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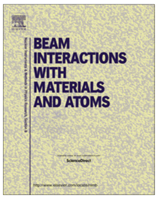

Ion track symmetric and asymmetric nanopores in polyethylene terephthalate foils for versatile applications

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ABSTRACT

In this report we present several fabrication methods which allow production of ion track nanopore membranes with different pore configurations. Polymer foils, typically polyethylene terephthalate with a thickness of 5–23 μm, are irradiated with accelerated heavy ions (energy of 1–10 MeV/u) and then subjected to different physico-chemical treatments. Depending on the procedure, symmetric or asymmetric pores with nanoscale-sized narrowing are obtained. The asymmetric configurations include conical, funnel-like and bullet-like shapes. In electrolyte solutions the asymmetric nanopores exhibit diode-like properties which strongly depend on the pore shape. The peculiar features of such pores provide a basis for various applications.

1. Introduction

Nanopores in polymer foils and inorganic materials have attracted tremendous interest due to their application as biomimetic systems and as miniaturized devices, e.g. ion pumps, molecular sensors, logic elements, and others [1–8]. A well-known method for the production of uniform pores in dielectrics is particle track etching [9,10]. Considerable research activity has been focused on the nanometer-sized ion track-etched pores in polymers in recent years [10–17]. The technique of production of single ion tracks in thin films has become a milestone in advanced studies of artificial narrow pores [10]. Conical and doubly-conical nanopores have been found to be a promising instrument in studying novel ion transport phenomena. Various chemical modifications make it possible to impart useful functions to the pores fabricated in polyethylene terephthalate (PET) or polyimide foils [13,14,16–21]. The performance of a nanopore critically depends on the size and shape of its narrowest region. Further developments require a controllable fabrication of nanopores with pre-determined geometrical characteristics. This paper reviews our main results obtained with the help of different versions of track-etching technique applied to ion-irradiated PET foils.

2. Experimental

Polyethylene terephthalate films (Hostaphan, 5, 12 and 23 μm thick) were irradiated with accelerated heavy ions with specific energy ranging from 1 to 11 MeV/u. The irradiations were performed using the IC-100 and U-400M cyclotrons (FLNR JINR, Dubna) and UNILAC (GSI, Darmstadt). Single- and multi-track samples were employed in experiments. The tracked films were exposed to ultraviolet (UV) radiation from a source that provided $3\,\mathrm{W\,m^{-2}}$ and $4\,\mathrm{W\,m^{-2}}$ of electromagnetic power in ranges B (280–320 nm) and A (320–400 nm), respectively, on the specimen surface. Samples were etched with sodium hydroxide solutions of different molarities (from 1 to 9 mol/L). Anionic surfactant Dowfax 2A1 (Dow Chemicals) was added to etching solutions to obtain special pore geometry. Conductometric monitoring of the etching process for single-track samples inserted in a two-compartment electrolytic cell (see Fig. 1) was performed in AC mode using a PC-controlled LCR-meter (HiTESTER 3522-50, HIOKI, Japan). The current–voltage characteristics of the produced nanopores in a neutral electrolyte (KCl) were measured with the same instrument. The transmembrane current was measured by stepping the voltage between +1 and −1 V. Depending on the required resolution and

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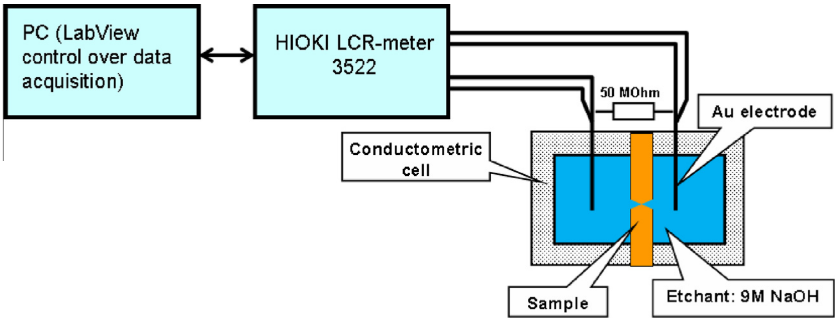

Fig. 1. Set-up used for conductometric etching of samples with single tracks.

magnification, multi-pore samples were examined using either an SEM (JSM-840) or an FESEM (LEO-1530, Zeiss Ultra Plus) instrument. Other details of the sample preparation and examination have been reported previously [15,22].

3. Symmetric doubly-conical pores

Double cone is the trivial geometry that can be obtained using the conventional approach to ion track etching. Chemical etching of an ion-irradiated foil from both sides creates an hourglass-shaped pore with a narrowest part in the middle [23]. The degree of taper, i.e. the cone angle, depends on the track-to bulk etch rate ratio. The size and shape of the pore constriction is of special importance when studying the ion, molecule and particle transport processes in restricted volumes. Such important parameters as electrical field, dwell time, and ionic selectivity critically depend on the pore constriction geometry. The algorithm suggested in Ref. [24] provides a method for a more accurate characterization of the pores produced by symmetric two-sided etching. The method includes conductance measurements performed during the chemical etching of a foil containing single ion track and FESEM measurements on multi-track samples etched in parallel.

The model for the two-sided track etching considers the structure of the latent track to explain the observed dynamics of pore growth. Within a cylinder of approximately 100 nm in diameter, the polymer is substantially modified by ion-induced radiolytic reactions. In the track core (radius < 5 nm), the etch rate V_T is typically several orders of magnitude higher than the bulk etch rate. In the halo (radii between 5 and 50 nm), the track etch rate is slower than the bulk etch rate. With increasing pore diameter, the local etch rate recovers gradually and reaches the bulk etch rate at the outer halo diameter. As a result, double-funnel-shaped (or "quasi-doubly-conical") pores form after breakthrough. The longitudinal profile of the pore is determined by the spatial distribution of radiation effects in the latent track. It is essential that the pore be symmetrical with respect to the center plane of the foil and that its evolution can be regarded as an imaginary (virtual) movement of its two halves towards each other at a speed V_T. Such a consideration allowed us to derive the following equation, which relates the measured conductance of the pore G to its geometrical parameters R and r [24]:

$$\frac{(1 - V_B/V_T)}{R^2(t)} - \frac{1}{r^2(t)} = \left(\frac{k\pi}{2V_T}\right)\frac{d}{dt}(1/G(t)) \qquad (1)$$

here R and r are the radii of pore opening and the constriction in the middle, respectively; k is the specific conductivity of etching solution; t is etching time. Using Eq. (1), the constriction radius $r(t)$ can be calculated using the measured values of $R(t)$, $G(t)$, V_T, V_B, and k. This model of pore development as the movement of two mirror halves makes it possible to obtain the longitudinal profile of the pore, based on the fact that the time dependence and the distance dependence of the radius are linked to each other via the parameter V_T. Fig. 2a shows the profiles of symmetrical pores obtained via the two-sided etching of a U ion single track. The pore's central segments, with a length of 2000 nm, are shown at four different etching times. The deviation from the ideal double-cone geometry extends in an axial direction for up to ±500 nm from the center plane. As the pore widens, its geometry gradually approaches the doubly-conical shape. A prolonged etching is required to approach a conical geometry, which is attained at a constriction radius of approximately 15–20 nm. FESEM observation qualitatively supports the conclusions derived from conductometric data (Fig. 2b). Considering the actual dimensions and shape of the quasi-doubly-conical nanochannels can help improve the quality of future experiments on the transport of ions, molecules and particles in restricted volumes.

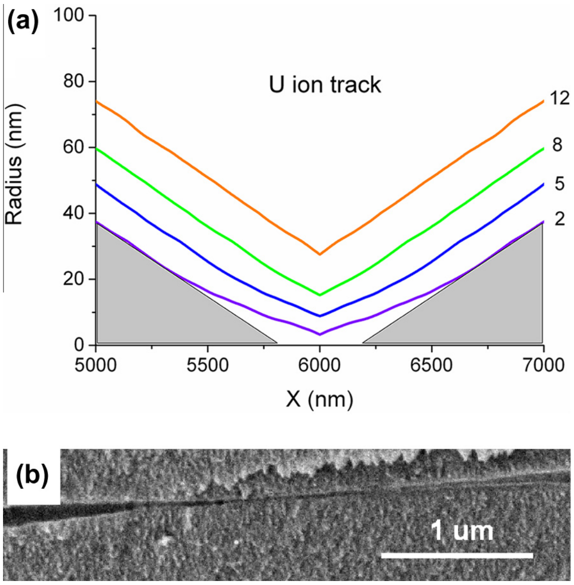

Fig. 2. (a) Central part of reconstructed pore profiles for a U ion track, etched from both sides in 9 M NaOH at room temperature. Center plane: $x = 6000$ nm. The numbers at the curves denote the etching time after breakthrough, in minutes. Inscribed triangles show the deviation from double-cone geometry. (b) FESEM image of central part of pore obtained by two-sided etching of Au ion track. The ions' energy was between 5 and 11 MeV/u.

4. Symmetric cigar-like pores

The principle of the surfactant-enhanced ion track etching resulting in the cigar-like (or spindle-like) pore geometry is