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Electron induced (surface) conductivity of FEP

J. P. Jog, S. J. Walzade and S. V. Bhoraskar
Department of Physics, University of Poona, Poona 411 007, *India*

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Introduction

The incidence of electrons on an insulating material generates electron-hole pairs within the lattice and under the influence of an applied electric field the passage of charge carriers from one electrode to another constitutes a conduction current. This is the phenomenon of electron beam induced conduction and can be classified into *EBIC* (Bulk) and *EBIC* (Surface). The former is identified when the electric field is applied across the thickness of the sample and the latter when the electric field is applied parallel to the surface. *EBIC* (Bulk) is often used to study the diffusion lengths[1] and mean life time[2] of the charge carriers in semiconductors. The mobilities and transit times for holes and electrons have been determined[3,4] using the *EBIC* (Bulk), while Blumtrill[5] *et al.* have utilized this to investigate the dislocations in semiconductors.

Although an extensive work has been reported in the field of *EBIC* (Bulk) in oxides[6,7] and polymers[8-10], the *EBIC* (Surface) has not been studied in the literarure. In this communication we report the *EBIC* (Surface) in the copolymer: Fluorinated Ethylene-Propylene (FEP) as a function of incident electron flux and electron beam energy. The electric field in the measurement is applied parallel to the surface and the change in the conductivity due to the incidence of electrons near the field region is noticed. An attempt has been made to determine the spatial depth of trapping levels in FEP using the *EBIC* (surface).

Experimental

The experiments were performed on 250 μm thick films of fluorinated ethylene-propylene (11%-18% HFP in PTFE Du Pont de Nemours) at pressures less than 10^{-6} torr using an electron beam from an electron gun and accelerating column. Two concentric annular electrodes of silver with radial width of 1 mm each were vacuum deposited on one of the surfaces of the sample. The radial separation between the two rings and the inner diameter of the inner electrode were 2 mm each. A bias voltage was applied across the two electrodes making the outer electrode positive with respect to the inner electrode and a focussed beam of 1 mm diameter was allowed to fall at the centre of the annular electrodes, region X. A conical cage was mounted so as to establish contact with the inner electrode and to avoid any stray electrons from reaching the outer electrode directly. The current was recorded on the outer electrode using an electrometer amplifier. The beam energy was varied from 6 KeV to 30 KeV and the beam current was varied from 2×10^{-9} Amp to 2×10^{-8} Amp. The electron beam induced current I_s was recorded for the bias voltages ranging from 0 to 1000 V. The incident beam current I_p was measured on the conical cage when the beam was deflected using the beam scanning assembly. The experimental setup is shown in *Figure 1*.

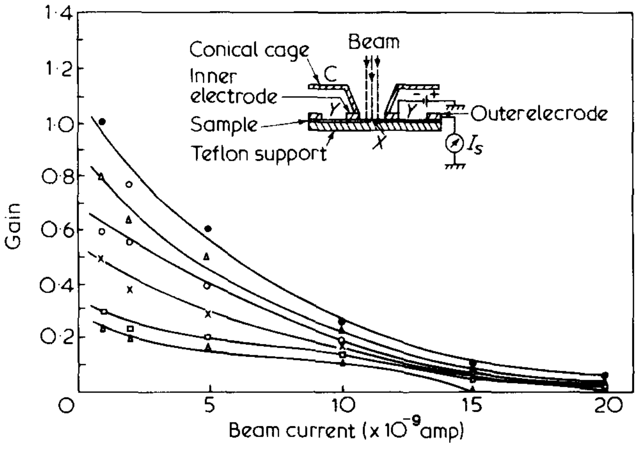

Figure 1 Effect of incident electron beam current on *EBIC* gain at constant beam energy for different biasing voltages and schematic diagram of experimental assembly. (●), 1000V; (▲), 900V; (○), 700V; (X), 500V; (□), 400V; (△), 300V: beam energy = 6KeV

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Results and discussion

The dark current I_0, flowing in the annular gap on the sample surface was measured for each bias voltage. This was of the order of 10^{-9} Amp, the magnitude of which increased when the electron beam was incident on the field free central region ('X'), the order remaining the same. The gain in *EBIC* 'g' was calculated using the relation

$$g=\frac{I_s-I_0}{I_p}$$

The observed variation of 'g' with incident electron flux and the electron beam energy for various bias voltages are shown in *Figure 1* and *Figure 2*. A maximum gain of 5 was obtained for this sample.

The increase in the conduction current in the region Y when the beam is incident at X can be explained by encountering the contribution of the bulk to the surface conduction in presence of the electron beam. The incident electrons, a part of which is reflected from the surface of the sample, penetrate into the sample up to a distance depending on their energy. The penetrating electrons, during their passage through the sample produce electrons and holes. Consequently the incoming electron beam creates a negative space charge region at its incidence and holes move towards this region where they are either compensated or neutralized. The electrons, however, drift towards the non-irradiated region and increase its conductivity. The contribution of a charge carrier towards the conductivity is proportional to the distance it drifts along the direction of the electric field without recombination or being captured.

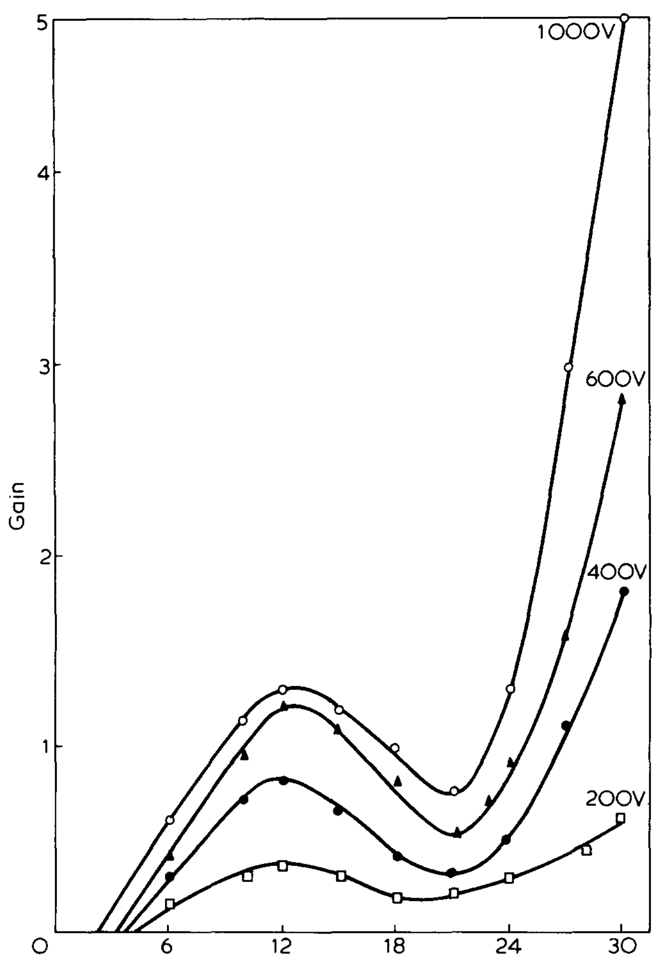

Figure 2 EBIC gain as a function of electron beam energy at constant electron beam current. Beam current = 2×10^{-9} Amp

Figure 1 illustrates the gain characteristics plotted as a function of incident flux, I_p, at a constant beam energy of 6 KeV. As the electron beam current is varied from 2×10^{-9} Amp. to 2×10^{-8} Amp, the gain is observed to decrease with increasing incident flux for each bias voltage. This can be explained on the basis of a recombination phenomenon in the sample. As the incident flux is increased the carrier density increases and there is a higher probability of the moving electron recombining with an opposite charge created by another primary electron. Thus the number of charge carriers contributing to the *EBIC* current decreases with increasing beam flux. However, when the incident flux is decreased the probability of such a recombination is low and the mean drift distance of the charge carrier increases which in turn results in increased conductivity. Similar results have been obtained by Ehrenberg and Ghosh[11] in the case of AS_2S_3 and by Beckley *et al.*[8] for PET while measuring *EBIC* (Bulk).

The effect of beam energy on *EBIC* gain has been studied for the incident beam current of 2×10^{-9} Amp. The results are somewhat unusual (*Figure 2*). The gain value increased with increasing electron energy except for certain values of beam energies. The gain energy plot showed a negative slope region which was later proved to be a characteristic of the sample under investigation. A set of five samples was studied to get consistent results.

The observed phenomenon can be explained on the basis of the range energy relation of the incident electrons and the contribution of the bulk conduction to the surface conduction in presence of electron beam. In this experimental set up the electric field is applied parallel to the surface and the conductance which one measures is the 'sheet' conductance which may be defined as an integral of the surface conductivity over the thickness corresponding to the range of the electrons. It was observed that the gain in general had a tendency to increase with incident electron energy. This is clearly so as the irradiated region increases with increasing penetration depth of electrons and effectively produces a larger number of secondaries which can contribute to the conduction. Accordingly one should expect a continuous increase in the gain with electron beam energy. However, the existence of negative slope indicates a phenomenon which dominates the conduction mechanism over some part of electron energies. Over the energies of negative slope, the *EBIC* gain decreases to a quite low value indicating a decrease in the number of charge carriers reaching the collector electrode. Such a phenomenon can occur if the charge carriers are immobilized due to the existence of localized electron traps near the surface. The nature of such traps cannot be described exactly but these may be the result of broken chains, adsorbed molecules, oxidation product, chemical impurities and chain folds[12-14].

The existence of negative slope in the energy range 12 KeV to 21 KeV roughly indicates, therefore, the spatial width of trapping levels in FEP. The penetration depth of electrons was determined by Gross *et al.*[15]. Referring to this, these energies correspond to 0.7 μm and 2.2 μm respectively.

Our experiments, therefore, indicate the presence of a trapping layer ranging in depth from 0.7 μm to 2.2 μm from the surface. The presence of near surface traps have also been reported in Teflon FEP by Seggern[16] from his t.s.c. experiments in electron bombardment and corona charged samples. The spatial depth of near surface trapping centres as reported by them are in the range of 0.5 μm to 1.8 μm from the surface. Our results are in close agreement with the reported ones. This method is now being used to study the effect of surface treatment on the spatial depth of traps in grafted FEP and positive results have been obtained which will be communicated in the near future.

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Thermal conductivity of polymers: A new correlation*

M. G. Kulkarni and R. A. Mashelkar
Department of Chemical Engineering, National Chemical Laboratory, Pune 411 880, *India*
(*Received* 10 *September* 1980; *revised* 24 *February* 1981)

Introduction

Study of transport properties of polymers is important from two view points. It provides an insight into the structure of the polymer and it helps to predict product performance during specific applications. A review of the literature reveals that the effects of such parameters as molecular weight, molecular weight distribution, crystallinity and orientation have been studied in great detail and empirical correlations have been established. Although thermal properties of polymers play an important role in polymer processing, in studying structure–property relationships and choosing materials for specific applications, thermal transport is still not clearly understood.

Theories of mechanism of heat transfer in polymers have not been well developed compared with the theories of mechanism of heat transfer in gases and liquids, primarily due to the lack of reliable data, which in itself has been attributed to difficulties involved in the experimentation. A qualitative description of the temperature dependence of thermal conductivity of polymers over a wide range has been given by Hands[1].

In view of the lack of experimental data and difficulties involved in accurate measurements, approximations are often used. A number of correlations associating such structural variables as molecular weight of the polymer, crystallinity, orientation etc. with the thermal conductivity have been proposed[2–5]. Thus Luba *et al.*[5] proposed empirical correlations for thermal conductivity of amorphous polymers in the temperature ranges above and below T_g as well as for semicrystalline polymers above and below T_m. The thermal conductivity of amorphous polymers at 173K was correlated with the refractive index of the polymers. It is not clear as to whether the same relationship would be valid at other temperatures as well, since the authors themselves have stressed the need to establish the correlation at temperatures other than 173K.

Search for a new correlation

Attempts to explain the temperature dependence of the thermal conductivity of polymers on theoretical considerations have not been successful. Uberreiter and Nens[6] assumed that thermal energy is transferred along the length of the polymer chain and the transverse waves set up above the glass transition temperature tend to dampen the process of transfer, resulting in decreased conductivity above the glass transition temperature. The concept is analogous to that proposed by Eucken[7] to explain the temperature dependence of the thermal conductivity of low molecular weight amorphous materials. According to Eucken[7] such a material can be looked upon as a quasi-lattice structure. Thermal conduction in such a structure takes place as a result of excited coupled intermolecular and intramolecular vibrations of the quasi-lattice structure. An increase in the temperature when the structure is much below its T_g results in an increase in population density of these interactions resulting in an increase in thermal conductivity. However, an increase in temperature also leads to an increase in the free volume which disrupts the lattice and the propagation of the vibrations. The net result of the two opposing effects is a decrease in the thermal conductivity. With a further increase in temperature, the population density of excited

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