surfaces on quartz as compared with films grown on glass can be explained by considering the smooth surfaces of quartz having roughness of 10 nm in comparison to glass having roughness of 110 nm which results in better crystallinity and hence more roughness [22].

It has also been pointed out that average grain size of film deposited on quartz substrate was 10 μm which is more than that of film deposited on glass substrate, which was about 8 μm as observed from AFM investigations. It was found that grain was more uniformly and densely distributed over the entire surface of the sample grown on quartz as compared with those of grown on glass. Most of the grains of the sample were found to be of agglomerated rods like shape. The samples show an improvement in crystallinity on quartz substrate as compared to glass. The line profile charts (Figs. 4 and 5) shows continuous roughness results for the selected profiles.

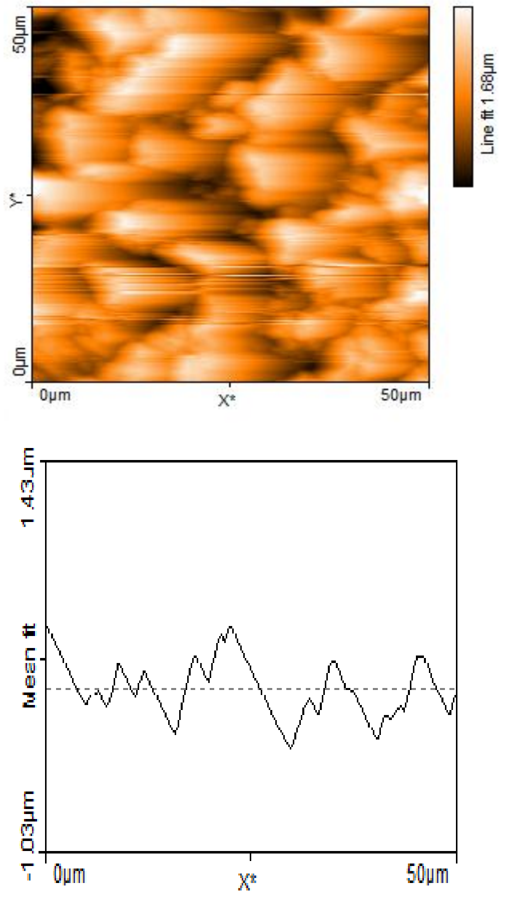

Fig. 4. (a) AFM image and the line profile graph of the CuTsPc films deposited on quartz substrate.

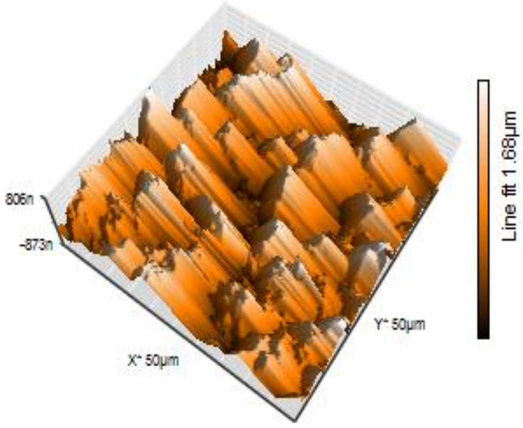

Fig. 4. (b) Three dimensional image of the CuTsPc films deposited on quartz substrate.

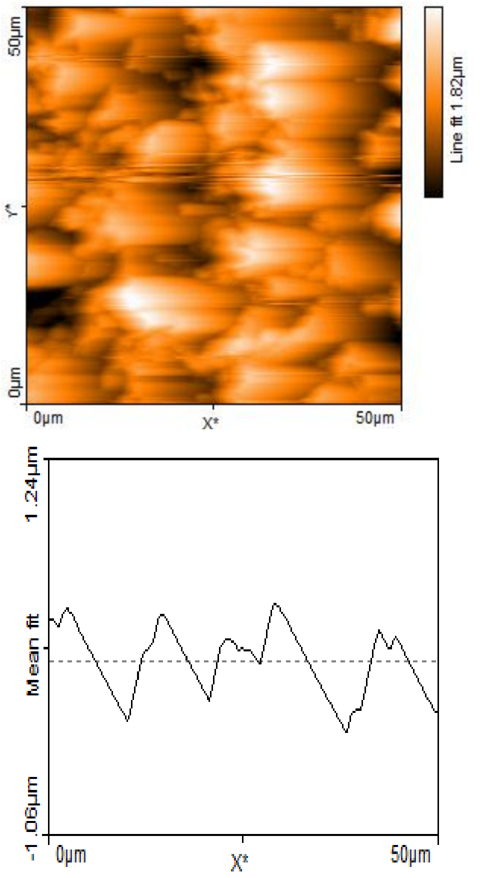

Fig. 5. (a) AFM image and the line profile graph of the CuTsPc films deposited on glass substrate.

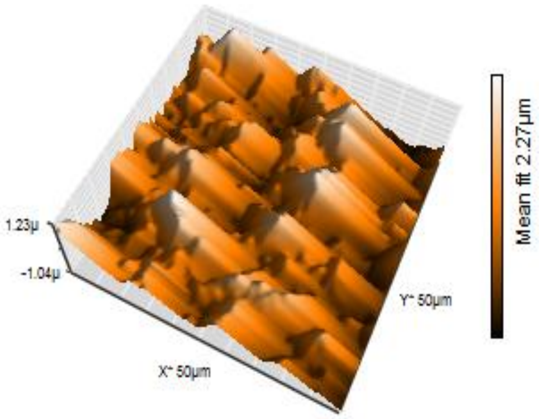

Fig. 5. (b) Three dimensional image of the CuTsPc films deposited on glass substrate.

3.2 Optical studies

Fig. 6 shows UV-VIS absorption spectra of CuTsPc film deposited on glass and quartz substrate. There are two absorption peaks 341 nm and 612 nm for films grown on quartz and at 295 nm and 606 nm for glass deposited films. The peaks at 606 and 612 nm correspond to the π to π^* transition centered on the macro cycle of CuTsPc molecules, which are Q bands of the dimer and monomer of Pc molecules, whereas the absorption peaks at 341 nm and 295 nm corresponds to the Soret Band of the phthalocyanine ring [25]. Band gap has been calculated using the equation of Bardeen et. al [29].

$$(\alpha h\nu)^2 = A\,(h\nu - E_g) \qquad (3)$$

where Eg is the optical band gap, A is constant and ν is the frequency of the incident light. The extra-polation to the linear portion $\alpha h\nu = 0$ gives the optical band gap 1.55 and 3.88 eV for films grown on glass and 1.7 and 4.04 eV for films grown on quartz substrates, respectively. The linear portion of plot near the absorption edge is due to the semiconducting behavior of the materials. The increase in the optical band gap and decrease in optical absorbance for CuTsPc films on quartz substrate as compared to those deposited on glass may be attributed to the fact that they exhibit large grain size and show more ordered structure, which give comparatively less contribution to the absorption [22]. These results are good in agreement with those reported for other phthalocyanine based materials [27-29].

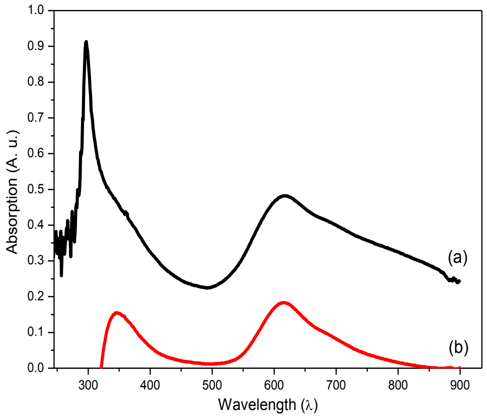

Fig. 6. The UV-absorption spectra for CuTsPc film deposited on (a) glass and (b) quartz substrate.

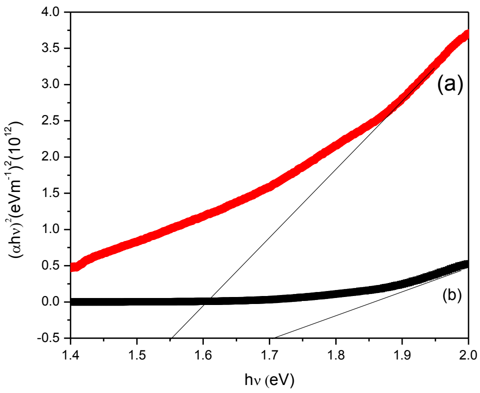

Fig. 7. (a) variation of $(\alpha h\nu)^2$ vs Energy for CuTsPc film deposited on (a) glass and (b) quartz substrate.

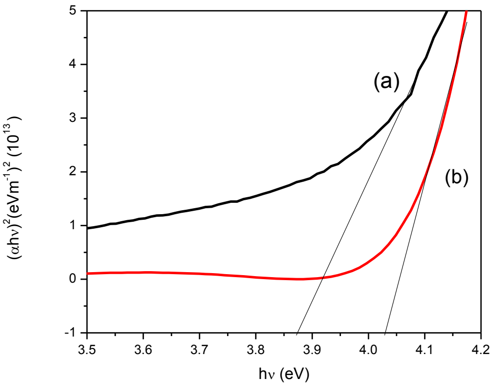

Fig. 7. (b) variation of $(\alpha h\nu)^2$ vs Energy for CuTsPc film deposited on (a) glass and (b) quartz substrate.

The extinction coefficient (k) is calculated using the equation

$$k = \alpha\,\lambda / 4\pi \qquad (4)$$

where α is the absorption coefficient and λ is the wavelength. The variation in refractive index (n) is observed using the equation

$$n = (1 + (1 - T^2)^{1/2})/2T \qquad (5)$$

where T is the transmittance. Fig. 8 shows the variation of refractive index n and the extinction coefficient k with the photon energy hν for the CuTsPc films grown on the glass and the quartz substrate. The value of k and n lies in the range 3.12 to 7.09 and 2.99 to 5.88 for films grown on glass and 1.08 to 2.80 and 1.2 to 2.67 for films grown on quartz substrates, respectively. This data show that the CuTsPc films can be potentially used for harnessing solar energy.

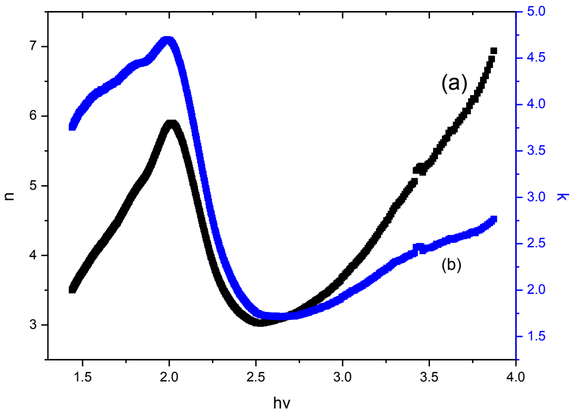

Fig. 8. (a) Dependence of refractive index n and extinction coefficient k on the photon energy hν (eV) for the CuTsPc films deposited on the glass substrate.

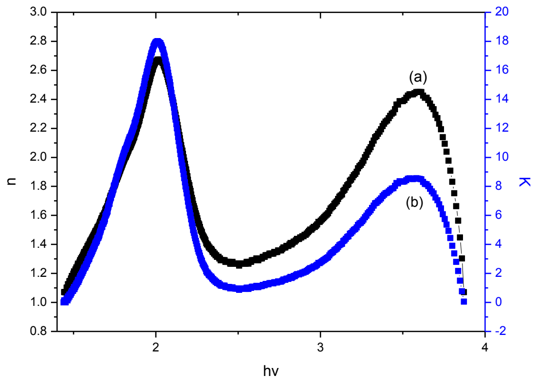

Fig. 8. (b) Dependence of refractive index n and extinction coefficient k with the photon energy hv (eV) for the CuTsPc films deposited on the quartz substrate.

3.4 Electrical studies

The current-voltage (I-V) studies CuTsPc films have been made and variation are found to be linear, which indicate the ohmic conduction in these films. Arrhenius plot of electrical conductivity of CuTsPc films on quartz and glass substrates are shown in Fig. 9. It has been observed that electrical conductivity of the films increases with increase in absolute temperature within the experimental temperature range investigated. Such dependence indicates semiconducting behavior of the films. The activation energy was obtained using the relation

$$\sigma = \sigma_0 \exp(-E_a / KT) \qquad (6)$$

where E_a is the activation energy for conduction, σ_0 is constant, K is Boltzman constant and T is the absolute temperature. The activation energy for conduction corresponding to the slope of $\ln(\sigma)=f(10^3/T)$ is found to be 0.0088 eV and 0.0090 eV for the sample grown on glass and quartz substrate, respectively.

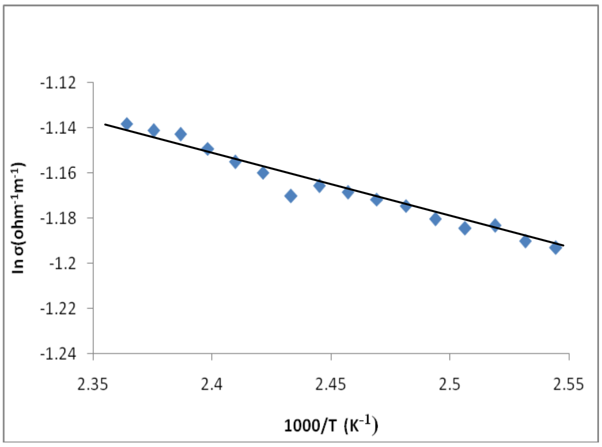

Fig. 9. (a) Plot of In σ vs 1000/T for CuTsPc thin films deposited on glass substrate.

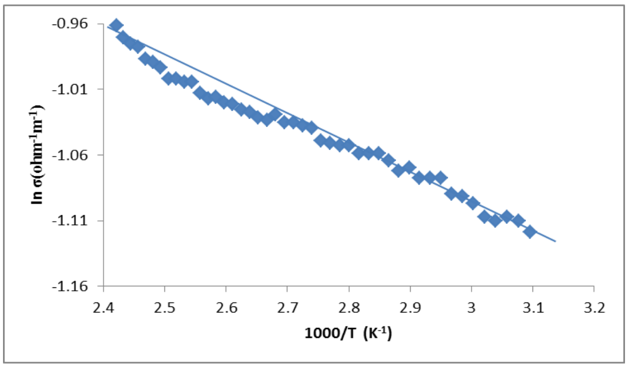

Fig. 9. (b) Plot of In σ vs 1000/T for CuTsPc thin films deposited on quartz substrate.

4. Conclusions

The structural, optical and electrical properties of CuTsPc thin films grown by drop cast method have been investigated. XRD measurements suggest the growth of CuTsPc films are of polycrystalline nature. The optical measurements show that band gap of the films lies in the range 1.5 and 4.05. Electrical studied have shown the semiconducting behavior of films with activation energy 0.0088 eV for films grown on glass and 0.0090 eV for films grown on quartz substrate. The properties are found to be influences by the choice of substrate. The present study suggests that highly crystalline CuTsPc films can be processed by drop caste method at low temperature.

References

[1] S. R. Forrest, Nature **428**, 911 (2004).
[2] K. Xiao, Y. Liu, G. Yu, D. Zhu, Appl. Phys. A **77**, 367 (2003).
[3] Sukhwinder Singh Brar, A. Mahajan, R. K. Bedi, Optoelectron. Adv. Mater. –Rapid Commun. **5**(8), 815 (2011).
[4] K. Kudo, D. X. Wang, M. Lizuka, S. Kuriyoshi, K. Tanaka, Synth. Met. **111**, 11 (2002).
[5] Mutabar Shah, M. H. Sayyad, K. S. Karimov, Journal of Semiconductors **32**, 4 (2011).
[6] N. R. Amstrong, J. Porphyrins Phthalocyanine **4**, 417 (2000).
[7] R. D. Gould, Coord. Chem. Rev. **156**, 217 (1996).
[8] S. Schumann, R. A. Hatton, T. S. Jones, The Journal of Physical Chemistry **115**, 4916 (2011).
[9] C. G. Claesssens, U. Hahn, T. Torres, Chem. Rec. **8**, 75 (2008).
[10] A. W. Hain, Z. Liang, M. A. Woodhouse, B. A. Gregg. Chem. Rev. **110**, 6689 (2010).
[11] A. Kumar, A. Singh, A. K. Debnath, S. Samanta, D. K. Aswal, S. K. Gupta, J. V. Yakhmi, Talenta **82**, 1485 (2010).

[12] K. Kato, N. Watanabe, S. Katagiri, K. Shinbo, F. Kaneko, J. Locklin, A. Baba, R. C. Advincula, Jpn. J. Appl. Phys **43**, 2311 (2004).
[13] Xinze Luo, Lin Xu, Binbing Xu, Fengyan Li, Applied Surface Science **257**, 6908 (2011).
[14] G. Chaidogiannos, F. Petraki, N. Glezos, S. Nespurek, Appl. Phys. A **96**, 763 (2009).
[15] R. A. Hatton, N. P. Banchard, V. Stolojan, A. J. Miller, S.R.P. Silva, Langmuir **23**, 6424 (2007).
[16] S. Berhanus, F. Tariq, T. Jones, D. W. McComb, J. Mater Chem. **20**, 8005 (2010).
[17] M. A. McLchlan, D. W. McComb, S. Berhanu, T. S. Jones, J. Mater. Chem. **17**, 3773 (2007).
[18] Himani Gupta, Aman Mahajan, R. K. Bedi, Indian Journal of Pure and Applied Physics **46**, 435 (2008).
[19] O. P. Laseentha, C. S. Menon, J. Matter Sci. Mater Electron **19**, 602 (2008).
[20] Himani Gupta, R. K. Bedi, Aman Mahajan, J. Appl. Phys. **102**, 073502 (2007).
[21] A. O. Abu-Hilal, M. Saleh, R. D. Gould, Mater. Chem. Phys. **94**, 165 (2005).
[22] Dinesh Pathak, R. K. Bedi, Davinder Kaur, Journal of Korean Physical Society **56**, 836 (2010).
[23] L. S. Birks, J. Fried, J. Appl. Phys. **16**, 687 (1946).
[24] D. Pathak, R. K. Bedi, D. Kaur, Optoelectron. Adv. Mater.-Rapid Commun. **4**(5), 657 (2010).
[25] H. Ding, X. Zhang, M. K. Ram, C. Nicolini, J. Colloid and Interface Science **290**, 166 (2005).
[26] J. Bardeen, F. J. Blatt, L. H. Hall, R. Breckenridge, B. Russell, T. Hahn (eds.) Proc. Photoconductivity Conf. (Willey New York), (1956).
[27] R. A. Collins, A. Krier, A. K. Abass, Thin Solid Films **229**, 113 (1993).
[28] G. Kumar, J. Thomas, N. Gearege, P. Radkaharishnann, Phys. Chem. Glass **41**, 89 (2006).
[29] M. M. El-Nahass, Z. El-Gohary, H. S. Soliman, Opt. Laser Technol. **35**, 523 (2003).

---

[*] Corresponding author: dineshpathak80@gmail.com