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Addresses for correspondence: The Chief Editor, East African Journal of Physical Sciences, School of Pure and Applied Sciences, Kenyatta University, P.O. Box 43844, Nairobi, Kenya. *E-mail*: scchhabra@avu.org

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Current-voltage characterization of doped polystyrene thin films with view to gas sensing

A.B. Wafula* and G. Katana

Physics Department, Kenyatta University, P. O. Box 43844, Nairobi, Kenya

*corresponding author

Current-voltage measurements of iodine doped polystyrene thin films as a function of dopant concentration, temperature and radiation have been carried out. The thin films were prepared by solution casting method taking the constituents in right proportions. All devices showed memory and threshold switching except for doped annealed samples that lost both memory threshold switching at a temperature of 90°C. The thickness was varied from 3-7µm while the concentration of iodine varied from 0.025 to 0.100 g. The threshold voltage was lower in pure samples than in doped samples indicating an increase in disorder in the arrangements of the atoms. Irradiated and annealed devices showed a marked increase in threshold voltage. Once the pure samples switched from OFF-state to ON-state they remained in the ON state but the doped samples returned to their original state after 33 minutes to 3 hours of switching depending on the concentrations.

The space charge limited current theory is a suitable model to explain condition in these polymeric materials. The ON-state was ohmic while the OFF-state obeyed Child-Langmuir law.

Key words: memory, switching, doped, polymer, polystyrene.

INTRODUCTION

Many studies on switching phenomenon have been done in inorganic materials such as chalcogenide glasses and oxides but few in polymers materials (Pendar & Fleming, 1975). For a long time polymers were considered as electrically inactive materials and their main function in electrical technology was to furnish electrical insulation. However, about 1940, it was observed (Mott & Gurney, 1940) that, based on the energy-band viewpoint, it should be possible to obtain injection of electrons from a suitable contact into an insulator, in a manner analogous to their injection from thermionic cathode into vacuum. Later on the bipolar transistor in solid state electronics was successfully done and ever since there has been a continually growing interest in the properties of currents injected into more insulating materials.

During the 1950's and 1960's the development of transistors physics led to new insights into the nature of crystalline semiconductors. Pendar and Fleming (1975) have reported memory switching in evaporated thin anthracene films in which they found that the ohmic relations in the low impedance rate is caused by space charge conduction. Sakai *et al.* (1984) also observed these phenomena in polystyrene (PS) and other polymeric thin films. However, relatively little work has been done on the subject of threshold and memory switching in polymeric thin films. Siro (1997) worked on polymethacrylate (PMMA) thin films and found that threshold voltage increases with dopant concentration and decreases with temperature. Threshold and memory switching disappeared at high temperatures. Musyoki (1998) studied switching, memory and photoelectronic effects in thin films. He found that irradiating samples of PS and PMMA for a particular period of time removes memory and the duration for irradiation before removal of memory differed in the two polymers. He also found that in PS, transition voltage, V_{th} , decreased with irradiation time while in PMMA the reverse behaviour was noted. However, no sufficient explanation has been given in terms of structural changes. In work detailed measurements of I-V

characteristics for doped PS have been taken with view of obtaining devices for application in gas sensors, memory storage equipment, FETs, and lasing devices.

EXPERIMENTAL

Aluminium (Al) was deposited on a clean slide in a HIND-HIVAC vacuum chamber model No. 12 A 4 at a pressure of about 1×10^{-6} torr. Films approximately $0.2 \mu\text{m}$ thick were obtained. Afterwards the slides were coated with polystyrene using solution casting method (Siro, 1997). 0.1 g of PS granules/pellets were mixed with 100 cm^3 of benzene and stirred periodically. During the stirring the beaker was tightly covered with Al foil to avoid evaporation of the solvent. The mixture was stirred for about 2 hours for all PS to dissolve. The resulting solution was then divided into volumes 15, 20, 30, 35 cm^3 in four identical petri dishes each containing one clean and a metal-coated glass slides. The petri dishes were also covered with Al foils and small holes were made on them to control the rate of evaporation. The set up was left overnight for casting. Different volumes of solutions in each petri dish give different corresponding thickness of the films formed.

For the doped films, 0.1 g of polymer and iodine of the varying proportions were both dissolved in a 100 cm^3 of benzene. The mass of iodine used was varied: 0.025, 0.050, 0.075 and 0.100 g. After the films had been prepared, the outer electrode of Al was deposited through Al masks of area 0.04 cm^2 in a vacuum chamber. Very thin copper wires were then connected to the lower and upper point contact electrodes of conductive silver paste. For voltage measurements, a Digital Multimeter Gold Star DM-311 was employed and a high stability 35 and 350 V dc power supply Philip Harris model was used to supply current. For high temperatures, an oven with a variac was used. A digital thermometer NiCr-Ni GTH 1160 was used to measure temperature. Some samples were irradiated by a NE-laser light of wavelength 632.8 nm before the upper electrode was deposited.

RESULTS AND DISCUSSION

Figure 1 shows $\log V$ Vs $\log I$ for pure polystyrene. The Figure has 4 sections, namely: AB, BC, CD, and CE. This V_{trans} is related to other parameters of the sample the following equation (Mott & Gurney, 1940).

$$V_{\text{trans}} = \frac{en_{\text{co}}d^2}{2\epsilon\epsilon_0} \quad (1)$$

where e is the electronic charge, n_{co} is the initial charge carriers, d is the electrode spacing, ϵ permittivity of the sample and ϵ_0 permittivity of vacuum.

The transition voltage, V_{trans} , was $1.04 \pm 0.001 \text{ V}$ for $t = 2.6 \mu\text{m}$, where t is its thickness. It is evident that at low voltages, just below switching, OFF state current conduction is non ohmic. The slope for AB is 1.6 ± 0.08 which is in agreement with other results (Musyoki, 1998).

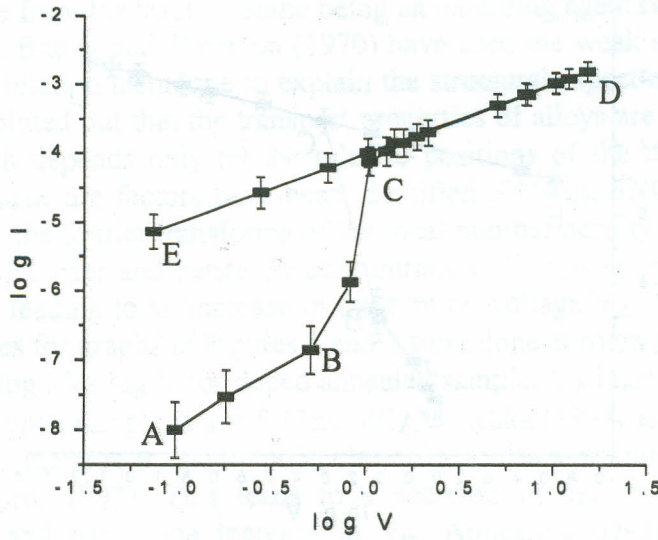


Figure 1. Log I Vs log V for pure polystyrene.

Above the V_{trans} the slope for BC is 10.1 ± 0.62 . Here is the region for Space Charge Limited Conduction (SCLC) as given by equation 2.

$$I = k V^n \quad (2)$$

where I is current, k is a constant and V if the voltage supplied with n more that 2 for SCLC.

At point C all traps are filled and remain filled. At this point the voltage across the sample is related to the other parameters by the equation 3.

$$V_{tf} = \frac{ed^2 N_t}{2\epsilon} \quad (3)$$

where N_t stands for the total concentration of traps in the sample.

Section CE is the memory section and the slope is $1.00 \pm 2.04E-16$ showing ohmic relationship. An interesting observation for the pure polystyrene samples was that once they switched from an OFF-state to an ON-state, they remained in the ON state. This is very a useful observation, showing the practical use of these materials, that such materials can be used in storage of vital information.

The shape of Figure 2 is similar to that of the pure sample showing doping has no effect on the shape. The slope for AB was 5.91 ± 0.99 , for BC, 14.41 ± 0.99 and for CD, 1.00 ± 0.99 showing again ohmic relation in ON-state region. V_{th} increased with iodine concentration showing a sigmoidal variation. This variation was due to an increase in total trap concentration with doping, and is not dependent on the increase of charge carrier concentration. The increase in traps can be

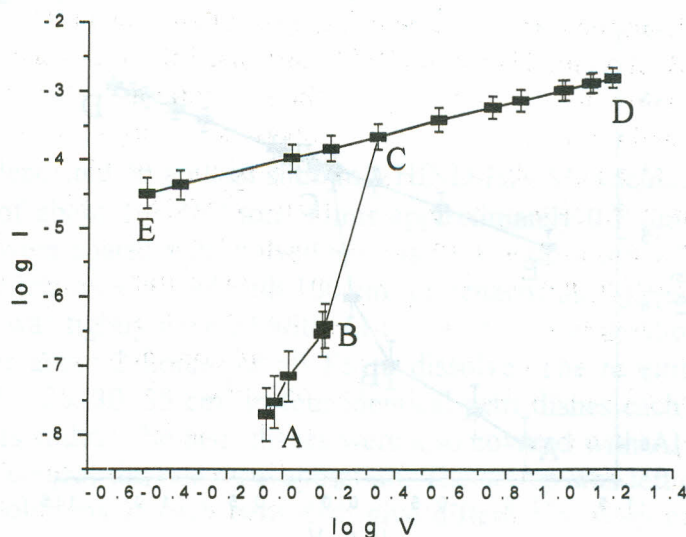


Figure 2. Log I Vs log V of doped polystyrene.

attributed to the structural changes in PS due to the presence of iodine atoms within its structure. Theoretical structural studies on doped polymers have indicated that doping increases structural disorder and the polymer goes into a more amorphous state (Sperling, 1992). The change in order and hence in concentration of traps seem to reduce the effective internal field strength leading to an increase in the turn-on voltage V_{th} . Iodine induced structural changes and also increased the concentration of traps and carrier concentration. An interesting observation is that, unlike the pure samples, the doped samples do not remain in the ON-state for long but return to the OFF-state after sometime as shown in Table 1. The revert to OFF state depended on the concentration of the dopant.

Table 1. Dopant conc. of doped polystyrene against recovery time.

Conc. (g)	Time (mins)	t (μ m)
0.05 ± 0.01	120 ± 1.2	4.04 ± 0.01
0.075	53	2.51
0.10	33	4.64

The results indicate that the higher the concentration, the short the recovery time. Recovery is possible since iodine forms a covalent bond with PS. Such a bond is the least stable among the halogens because iodine forms only weak bonds with the non-metals (Pierce, 1970). From the results it appears that the bonding is broken at voltages higher than V_{th} from the heat generated. Below this voltage, the bonding forms again after heat is lost to the environment. The more the concentration, the weaker the bonding. Van der Waals forces play a major role at higher

concentration than covalent forces. Hence the short recovery time at higher concentration. Another explanation for this behavior is that after current has been switched off, charge carriers are extracted by iodine from the traps – iodine being an oxidizing agent. Hence the sample reverts back to the OFF state. Bhatia and Thornton (1970) have used the weak scattering approximation and the Van Hove correlation technique to explain the structural aspect of electrical resistivity of binary alloys. They pointed out that the transport properties of alloys are strongly dependent on a structure factor, which depends only on the relative positions of the charge carriers and atom factor. Three partial structure factors have been identified $S_{NN}(q)$, $S_{NC}(q)$ and $S_{CC}(q)$, which could be derived from the fourier transforms of the local number density and concentration of the alloy. The change in disorder and hence on concentration of traps seem to reduce the effective internal field strength leading to an increase in the turn on voltage V_{th} . Measurements of current and voltage for samples for graphs in Figures 1 and 2 were done at room temperature of 23°C.

Figure 3 shows log I Vs log V for doped annealed sample. V_{th} increased with annealing. For example for 0.075 g doped sample, $V_{th} = 5.12 \pm 0.001$. Musyoka (1998) reported a similar increase in doped PMMA. This increase is due to molecular diffusion as a prominent factor arising during annealing process (Siro, 1997). This leads to a decrease in the magnitude of the negative dielectric anisotropy and hence the increase in V_{th} . Annealing destroys both switching and memory properties. C—H bonds are weak and annealing the films at high temperature may cause dissolving of the C—H bonds and the subsequent effusion of the H atoms from the films (Magnaldo *et al.* 1996). This may lead to complete distortion of the polymers structure causing the complete loss of the switching and the memory effect.

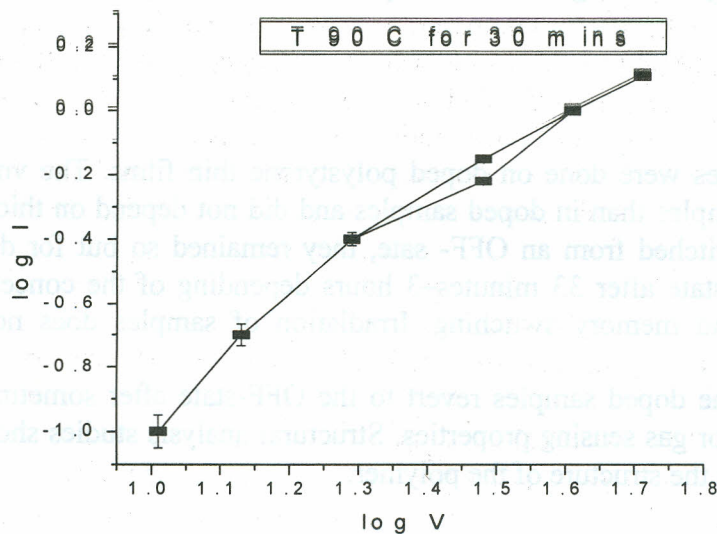


Figure 3. Log I Vs log V for doped and annealed polystyrene.

Figure 4 shows log I Vs log V of irradiated, doped sample. The threshold voltage increased with irradiation time. For example for 0.100 g doped sample, $V_{th} = 5.50 \pm 0.001$. Musyoka (1998) reported a similar increase in doped PMMA. This is attributed partly to the changes of the concentration of traps due to disorder changes and also due to degradation of the polymer (Salim,

2000). However, from Figure 4, the samples still exhibit threshold and memory switching. It was also true at higher times of irradiation. Therefore irradiation of doped polystyrene does seem to clear memory of the samples at all.

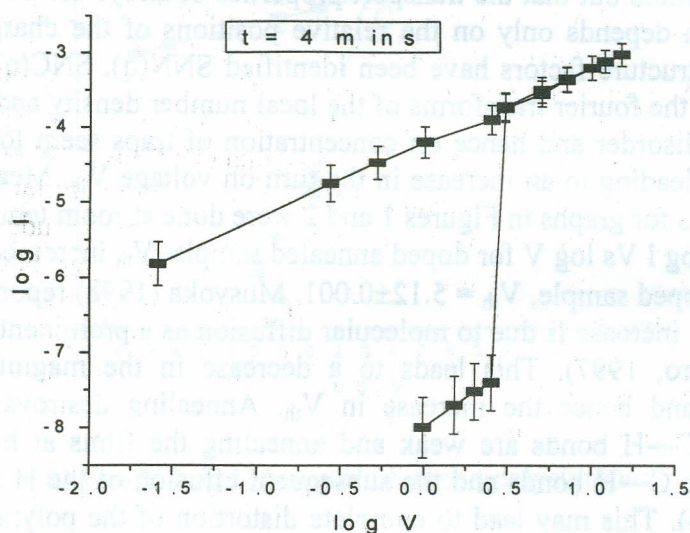


Figure 4. Log I Vs V for doped and irradiated polystyrene.

CONCLUSION

Current-voltage studies were done on doped polystyrene thin films. The voltage for switching was lower in pure samples than in doped samples and did not depend on thickness. For the pure sample, once they switched from an OFF-state, they remained so but for doped samples, they returned to the OFF-state after 33 minutes–3 hours depending of the concentration. Annealing removes threshold and memory switching. Irradiation of samples does not seem to remove memory at all.

From the fact the doped samples revert to the OFF-state after sometime, we suggest that they be investigated for gas sensing properties. Structural analysis studies should be done to find out how iodine affects the structure of the polymer.

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