JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 15, No. 11-12, November - December 2013, p. 1417 - 1422

Temperature dependent dark current-voltage study of thionine dye doped solid state photo electrochemical cell (PEC)

S. MAITY, P. DALAPATI, N. B. MANIK*
Condensed Matter Physics Research Center, Department of Physics,Jadavpur University, Kolkata – 700032, India

Solid state electrochemical systems doped with different dyes have been studied for their optoelectronic application possibilities. In the present study we have investigated the dark current-voltage property of Thionine dye dopes PEC in a range of temperature 251-329K to estimate the trap states of the system. The dark I-V characteristics suggest two distinct regions of current separated by transition voltage – below it, the current follow Ohmic nature and above it, current conduction is Space–Charge–Limited–Current (SCLC) controlled by exponentially distributed traps. The separation between conduction band (CB) edge (E_C) and equilibrium Fermi level (E_{F0}) for different bias voltages (below transition voltage) have been calculated from the Ohmic region for bias voltages of 0.6, 1.0, 1.5 and 2.0 Volts and a upward shifting of E_{F0} is found with increasing applied voltages. Values of the product of mobility and effective density of states at CB ($\mu_0 N_C$) have also been estimated for the said applied biases. From the slops of Current-voltage characteristics in SCLC region for different temperatures we have estimated characteristic energies for trap distribution at different temperatures. Results show that at low temperature trap density changes sharply with energy than that at high temperature.

(Received November 13, 2012; accepted November 7, 2013)

Keywords: Temperature dependent Dark I-V; Thionine dye doped PEC; Band gap energy; Exponentially distributed traps;

1. Introduction

Recently different organic materials are being studied widely to develop organic photovoltaic devices [1-5]. These devices may be fabricated over a large area on flexible substrate from solution of organic materials by simple processing techniques, such as sol-gel, spin coating, solvent casting, sublimation, dip coating etc [6-8]. The materials used in these devices have some advantages of relatively excellent film forming properties. Suitable doping can vary the electrical and optical properties.

Organic molecules such as dye have tremendous possibilities in photovoltaic studies [9-12]. They can be used as photosensitive element as well [13, 14]. Different dyes are available with different band gap and can be used to respond with various frequency bands of sunlight. Our earlier studies on such dye doped systems showed some unusual nature in their electrical and optical measurements, which was attributed to the disorder nature of the systems [11, 13, 14]. Particularly for dark current–voltage results, the non exponential natures have been found; which is the indication of the presence of traps in the system. For each case we got two distinct regions of current, above and below a transition voltage. It has been found to be the best technique for the estimation of the approximate band gap and probable traps of solid state semi-conducting inorganic thin films by the measurement of I-V in a wide range of temperature [15]. Different diode parameters like, ideality factor, temperature coefficient of forward voltage i.e. K co-efficient, zero bias barrier height, reverse breakdown voltage etc. can also be measured from temperature dependent I-V characteristics [16-20]. In the present study we have investigated the probable charge transport process and also estimated the traps by temperature dependent dark I-V study of Thionine dye doped solid state PEC in the temperature range 251K-329K. In this work the PEC contains a blend of Thionine dye dispersed in transparent Polyvinyl Alcohol (PVA) and Polyethylene Oxide (PEO) complexes with Lithium perchlorate ($LiClO_4$), Ethylene Carbonate (EC) and Propylene Carbonate (PC). Thionine dye is used as an optically active material; where as PVA acts as an inert polymer binder. $LiClO_4$ is mixed with polymer matrix PEO to form the solid state ionic conductor. To enhance the mobility of the charge carriers EC and PC has been used as plasticizers [11]. A solid film of this blend is then sandwiched between two electrodes. Normally one electrode is transparent (usually ITO coated glass plate) and the other is Alluminium.

2. Experimental

2.1 Sample and cell preparation

In a test tube, 1 g of Polyvinyl Alcohol (PVA) was mixed with 15 cc of distilled water, then is warmed gently and stirred to make a transparent viscous solution of PVA. Thionine dye (2mg) was mixed with this solution. A solid electrolyte was prepared in another beaker by mixing Polyethylene Oxide (PEO), Lithium perchlorate ($LiClO_4$), Ethylene Carbonate (EC), and Propylene Carbonate (PC) in the ratio of 60 mg: 14.12 mg: 38 mg: 30 mg. The mixture is stirred for 5 hrs. This gel like solid electrolyte is now mixed with the previously prepared solution of PVA and the dye to form a blend. This blend is stirred properly to mix well.

This viscous gel solution then is spin coated on Indium Tin Oxide (ITO) coated glass plate at 1200 rpm and is sandwiched by placing another Al electrode on the spin coated film. The device structure is shown in Figure 1 along with structure of the dye. Two plates act as the two contact electrodes. Two electrical leads are then taken out of the two ends of the electrodes**.** The complete cells were vacuum dried for 6 hours before using them for characterization.

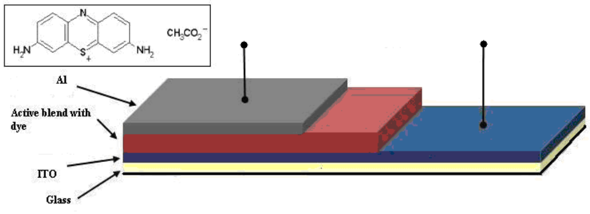

Fig. 1. Active blend of dye mixed electrolyte is spin coated to get a thin film and sandwiched between two electrodes ITO and Al.

2.2.Measurements

The current-voltage characteristics of the cell were measured in the temperature range 251K – 329 K in the dark by using a cryostat, designed and made in our laboratory; which was evacuated to a pressure of 10^{-4} Torr by using a high vacuum pumping unit (Model No. PU-2 CH-8, manufactured by Vacuum Products & Consultants). Temperature measurements were performed by a K-type thermocouple (Cromel-Allamel) with an accuracy of ± 0.15 K. The I – V measurements were performed by a Keithley 2000 multimeter and a Keithley 2400 source meter.

3. Results and discussion

The value of current upon application of a bias voltage under dark on different temperature is presented in Figure 2. The non exponential nature of the curve indicates the presence of traps. To analyze the charge transport process the I-V curve is redrawn in Logarithmic scale and presented in Figure 3.

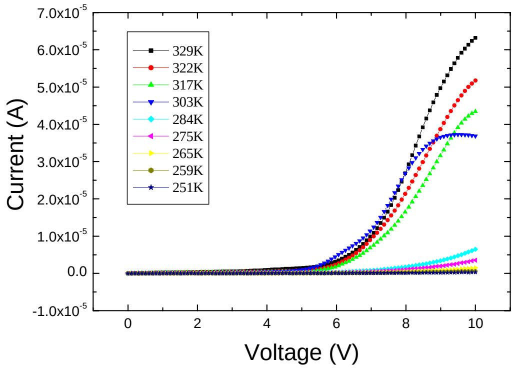

Fig. 2. Typical dark current voltage curve for the PEC cell with Thionine dye of structure ITO/PVA+Thionine+PEO+LiClO$_4$+EC+PC/Al in the temperature range 251 – 329 K.

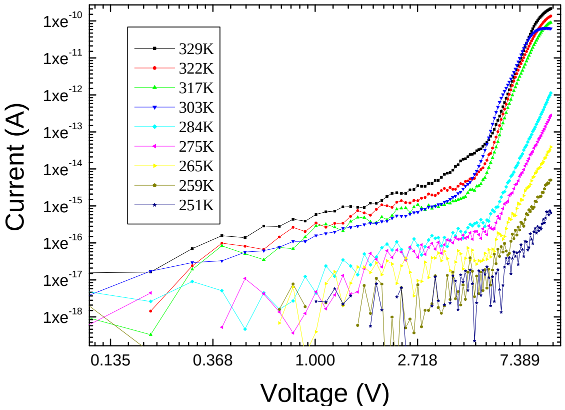

Fig. 3. Logarithmic plot of Fig. 2. Slopes of every curve are different about a particular voltage called transition voltage.

There are two distinct regions for every temperature about a particular voltage called threshold or transition voltage. The Table below shows the values for threshold voltages, exponents for two regions with varying temperatures.

Table 1. Data extracted from log-log plot of dark I-V.

Temperature (K)	Transition voltages (volt)	Exponent below Transition voltage	Exponent above Transition voltage
251	2.196	0.72	3.37
259	3.096	0.29	4.14
265	2.524	0.54	4.75
275	2.544	0.90	5.46
284	3.059	078	5.85
303	1.326	0.77	6.28
317	2.420	0.64	7.06
322	1.470	0.90	6.94
329	2.178	0.95	7.27

Exponents below the transition voltage can be approximately taken as 1, which is an indication of Ohmic conduction below the transition voltages. For Ohmic conduction the current density j can be written as

$$j = qn_0\mu V / d$$

Where q is the electronic charge, n_0 is the concentration of the thermally generated free electrons in the conduction band (CB) at thermal equilibrium, μ is the electron mobility, V is applied voltage, d is the thickness of the film.

The concentration n_0 can be written as

$$n_0 = N_c e^{-(E_c - E_{F_0})/kT}$$

N_c is the effective density of states in CB, $E_C - E_{F0}$ is the separation of equilibrium Fermi level from CB edge, k is Boltzmann constant and T, absolute temperature.

Considering the system with some faults with fault barrier potential E_{SF}, mobility of the film may be represented as [15] $\mu = \mu_0 \exp(-E_{SF} / kT)$, μ_0 is the mobility of unfaulted system. Considering A as the area of the film current can be expressed as

$$I = jA = qA\mu_0 N_C \exp[-\frac{(E_C - E_{F0} + E_{SF})}{kT}]\frac{V}{d}$$

This equation may be considered as the complete current equation. The exponents can be calculated by the plot of *ln* (I/V) vs 1/T for any particular applied voltage. Figure 4 below show the variation of *ln* (I/V) vs 10^3/T for voltages 0.6 V, 1.0 V, 1.5 V and 2.0 V respectively. The nature of the curve can be considered as a straight line for the high temperature region (above 265 K). The slopes differ in the low temperature region (below 265 K). The straight line fitting have been done for the high temperature region. However low temperature region has been left alone in our discussion because of the limitations in experimental facility we have. But this region is important for the calculation of the fault barrier potential (E_{SF}). In the range of low temperature (LT), the electron concentration is essentially independent of temperature, and the activation energy of conductivity could be related to the activation energy of mobility, i.e., the fault barrier potential E_{SF}. But this part is beyond our scope in present discussion. In this assumption *ln* (I/V) can be written as

$$\ln(I/V) = \ln(\frac{Aq\mu_0 N_C}{d}) - \frac{E_{SF}}{10^3 k}\frac{10^3}{T}$$

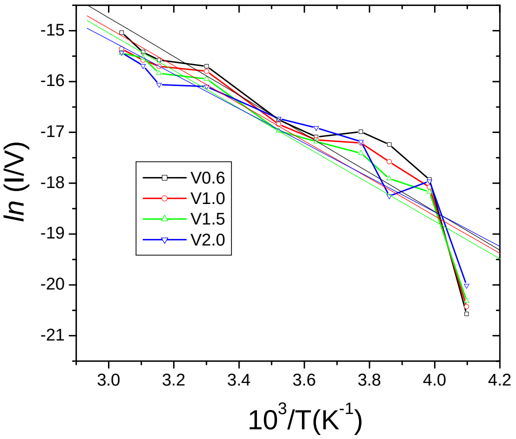

Fig. 4. Dependence of ln (I/V) on the reciprocal temperature 10^3/T at different V, for the cell. The straight lines are the fitting lines of the curves at high temperature region. Slope of the curves give $E_C - E_{F0}$ and cross-section of straight lines with vertical axis give $\mu_0 N_C$/d.

In the range of high temperature (HT), the thermal excitation of the electrons in the conduction band becomes important and *ln* (I/V) can be written as

$$\ln(I/V) = \ln(\frac{Aq\mu_0 N_C}{d}) - \frac{E_C - E_{F0}}{10^3 k}\frac{10^3}{T}$$

the slope of the straight line, in the range of HT, gives the values of $E_C - E_{F0}$ ≅ 0.33 eV, 0.32 eV, 0.31 eV and 0.29 eV for V=0.6, 1.0, 1.5 and 2.0 volt respectively, taking $10^3 k = 8.652 \times 10^{-2} eV$. The decreasing value of $E_C - E_{F0}$ with increasing V suggests a considerable amount of upward shift of equilibrium Fermi level.

In accordance with the above equation if we extrapolate the straight lines in HT range, the point of intersection with *ln* (I/V) axis will give value of first part of the equation. From this value the product $\mu_0 N_C$ was obtained for A=1 cm^2 and for constant ‘d’ with values $3.626\times10^{16}\times$d C^{-1}m^{-1} for 0.6 volt, $2.939\times10^{16}\times$d C^{-1}m^{-1}, $2.633\times10^{16}\times$d C^{-1}m^{-1} and $2.200\times10^{16}\times$d C^{-1}m^{-1} corresponding to 1.0, 1.5 and 2.0 volt respectively. The exact reason behind the decreasing characteristics of the product is not clear to us; however, it may be due to change of either of μ_0, N_C or both of them with change of applied bias.

The decreasing nature of $E_C - E_{F0}$ and the product ($\mu_0 N_C$/d) with increasing applied voltage is shown in Figs. 5 and 6 respectively.

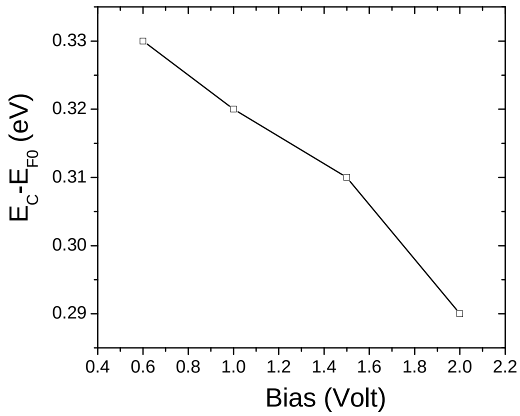

Fig. 5. Decreasing nature of $E_C - E_{F0}$ with four different applied bias voltages.

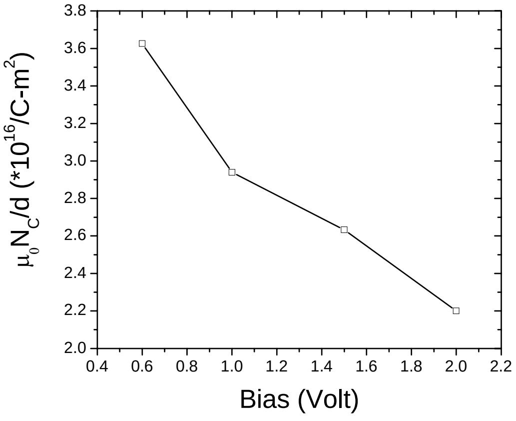

Fig. 6. Decreasing nature of $\mu_0 N_C$/d with four different applied bias voltages.

For applied voltages greater than the transition voltages slopes of *ln*I vs *ln*V characteristics, as in Figure 3, are in the range of 3.37 to 7.27. In current-voltage characteristics, slopes with value greater than 2 indicate the Space-Charge-Limited-Current controlled by exponentially distributed trap levels. According to Lampert [21], such type of current conduction with exponentially distributed traps the current density can be written as

$$j_{SCLC} = q\mu N_C (\frac{\varepsilon}{qN_t})^m \frac{V^{m+1}}{d^{2m+1}}$$

Where, in addition to the symbols defined before, ε is the electrical permittivity of the material of the film, N_t represents the total density of trapping levels in the exponential distribution and m is the ratio of temperature parameter T_C and experimental temperature T.

The exponential trap distribution may be described in terms of T_C as:

$$N(E) = \frac{N_t}{kT_C} \exp(-\frac{E}{kT_C}) = N_0 \exp(-\frac{E}{kT_C})$$

Where N(E) is the trap density per unit energy range at an energy E below the CB edge and N_0 is the value of N(E), i.e., the density of trapping levels per unit energy at CB. The extracted data from the Figure 3, which are listed in Table1, suggest that the values of m increases as the experimental temperature increases. For every value of m, the temperature parameters T_C (in K) as well as the product kT_C (in eV), may be called as characteristic energy of the trap distribution, have been calculated. The values are 0.051, 0.07, 0.086, 0.106, 0.119, 0.138, 0.166, 0.165, and 0.178 eV corresponding to the temperatures 251, 259, 265, 275, 284, 303, 317, 322, and 329 K respectively. The increasing nature of characteristic energy with temperature is shown in Fig. 7; and it indicates the fact that, as temperature increases the trap distribution changes its shape. The variation of distribution function $N(E) = N_0 \exp(-\frac{E}{kT_C})$ with E for the calculated values of kT_C (i.e., for different temperature) is drawn in Figure 8 below, for $N_0 = 10^{20}$ ev^{-1}.

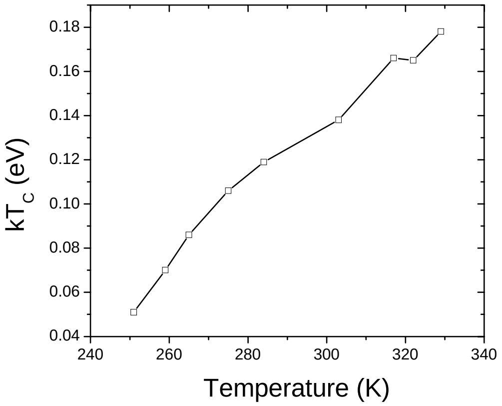

Fig. 7. Temperature (T) vs kT_C curve, showing proportional nature. It indicates the fact that as temperature increases the electrons of deep traps dominates in the current.

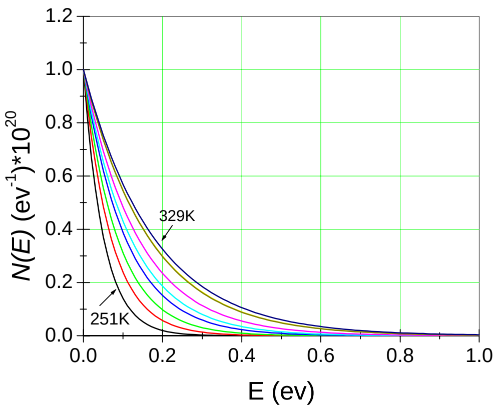

Fig. 8. Representation of variation of N(E) with E for different temperature. As temperature decreases the curve decayed more sharply compared to high temperature.

So it can be concluded that at temperature 251K the trap density per unit energy at the energy 0.051 ev is N_0/e (1/e times the value at the CB edge) and that value of N(E) can be found for temperatures 259, 265, 275, 284, 303, 317, 322, and 329 K at the energies 0.086, 0.106, 0.119, 0.138, 0.166, 0.165, and 0.178 eV respectively.

According to Lampert [22] and others [23, 24] the trapped injected carriers and the transition (crossover) voltage are proportional to kT_C by the relations

$$n_t = kT_C N_0 \exp(\frac{F - E_C}{kT_C}) \text{ and}$$

$$V_t = ekT_C \frac{d^2}{\varepsilon} N_0 \exp(\frac{F - E_C}{kT_C}) \text{ respectively.}$$

These two relations suggest the possible variation trapped injected carriers as well as current contributed by it and the transition voltage with temperature. We have found some variations in transition voltage in our experimental results, but these are not in agreement with the above equation. It may be the future scope of the work and presently left for future study.

In Fig. 9 the schematic picture of energy level diagram of the cell for both low and high voltage region is presented.

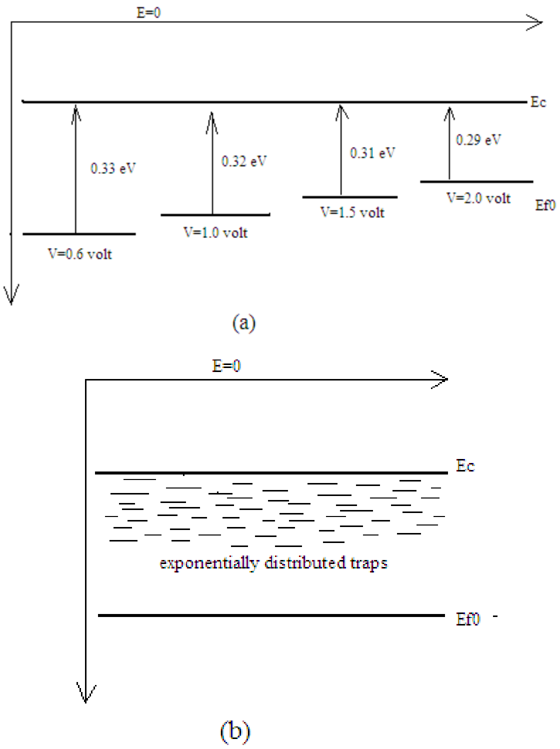

Fig. 9. Schematic representation of energy diagram (a) below and (b) above transition voltage; (a) represent the upward shifting of E_{F0} with increasing applied voltage, (b) shows the trap levels (of exponentially distribution) with few calculated values of characteristic energy (in eV).

4. Conclusion

Using the measurement of I-V characteristics for different temperatures in the range of 251-329K the effect of trap states on electrical properties of Thionine dye dopes solid state PEC was investigated in the present study. In the range of low voltage applied on the film is observed to be an Ohmic conduction. The temperature dependent study shows a shift of equilibrium Fermi level towards Conduction band as applied bias increases. The same study also indicates the decrease of product ‘mobility and density of states’ as applied bias increases. In the range of high applied voltages the current conduction is Space–Charge–Limited–Current (SCLC) controlled by exponentially distributed traps placed in band gap. The analysis of current characteristics in the frame of SCLC theory offers a possibility of getting parameters characterizing trap distribution. The study also showed some expected variation in current, contributed by trapped injected charges, and transition voltage with varying experimental temperature of the device.

Acknowledgement

The authors would like to thank Defence Research and Development Organisation (DRDO), UGC and CSIR, Govt. of India for providing financial support. We are thankful to Professor A. N. Basu, Emeritus Professor of Department of Physics, Jadavpur University for his valuable suggestions to analyse the experimental data.

Reference

[1] C.W. Tang, Appl. Phys. Lett. **48**, 183 (1986).
[2] B. O'Regan, M. Gratzel, Narure. **335**, 737 (1991).
[3] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Synth. Metals **59**, 333 (1993).
[4] M. Gratzel, Narure. **414**, 338 (2001).
[5] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science **270**, 1789 (1995).
[6] J.C. Hummelen, B.W. Knight, F. LePeq, F. Wudl, J. Yao, C.L. Wilkins, J. Org. Chem. **60**, 532 (1995).
[7] N.S. Sariciftci, D. Braun, C. Zhang, V.I. Srdanov, A.J. Heeger, G. Stucky, F. Wudl,Appl. Phys. Lett. **62**, 585 (1993).
[8] G. Yu, K. Pakbaz, A.J. Heeger, Appl. Phys. Lett. **64**, 3422 (1994).
[9] A. Haldar, S. Maity, N. B. Manik Ionics **14**(3) 263 (2008).
[10] A. Haldar, S. Maity, N. B. Manik Ionics **14**(5), 427 (2008).
[11] S. Maity, A. Haldar, N. B. Manik Ionics **14**(6), 549 (2008).
[12] A. Haldar, S. Maity, N. B. Manik Ionics **15(**1), 79 (2009).
[13] S. K. Dey, N.B. Manik, S. Bhattacharya, A. N. Basu; Syn. Met.; **18**, 19 (2001).
[14] S. K. Dey, Md. R. Islam, N.B. Manik, A. N. Basu; J. Mat. Sci.; **38**, 93 (2003).
[15] S. Antohe, L. Ion, V. A. Antohe; J. Optoelectron. Adv. Mater. **5**(4), 801 (2003).
[16] Rajinder Sharma, Journal of Electron Devices, **8,** 286 (2010).
[17] M. Ravinandan, P. Koteswara Rao, V. Rajagopal Reddy, J. Optoelectron. Adv. Mater. **10**(10), 2787 (2008).
[18] R Singh, S K Arora, Renu Tyagi, S K Agarwal, D Kanjilal; Bull. Mater. Sci., **23**(6) 471 (2000).
[19] W. Mtangi, P.J. Janse van Rensburg, M. Diale, F. D. Auret, C. Nyamhere, J.M. Nel, A. Chawanda, Materials Science and Engineering: B, **171**(1–3), 1 (2010).
[20] M.K. Hudait, S.B. Krupanidhi, Physica B **307,** 125 (2001).
[21] M. A. Lampert, P. Mark, Current Injection in Solids (Academic Press, New York, 1970) 33.
[22] M. A. Lampert, Volume-controlled current injection in insulators: Rep. Prog. Phys. **27**, 329 (1964), doi:10.1088/0034-4885/27/1/307.
[23] S. Antohe, L. Ion, V. Ruxandra; J. of Appl. Phys. **90(**12), 5928 (2001).
[24] L. Ion, S. Antohe, M. Popescu, F. Scarlat, F. Ionescu; J. Optoelectron. Adv. Mater. **6(**1), 113 (2004).

---

[*] Corresponding author: nbm_juphysics@yahoo.co.in