PERGAMON

Production parameters for the formation of metallic nanotubules in etched tracks

D. Fink[a,*], A.V. Petrov[a,b], V. Rao[c], M. Wilhelm[a], S. Demyanov[b], P. Szimkowiak[a], M. Behar[d], P.S. Alegaonkar[a,e], L.T. Chadderton[f]

[a] *Hahn-Meitner-Institut, Glienicker Str. 100, D-14109 Berlin, Germany*
[b] *Institute of Solid State Physics, NASB, P.Brovka Str. 17, 220072 Minsk, Belarus*
[c] *Mangalore Univ., Mangalagangotri 574199 Karnataka, India*
[d] *Instituto de Física, UFRGS, Campus do Vale, 91501-970 Porto Alegre, Brazil*
[e] *Department of Physics, University of Pune, Pune 411007, India*
[f] *Institute of Advanced Studies, ANU Canberra, GPO Box 4, ACT, Australia*

Abstract

The formation of conducting nanotubules in etched tracks is reported in literature since about a decade. However, up to now precise production recipes are scarce. For this sake we present here a systematic study on some important factors that influence the formation of metallic nanotubules. In the case of chemical deposition, the first question to be answered is the choice of the activation technique to produce the required activation centers. Both the time of activation and the time of subsequent chemical deposition are crucial parameters in this connection. Finally, the maximum temperature is determined up to which thermal stability of the etched tracks and of the tubules therein is given. This study should allow one to predict better the efficiency of conducting nanotubule formation.
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Keywords: 81.07.De; 81.16.Be; 61.41.+e; 61.80.Jh

1. Introduction

First a note for clarification: The zones of continuous local damage along the trajectories of swift heavy ions impinging into insulators are denoted as "nuclear tracks", "ion tracks", "latent tracks", or simply "tracks" by the different authors. After etching these tracks, i.e. after removing the radiochemically modified matter therein, pores emerge. Though these pores are no more tracks, they are called slipshodly "etched tracks" or sometimes even simply "tracks" since half a century. In order not to confuse the reader, we follow this historical custom here, too.

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* Corresponding author. Tel.: +49-30-8062-3029; fax: +49-30-8062-2293.

E-mail address: fink@hmi.de (D. Fink).

Matter inserted into these pores—the "etched tracks"— arranges either in the form of nanotubules or of nanowires, also called "nanofibrils" (Martin, 1994). The outer shape of these nanostructures is a direct replica of the inner shape of the etch track templates which is usually cylindrical, conical, or hyperbolical. This is known since long and has been applied already at many opportunities (Martin, 1994); more applications are expected to follow soon (Fink et al., 2003). However, it is strange that, in spite of the great success story of these nanostructures, there has hardly been done any systematic measurement on the parameters that govern the emergence and behavior of these structures. Therefore we have recently presented the first results on the dependence of the wall thickness, crystallinity, and conductivity of Ag nanotubules on the tubule production time (Petrov et al., 2002). This paper intends to continue that work.

2. Experimental fundamentals and results

2.1. Track etching

We have selected several common polymer foils for this study such as polyethylene terephthalate (PET, Mylar©), polyimide (PI, Kapton©), polycarbonate (PC, Makrofol), and silicone rubber. Due to lack of space we compare here only the results in ∼10–20 μm thick PET and PI foils from Goodfellows Ltd. or from Russian provenience with each other. These foils have been irradiated with ∼300–500 MeV Ar, Kr or Xe ions up to fluences between ∼1×10^6 and ∼5×10^8 cm^{-2} at the heavy ion accelerators of either the JINR Dubna (Russia) or of the HMI Berlin (Germany). It is the choice of the projectile and its energy that gives the magnitude and distribution of the transferred energy density along the ion track, which vice versa determine the track-to-bulk etching speed ratio and hence also influence the shape of the emerging pores (the "etched tracks") after etching. Whereas PET irradiated as described above and etched in typical conditions yields rather cylindrical tracks, those ones in PI are usually conical (or hyperbolical if etched from both foil sides), the cone angle χ increasing with decreasing projectile atomic number. Here, $\chi \sim 20°$.

For the etching of the PET foils we used 3 mole/l NaOH at 45°C. Systematic checks of the track shape were made in regular intervals by means of the ion transmission spectrometry (ITS) (Vacík et al., 2000). This technique monitors the energy spectrum of nearly monoenergetic (5.49 MeV) α particles from a 40 kBq ^{241}Am α source, transmitted through the etched foils. When the first α particles are transmitted through the foils without any energy loss, etchant breakthrough has been achieved; the fraction of such particles allows one to calculate the track radius, provided that one knows the areal track density (Stolterfoht et al., 2002). We etched the tracks up to diameters between ∼100 nm and a few μm.

2.2. Production of metallic tubules: chemical deposition

We have produced conducting tubules inside the etched tracks by deposition of Ag, Cu, and Ni. For the metal deposition within the etched tracks we applied the well-known chemical or "electrodeless" deposition (ELD) technique (Lincot et al., 1999). For the deposition of Cu and Ni we used commercial solutions obtained from Doduco Ltd,[1] and for Ag deposition we followed the historical recipe of St. Gobain (Brockhaus, 1895; Thöne, 1955), due to its environmental friendliness. Both Cu and Ag were deposited at ∼24°C, and Ni deposition took place at ∼88°C, following the company's recommendation. In contrast to observations by Martin, neither a strong surface-near reduction of the

inner tubule diameter nor a complete tubule closure was found.

2.3. Nucleation centers

2.3.1. Chemical activation

The formation of durable metal layers on polymeric substrates requires the existence of nucleation centers (poetically called "molecular anchors" by Martin, 1994) on the polymer surface where the metal atoms should precipitate. For the highly advanced commercial polymers used here, the areal density of the naturally abundant intrinsic surface defects which allow metal precipitation and nucleation is too low for the formation of a continuous metallic layer; in this case discontinuous tubules emerge (Fig. 1a). The creation of additional nucleation centers to form continuous tubules (Fig. 1b) can be initiated either chemically by bonding suitable metal atoms (e.g. Sn, Pd) onto the polymeric surface, or physically by creation of dangling surface bonds by laser or ion irradiation.

We used the resistivity along the tubule axis to describe the quality of the emerging tubules. For sufficiently high resistivities, this was done by contacting both front and back sides of the tubule-containing polymer foils with Au electrodes under gentle pressure. To determine very low resistivities, special foils were irradiated through tiny pinholes to reduce considerably the total number of examined tubules (which were counted).

Fig. 2 shows the dependence of the Cu tubule quality on the activation time necessary to produce a sufficient number of nucleation centers. The resistivity of non-activated samples (not shown here), closely resembling to that one after 1 s activation time (Fig. 2), is determined exclusively by the metal deposited at intrinsic defects. As can be seen, already a few seconds exposure to the activation solution improve the tubule quality by several orders of magnitude. Once the nucleation center density has come to saturation, further exposure to the activation solution is inefficient.

The quality of the metallic tubules is correlated with the roughness of their inner surfaces, which is the larger the less nucleation centers were available during the initial tubule growth phase. A high nucleation center density yields smooth inner tubule walls and high conductivity. Also the smoothness of the outer tubule surfaces (as determined by the roughness of the etched track inner walls, depending on the etching conditions such as the etchant concentration) is of some importance. This is nicely demonstrated by the comparison of the quality of tubules in PET and PI prepared under identical conditions. Tubules in PI have much better quality, due to their greater smoothness of both the inner and outer tubule walls.

2.3.2. Formation of nucleation centers by ion irradiation

Instead of applying chemical activation, ion irradiation can be used. Possibly, its main action is to activate by electronic energy transfer e.g. ring structures of the target

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[1] AMI DODUCO GmbH & Co., Geschäftsfeld Oberflächentechnik, Im Altgefäll 12, D-75181 Pforzheim, Germany.
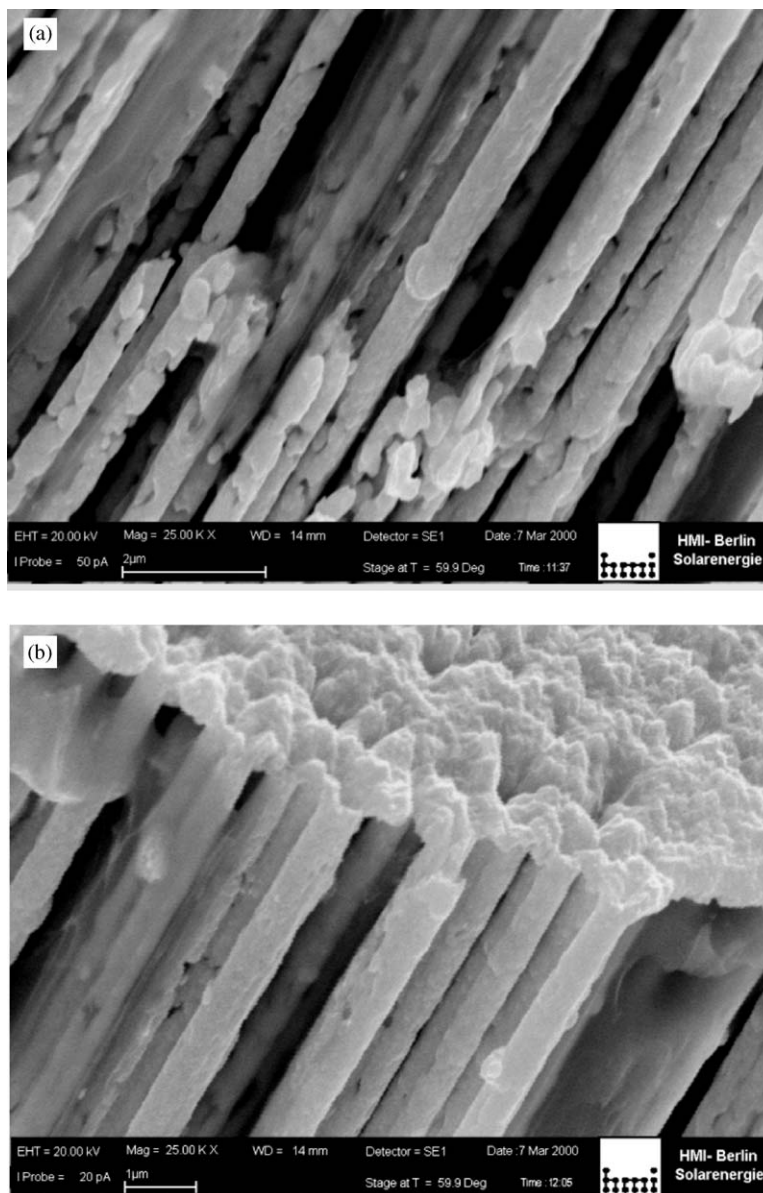
Fig. 1. Comparison between (a) intermittent and (b) continuous ELD-deposited tubules of Ag in PET. Preparation (a) without, (b) with addition of chemical activation centers. Polymer etched away after sample preparation, for better visibility of the tubules.

polymer, so that oxygen can be attached, the latter one enabling the metal addition. First test experiments on the nucleation center formation by 30–300 keV He^+ to Xe^+ ion irradiation have been performed by us, according to which reasonable polymer surface activation is already achieved at fluences of 10^{13} cm^{-2}, rather independent of the used projectile. Further ion irradiation does not alter the findings, which signifies that saturation in the surface activation was reached.

Metal layers deposited on ion-activated polymers appear to be smoother than those ones deposited onto chemically activated ones which points at a higher nucleation center density after irradiation. As ion induced activation takes place only within the particles' range, this approach enables one to tailor the metal deposition along the track axis, so that e.g. cylindrical metal contacts for sensors embedded in tracks can be produced on both sides of a track.
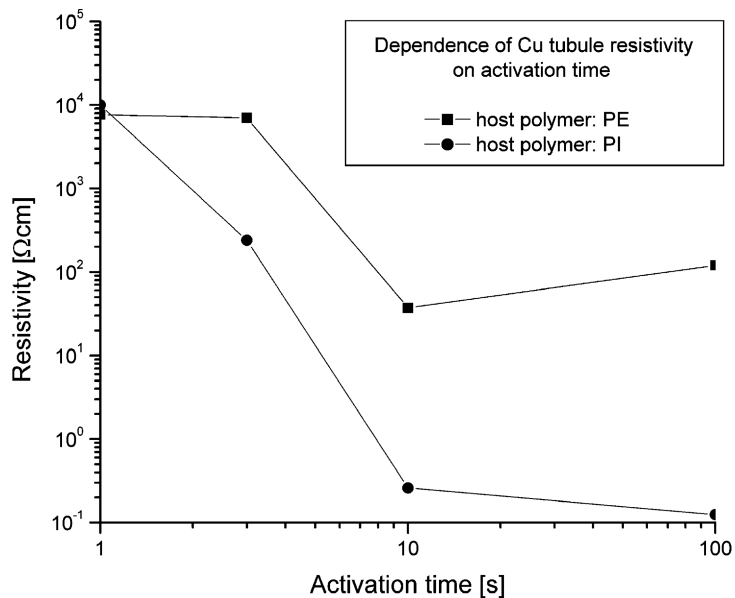
Fig. 2. Dependence of resistivity of microporous PE and PI foils with embedded Cu tubules along the foil's surface normal (i.e. along the tubule axis) on the activation time. Conditions for chemical activation and ELD deposition in all cases given by DODUCO company standard recipes; 5 min ELD solution exposure.
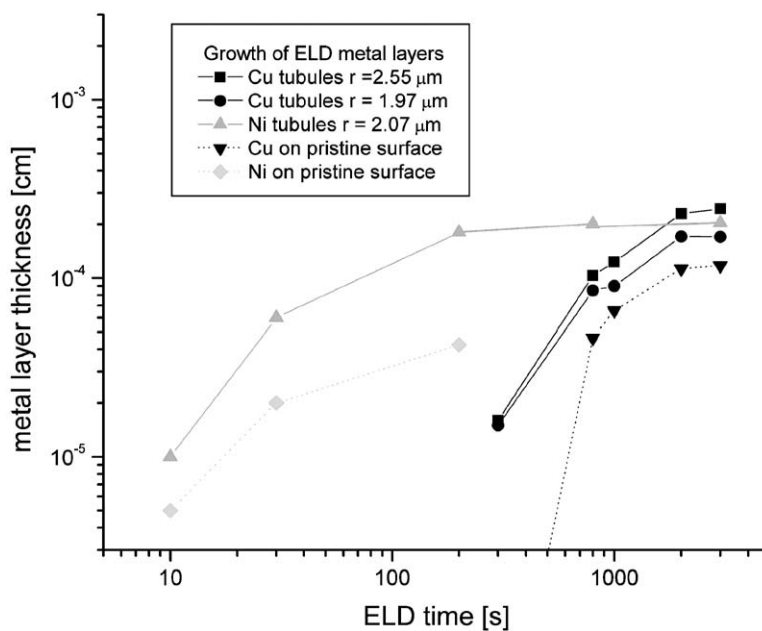

Fig. 3. The growth of metallic layers on PI by ELD. Comparison between growth on surfaces of pristine polymer foils and growth in the interior of etched tracks, for both Cu and Ni.

2.4. Tubule characterization

ELD deposition of metals in tubules sets in after a system dependent incubation time (Ni :∼5 s, Ag :∼1 min, Cu :∼1 1/2 min). At elevated temperature the tubule for-

mation speed is faster (Petrov et al., 2002). Fig. 3 compares the ELD deposition speed at ambient temperature within the etched tracks with that one on unirradiated polymer foil surfaces. The metal layers start growing ∼2 times earlier within the tubules than on the pristine surfaces. This is

attributed to the higher density of activation centers in the etched tracks as compared with the pristine surfaces, as radiation-damaged inner track walls are expected to bond the sensitizers better than inert pristine polymer surfaces. The metal deposition both in the tubules and on unirradiated surfaces continues up to hours with steadily decreasing deposition speed—the latter one either stemming from the exhaust of the given solution, or in the case of narrow tracks, from their complete filling. There is no remarkable difference in the deposition speed on pristine surfaces and tubule walls, for whatever tubule radius, which demonstrates, that the diffusion speed of the ELD solution even within very narrow tracks is no decisive parameter.

The direct consequence of the increasing metallization of the microporous foils is a dramatic change in their conductivity. In the initial stage of metal deposition the resistivity falls by many orders of magnitude from the insulating via semiconducting to conducting state, until a continuous metal layer has been formed. Thereafter, the further decrease in resistivity is determined by the increase in layer thickness. The resistivity improves faster inside the tracks than on the foil surfaces, consistent with the enhanced metal layer growth within the tracks.

We could prove by SEM, conductivity measurements, and ITS (not shown here in detail) that the metallic tubules are continuous and hollow throughout the whole thickness of the polymer foil. Rutherford Backscattering measurements have revealed, however, some variation of the tubule wall thickness along the tubule axis. This will be reported in more detail elsewhere.

2.5. Thermal stability of etched tracks and metallic nanotubules

As many proposed ion track applications require high temperatures, either for device preparation or application, the behavior of tracks and the structures embedded therein must be known. First examinations of that kind have already been made (Vacík et al., 1999). According to these findings, etched tracks in PE first widen slightly upon annealing due to release of bond water (from the etchant), then become narrower due to the onset of glassy flow, and finally widen again rapidly due to carbonization. Ag tubules embedded in such tracks appear to lose their parallel alignment above the glass transition temperature T_g so that their transmission rapidly decreases upon annealing. For PI however, the tracks maintain their shapes well up to $\sim 450^\circ$C, and thereafter, concomittent with the onset of carbonization, they increase in width. Silver tubules embedded in these tracks lead to stable structures up to $\sim 650^\circ$C.

3. Conclusions

The number of reported ion track applications is rapidly growing. These applications frequently make use of structures such as nanowires or nanotubules embedded in these tracks. Therefore we have studied the production and behavior of these nanostructures in more details, specifically looking at the parameters of activation and chemical deposition, and at the thermal stability of the tubules. These results should enable one to better tailor their production strategies and to better predict the functionality of nanotubules in future devices.

Acknowledgements

References

Brockhaus, K.-L., 1895. Brockhaus, 14th Edition, Leipzig, Berlin und Wien, Vol. 15, p. 149 (in German).

Fink, D., Alegaonkar, P.S., Petrov, A.V., Fahrner, W.R., Berdinsky, A.S, Rao, V., Müller, M., Dwivedi, K.K., Chadderton, L.T., 2003. The emergence of new ion track applications, Radiat. Meas. this issue, doi:10.1016/S1350-4487(03)00209-9.

Lincot, D., Froment, M., Cachet, H., 1999. Chemical deposition of chacogenide thin films from solution. Adv. Electrochem. Sci. Eng. 6, 165–235.

Martin, C.R., 1994. Nanomaterials: A membrane-based synthetic approach. Science 266, 1961–1966.

Petrov, A., Fink, D., Müller, M., Sieber, I., Wilhelm, M., Stolterfoht, N., Papaleo, R., Schulz, A., Vacík, J., Červená, J., Hnatowicz, V., Chadderton, L.T., Berdinsky, A., Fahrner, W., 2002. Nanotubule formation by heterogeneous nucleation of silver along etched nuclear tracks in polyethylene terephthalate (PET). Proceedings of the Third Sibirian Russian Workshop and Tutorials on Electron Devices and Materials (EDM2002), Erlagol, Altai (Russia), July 1–5, 2002 (IEEE 02EX518, ISBN 5-7782-0380-1), Vol. 1, pp. 31–35.

Stolterfoht, N., Fink, D., Petrov, A., Müller, M., Vacík, J., Červená, J., Hnatowicz, V., Chadderton, L.T., Berdinsky, A.S., 2002. Characterization of etched tracks and nanotubules by ion transmission spectrometry. Proceedings of the Third Sibirian Russian Workshop and Tutorials on Electron Devices and materials (EDM2002), Erlagol, Altai (Russia), July 1–5, 2002 (IEEE 02EX518, ISBN 5-7782-0380-1), Vol. 1, pp. 36–39.

Thöne, K., 1955. Chemie im täglichen Leben., Hallwag, Bern, pp. 14–16 (in German).

Vacík, J., Červená, J., Hnatowicz, V., Fink, D., Kobayashi, Y., Hirata, K., Apel, P.Yu., Strauß, P., 1999. Study of latent and etched tracks by a charged particle transmission technique. Radiat. Meas. 31, 81–84.

Vacík, J., Červena, J., Hnatowicz, V., Posta, S., Fink, D., Klett, R., Strauss, P., 2000. Simple technique for characterization of ion-modified polymeric foils. Surf. Coat. Technol. 123, 97–100.