J MATER SCI **41** (2006) 2417–2421

Electrical properties of Schottky diodes based on Carbazole

SREEJITH K. PISHARADY*, C. S. MENON, C. SUDARSHANAKUMAR
School of Pure and Applied Physics, Mahatma Gandhi University, Priyadarshini Hills, Kottayam (Dits), 686 560, Kerala
E-mail: skpishar@Yahoo.co.in

Sandwich structures of Carbazole thin films have been prepared by using vacuum deposition technique. The plot of current density versus voltage (*J–V* characteristics) shows two distinct regions. In the lower voltage region ohmic conduction and in the higher voltage region space charge limited conduction (SCLC) is observed. Number of states in the valence band (*Nv*) is calculated from the temperature dependence of *J* in the ohmic region. From the temperature dependence of *J* in the SCLC region trap density (*Nt*) and activation energy are determined. The values of *Nv* and *Nt* are in the order 10^{23} m^{-3} and 10^{27} m^{-3} respectively. The value of activation energy is nearly equal to 0.1 eV and that of the effective mobility is 4.5×10^{-7} $\text{cm}^2\ \text{V}^{-1}\ \text{S}^{-1}$. Schottky diodes are fabricated using Aluminium (Al) as Schottky contact. It is observed that gold (Au) is more suitable for ohmic contact compared to silver (Ag). From a semi logarithmic plot of *J* versus *V*, the barrier height (ϕb), diode ideality factor (n) and saturation current density (J_0) are determined. The value of n increases and ϕb decreases on annealing.

1. Introduction

Carbazole (Cz) and its derivatives receive more attention because of their wide variety of electronic and electro optical properties together with their high hole transporting mobility [1]. The polymer forms of Cz such as Poly (Vinyl Carbazole) PVK, Poly (*N*-Vinyl Carbazole) are found to be efficient as an emitting layer in many Organic Light Emitting Diodes (OLEDs). It is also found that the performance of OLEDs can be improved by using multi layers of Cz and Cz blended with other polymers [2–4].

In this work we investigate the electrical properties of Cz and Schottky diode characteristics using Cz as an active layer for first time. Current voltage characteristics can provide information about the conduction mechanism through the film and the temperature dependent conductivity can be used to calculate a number of parameters such as trap density (*Nt*), number of states in the valence band (*Nv*) and activation energy. These parameters are very useful for understanding the semi conducting property of the material and in designing thin film devices.

The importance of Schottky diode is the speed at which they can be switched from OFF state to ON state. This speed is enabled by the fact that only the majority charge carriers control their performance. The use of Cz as an active layer provides comparable electrical and optical properties to their polymer unit and avoids the effect of shortening the polymer chain length during evaporation [5]. Here we discuss the fabrication and characteristics of Schottky diode with Al as Schottky contact. Effect of various Ohmic contacts is investigated in this work.

Thermal annealing is a standard technique used to improve the efficiency of Inorganic and Organic semiconductor devices. Liu *et al* reported that annealing at a temperature higher than glass transition temperature (Tg) before the cathode deposition improves the efficiency of hole ejection in the case of poly (2-methoxy-5- (2′-ethyl-hexyloxy)-l, 4-phenylene) MEH-PPV) light emitting diodes increases the maximum light output but lowers the quantum yield [6]. However they found that annealing after the metal deposition enhances device efficiency [7]. In this work we investigate the effect of air annealing on the Schottky diode characteristics.

2. Experimental

Natural Cz is originally procured from Aldrich chemical company (U.S.A.). Highly polished and thoroughly cleaned micro glass slides are used as substrates. The

---

*Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-5078-1

evaporation is carried in a molybdenum boat using Hind Hivac12A4 vacuum coating machine, under a base pressure of 5 × 10^{-6} Torr. Thick nesses of the films are determined by Tolansky's multiple beam interference technique [8]. For studying J-V characteristics a Cz layer is sandwiched between two Silver electrodes (Ag/Cz/Ag) structure. For fabricating Schottky diode a thin layer of thickness 60 nm is first vacuum deposited which provides necessary ohmic contact. Ohmic electrodes are first deposited because hole-blocking Al forms an oxidizing layer, which has an effect on Schottky behavior. Over this bottom electrode Cz layer of suitable thickness is deposited. The thickness of Cz layer is selected to produce effective Schottky behavior. A very thin layer produces shorting between electrodes and a thick layer has a resistance comparable to depletion resistance. Finally an Al layer of thickness 100 nm is deposited. Suitable masks are used for each deposition. The effective area for electric conduction is 0.06 cm^2. The electrical characteristics are studied using a programmable Keithley electrometer (Model No. 617). Films are annealed using specially designed furnace equipped with digital temperature controller cum recorder. Since Cz is photo conducting all the measurements are done in darkness and in a vacuum of the order of 10^{-3} Torr to avoid any possible contamination of the films.

3. Results and discussions

3.1. Electrical properties

Fig. 1 shows the *J–V* characteristics of Carbazole film of thickness 2480 Å. The graph shows two distinct regions. In the lower voltage region slope is nearly equal to unity and in the higher voltage region slope is nearly equal to two. The conduction at low voltages is by ohmic conduction and at higher voltages SCLC is dominant. Assuming a *p*-type conduction to exist in Cz, then current density is related to applied voltage under the relation [9]

$$J = e\rho_0\mu_p\frac{V}{d} \tag{1}$$

Where ρ_0 is the thermally generated holes in the valence band, μ_p is the hole mobility, e is the electronic charge and d is the thickness of the film. The concentrations of holes at thermal equilibrium is given by

$$\rho_0 = Nv\exp\left[\frac{-(Ef - Ev)}{kT}\right] \tag{2}$$

Using equations 3 equations 2 becomes,

$$J = e_0(\mu_p Nv)\frac{V}{d}\exp\left[\frac{-(Ef - Ev)}{kT}\right] \tag{3}$$

Where Nv is the effective density of states in the valence band, $(Ef - Ev)$ is the separation between valence band edge and Fermi level.

TABLE I Variation of different parameters as function of film thickness

Thickness (A^o)	μ_pNv (m^{-1} v^{-1} s^{-1}) 10^9	Nv (m^{-3}) 10^{21}	$(Ev - Ef)$ eV	Nt (m^{-3}) 10^{27}	$(Ev - Et)$ eV
1345	0.33	2.07	0.17	1.1	0.10
1821	3.6	22.09	0.15	2.4	0.10
2480	21.7	133.21	0.17	5.9	0.11

From the Equation 3 it is clear that a plot of $\ln(\frac{J}{V})$ versus$(\frac{1}{T})$ is a straight line whose slope gives $(Ef - Ev)$ and the intercept at $(\frac{1}{T}) = 0$ gives μ_pNv. A typical plot of Cz film of thickness 2480 Å with a constant biasing voltage of 10 V is shown in Fig. 2. By assuming the mobility of holes in the Cz thin film is equal to 1.63 × 10^{-6} cm^2 V^{-1} s^1 report by E.G. Thianche *et al.* [10] for PVK Nv has been calculated. The value of $(Ef - Ev)$ and the variation of μ_pNv with different thickness are listed in Table I.

The expression for current density described by the Equation 1 is true only in the case of a trap less insulator or for small applied voltages. But above a particular value

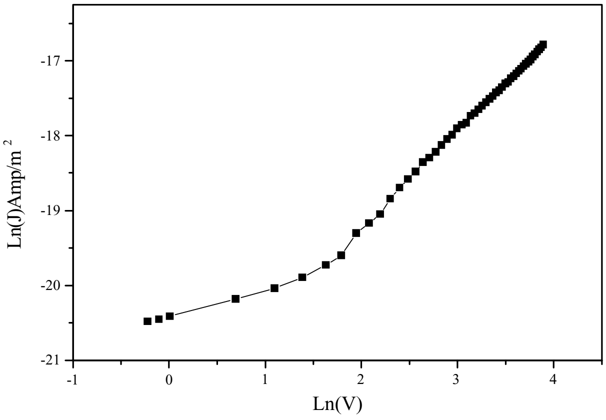


Figure 1 J–V characteristics of Carbazole thin film.

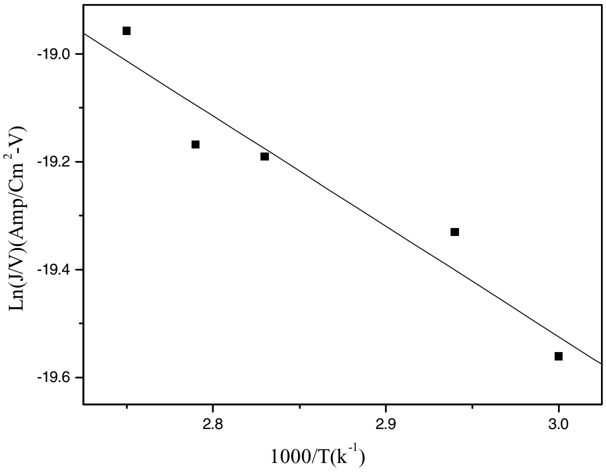


Figure 2 A plot of $\ln(\frac{J}{V})$ versus $(\frac{1000}{T})$ for Cz thin film in the ohmic range.

TABLE II Variation of different parameters with electrode

	Au-Al	Ag-Al	Ag-Ag	Zn-Al
Saturation current density $J_0 \times 10^{-9}$ (Amp/cm^2)	5.33	1.07	1.6	0.296
Diode ideality factor (n)	1.03	3.5	15.76	18.84
Barrier height $\phi\, b$(eV)	0.86	0.91	0.89	1.07

of voltage, called threshold voltage the expression for current density can be modified as [11]

$$J = \frac{9}{8}\varepsilon\mu_p\theta\left[\frac{V^2}{d^3}\right] \tag{4}$$

Where ε is the permittivity of Cz, which is equal to 4.2 × 10^{-9} F cm^{-1} [11] and θ is the ratio of free to trapped charge carriers given by,

$$\theta = \frac{Nv}{Nt}\exp\left[\frac{-(Et - Ev)}{kT}\right] \tag{5}$$

Using equations 5 equations 4 becomes,

$$J = \frac{9}{8}\varepsilon\mu_p\left[\frac{V^2}{d^3}\right]\frac{Nv}{Nt}\exp\left[\frac{-(Et - Ev)}{kT}\right] \tag{6}$$

From the above expression it is clear that a plot of $\ln(\frac{J}{V^2})$ versus $(\frac{1}{T})$ is a straight line. Such a plot for film of thickness 2480Åis as shown in Fig. 3. The value of $Et - Ev$ (activation energy for holes) is obtained from the slope and the intercept at ordinate gives the value of trap density. The activation energy and trap density for Cz film for different thickness is listed in the Table II. The total trap density calculated is of the order of 10^{26} m^{-3}. These values are comparable to the value 10^{27} m^{-3} reported by Unni and Menon for Metal free Phthalocyanine [12].

Fig. 4 shows a plot of $\ln(\frac{J}{V^2})$ versus d^{-3}. As expected from the Equation 6 the graph is a straight line. The slope of the graph gives the effective mobility $\mu_{eff} = \mu_p\theta$ [13]. The calculated value of μ_{eff} is 4.5 × 10^{-7} cm^2 V^{-1} S^{-1}. The value determined here shows a deviation nearly equal to one order of magnitude from the value reported by Thianche *et al.* for PVK [8]. This variation may be due to the fact that a large number of charge carriers get trapped themselves on their movement through the film in the SCLC region.

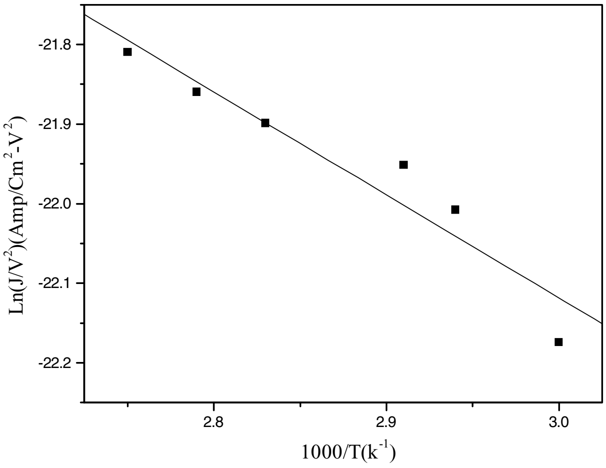


Figure 3 A plot of $\ln(\frac{J}{V^2})$ versus$(\frac{1000}{T})$ for Cz thin film in the SCLC range.

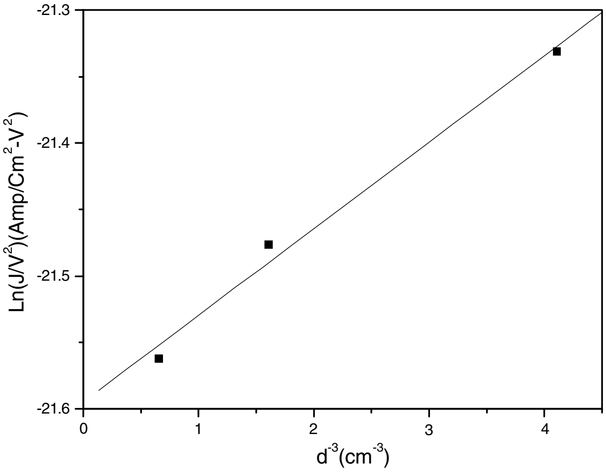
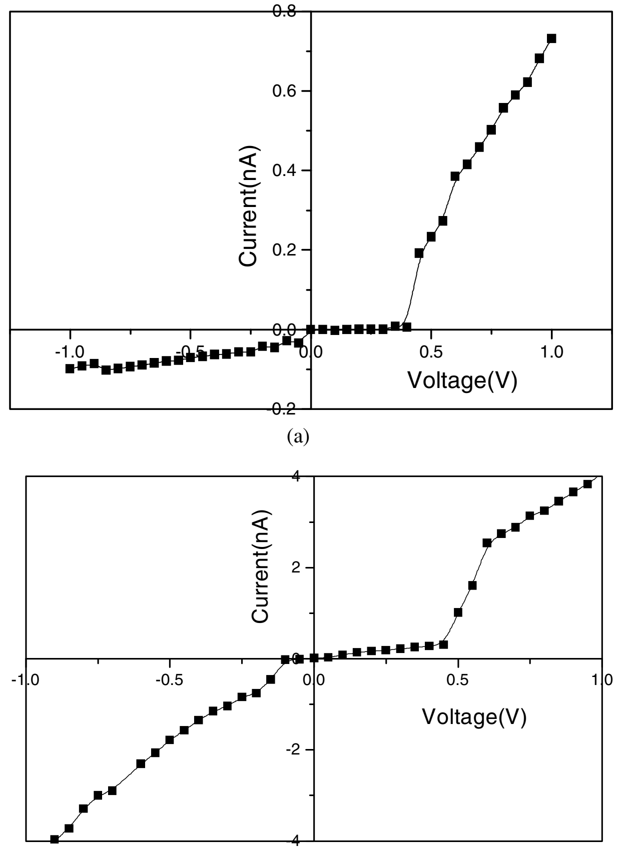


Figure 4 A plot of $\ln(\frac{J}{V^2})$ versus d^{-3}.

3.2. Schottky diode characteristics

3.2.1. Effect of various ohmic contacts

The *I–V* characteristics of a Schottky diode with Al as Schottky contact and Gold (Au) as ohmic contacts is given in Fig. 4a and Silver (Ag) as ohmic contact is given in Fig. 4b. The low work function Al (ϕAl = 4.0 eV) forms a schottky contact with Cz and high work function metals such Au (ϕAu = 5.1 eV) and (ϕAg = 4.73 eV) forms ohmic contact. In the forward a negative voltage is applied to the Al electrode. The I–V characteristics are asymmetric on both polarities and show an exponential trend. This rectifying behavior is due to the charge carriers ejected from the electrode. In both cases the current does not increase appreciably with the applied voltage up to a particular value voltage called turn on voltage (*Vt*). The value of *Vt* found is 0.45 V for Ag/Cz/Al diode and is 0.4 V voltage for Au/Cz/Al diode. The characteristics observed here are similar that of conventional Silicon based diode. Fig. 6 and 7 shows diode characteristics for Zinc/Cz/Aluminium (Zn/Cz/Al) and Ag/Cz/Ag diodes. The I–V characteristics are symmetric on both polarities and ohmic type conduction exists in these cases. The characteristics of Ag/Cz/Ag diode indicates that the observed results in Au/Cz/Al and Ag/Cz/Al is not a surface phenomenon but is due to the difference in work functions of the Al electrode and Cz. Ohmic conduction exists in Zn/Cz/Al diode due to the



(a)

(b)

Figure 5 *I–V* characteristics of (a) Au/Cz/Al diode and (b) Ag/Cz/Al diode.

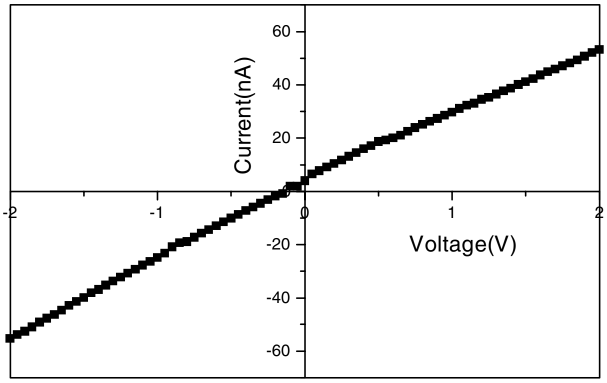


Figure 6 *I–V* characteristics of Zn/Cz/Al diode.

small difference (0.3 eV) in work function between Zn and Al electrodes.

The rectifying behavior of a schottky barrier diode is assumed to be follow a standard thermionic emission theory for conduction across the junction. Based on this theory the current voltage relationship can be expressed as [14]

$$J = J_0\left(\exp\left(\frac{qV}{nkT}\right) - 1\right) \tag{7}$$

where J is the instantaneous current density, J_0 is the saturation current density, q is the electronic charge, V is

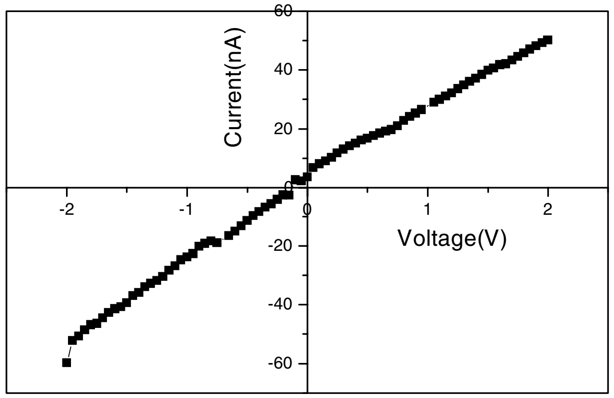


Figure 7 *I–V* characteristics of Ag/Cz/Ag diode.

the applied potential, n is a constant called diode ideality factor, k is the Boltzman constant and T the absolute temperature.

J_0 is given by

$$J_0 = A^* T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \tag{8}$$

Where ϕ_b is the junction barrier height and

$$A* = \frac{-4\pi m^* K^2}{h^3}$$

Where m^* is the effective mass of the electron; h is the Planck's constant.

Since $\frac{qV}{nkT} \gg 1$ a semi logarithmic plot of current density versus applied voltage is expected to be linear with a Y intercept corresponding to J_0. Fig. 8 shows such a plot of Au/Cz/Al diode. From the figure it is clear that a linear relationship exist for small applied voltages and for large applied voltages the graph deviates from linearity. The voltage drop across the series resistance in the natural region of the semiconductor causes this deviation. From the slope value of n is calculated. The various parame-

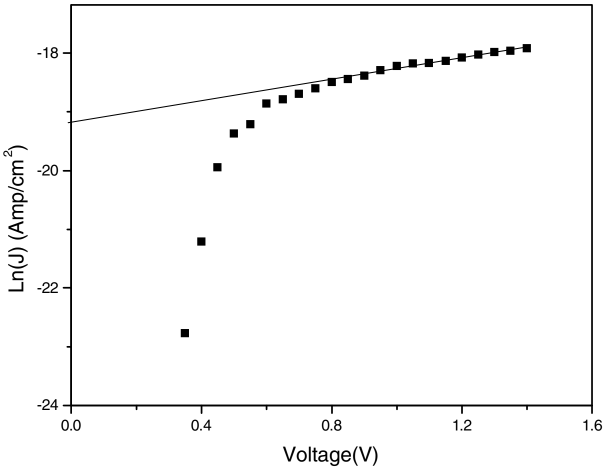


Figure 8 A semi logarithmic plot of Current density versus Applied voltage.

TABLE III Variation of different diode parameters as a function of annealing period

	As Deposited	Annealed		
		15 M	30 M	1 H
Saturation current density $J_0 \times 10^{-9}$ (Amp/Cm^2)	5.33	10	13.51	14.43
Diode ideality factor (n)	1.03	1.59	4.52	33.43
Barrier height ϕb	0.86	0.84	0.83	0.83

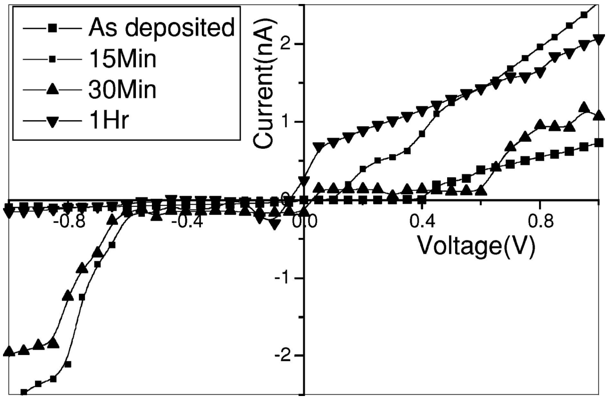


Figure 9 *I–V* characteristics of Au/Cz/Al diode annealed for different periods of time.

ters related to the above described diodes are listed in the Table II. Both Ag/Cz/Al diode Au/Cz/Al diode have rectifying nature the diode ideality factor is nearly equal to one for Au/Cz/Al diode. This indicates that Au provides good ohmic contact compared to Ag.

3.2.2. Effect of air annealing on diode characteristics

Fig. 9 Shows the *I–V* characteristics of air annealed Au/Cz/Al at a constant temperature of 75°C, for different periods of time. The values of J_0, ϕb and n for these diodes are listed in Table III. As annealing period increases barrier height decreases and ideality factor increases. This deviation in ideal rectification property is attributed to inter diffusion between Au and Cz. The reduction in barrier height is due to some surface morphological change. When a metal is deposited on to an organic layer at a higher temperature a rough metal surface is formed due to difference in thermal expansion coefficient between metal and underlying organic layer [15]. This surface roughness can induce degradation of contacts. If a proper annealing is applied before the deposition of top electrode this roughness can be minimized and get a sufficiently good contact between Cz and Al electrode [16].

4. Conclusion

In this paper the electrical properties of Cz thin film sandwiched between two Ag electrodes and the Schottky diode characteristics are investigated. The J-V characteristics show ohmic type conduction at low voltages and at high voltages conduction is SCLC. The thermally generated hole concentration is of the order 10^{21} m^{-3} and Fermi level is about 0.17 eV above the valence band. With increasing thickness charge concentration in the valence band is observed to increase. The total trap density is of the order 10^{27} m^{-3}, and activation energy is equal to 0.1 eV. The trap density also increases with thickness of the film. The value of effective mobility is 4.5×10^{-7} cm^2 V^{-1} S^{-1}. Ag and Au are found to give good ohmic contact for Cz with Al as Schottky contact. Zn/Cz/Al and Ag/Cz/Ag diodes show ohmic type conduction in both polarities. As annealing period increases diode ideality factor increases due to inter diffusion between Au and Cz atoms and barrier height decreases due to surface modifications.

References

1. J. SWORAKOWSKI and J. ULANSKI, *Annu. Rep. Prog. Chem Sect. C* **99** (2003) 87.
2. G. WANG, C. YAN, H. WU and Y. WEI, *J. Appl.Phys.* **78** (1995) 2679.
3. B. HU, Z. YANG and F. E. KRASZ, *ibid.* **76** (1994) 2419.
4. C. ZHANG, H. VON. SEGGEM, K. PAKBAZ, B. KRAABEL, H. W. SCHIMIDT and H. J. HEEGER, *Synth. Met.* **62** (1994) 35.
5. K. D. ALMEIDA, J. C. BERNEDE, S. MARSILLAC, A. GODOY and F. R. DIAZ, *Synth. Met.* **122** (2001) 127.
6. J. LIU, R. GUO and Y. YANG, *J. Appl. Phys.* **91** (2002) 1595.
8. L. I. MAISSEL and R. GLANG, "Hand Book of Thin Film Technology" (Mc Graw Hill, New York, 1983) pp. 11.
9. M. A. LAMPET, *Rep. Phys.* **27** (1964) 329.
10. E. GAUTIER-THIANCHE, C. SENTEIN, A. LORIN, C. DENIS, P. RAIMOND and J.-M. NUNZI, *J. Appl. Phys.* **83** (1998) 4236.
11. R. CLERGERAUX, I. SEGUY, P. JOLINAT, J. FARENC and P. DESTRUEL, *J. Phys. D. Appl. Phys.* **33** (2000) 1947.
12. K. N. NARAYANAN UNNI and C. S. MENON, *Indian Journal of Pure and Applied Physics.* **39**(2001) 156.
13. V. N. SAVVATEEV, M. TARABIA, H. CHAYET, E. Z. FARRAGI, G. B. CHOHEN, S. KRISTEIN, D. DAVIDO, Y. AVNY, and R. NEUMANN, *Synth. Met.* **85** (1997) 1269.
14. S. M. SZE, "Physics of Semiconductor Devices" (Eastern Wiley, New Delhi, 1981) pp 637.
15. N. BOWDEN, S. BRITTAIN, A. G. EVAS, J. W. HUTCHINSON and G. M. WHITESIDES, *Nature* **93** (1998) 146.
16. J. KIM and H. H. LEE, *J. Polym.Sci. Part-B: Polym. Phys.* **39** (2001) 1122.

Received 24 November 2003
and accepted 9 May 2005