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NEW RESULTS ON THE DESCRIPTION OF THE ETCHING PROCESS IN POLYMERS IRRADIATED WITH HEAVY IONS AND THE SYSTEMATICS OF PORE OPENING WITH THE HELP OF THE MODEL OF LOW-ENERGY EXCITATIONS

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The interaction of heavy ions with solid (thin films) produces a narrow radial core of primary damage. The actual nature of the damage and the mechanism of its formation is not yet fully understood. In some recent publications [3,4,5,6] a new model was introduced which is based on the theory that the incident ion causes a disturbed structure directly around its trajectory and is characterized by vitreous properties. It is termed as the model of low-energy excitations. A method to determine the systematics of pore formation has been shown. The thin films have been etched by electrochemical technique and the first results obtained about the opening process of the smallest track have been presented.

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

Новые результаты в описании процесса травления в полимерах, облученных тяжелыми ионами, и систематика вскрытия пор на основе модели низкоэнергетических возбуждений

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Взаимодействие тяжелых ионов с твердым телом (тонкими пленками) создает узкую радиальную сердцевину первичного повреждения. Действительная природа этого повреждения и механизм его образования еще не до конца понятны. В ряде недавних публикаций [3,4,5,6] была описана новая модель, основанная на гипотезе, что налетающий ион производит повреждение структуры непосредственно вокруг траектории своего движения и характеризуется свойствами стеклообразного тела. Она получила название — модель низкоэнергетических возбуждений. Представлен метод определения систематики образования пор. Представлены первые результаты по процессу вскрытия наименьших треков в тонких пленках, подвергнутых травлению по электрохимической методике.

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1. Introduction

It is more than 30 years since Young (1958), Silk, and Barnes (1959) published the first results on nuclear tracks in solids. These investigations were only the begining of the development of new track detectors in nuclear physics. At present, a wide spectrum of problems exists, concerning the etching of materials irradiated by heavy ions.

The explanation of the interactions of heavy ions with solids along their trail, especially the so-called core of the track, is now as ever an actual problem. The core is the range, where an ion generates a primary disturbance. By recent publications a new model is introduced [1]. This model bases on the theory that the incident ion is disturbing the structure directly around its trajectory, described by vitreous properties [2].

Since, for instance, in irradiated polymers the radius of the core is smaller than 10nm, a high quality technique of measurement is necessary to reach out the range of pore radius smaller than 1nm. For calculating the effective radius

$$\bar{r}(t) = \sqrt{\frac{1}{\kappa(R(t) - R_L)}\frac{d}{NS\pi}}, \tag{1}$$

with $\bar{r}$ being effective pore radius at the time t; κ, conductivity of the etchant; $R(t)$, electrical resistance of the conductance cell with membrane at the time t; R_L, resistance of the conductance cell without membrane; d, thickness of the solid film; S, area of the sample in the case of high track density; and N, track density, some important assumtions are provided:

— cylindrical shapes of the pores

— very thin films of solids (polymer films).

If it is possible to measure the time development of these small radii, there arises a new question, namely, the statistics of the opening process of the pores.

The time dependence of pore opening can be developed by applying the model of low-energy excitations. This paper presents an experimental set-up connected with a method which allows one to determine the statistics of the pore origin and to modulate the etching process for values of radii smaller than 5nm. The advantages and disadvantages of this measuring method, its limits and alternatives to raise the accuracy of the measurement are also displayed.

2. The Model of Low-Energy Excitations

In general, all the processes which can be described by the model of low-energy excitations are determinable by the following characteristics:

1) An external perturbation initiates an internal interactive process resulting from an abrupt potential change within a system investigated.

2) This potential change, in turn, causes response phenomena, i.e., there is a reaction to this potential change.

The irradiation of solid produces local regions, where charged particles or dipoles are not compensated completely. Though the solid is electrically neutral, i.e., the sum of all charges is zero, separate regions can have charges causing the polarization. The separate regions are interconnected and if there is a change of polarity in one of them the others will "feel" it. The charge of the solids structure along the latent trail expresses the energy loss of the ion in its travel through the matter.

During the etching process the deposited energy is transferred to the whole solid. The influence of etching reactions can effect a change of polarization in a separate region by the transition of a free charge or a dipole from one state of equilibrium into another. The energy barrier between these states of equilibrium is very small, and so a transition from one into the other is possible. These are the so-called two level systems. But a transition of a charge or a dipole into another state of equilibrium is connected with a change in polarization in the surrounding. The neighbouring regions react to this change and this response can be compared with an oscillation of the regional units. These are low-energy excitations. That's why the model is called the Model of Low-Energy Excitations. A response function, describing the reaction of the solids on the external disturbance, i.e., the penetrating ion, released by the etching process,

$$\psi(r) = \frac{a_0^2}{k_B T e^{n\gamma} l_0 k_c^n} r^{-n}.$$

$$\exp\left(- \frac{r^{1-n}}{(1-n) e^{n\gamma} l_0 k_c^n} \right), \qquad (2)$$

can be calculated by the model. Thereby, r is the pore radius; k_c, the maximal wave number of the low-energy excitations; l_0, the distance between two states of equilibrium if no correlations occur; a_0, the polarization density; n, the so-called interaction parameter; k_B, the Boltzmann constant; T the absolute temperature; and γ, the Euler constant.

The response function is proportional to the radial etching rate in the case of only one pore at the investigated solid.

In the case of high pore density at the solid, the radial etching rate is proportional to the imaginary part of the Fourier-transformation of the response function

$$\chi'' = \int dr \psi(r) \sin(kr) \qquad (3)$$

with $k = \frac{1}{\bar{r}}$. The value $\bar{r}$ is the effective radius.

3. A Possible Variant to Calculate the Statistics of Pore Opening

The shape of the curve of etching rate versus the effective radius is shown schematically in Fig.1. Hereby, the stars represent the measured points and the solid line shows the shape of the curve as a result of the influence of the low-energy excitations during the etching process. The value r_L was selected as the upper limit of the range where the model of low-energy excitations is valid. This value is connected with parameter l_0 characterising the mean distance between the two states of equilibrium and depending on the size of the locally polarized regions. The number of local polarized regions decreases for values greater than r_L, because the etching process itself removed some of these regions. A deviation between the experimental and the theoretical curves can be observed for values lower than r_V.

Equation (1) is used to determine the experimental curve of the etching rate $\bar{v}_R(\bar{r})$, where

$$\bar{v} = \frac{d\bar{r}}{dt}.$$

The number N of tracks per sqcm is assumed to be constant in eq.(1): $N = N_{\mathrm{const}}$. Assuming the etching mechanism is also connected with the generation of low-energy excitations for values $\bar{r} < r_V$, we see that the values of tracks must be lower than N.

This means, that the pores do not open simultaneously, but as a function of time:

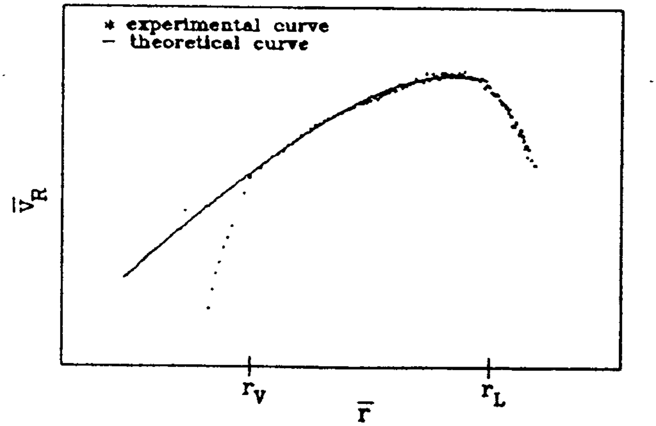

Fig.1. Schematical shape of the etching rate versus the effective radius

$$N = f(t) \quad \text{for} \quad \bar{r}(t) < r_V. \tag{4}$$

With the help of the model of low-energy excitations it is possible to derive the time distribution of the number of opening pores N_{exp}. To calculate this distribution the following steps are necessary:

—Fitting the parameters of the model with the experimental data in the interval $[r_V, r_L]$ (see Fig.1);

— Then the modelized curve will be extended to values lower than r_V;

— Calculation of $\bar{r}(t)$ from the theoretical etching rate $\bar{v}_R$. These values will be destinated as $\bar{r}_{lee}(t)$ (lee ... low-energy excitations).

It is now possible to derive the time distribution of the number of opening pores N_{exp} by including the mentioned difference between the experimental and theoretical curves:

$$\frac{\bar{r}(t)}{\bar{r}_{\text{lee}}(t)} = \sqrt{\frac{N_{\text{const}}}{N_{\text{exp}}}}, \tag{5}$$

the time dependence of N_{exp} can be calculated

$$N_{\text{exp}} = N(t) = N_{\text{const}} \cdot \frac{\bar{r}^2_{\text{lee}}(t)}{\bar{r}^2(t)}. \tag{6}$$

4. Experiment

The experimental set-up is shown in Fig.2. A great number of samples has been measured, each with a different reference resistance, in order to determine the $\bar{r}(t)$-curve very exactly.

The $\bar{r}(t)$-curve has been composed only by intervals of the $\bar{r}(t)$-curves of each measurement, where the resistance of the foil lies in the order of magnetude of the reference resistance:

$$0{,}3R_{\text{Ref}} \le R(t) \le 3R_{\text{Ref}}. \tag{7}$$

With the help of the introduced method the $N(t)$-dependence can be ascertained from the functions which are shown in Figs.3 and 4. This dependence is to be seen in Fig.5. Now the $N(t)$-distribution is known and the $\bar{r}(t)$-function can be corrected. This correction is necessary because the number of opened pores was taken as a constant at the determination of the $\bar{r}(t)$-pairs from the values of foil resistance (see eq.(1)). The result of such a correction is shown in Fig.6, whereby a sample with $1.5 \cdot 10^9$ tracks/cm^2 has been mea-

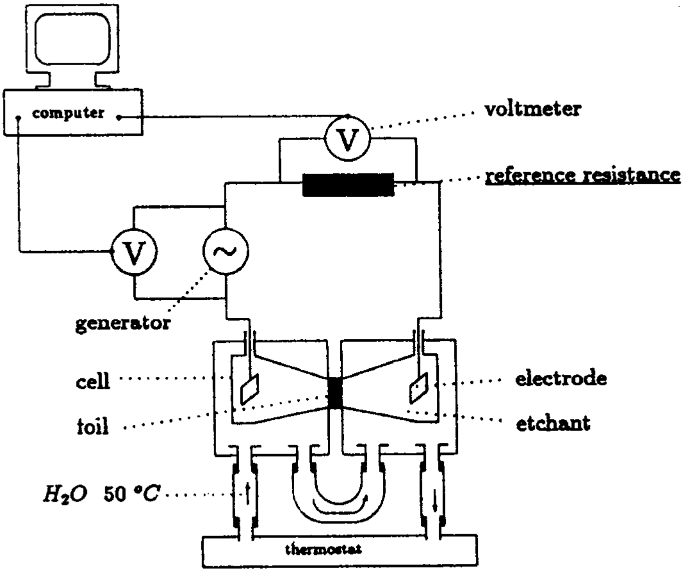

Fig.2. Schematical representation of the experimental set-up

sured. The corrected $\bar{r}(t)$-curve raises for $t < t_{\text{min}}$. A minimum occurs, which cannot be explained theoretically. This means that for values $\bar{r}(t)$ at lower than t_{min} the determined resistances must be wrong, their values are to low. Here are the limits of the experimental set-up. The foil capacity and the

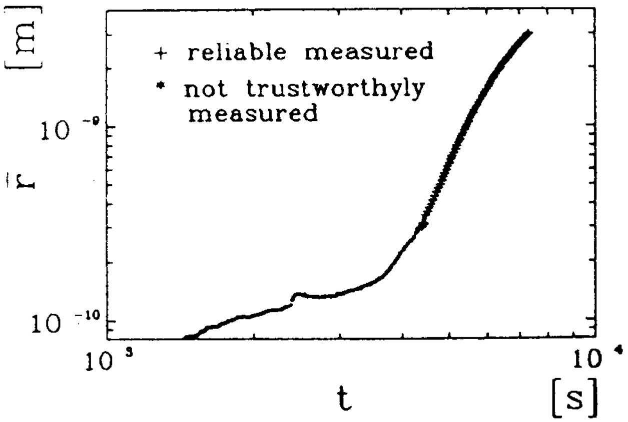

Fig.3. The measured effective radius in dependence on the time

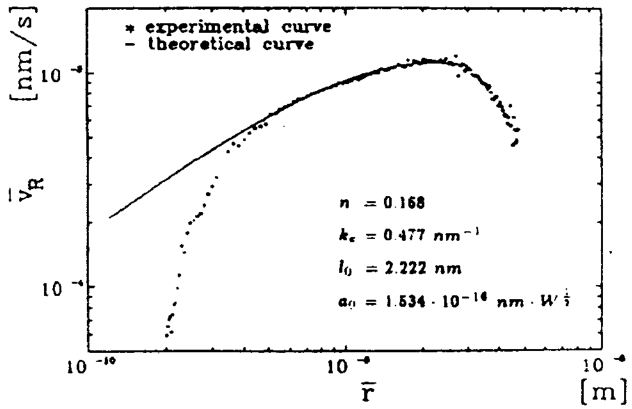

Fig.4. The etching rate versus the effective radius of etched pores

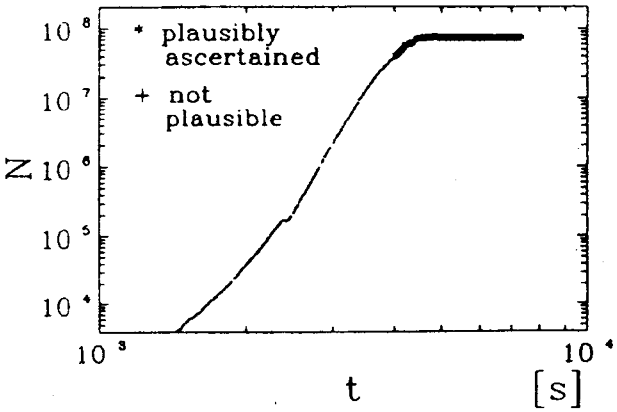

Fig.5. The number of opened pores in dependence of the time

entrance resistances of the voltmeters influence the measurement in such a manner that the values of foil resistance exceeding $5 \cdot 10^5\ \Omega$ cannot be measured exactly.

The $\bar{r}(t)$-curve should approach the curve calculated with the model of low-energy excitations, because it has been determined with constant N for decreasing t-values (see Fig.6: shape of lee-curve). Comparing Figs.3 and 6 it is to be seen that $\bar{r}(t)$ for a foil with $1.5 \cdot 10^9$ tracks/cm^2 can be determined exactly at lower values of $\bar{r}$ yet. The reason is, that the number of tracks per

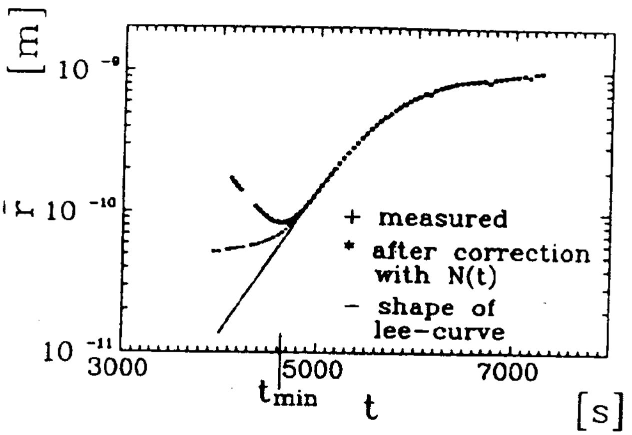

Fig.6 The measured and corrected effective pore radius and its shape calculated with the model of low-energy excitations

sqcm is greater and so the measured resistance, from which $\bar{r}$ is calculated, is already lower than $5 \cdot 10^5\ \Omega$.

5. Conclusions

Using the presented experimental set-up and the introduced method one can show that the pore opening depends on time. The measurements indicate that the pore opening during the etching process has a legal behaviour.

The results also show the limits of the used measuring method. The measuring equipment, which is equivalent to the measurement of resistance, cannot be used to determine resistances greater than $10^6\ \Omega$.

Because the starting value of the resistance lies in the order of magnitude of $10^{12}\ \Omega$ the data greater than $10^6\ \Omega$ in the actual experimental set-up are lost. So, a completely different principle of measurement becomes necessary, just as for measurements with foils, where the number of tracks is lower than that in this paper.

One possible method to solve this problem is the measuring equipment, where the difference between resistances can be determined. This will be the subject of a later paper.

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