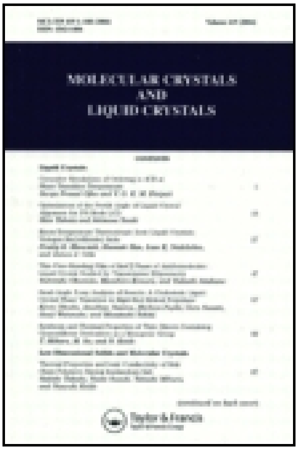

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Thermo Electric Power Versus Temperature in Implanted Polyparaphenylene (PPP)

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THERMO ELECTRIC POWER VERSUS TEMPERATURE IN IMPLANTED POLYPARAPHENYLENE (PPP)

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Abstract: Polyparaphenylene (PPP) samples were implanted with alkali metal ions using different energies. They were characterized and the evolution of thermo electric power versus temperature was followed. The results may be analyzed in terms of a variable range hopping process between localized states induced near the Fermi level through implantation. Furthermore with samples implanted at low energy, a transition toward values characteristic of the expected doping shows up (n type doping with alkali metals).

INTRODUCTION

In previous papers (1, 2) we have shown that electroactive PPP may be doped by ionic implantation. Depending on ion nature and implantation parameters (energy, fluence...). For "chemically active ions", conductivity varies as a function of those parameters. Specifically for energy [1] two domains may be deduced : at low energies (E ≤ 100 keV) conductivity increases as energy decreases whereas at higher energies (E > 100 keV) conductivity is enhanced with energy. Measurements of Seebeck coefficients were carried out in order to deduce the type of conductivity involved [2] in the process. Figure 1 reproduces variations of the Seebeck coefficient with energy (1-a) and fluence (1-b) One can see that, provided smooth parameters are used, n type conductivity is obtained with alkali metal ions and p type conductivity with halogens. It is to be noted that p type conductivity occurs at higher energies whatever the ion.

We have shown by studies of conductivity versus temperature [2] that at high temperature some thermally activated mechanisms (with activation energy in the range 0 1.eV) are involved while, at low temperature, variable range hopping mechanism seems to dominate. It was thus important to study the variation of Seebeck coefficient as a function of temperature in an attempt to clarify this point.

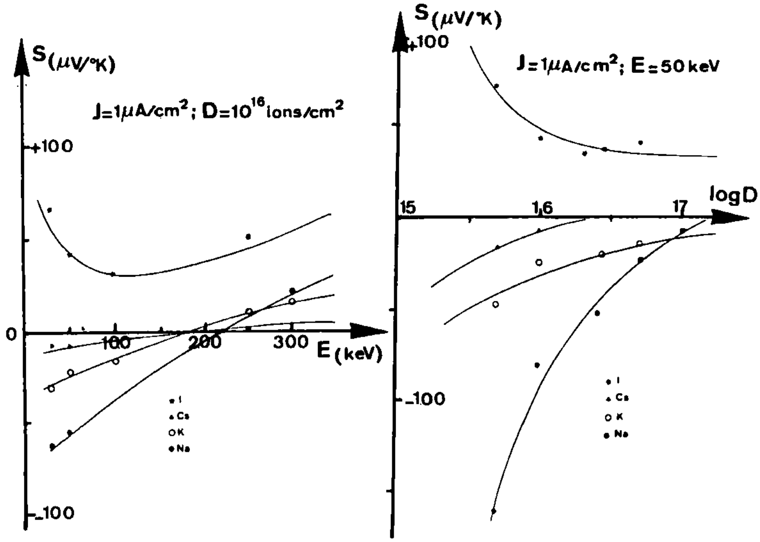


Figure 1 : Evolution of Seebeck coefficient (S) on implanted polyparaphenylene with different ions (Iodine, Cesium, Potassium, Sodium)
a) - as a function of Energy (E) b) - as a function of Fluence (log D)

EXPERIMENTAL

A special set up was built for measurements of Seebeck coefficients at a large range of temperature. Good contact between probes and implanted layer was insured by using a mobile assembly (see figure 2) which composed of two probes located inside a hell jar linked to a micromanipulater outside through a "tomback". Samples thus stood in a dry atmosphere to avoid any water condensation and ohmic contacts were made without heavy damage to the implanted layer whatever the temperature.

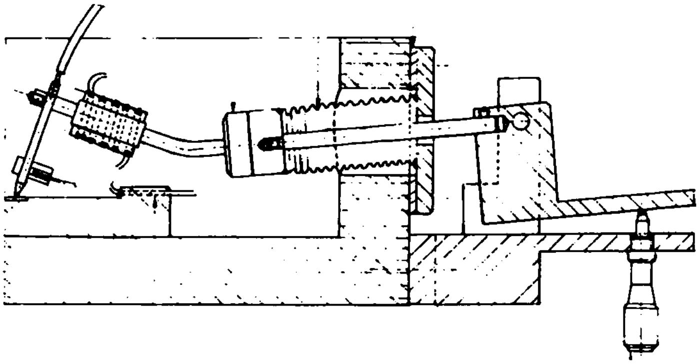


Figure 2 : Schema of the mobile assembly used to insure good ohmic contact to the implanted sample

Even in the absence of temperature gradients between the probes, there exists a residual voltage whose magnitude depends upon temperature which will be superimposed on the thermoelectric potential. This type of drawback was already described by Nagels [3] in the case of vitrous systems. From our data we can infer that the lower the temperature, that is the higher the sample resistance, the higher the residual voltage which indeed could come from contact efficiency. It is why we have used an automated measurement set-up with an IEEE bus as schematized in figure 3. The residual offset voltage was first registered before the temperature gradient was set. The voltage was then measured when gradient reached 12°. The offset voltage was substracted from the thermoelectric voltage to calculate the Seebeck coefficient, S.

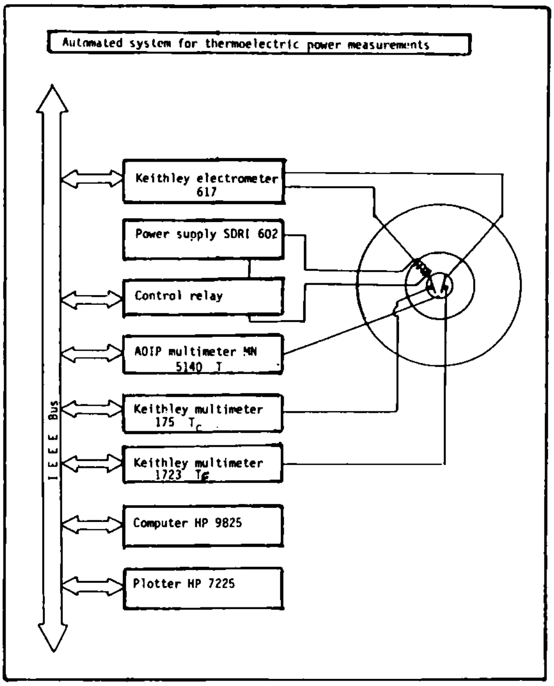


Figure 3: Automated system for measurement of thermoelectric power through an IEEE bus

RESULTS - DISCUSSION

As an example we have reproduced in figure 4-a what could be the evolution of S versus reciprocal temperature if the residual voltage was not taken into account. This evolution would be quite erroneous as compared to figure 4-b showing the same data (PPP sample implanted with Cs ions with an energy of 30 keV) when the offset voltage is deducted.

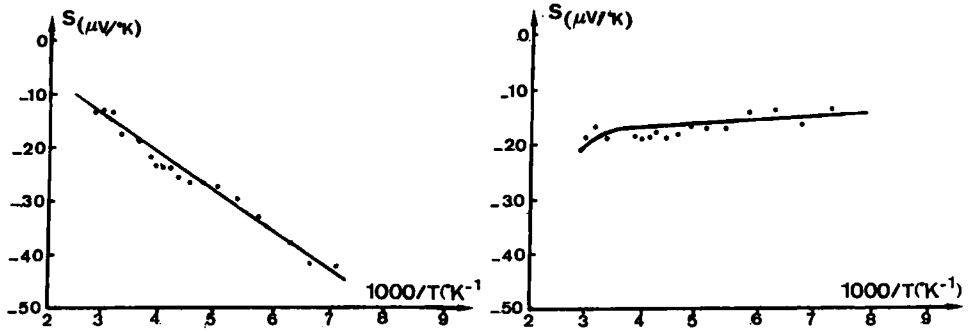


Figure 4 : Plot of S as a function of 1000/T for Cs implanted polyparaphenylene
($E = 30$ keV ; $j = 1$ μA/cm^2 ; $D = 5\ 10^{15}$ ions/cm^2)

a) - as measured without deducting the offset voltage

b) - taking into account the residual voltage

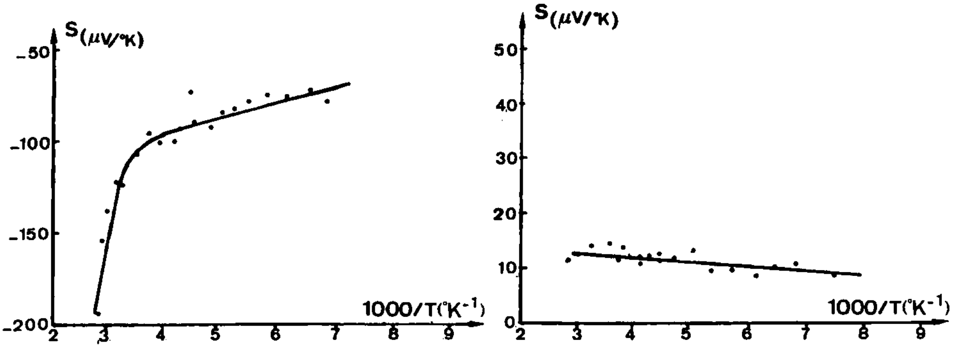


Figure 5 : Plot of S versus 1000/T for Na implanted PPP
$j = 1$ μA/cm^2 ; $D = 5\ 10^{15}$ ions/cm^2

a) - $E = 30$ keV

b) - $E = 300$ keV

Figure 5 collects results of variation of S with reciprocal temperature in the case of Na implanted polyparaphenylene at different energies (5-a : 30 keV and 5-b : 300 keV).

Generally, three different contributions take place in the overall process and the relationship is given by [4] :

$$S = \frac{1}{\sigma_p + \sigma_n + \sigma_H}\left[\sigma_p \underbrace{\left(\frac{E_p^\alpha}{qT} + A\right)}_{S_p} - \sigma_n \underbrace{\left(\frac{E_n^\alpha}{qT} + A\right)}_{-S_n} + \sigma_H S_H\right]$$

where (σ_p, S_p), (σ_n, S_n) and (σ_H, S_H) are respectively conductivity and contribution to the thermoelectric factor of holes, electrons and variable range hopping processes. From figures 4-b, 5-a and 5-b it is evident that the process does not obey an Arrhenius law , especially in the low temperature domain where S shows very weak and almost constant absolute values ($S < 100$ µv/K). This type of behaviour is characteristic of a variable range hopping process in which the thermoelectric power for a tridimensional model follows the law :

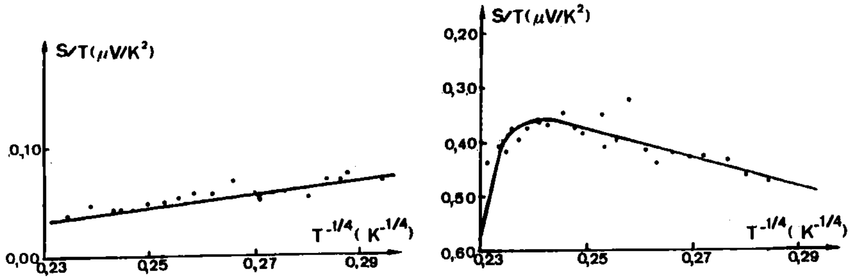
$$\frac{S}{T} = \frac{\pi^2 k^2 \gamma}{12q}\left(\frac{T_o}{T}\right)^{1/4}$$

assuming the density of states near the Fermi level varies according to [5, 6] :

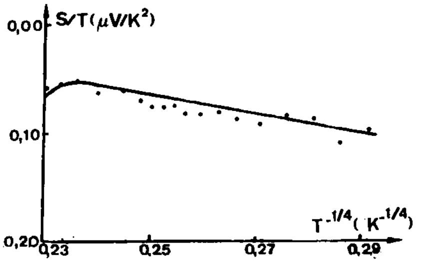
$$N(E) = N(E_F)\,[1 + \gamma(E - E_F)]$$

We have plotted $S/T = f(T^{-1/4})$ for different samples. Figure 6-a, shows a plot of the high energy sample (Na, 300 keV) . A linear evolution exists in the whole temperature domain. However with samples implanted at low energy (Na and Cs, 30 keV) figures 6-b and c demonstrate that the linear realtionship is restricted to the low temperature domain. Furthermore it is to be noted that for those samples showing a negative S, one gets $\gamma > 0$ whereas $\gamma < 0$ on samples implanted with high energy ions whose Seebeck coefficient is positive (figure 6-a). This is in agreement with previous reports [5, 6] and supports recent conclusions by Nagels et al [7] that transport processes in polymetaphenylene networksfollow a variable range hopping law. The similarity would come from disorder whose effect dominates at low temperature for low energy implanted samples, or from disorder brought about by ion implantation at high energy, generating tridimensional network behavior.

Figure 6 : Plot of S versus T $^{-1/4}$ for implanted PPP - J = 1 μA/cm^2; D = 5 10^{15} ions/cm^2



a) - Na implanted sample E = 300 keV b) - Na implanted sample E = 30 keV



c) - Cs implanted sample E = 30 keV

It must be pointed out that a large difference appears at high temperature between high energy Na implanted samples (figure 5-b) and low energy Na implanted ones (figure 5-a). Above room temperature the latter finally show n-type behavior characterized by a dramatic increase in the absolute value of S with temperature. Yet in the case of Cs this increase is less pronounced or would occur at higher temperature (figure 4-b). This may be interpreted in terms of ionic volume. Cs is a bigger ion than Na and should induce many more defects upon penetration in PPP samples which in turn would lead to larger disorder and thus to a more pronounced tridimensional behaviour governed by variable range hopping processes.

It is interesting to note that low energy implanted PPP samples (particularly Na) present the same type of behaviour as amorphous semiconductors (a Si, a Ge, a Ga As...)obtained by low rate growth and subsequently annealed at high temperature^4.

In the high temperature domain a Si shows the standard electronic conduction and we are presently studying implanted PPP in the high temperature domain as well. Whether transport properties, at high temperature, of low energy implanted samples result from majority carrier conduction (electrons with alkali metal implantation or holes with halogens) in the band tails where localized states coming from defects might be introduced will be the subject of a forthcoming paper. The activation energy of the process will hopefully clarify the problem.

CONCLUSION

Variable range hopping theory accounts well for the thermoelectric power at low temperature of ion implanted PPP whatever the implantation energy. However with low energy implantation the variation in the high temperature domain is that of n-type material.

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