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ELECTRICAL BEHAVIOUR OF THIN LAYER Au-POLYETHYLENE-Al SANDWICHES

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ABSTRACT

The electrical conduction of 1-2,000 Å thick polyethylene films could be increased after electroforming processes. There was an intermediate range over which the sandwich could be switched reversibly from a lower to a higher conduction. This conduction was restricted to very localized regions and led to destruction of the system at inputs above 10^{-4} W. The breakdown resistance of the residual part was not, however, reduced.

KIVONAT

Az 1000-2000 Å vastagságu polietilén filmek elektromos vezetése elektroformálással megnövelhető. Létezik olyan átmeneti tartomány, amelyben a szendvics reverzibilisen átkapcsolni képes kis és nagy vezetésü állapotai között. Ez a vezetés igen kis keresztmetszetre korlátozódik, és 10^{-4} W teljesitmény felett a rendszer roncsolódását okozza. A sértetlen maradó keresztmetszet-rész átütési ellenállása mindazonáltal megkimélődik.

РЕЗЮМЕ

Электрическая проводимость полиэтиленовых пленок толщиной 1000-2000 Å может быть увеличена путем электрического формирования. Существует переходный диапазон, в котором сэндвич (Au-полиэтилен-Al) может обратимо переключать между состояниями низкой и высокой проводимости. Эта проводимость ограничивается на весьма малое сечение и при значениях мощности, превышающих 10^{-4}, вызывает разрушение системы. Сопротивление пробоя части сечения, которая не подвергается разрушению, тем не менее уцелеет.

INTRODUCTION

Since the discovery of switching and memory effects in inorganic amorphous semiconductors by Ovshinsky [1] extensive studies have been carried out to establish what are the basic processes taking place in the phenomenon. Yet there still remains some controversy over whether the switching is initiated by electronic and/or thermal processes [5]. The present work aiming to observe switching in thin polyethylene films, was prompted by earlier reports of memory effects in thin amorphous tetracene films [2] and of a negative differential resistance in the I-V characteristics of semiconducting polymers [3]. This paper is a preliminary account of the results obtained so far from studies of the electrical properties of polyethylene films and the modifications that can be induced in them by gamma irradiation.

EXPERIMENTAL

Thin-film Au-polyethylene-Al sandwiches were prepared by vacuum evaporation on to 25x75 mm glass substrates /microscope slides/ previously washed with detergent and cleaned in an ultrasonic bath. First, two 1 mm wide gold strips, symmetrically spaced 1 mm apart about the longitudinal axis of the glass slide, were deposited from a molybdenum boat at $2x10^{-5}$ torr, to thickness of 1-2,000 Å. These were then covered with a 6 mm wide polyethylene film, and finally 1 and 2 mm wide aluminium electrodes were deposited from a tantalum boat /using an appropriate mask/, again to a thickness of 1-2,000 Å.

This sequence of deposition prevented the formation on the electrodes of intermediate oxide layers which might affect the conduction properties under investigation. Studies by capacitor manufacturers have established that polyethylene can be evaporated quite well at 280-400^{o}C. The more volatile, low molecular weight components evaporate during the early stages of heating, but above 350^{o}C the melt begins to sputter droplets on to the substrate which form a film polymerizing more readily, and having properties more like those of the bulk material, than the film produced from the initial volatile fractions.

The thickness of the polymer layer was estimated from the capacity of the sandwich measured at 1000 Hz dielectric constant of $\varepsilon = 2$ for the polyethylene film, the measured capacity of 80-90 pF per mm^2 around 2000 Å.

The samples were investigated in a closed chamber evacuated to about $3x10^{-3}$ torr in order to avoid disturbing effects of the atmosphere. Current vs applied voltage characteristics were measured at room temperature with the circuit depicted in Fig.1. Here R and C denote the resistance and capacitance of the sample; R_m is the measuring resistor needed for the determination of the current passing through the sample, usually much smaller than R. The voltage at point X is thus about the same as that applied to the sample /with correction where necessary/.

To measure currents below 10^{-8} A the output at point Y was fed to an electrometer and thence to a X-Y recorder, but for measurements of higher currents points X and Y could be plugged directly to the recorder or an oscilloscope. Potentiometer P of 20 kOhm impedance was replaced by a 400 Ohm potmeter if resistance R became low. Capacitor C_o = 50 µF served for damping voltage surges caused by screwing the potmeter when sample resistance was high /time constant ~1 second/, in order to avoid the disturbing effects of sudden voltage changes on the differentiating circuit formed by capacitor C and R_m, which is of relatively high resistance at the initial stage.

As oxide and organic amorphous semiconductor sandwiches with Al and Au electrode pairs generally exhibit a negative differential resistance /i.e. memory-switching behaviour/ only if a positive bias is applied to the Au plate, this was the case studied most thoroughly, though checks were also made of the behaviour under reverse bias.

Sandwiches could be considered as remaining intact as long as the current passed through the polyethylene film did not exceed 10^{-11} A. Relatively high bias voltages of about 300 mV /Au positive/ were observed at the electrode terminals with impedances above 10^{12} Ohm. Leakage resistance due to conduction between the electrodes on the glass surface was about the same order of magnitude.

RESULTS

Polyethylene films about 2,000 Å thick generally displayed a resistance of $2x10^{12}$ Ohm at applied voltages of a few volts, though a few samples had resistances ranging from 20 MOhm down to as low as 170 Ohm already on the first measurement. If the Au electrodes were positively biased, the first breakdown usually occured at 8-25 V. Assuming uniform polymer thickness throughout the sandwiched layer and flawless electrode surfaces, the average breakdown field can be estimated from this to be $4x10^5$-10^6 V/cm.

Up to breakdown there was little variation in resistance of the sample with applied voltage.
100 to 1000 fold gain in current occurring at breakdown changed the electrical conduction of the sample only if the current was sustained long enough /several tens of seconds/ or if the procedure was repeated a number of times. Otherwise, the characteristic measured after breakdown hardly differs from the pre-breakdown trend.

The use of relatively low /e.g. 10^3-10^4 Ohm/ measuring resistors, with the intention of facilitating the build up of fairly large currents of mA order, did not help, since in this case the rapid current surge could not be stabilized but instead destroyed the conducting state. The most effective means of obtaining systems of lower resistivity was, in fact, to restrict the current with a 10^8 Ohm protective resistor. Nevertheless, even after the first durable breakthrough the resistivity of the sandwich did not remain particularly low once the applied voltage was removed. A second voltage run produced an exponentially increasing conduction with the voltage dependence of the resistance following the form $R/u/ = 10^n e^{-\alpha u}$ /n = 8.5-10.5; $u = U/U_{breakdown}$; $\alpha = 5.4$/ as can be seen in Fig.2. This run was characterized by very considerable local fluctuations, sometimes as much as 100 %. The second breakdown with a 10^6 Ohm protective /and measuring/ resistor occurred at the same or a lower applied voltage as the first. The resistance of the conducting system could be lowered to the same order of magnitude as well. Continueing the procedure with, say, 10^4 Ohm it was eventually possible to lower sample resistance to a few hundred Ohm with a measuring resistor of 100 Ohm.

The above sequence of operations is further evidence for the thermal character of the switching, since it shows that above a certain point of instability the conduction increases stepwise with applied power density. Up to this point the curves are slightly superlinear and can be reset to 0 without hysteresis.

It seems obvious that with the onset of instability the conductive regions formed as a result of warming, Au diffusion and other factors grow either in extent or in degree of contamination or both. The relationship between the average power and the resistance in this region of forming process can be seen in Fig.3. Entering the lower limit /dotted line/ the characteristics show hysteresis. The upper line connects the points where sudden changes in resistance occur. The two lines coincide in the region of small resistances.

The degree of degeneration of the initially well insulating polyethylene film is well documented by the fact that under an applied voltage of 1-2 V the sandwich is capable of transducing currents as high as 10 mA. The maximum observed power at which the conducting state did not deteriorate was 3.5×10^{-2} joule/sec.

With a 20 V pulse of $2x10^{-7}$ second duration taken from a pulse generator having an output impedance of 100 Ohm the sample could be switched back to the pre-breakdown state or the state directly after that, with a resistance in excess of 10^{8} Ohm.

The single small hole visible to the naked eye that was left behind on the Au-polyethylene-Al structure when the switching cycle was completed proves that conduction must have been restricted to a tiny area and that it was ended because of evaporation of the material. When the sample had reached its megohmic oscilloscope trace state it could be controlled by triangular pulses to produce a characteristic with a negative differential resistance differing only in detail from that obtained with sandwiched aluminium oxide [4] and tetracene [2] thin layers.

1000 Å and thinner polymer films broke down easily in such a manner that the Au and Al films of the sandwich adhere to each other and hence the resistance was limited only by that of the metallic electrodes. If striking extended over the entire 1 mm^2 area covered by the crossed electrodes the structure would not function any more. This occurred especially easily with samples pre-exposed to substantial gamma-ray doses /$4x10^{19}$ $eVcm^{-3}$/. The resistance of these samples, even before breakdown, was as low as 10^3-10^4 Ohm. This could be increased up to 20-25 megohm by applying 5-6 V pulses but attempts to produce low-resistance states usually finished up with the creation of 15-20 Ohm short circuits.

Essentially different behaviour was observed when a negative bias was applied to the Au film. In this case the polyethylene could not be brought into a durably conducting state. Higher currents flowed only when the applied voltage was raised; on switching to lower voltages the conduction was the same as that while the applied voltage was being increased. The breakdown voltage was variable and the pre-breakdown I-V characteristic was also quite different. Some samples, for instance, were observed to break down at 80 V while others at 6-7 V, though the thickness was in both cases around 2000 Å.

The current vs voltage characteristic is depicted in the Fig.4. Though the field strength and the current reached much higher values in this case, still the irreversible forming of samples did not appear and there was no lasting increased conduction. On the other hand, samples previously broken down and formed with positively biased Au electrode exhibited the same behaviour with negative Au as the other ones after similar treatment with positive Au /see Fig.2./.

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FIGURE LEGENDS

Fig.1 Sketch of the circuit for the measurement of I-V characteristics

Fig.2 Voltage dependence of the impedance of a 2000 Å thick polyethylene sandwich with positively biased Au electrode

Fig.3 Correlation between forming energy and resistance of the Au-polyethylene-Al sandwich

Fig.4 Voltage dependence of current in a polyethylene film with negatively biased Au electrode /d = 2000 Å/

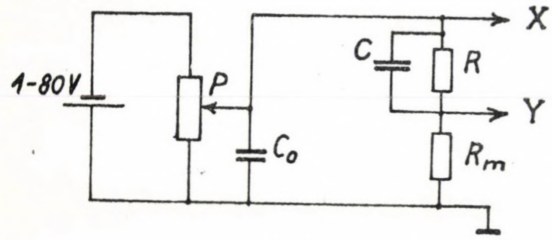

Fig.1.

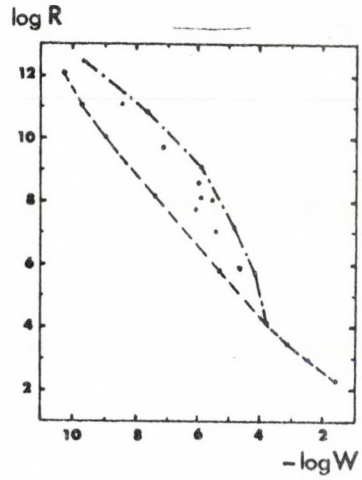

Fig.3.

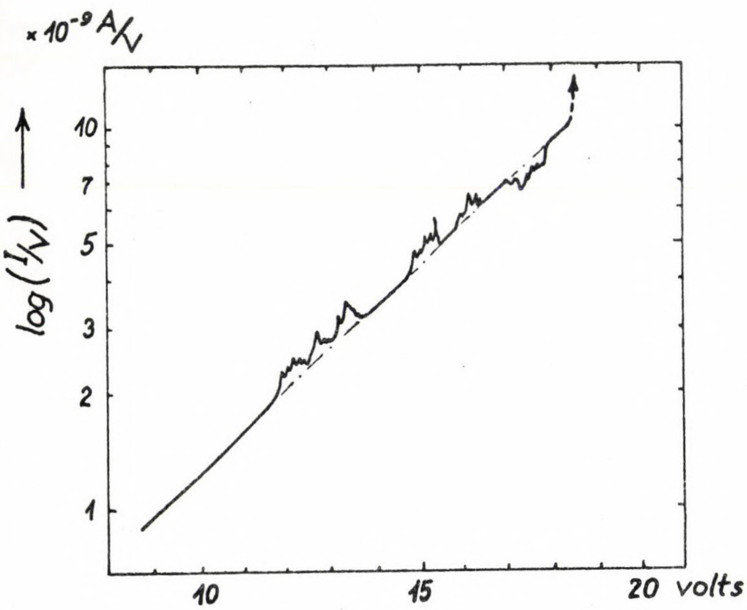

Fig.2.

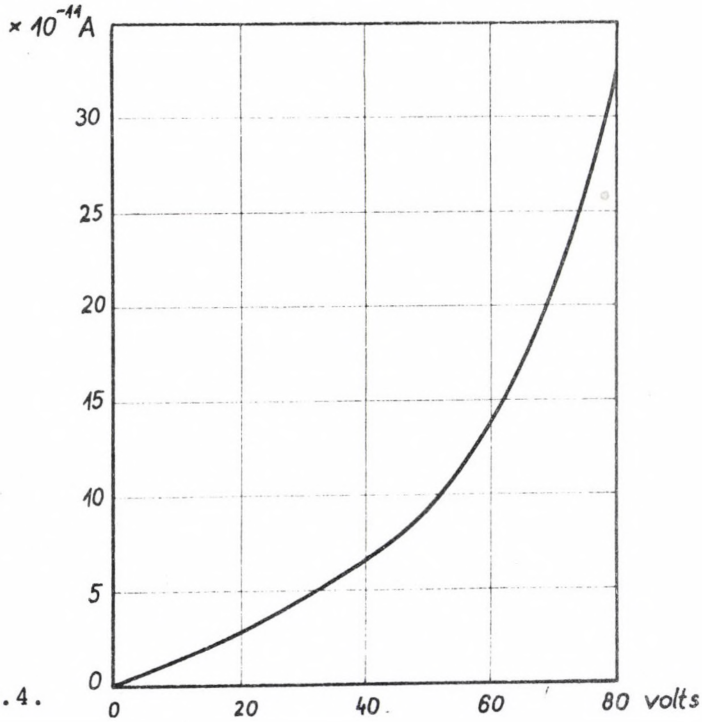

Fig.4.

Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Kiss István, a KFKI Szilárdtestkutatás
Tudományos Tanácsának szekcióelnöke
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Budapest, 1973. október hó