Nuclear Instruments and Methods in Physics Research B 306 (2013) 99–103

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Use of STIM for morphological studies of microstructured polymer foils

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ARTICLE INFO

Article history:
Received 25 July 2012
Received in revised form 27 September 2012
Available online 9 November 2012

Keywords:
Scanning transmission ion microscopy
Proton beam writing
Ion beam imaging techniques
Scanning electron microscopy

ABSTRACT

In this work, morphological characterization of microstructures produced by focused 3 MeV H^+ beams and chemical etching on poly(ethylene terephthalate) foils was investigated by on- and off-axis scanning transmission ion microscopy (STIM). STIM images were obtained from different energy regions of the transmitted energy spectra. STIM performance was compared to scanning electron microscopy (SEM) used as a reference. STIM and SEM images provided similar morphological information. The deviations observed between the measured dimensions obtained from both techniques were within the uncertainties of the experiment. Moreover, the scaling of the structures' size versus etching time (i.e. the etching rates) extracted from STIM and SEM data were equivalent. Prolonged etching times of up to 60 min were performed to check the effect of the irradiation on the non-bombarded vicinity of the structured lines. STIM images clearly revealed a distribution of cavities and porosity along the structured walls for etching times above 20 min. This is attributed to thermal effects and outgassing during the proton beam writing, which probably create voids that are enlarged by the long exposure to the etching solution.

1. Introduction

Proton beam writing (PBW) is an important technique for patterning of materials such as glasses, polymers or semiconductors at high spatial resolution [1]. It has found applications in many areas, such as microfluidics, microphotonics, filtering, physiology and tissue engineering among others [2–5]. Scanning transmission ion microscopy (STIM) is a powerful tool for *in situ* morphological characterization of such structures due to its sensitivity to local mass density and thickness. In a homogeneous substrate, this technique can contrast the fabricated structures from the non-irradiated portion of the sample, thus enabling the determination of their dimensions and geometry [6–9]. Besides STIM, Scanning electron microscopy (SEM) is an important tool for morphological studies of polymers irradiated with high energy ions [10]. Despite the undisputable advantages of SEM, one of the drawbacks is that the sample must be coated with carbon or metals like gold because of the insulating properties of polymers. In this case, STIM could be used instead, since it does not require any further sample preparation.

STIM image formation is based on the energy loss contrast between different areas of the sample that are scanned by a focused MeV ion beam. Different strategies for image formation are employed. For instance, strategies based on the energy averaging technique or median filtering technique can lead to images with reduced noise [6]. Another imaging technique uses windowing of the transmitted energy spectrum, taking into account only those ions whose energy fall in a pre-selected window. Although it may produce rather noisy images, it may be useful for the analysis of simpler structures [6–9] because of the gain in structural discrimination, as it is demonstrated in this paper.

The main experimental arrangement for STIM measurements is the so called on-axis configuration, in which the detector is positioned directly behind the sample and thus aligned with the beam. In this case, the primary interaction occurs between the projectile and the target electrons, leading to relatively small scattering angles. Beam currents must be considerably reduced in this configuration (to several thousand ions per second) in order to avoid damage of the detector. The drawback with this configuration is that it cannot be combined with other measurements such as micro-PIXE or micro-RBS which require higher currents. This problem can be overcome by using the off-axis configuration, in which an

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http://dx.doi.org/10.1016/j.nimb.2012.10.024

angle between the sample axis and the detector (typically between 20° and 45°) is established. This arrangement, however, broadens the spectral peaks, since the ion energy loss includes also interactions with target nuclei, compromising energy and thus spatial resolution [11].

In the present work, on- and off-axis STIM are evaluated as a method for characterization of polymer foils microstructured by PBW. The results are compared to those obtained using SEM in order to assess STIM analytical capabilities.

2. Experimental procedure

Polyethylene terephthalate (PET – Mylar®) foils of 1 cm^2 and 12 μm thick were irradiated at room temperature with 3 MeV protons. The microprobe station consists of an Oxford Microbeams® system operating in triplet mode. A fixed fluence of 6×10^{15} ions/cm^2 and currents varying from 100 to 200 pA were employed for pattering lines on the foils. These lines were drawn in a (100×1) pixels pattern, with a step of writing of 1 μm. The beam spot size was typically 2.0×2.5 μm^2. After the irradiation, the samples were submitted to a 6 M NaOH etching solution in a thermal bath at (60 ± 1) °C with continuous magnetic agitation. The etching time varied from 1 up to 60 min.

The samples were analyzed by on- and off-axis STIM, using a 1 MeV H^+ beam. The reduction of the H^+ energy for the STIM measurements allowed a better assessment of buried structures generated in the polymer without compromising the transmission of the ions. Surface barrier detectors (EG&G Ortec, model BU-011-025-100) with energy resolution of about 8 keV for protons were employed in the measurements. The scan area was 150×150 μm^2 with a 256 pixels matrix. For the on-axis measurements, the current was decreased to around 1500 counts/s at the detector and the total integration time was around 6 min. For the off-axis measurements, a beam current of ~30 pA was used and the number of counts per image is similar to that one obtained for the on-axis case. The angle between the off-axis detector and the beam axis was 24°. Finally, the beam current for on-axis STIM analysis was reduced on the source and not by reducing the slits aperture. This procedure maintained the spot size roughly the same as the one used for the PBW and allowed a straightforward comparison between the on- and off-axis measurements.

STIM maps were produced selecting an energy window encompassing 5–30 channels of the transmitted energy spectra and centered at different positions. In this way, one can highlight structures associated to a particular thickness range which may not be visible if the whole energy spectrum is used. Because of the energy windowing, noisy images are produced but with better detail contrast. The measurements of the length and width of the microstructures were performed with the software ImageJ®, which treats digital images from the STIM maps in terms of color depth. One profile along the major axis and three profiles along the minor axis of the structures were generated, and the resulting edges of the spectra were fitted with error functions in order to obtain the length and width of the structured lines. Fig. 1 shows a drawing depicting the major and minor axis and a typical profile obtained through this methodology.

After the STIM measurements, the same samples were coated with carbon films for the SEM analysis with a Jeol JIB4500 microscope. The samples were tilted by either 52° or 25° in order to measure the height of the walls of the microstructured lines and extract the thickness of the foils. The SEM images were also analyzed using the ImageJ® software. In this case, all dimensions were obtained directly from the images without any need of further treatment.

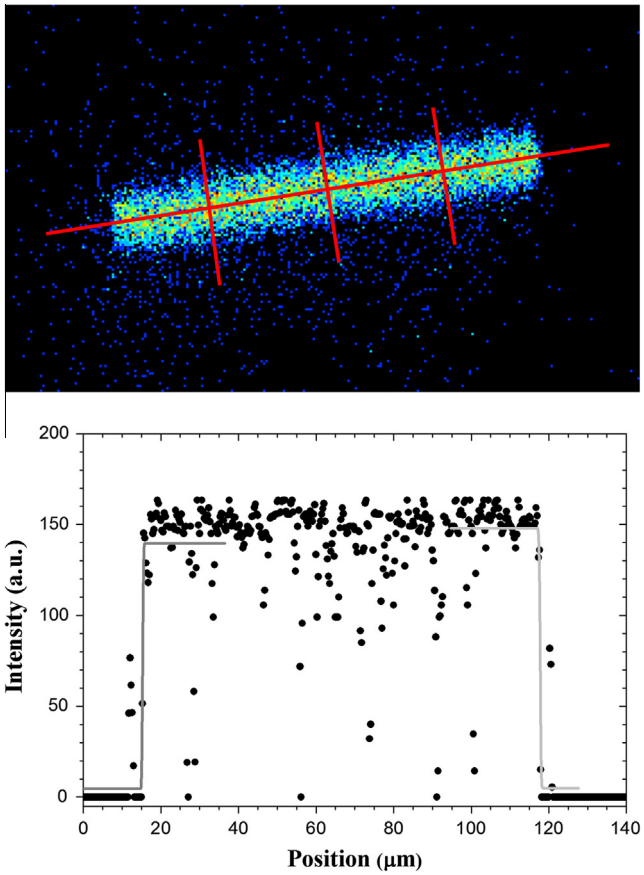

Fig. 1. On-axis STIM image obtained after 10 min of etching. The lines on the top panel represent the major and minor axis from which the profiles were obtained. One typical profile for the major axis is shown with the respective fittings at the edges. The dimensions were calculated from the difference between the centroids of the error (erf) and the complementary error (erfc) functions marked in dark and light gray respectively.

3. Results and discussion

On-axis STIM spectra of all etched samples were characterized by two distinct peaks as shown in Fig. 2. One of them represents the perforation on the sample, i.e. the region where the beam does not loose energy (panel A, energy region D). The lower energy peak (panel A, energy region B) represents the non-irradiated part of the foil where the etching is less effective. In the following discussion, higher and lower energy peaks are referred to as "hole" and "foil" peaks respectively. With increasing etching times, the foil peak approaches the hole peak as expected (panel A in Fig. 3), due to the reduction of the non-irradiated polymer thickness by the etchant. We note that for a sample *not* subjected to post-irradiation etching, the STIM spectrum shows only one broad peak since no hole is directly formed by the writing procedure. In this case, the STIM map obtained by selecting this broad peak shows no contrast in the image. The slight thickness difference at the irradiated line due to sputtering caused by the H^+ beam is apparently too small to be detected in this configuration. By selecting, however, only a narrow shoulder at lower beam energies a STIM map with good contrast at the non-etched bombarded region could also be produced.

STIM maps of etched samples clearly show the hole area, independent of the energy region selected as can be seen in Figs. 2 and 3 (panels B, C and D). The only visible changes are the type of contrast at the hole (negative or positive) and the number of counts of the image. However, additional information could be obtained in samples prepared after longer exposure times to the etchant by selecting the intermediate energy region between the hole and foil