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Electrical Conduction in Solution Grown Thin Films of the Complex of Zr(IV) with Cyclodichlorophosphazene Trimer

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Abstract

Current transport mechanism in thin films of complex of Zr(IV) with Cyclodichlorophosphazene trimer $(PNCl_2)_3$ have been studied under normal and different illuminating conditions. It is found that at low field the film exhibits ohmic behaviour and the high field region is dominated by Richardson-Schottky (RS) mechanism.

Keywords : Cyclodichlorophosphazene trimer, Richardson-Schottky, Ohmic behaviour

Introduction

Polymers have been studied extensively with a view to access their suitability for application to electronic devices (Tammula and Rymaszewski,1989). Polymers like Polyvinylidene fluoride-chloro trifluoroethylene (Mehendru *et al*., 1985), Polyimide (Ansari and Al-Marzouki, 1999) have been found attractive, in electronics and microelectronics applications because of better stability, enhanced conductivity and to exhibit a number of dielectric relaxations (Dhumure and Lokhande, 1992; Singh and Singh, 1995). Conduction in thin films can be enhanced by interaction with light (Frenkel, 1938). Recently conduction in thin films of inorganic heterocyclics like cyclohexathiazenium chloride $(S_6N_4)^{2+}Cl_2^-$, (Sharma and Upadhyay,1998), cyclodichlorophosphazene trimer $(PNCl_2)_3$ (Sharma and Kumar, 2004) and complex of Fe(II) with $(PNCl_2)_3$ have been studied (Sharma, 2005[a] , 2007). In view of this complex of $ZrOCl_2$ with $(PNCl_2)_3$ has been prepared and studied for its electrical conduction under normal and illuminating conditions with sodium and mercury light.

Materials and Methods

The complex of Zr(IV) with $(PNCl_2)_3$ having composition $[P_3N_3Cl_4ZrOCl_4]^{2-}$ was prepared by refluxing equimolar solution of $(PNCl_2)_3$ and $ZrOCl_2$ in benzene for about 24 h (Sharma, 2005b). The cream colored product settled out, collected and washed with benzene for removal of unreacted reactants if there was any. The product was dried and stored in vacuo over fused $CaCl_2$. The complex obtained has the composition $[P_3N_3Cl_4ZrOCl_4]^{2-}$ (Sharma, 2005b). The film of the complex was deposited on to an ultrasonically cleaned glass slides in benzene solution maintained at 300 K using isothermal immersion technique (Maissel, 1970). The film was vacuum dried for about 24 h to remove any residual solvent. The thickness of the film was measured by means of a mechanical stylus arrangement. A bare copper wire was placed across the film of the complex on the glass slide prior to vacuum deposition of copper electrode. After deposition the copper wire was removed and a width of 0.26 cm was obtained. Illumination of the films were done with the help of 60 Watt sodium lamp (44.17 W/cm^2) and 80 Watt mercury lamp (58.89 W/cm^2) and I-V characteristics of the films under different illuminations have been measured.

The schematic diagram of the experimental set up for I vs V measurement is given in Fig.1.

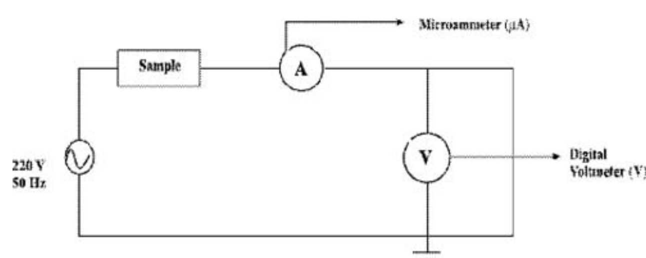

Fig. 1. Expeimental setup for I vs V measurement

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Results and Discussion

Fig.1 (a) shows the I-V characteristics of $[P_3N_3Cl_4ZrOCl_4]^{2-}$ film under normal and illuminating conditions. Films were illuminated with sodium and mercury light of intensities 44.19 W/cm^2 and 58.89 W/cm^2, respectively. It is seen from these curves that magnitude of current depends on the type of illumination.

The log I vs log V plots (Fig. 1(a)) are mostly linear in low fields for all the three films under study. Normal, sodium and mercury light illuminated films show two types of conduction. The calculated slope in low field region are 0.52, 0.89 and 0.93 for the respective curves. Thin films illuminated under normal, sodium light and mercury light have slopes of 0.63, 1.26 and 0.28 respectively, in high field region. The linearity for all illuminating conditions in the lower voltage region is due to independence of velocity of charge carriers on applied field indicating ohmic region while curvature is observed in high field region suggesting non ohmic region.

In high field region a remarkable increase in slope from 0.89 to 1.26 was observed in thin films illuminated with sodium light suggesting that sodium light has decreased the surface barrier thereby increasing the emission current. In thin film illuminated with normal light, there is a slight increase in slope from 0.52 to 0.63 in high field region due to independence of velocity of charge carriers with similar effect as observed in sodium illuminated thin film. However, in high field region slope of the thin film illuminated with mercury light changes from 0.93 to 0.28 suggesting that saturation of charge carriers has occurred due to space charge limited region (Iqbal and Hogarth, 1986). The data of Fig. 1(a) are replotted as log I vs $V^{1/2}$ for all the three films in Fig. 2.

The log I vs $V^{1/2}$ plots show linearity in high field region. This observation shows that current in this region obeys I α exp ($\beta V^{1/2}$) where β is a constant. Such a dependence of current on voltage will only be observed if high field conduction is being governed either by Richardson Schottky (RS) or Pool Frenkel (PF) effect (Lamb, 1967), the only point of distinction between the two being the values of β i.e. $\beta_{PF}=2\beta_{RS}$.

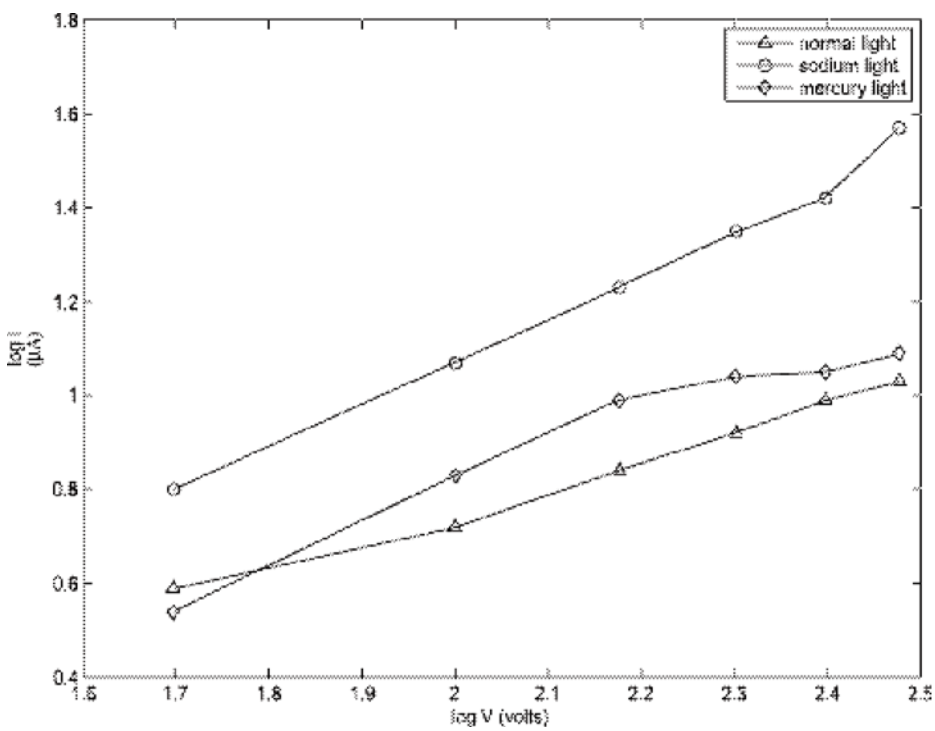

Fig. 1(a): Plot of log I vs log V of thin film under illumination by different lights

The theoretical values of β_{RS} has been calculated by Schottky relation:

$\beta_{RS}=(e^3/4\pi\varepsilon_o\varepsilon_r)^{1/2}$

$V^{1/2}$

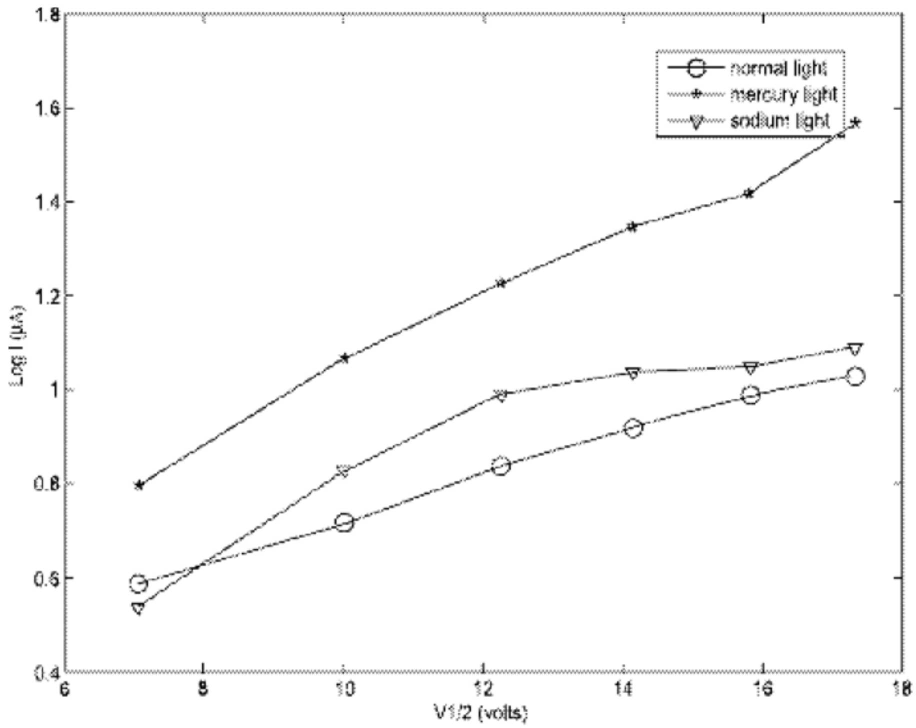

Fig. 2: Plot of I vs $V^{1/2}$ of thin film under illumination by different lights

where,e is the electronic charge (1.6×10^{-19} C), ε_r is the dielectric constant of the complex (3.65) and ε_o is the permittivity of free space (8.85×10^{-12} F/m).

The calculated value of β_{RS} is 3.17×10^{-22} and the experimental value of β_{PF} obtained from slopes of log I vs $V^{1/2}$ plots using relation:

$$\beta_{PF}=kT\times slope$$

and given in Table I. It is seen that $\beta_{RS} \approx \beta_{PF}$. This suggests that RS mechanism is the most dominating mechanisms of conduction at high fields for the film under three different illuminations.

Table I: Experimental values of β from the slopes of log I vs log V plots

Temp., K	Film under normal light		Film illuminated with Na light		Film illuminated with Hg light	
300	Slope	$\beta x10^{22}$	slope	$\beta x10^{22}$	slope	$\beta x10^{22}$
	0.072	3.01	0.077	3.22	0.088	3.68

Conclusion

From the observations it is concluded that sodium illuminated thin film shows better conduction in comparison to films illuminated with normal and mercury light. However all the three films are dominated by Richardson Schottky (RS) mechanism in high field region.

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