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CONDUCTOMETRIC DETERMINATION OF SINGLE PORES IN POLYETHYLENETEREPHTHALATE IRRADIATED BY HEAVY IONS

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Introduction

Most of previously published works devoted to electrolytic etching of latent heavy ion tracks usually examine the pore opening process in terms of an average picture represented by the measurement of conductivity. By this method only a crude analysis of the pore evolution starting from opening to further etching process going through so-called "core" and "halo" regions is possible. This has been described by Apel et al. (Apel et al., 1998; Apel et al., 2001). According to this work the effective diameter of one pore can be determined by the total diameter of N opened pores in the array and the resistance R of the foil of thickness l according to:

$$d_{\text{eff}} = \sqrt{\frac{4l}{\pi \cdot k \cdot N \cdot R}} \qquad (1)$$

In equation 1 the quantity k denotes the conductivity of the alkali electrolytic solution.

It should be noted that this expression does not take into account the real geometrical shape of pore channel, which becomes conical during the etching process. Further, it is supposed that all tracks will be etched simultaneously and identically. But in fact, the etching conditions may differ due to unequal degree of material damage along the path of the charged particle through the material. Such fluctuations can be explained by heterogeneous structure of the material caused by the manufacturing procedure of polymer foils. However, such fluctuations will be averaged at high particle fluences of more than 10^7-10^9 cm^{-2} but have an important influence on measurements at a very low track density of about 100 tracks per cm^2. Therefore, in this work special attention has to be paid for this effect.

In the present work, the method for a sequential observation of pore opening and further etching was established. In this way, a direct measurement of the conductivity is realized yielding a detailed picture of the sample resistance in the range of 10^6-$10^9 \Omega$. Moreover, samples with no more than $3.7 \cdot 10^3$ tracks per cm^2 were used. Because of such a low fluence, the conductivity values are very low and additional technical and methodical solutions must be developed to ensure reliable experimental conditions. This work continues the early investigations (Schulz, 1998). The special aim of the present work is to investigate the starting phase of etching in irradiated polymer samples in order to obtain the response from the opening of single pores.

Experiment

The set-up for electrolytic etching consists of two thermostatically controlled chambers. Between them the samples of irradiated polymer foils are placed. Every chamber has an electrode which is connected with a generator and a multimeter

correspondingly. The maximal resolution of the multimeter used in a voltmeter mode is 10^{-8} Volts and an internal resistance of 10^{10} Ω. In comparison with the device used previously (Schulz, 1998), no amplification of the electric signal was used.

As samples Hostaphan polyethylene terephthalate foils with a thickness of 20 μm were used. The samples have been irradiated in a stack of three foils performed at the UNILAC facility of GSI (Darmstadt, Germany). Bi ions having initial energy of 11.4 MeV/nucleon are directed perpendicularly to the surface and collimated in such way that only a circle of 1 mm diameter in the center of the sample was irradiated. Thus, only 10 to 30 tracks on a surface of 0.8 mm^2 could be achieved. Taking into account the geometry of the etching chamber it can be affirmed that all tracks are in etching zone. It is important to note that for current density higher than 10^{-6} A/cm^2, the main contribution to the signal results from polarization effects at the electrodes.

To avoid problems occurring from high sample resistance an additional reference resistance was switched parallel to the voltmeter. The voltage drops on it is proportional to the conductivity of the foil and, therefore, depending on the number of pores opened and etched in the etching process. Then the sample resistance R is given by:

$$R(t) = R_{ref} \cdot \left(\frac{U_0}{U_v(t)} - 1 \right) \qquad (2)$$

where U_0 is a voltage at the electrodes supported by the generator and U_v is the voltage drop on the reference resistance R_{ref}.

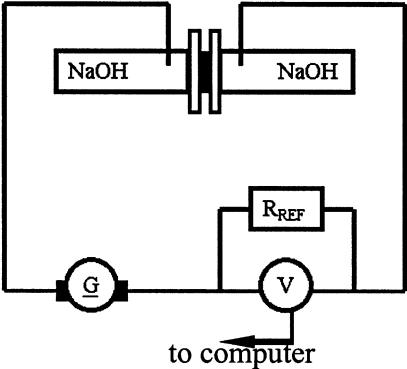A principal scheme of the experimental set-up is presented in Fig.1.

Fig.1. Scheme of the experimental set-up including the etching apparatus and the electric circuit.

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A voltage U_0 of 2V DC proved to yield optimal conditions in connection with a reference resistance of 11 kΩ. After preliminary experiments, sodium hydroxide (NaOH) with a concentration of 0.7N was chosen at a controlled temperature 50^0C. Furthermore, using the LabView program, a model for "step-by-step" track etching of the samples was developed for controlling the data collection and evaluation. The program takes into account the conical shape of pores appearing during the etching procedure at such conditions.

Results and discussion

In Fig.2 the results for $U_v(t)$ obtained with the equipment described above are presented.
As it can be clearly seen that the opening of any pore will result in a step in the function $U_v(t)$. The voltage increase measured at the reference resistance allows the identification of opening of single pores. It demonstrates that after opening of the first pore its diameter is growing and the next pore is opening in parallel. Thus, the etching procedure is characterized by a superposition of a permanent increasing number of pores.
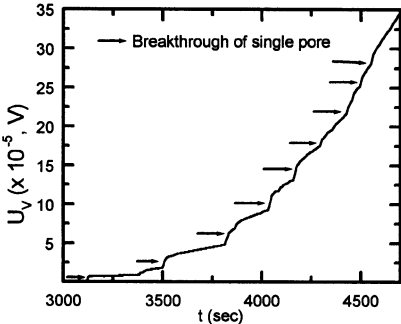

Fig.2. Measured voltage U_v in dependence on the etching time t. The breakthrough of the 1st to 9th pore is marked by arrows.
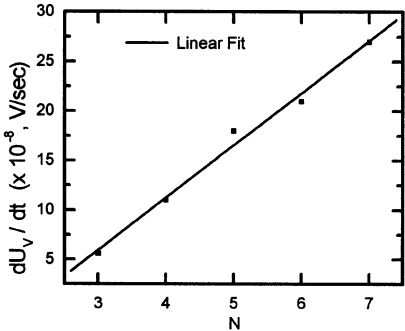
Fig.3. Rate of voltage increase at different steps in dependence on the number of opened pores.

After opening of first 10 pores, the rate of breakthroughs and etching increase rapidly resulting in a fast increase of the measured voltage U_v. Finally, this curve becomes a plateau caused by polarization effects at the electrodes limiting the registration process.
Basic restrictions of the measuring technique are caused by the resolution of the voltmeter which is in the order of $1\cdot10^{-6}$ Volts and corresponds to the typical resistance of the sample of about $2\cdot10^{10}$ Ω and, furthermore, by the velocity of the pore opening process. The time regime can be controlled by a proper choose of the concentration and temperature of the electrolytic solution and the generator voltage in accordance with the thickness and the conductivity of the sample.

The interpretation of the measured curve $U_v(t)$ can be done in two ways, i.e. the investigation of the steps and a calculation of the sample resistance in dependence on the etching time $R(t)$. In both cases results can be obtained concerning the number and the diameter of pores at the starting phase of the etching process.

Examining the slope dU_v/dt at each step a linear increase in accordance with the increasing number of opened pores was found and could be fitted as a straight line. This is shown in Fig.3. Obviously, the registration of opening of the first pore is quite difficult whereas the next pores can be observed very precisely.

Proceeding from equation 2 the time dependent sample resistance $R(t)$ can be calculated and represented in Fig.4. It is obvious that the resistance of the sample decreases proportionally to the number of opened pores. Clearly steps can be verified substantiating that the increasing conductivity is caused by opened pores only.

Comparing the results obtained in this work with a previous one (Schulz, 1998), it can be concluded that the new measuring technique yields an improved resolution which was achieved mainly by suppression of the signal noise. This is shown in Fig.5.
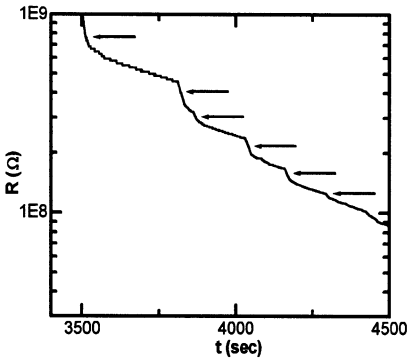

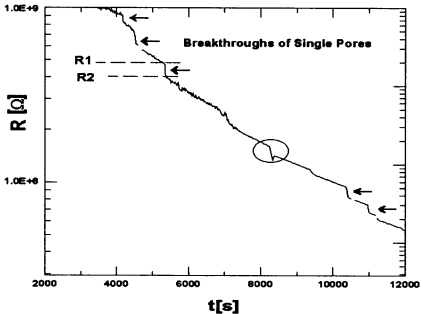Fig.4. The sample resistance $R(t)$ in dependence on the etching time measured in this work.

Fig.5. The sample resistance $R(t)$ in dependence on the etching time. Measurements are taken from (Schulz, 1998).

An estimation of the electrical resistance R_0 of one latent track can be done by using the fundamental relation:

$$R_0 = \frac{4l}{\pi k d_0^{2}} \qquad (3)$$

where k is the conductivity coefficient of the NaOH conductivity at 50^0C and a concentration of 0.7 N, l is the thickness of the polymer foil and d_0 is the latent track diameter. Whereas the quantity k was determined experimentally to

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k=0.2 Ω^{-1}cm^{-1} (Apel, unpublished) a precise value of d_0 is not yet known. Therefore, the approximate value of 10 nm taken from the literature (Fischer, 1983; DeSorbo, 1979) has been assumed. Such a value represents an average over the fluctuations of the latent track diameters arising from different degree of material damage along the charged particle path. This was noted in previous works already (Schulz, 1998; Enge, 1995). With these data a resistance $R_0=8\cdot10^{10}\Omega$ can be estimated.

Now the total diameter D(t) can be defined as the sum over the latent track diameter d_0 of N opened pores according to:

$$D(t) = \sum_{i=1}^{N}(d_{0i} + \Delta d_i(t)) \tag{4}$$

where d_0 is the breakthrough diameter of single pore and $\Delta d(t)$ is the growing of opened pore diameter.

The equation 3 can be reformulated in such way to describe the total resistance of the sample R(t) by:

$$R(t) = \frac{4l}{\pi k D^2(t)} \tag{5}$$

From this equation the total diameter can be determined using the measured sample resistance R(t) by the relation:

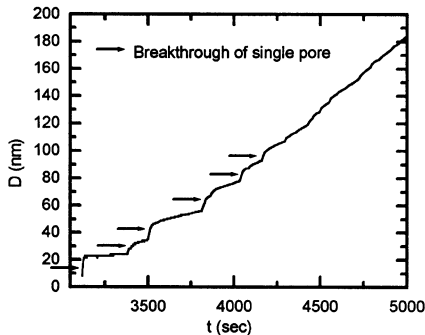$$D = \sqrt{\frac{4l}{\pi k R(t)}} \tag{6}$$

Fig.6. Diameter of all opened pores in dependence on the etching time.

The diameter equal 7-14 nm and it correlates with literature data. In the same time, it should be noted that the value presented on Y-axis of Fig.6 is a combination of two parallel processes described above.

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Comparing results of experiment and LabView model, good agreement was observed in analyzing range of conductivity. Calculations showed that values of current in this range are so small that we cannot take into account the effect of polarization.

Conclusion

A method for characterization of latent heavy ion tracks in polymers was developed using their sequent opening with increasing etching. The most important difference to former investigations is that it is possible now to recognize the sub-level of usual conductometric picture during the etching process. Due to changes in the method of measurement, significantly better results in comparison with previous work have been achieved. Using mathematical and graphical processing of the results, the suitability of this method has been confirmed. The registration of single tracks in the range of resistance from 10^8 to 10^{10} Ω was realized with good quality. The disadvantage of the method is that only opening of some first pores can be observed. Using this method, it is possible to register heavy ions at low fluences, particularly for tasks of dosimetry control if use foils as a detector. Determination of track parameters, such as diameter and etching rate is also available due to direct measurement.

Acknowledgements

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Кондуктометрическое определение одиночных пор
в полиэтилентерефталате, облученном тяжелыми ионами

В большинстве ранее опубликованных работ по проблеме формирования трека не уделялось достаточного внимания прямой регистрации открытия каждой поры в массиве, образованном за счет облучения полимерной пленки ионами. Такие измерения весьма сложны по причине очень высоких значений электрического сопротивления в момент открытия поры. В публикуемой работе приводится исследование пленок, облученных частицами с низкими значениями флюенсов, не превышающих $3{,}7 \cdot 10^3$ ионов/см^2.

В качестве образцов использована ПЭТФ-пленка типа Hostaphan толщиной 20 мкм, облученная ионами висмута с энергией 11,4 МэВ/нуклон. Благодаря оптимальным условиям травления и использованию компьютерной обработки данных, получены результаты, хорошо согласующиеся с теоретическими расчетами и моделью. Измеренный рост проводимости от момента открытия одиночного трека и до открытия следующего, в зависимости от времени травления и числа открытых пор, подтвердил предполагаемую модель процесса. В результате разработан метод регистрации треков, который может быть эффективно использован для описания последовательного появления каждой поры в процессе электролитического травления.

Работа выполнена в Лаборатории ядерных реакций им. Г. Н. Флерова ОИЯИ.

Oganessian V. R. et al. E18-2002-156
Conductometric Determination of Single Pores
in Polyethyleneterephthalate Irradiated by Heavy Ions

Most of previous works devoted to the problem of track formation processes did not pay enough attention to direct measurement of the appearance of every individual pore in an array of many pores induced by the irradiation of polymer films with ions. Such measurements are not easy to carry out due to the extremely high electric resistance in the moment of pore opening. In this work the analysis of films irradiated with low particle fluences up to $3{.}7 \cdot 10^3$ ions/cm^2 is described.

Polyethyleneterephthalate (PET) Hostaphan with a thickness of 20 μm was used. The samples were irradiated with Bi ions of 11.4 MeV/amu energy. Using optimized etching conditions and computer aided data evaluation we obtained results, which are in good agreement with theoretical predictions and model calculations. The measured increase of conductivity beginning from the breakthrough of a single track up to the next pore opening in dependence on the etching time and the number of opened pores confirm the assumed model. Thus, the developed «track-by-track» method can be used effectively for description of the sequential appearance of individual pores in an electrolytic etching process.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

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