Electron-stimulated insulator–metal transition in electrically active polymers

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A transition to a highly conducting state resembling a metallic state has been observed in polymer films with a nondegenerate ground state upon the application of an electron beam. The effect is discussed in terms of the properties of a polaron metal. © *1995 American Institute of Physics.*

The anomalously high conductivity of thin films of certain polymers with a nondegenerate ground state has attracted much interest.[1–3] So far, there is no acceptable model for this phenomenon. It has been suggested in several places[4,5] that the high-conductivity state becomes possible because a polaron lattice forms in certain regions of a polymer sample. For this to be true, however, at least two conditions would have to hold: 1) The density of charge carriers would have to be high. 2) There would have to be a corresponding energy structure which leads to an effective attraction between charges of the same sign. The reason why these conditions must hold is that the energy of the effective interaction of charges in a polymer system can be written

$$U_{\text{eff}} = U_p - U^*, \tag{1}$$

where U_p is the energy of the Coulomb interaction of two electrons at a given polaron, and U^* is the energy of the indirect interaction between electrons which results from an exchange of virtual phonons. This expression may contain various combinations of the constituent quantities. The case of most interest in the present letter is $U^* > U_p$. According to Refs. 6 and 7, the polaron band is three-dimensional in this case, and there may even be a superconductivity. One can alter the relation between U^* and U_p by, for example, exploiting their dependence on such energy parameters of the material as the width of the band gap.

The idea underlying the present experiment is as follows. We modify the energy-band structure by applying an electron beam to the polymer material, varying the space-charge density in the polymer by varying the bombardment dose in the presence of an electric field. We thereby obtain a high-conductivity state in the polymer sample, and we study its properties.

As test samples we selected polymers of the polyphthalidylidenearylene class.[8] Polymers of this class have two energetically stable states: the ground state and one excited state.[9] The ground state is neutral, and the excited state charged. Numerical calculations[10] have shown that positive charges assume positions in the skeleton of the molecule, while negative charges assume positions on side fragments. This charge redistribution reduces the width of the band gap to 1.5 eV.

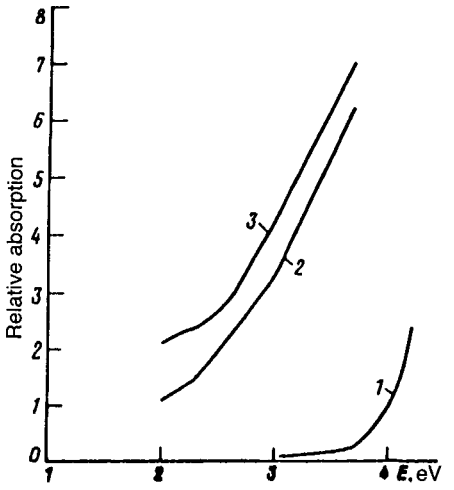

FIG. 1. Absorption spectrum of a sample versus the bombardment time. 1—Sample which has not been bombarded; 2—bombardment time of 30 min; 3—60 min.

The experimental apparatus was based on an RÉM-200 scanning electron microscope. A pulsed electron beam with a current density from 0.1 to 10 μA/cm^2, at an accelerating voltage of 10 kV, with a pulse length from 0.05 to 12.5 s, was used in the experiments. The bombardment dose rate was varied from 10^{-6} to 10^{-10} rad/s. The test sample was a multilayer metal–polymer–metal film sandwich. A Cr electrode deposited on the bombarded side was transparent to the electron beam. The transmission coefficient was 0.62, according to an estimate from the semiempirical relation of Ref. 11.

Figure 1 shows optical spectra of the polymer sample near the fundamental absorption edge for various durations of the electron-beam bombardment. As the bombardment time is raised, the absorption edge shifts into the near-IR region and changes shape, acquiring an approximate Urbach shape. The maximum shift observed in our experiments was about 3 eV. The new position of the edge after the bombardment corresponds to 1.8 eV, which agrees fairly well with the results calculated in Ref. 9. Those results predicted the formation of a structural feature in this part of the optical spectrum upon the onset of a charge state in a macromolecule.

Figure 2 shows the effect of the electron bombardment on the electrical conductivity of a polymer sample. At low bombardment doses, the current of the beam-induced conductivity, I_g, is proportional to the current of the primary beam, I_p. This current is due primarily to internal secondary electrons. Analysis of the measured current–voltage characteristics and current decay curves under time-varying conditions as the electron-beam current is turned off shows that the charge is transported by a mechanism controlled by trapping centers. Under the bombardment conditions corresponding to this condition, represented in the inset in Fig. 2, the beam-induced conductivity is monostable; i.e., when the electron beam is turned off, the original dark conductivity $\sim 10^{-14}$ S/cm is restored.

A study of the concentration of ESR centers as a function of the bombardment dose revealed that there is a singlet ESR signal, with an intensity which increases in proportion to the dose.

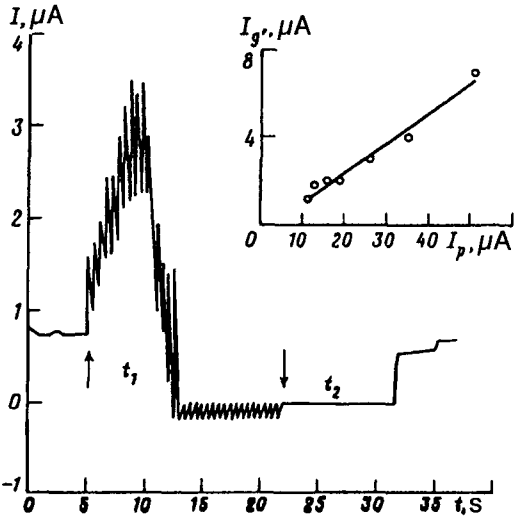

FIG. 2. Effect of electron-beam bombardment on the electrical conductivity of a polymer sample which was switched beforehand to the high-conductivity state. The arrows show the times at which the electrom beam is turned on and off. The inset shows the current beam-induced conductivity, I_g, versus the current of the primary beam, I_p.

At doses $\sim 10^{-1}-10^{-2}$ rad/s, a high conductivity $\sim 10^{0}-10^{-2}$ S/cm arises in the polymer sample. This conductivity is preserved even when the electron beam is turned off. We observe a "switching" to a conducting state with a "memory." This state corresponds to the maximum shift of the absorption edge (Fig. 1) and a linear, ohmic current–voltage characteristic.

The high dark conductivity could apparently be the consequence of a transformation of the electron subsystem in such a way that the band gap becomes narrower, while polaron states form as the result of an interaction of unneutralized charge carriers with phonons. At a sufficiently high concentration, the polarons can form a half-filled subband.

As the bombardment dose is varied, we observe a charge instability of the high-conductivity state, as shown in Fig. 2. It leads to a modulation of the current and of the high-conductivity state: The latter state is "turned off" when the electron beam strikes the sample, and the original high-conductivity state is "turned on" when the beam is turned off. The turn-off occurs with a time delay t_1 of a few seconds. The decrease in the conductivity is three or four orders of magnitude, and it persists during the application of the beam. When the beam is turned off, the high-conductivity state is restored with a time delay t_2, which is again a few seconds. This effect is quite reproducible on a large number of samples. The average number of switchings per sample is $\sim 10^3$.

Measurements of the current decay after the electron beam is turned off revealed that, as the polymer is bombarded with electrons, some trapping states with lifetimes of 2.9, 3.4, and 6.2 s arise in the sample. These times correlate well with the delays t_1 and t_2 in the switching of the conductivity off and on, as shown in Fig. 2.

We would like to offer the following explanation for the observed effects. We assume that a polaron subband forms in the band gap of the sample as a result of the bombardment. This subband must, by definition, be very narrow, if there is to be an effective interaction between electrons. One might suggest that the carrier mobility is

low, as it is in any polymer, and especially in this case because of the very large number of radiation defects in the sample. Furthermore, the band gap contains some trapping states, whose thermalization makes a separate contribution to the conductivity. The growth of the envelope in Fig. 2 can be explained in this manner.

These features set the stage for an increase in the density of free carriers in the subband and for a change in the position of the Fermi quasilevel. A shift of this level toward the edge of the subband can explain the current saturation in Fig. 2. A filling of the subband results in a cutoff of the conductivity. This quasiequilibrium state is maintained by a thermalization of the traps, which are continuously being filled with charge carriers from the electron beam. The delay in the turn-off of the high-conductivity state corresponds to the lifetime of one group of traps. The turn-on of the high-conductivity state occurs with a delay equal to the lifetime of the traps after they have trapped carriers from the subband.

Other explanations are apparently also possible; one would be the formation of a blocking layer of a $p-n$-junction type. However, an attempt to observe an effect of the polarity of the voltage applied to the sample showed that the influence of the polarity on the effect under discussion here was negligible.

In summary, it has been shown that conditions for the onset of a high-conductivity state—with electrical properties similar to those which have been seen previously in the excitation of a high-conductivity state by uniaxial pressure,[12] an electric field,[13] and a temperature change[14] can be realized by injecting charge into a polymer by means of an electron beam.

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