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Report

Ion-track membranes are thin polymer foils irradiated with energetic heavy ions having kinetic energies of several hundred MeV. Along the ion path chemical bonds are broken and new unsaturated bonds are created, leading to cylindrical volumes of increased chemical reactivity compared to the surrounding matrix material. By chemical etching, the tracks can be selectively dissolved and very uniform channels can be created. Nanoporous membranes are frequently used for filtration and as templates for electrochemical deposition of nanowires.

In our beamtime at ID01, we investigated different polymeric membranes such as polycarbonate (Makrofol, Bayer and Pokalon, LOFO), polyarylate (Aryphan, LOFO), polyethyleneterephthalate (Hostaphan, Bayer), and polyimide (Kapton) by small angle x-ray scattering. We fabricated ion track-etched membranes with pores of various sizes and diameters. We also examined membranes electrochemically filled with metal, i.e., nanowires embedded in the templates.

Small-angle x-ray scattering (SAXS) is a non-destructive method giving access to the three-dimensional structure of the investigated specimen, i.e., no further processing is needed after template creation. In addition, SAXS allows us to measure the size distribution of the pores [1]. Scanning electron microscopy also allows the investigation of size and shape of nanostructures, though it is only a surface sensitive technique. In order to obtain information about the pore geometry, a cross-section of the membrane has to be prepared which may result in a deformation of the pores and for investigating nanowires, the template has to be dissolved.

Results

The x-ray intensity as a function of the scattering vector *q* of one of our polycarbonate samples is depicted in Fig. 1 (left), showing strongly pronounced oscillations, as expected for cylindrical scattering objects. Such oscillations were found for Pokalon, Makrofol, and Aryphan membranes demonstrating the highly cylindrical shape of the nanopores as well as the perfect parallel alignment. Such oscillations were not found for Kapton foils neither when treated exclusively in hydrogen peroxide (90 °C, up to 5 h) nor when pre-treated (1 h) and subsequently etched in NaOCl (5 min). Experiments on unetched tracks also did not show any oscillations.

At present, it is not clear if the pores in Kapton do not have a cylindrical shape or exhibit a large size distribution, both effects would result in smearing out of the oscillations.
Small-angle x-ray scattering experiments performed on Pokalon membranes which were irradiated with various ion fluences ranging from 10^8 to $3*10^{10}$ ions per cm^2 and subsequently etched for different times in 5 M NaOH at 60 °C showed pronounced oscillations (Fig. 1 left) [2]. From the oscillation wavelength the mean pore diameter was calculated. From the pore size as a function of etching time, we deduced the radial etching velocity v_r which is plotted versus the ion fluence in Fig. 1 (centre). The etching rate slightly slows down for ion fluences larger than 10^9 ions per cm^2. This effect originates most probably from the fact that the track halos which are created by secondary electrons during the ion irradiation overlap for higher fluences. Cross-linked polymer chains in the halo may decelerate the etching process.
Ion track-etched polycarbonate and polyarylate membranes were investigated in the dry as well as in the wet state. After recording the SAXS data, the samples were stored in water over night and, subsequently, investigated once more. In addition, copper nanowires (Fig. 1 right) were electrochemically deposited in a second membrane that was etched simultaneously with the first foil. All experiments reveal that the diameter of the unfilled pores (both dry and wet sample) and the wire diameter agree with each other within the experimental uncertainties. These data also coincide with the wire diameter determined by scanning electron microscopy. This is a clear indication that the polymer does not swell significantly when stored in water and the wires do not alter the shape of the template due to crystallisation [3].
For polycarbonate, pore diameters measured by means of scanning electron microscopy are significantly smaller than the values determined from SAXS experiments and from size measurements on nanowires. Whereas the diameters obtained by SAXS and on nanowires are identical. The deviation between pore opening on the membrane surface and the inner diameter is attributed to surface tension which results in contraction of the pore opening.

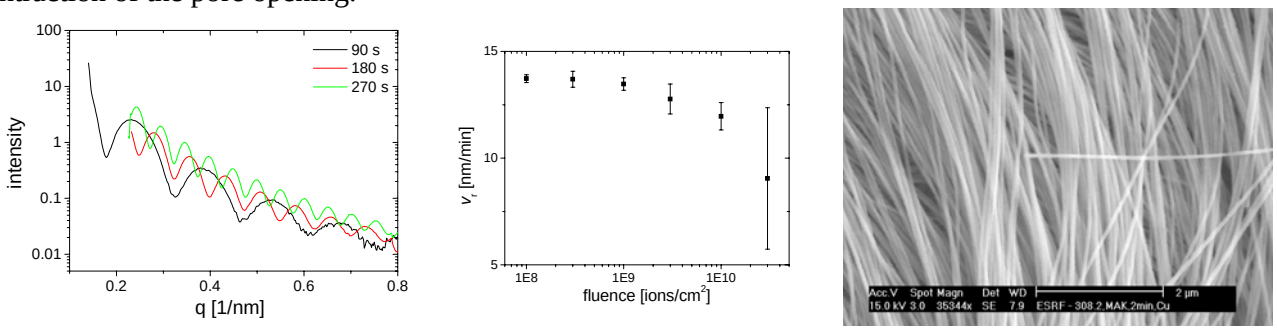

Fig. 1: (left) X-ray intensity as a function of scattering vector *q*. (centre) Radial etching velocity as a function of ion fluence. (right) Scanning electron microscopy image of nanowires.

Finally, it should be mentioned that we performed first test-experiments for in-situ chemical track etching. For this purpose, a special electrolytical cell was constructed fitting to the experimental conditions at the ID01 beamline at ESRF. We could demonstrate the feasibility of this approach, but various technical problems such as leaking have to be tackled in an improved cell version.

References

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