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Influence of a surfactant on single ion track etching: Preparing and manipulating cylindrical micro wires

Leo C.T. Man [a], Pavel Apel [b], T. Cheung [a], Lars Westerberg [c], K.N. Yu [a], Cristian Zet [d], Reimar Spohr [e,*]

[a] City University Hong Kong, Department of Physics and Materials Science, Hong Kong, China
[b] Joint Institute of Nuclear Research, Centre of Applied Physics, Dubna, Russian Federation
[c] Uppsala University, Svedberg Laboratory, Uppsala, Sweden
[d] Technical University Iasi, Department of Metrology, Iasi, Romania
[e] GSI and EuNITT, Darmstadt, Germany

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Abstract

The influence of the alkali resistant surfactant Dowfax 2A1 on single ion track etching in 30 μm polycarbonate foils is studied at low etch rate (5 M NaOH at 41.5 ± 2 °C) using electro conductivity measurements. At surfactant concentrations above 10^{-4} vol.% breakthrough times are predictable ($\Delta t/t < 0.25$). At high surfactant concentrations ($\geqslant$0.1 vol.%) the formation of cylindrical channels is favoured. The shape of these channels (length $\geqslant$ 26 μm, diameter $\geqslant$ 1.8 μm) is verified by electro-replication and SEM observation of the resulting wires. Agreement of radii is better than 0.1 μm. Depending on the current limit set during electro replication compact or hollow cylinders can be obtained. A technique for localizing and manipulating individual micro wires by their head buds is described.

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Introduction

Ion track etching [1] requires at least one energetic heavy ion or fission fragment to supply the energy necessary for rendering a cylindrical volume around the ion path developable in a dielectric solid. It opens a new route to micro technology decisively different from conventional lithography [2] while conventional lithography is based on a mask and on the collective interaction of many low-energy photons or electrons with a resist material, the ion track technique works usually without a mask. In contrast to lithography, the ion track technique can be applied to a wide selection of dielectrics [3]. This fact resides on the high energy density stored in the track core.

The ion track technique enables narrow, high aspect ratio structures with defined cutting angle whereby each structure is exactly due to one penetrating ion. Various other shapes are possible, such as narrow and wide cones, spherical troughs, barrels, and bottle necked structures [4]. Replica techniques are used to create spatially modulated textured objects such as wires with axially [5] or radially [6] varying composition.

Single ion tracks can serve as basic building blocks for larger aggregates or composites. Aimed single track structures are possible [7].

Track etching and electro-replication can be studied in real-time using electro conductivity measurements while

* Corresponding author. Tel.: +49 6151 376184; fax: +49 6151 376185.
E-mail address: r.spohr@gsi.de (R. Spohr).

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SEM can be used for verification. In this way, electro conductivity measurements can accelerate the exploration of new processes.

Surfactants improve the wetting of hydrophobic polymers. They form mono layers on the polymer surface [8] and reduce etch attack [9].

The report describes the effect of the (acid and alkali resistant) surfactant Dowfax 2A1 [10] on ion track etching at low etch rates. Above about 1 μm channel diameter, the result is essentially a cylindrical channel.

1. Experimental technique

1.1. Electrolytic cell

A 30 μm thick polycarbonate membrane with a single heavy ion track (11.3 MeV/u U-238, [11] is inserted into an electrolytic cell consisting of two cell halves with flat sealing surfaces facing the central membrane (Fig. 1, [12,13]). The membrane is etched on both sides with 5 M NaOH at (41.5 ± 2) °C while applying over the membrane an alternating voltage of 1 kHz frequency at 0.1 V amplitude using gold electrodes.

1.2. Phase sensitive detection

The phase shift between the applied ac voltage and the resulting current is determined by integrating the product of voltage and current over a number of voltage cycles, similar to a Lock-In Amplifier. During each cycle the double layer at the electrode/solution interface is continuously charged and discharged. At 0.1 V amplitude and 1 kHz frequency electrode impedance is purely capacitive and sufficiently small to be neglected in the equivalent circuit (Fig. 2).

The real part of the impedance reflects the geometry of the etched channel and the imaginary part of the geometry of the membrane. Phase-sensitive detection suppresses out-of-phase noise. From the break-through time, an approximate value of the track etch rate is determined. If the number of tracks and their length, as well as the conductivity of the etchant is known, the radial etch rate can be determined. Etching or electro deposition can be stopped at a preset value. Channel growth can be frozen at a prescribed diameter and wire growth at a prescribed length or bud size.

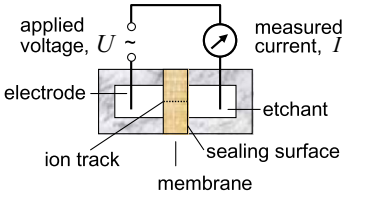

Fig. 1. Principle of electrolytic cell for real-time control of track etching and electro replication.

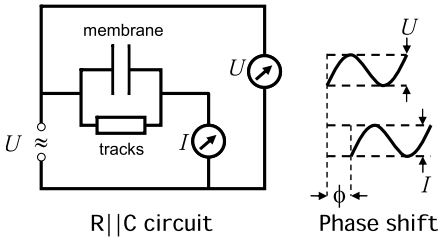

Fig. 2. Equivalent circuit for measuring membrane thickness and channel radius.

1.3. Track radius

Amplitude and phase of the resulting alternating current are measured as function of time. For sufficiently high track etch ratio the resulting channel can be approximated by a cylindrical channel of diameter $d = 2r$ and resistance $R = \frac{4t}{\sigma\pi d^2} \Rightarrow d = \sqrt{\frac{4t}{R\sigma\pi d^2}} \Rightarrow r = \sqrt{\frac{t}{R\sigma\pi d^2}}$, where t is the membrane thickness $(30 \pm 1$ μm), σ is the conductivity of the etchant (0.57 S/cm for 5 M NaOH at 41.5 °C), and $R = U/I$ is the ratio of the applied voltage amplitude U and the real part of the resulting current amplitude I.

2. Results

2.1. Break-through time

Polycarbonate membranes are hydrophobic. As it appears, the surfactant enables a reproducible contact between the etching medium and the hydrophobic membrane in the electrolytic cell. A small surfactant concentration ($\geqslant 10^{-3}$ vol.%) is sufficient for fairly constant break-through times of (345 ± 82) s (Fig. 3). This corresponds to 24% variation of the break-through times.

2.2. Radial etch rate

During etching the channel radius increases with time. The surfactant decreases but stabilizes the etch rate. With increasing surfactant concentration the radius becomes increasingly a linear function of time (Fig. 4). By differen-

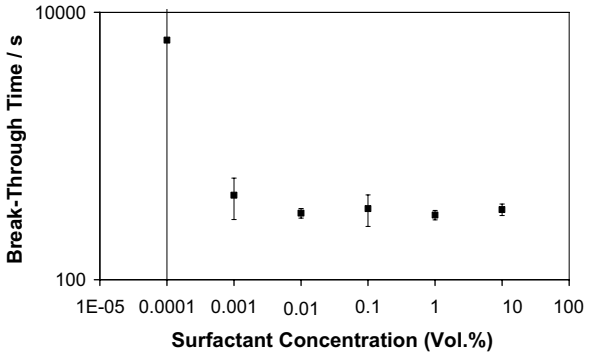

Fig. 3. Influence of surfactant concentration on break-through time. Above surfactant concentrations of 0.001 vol.% fairly reproducible break-through times are obtained. Each point corresponds to 3–5 single track membranes. Vertical bars are standard deviations.

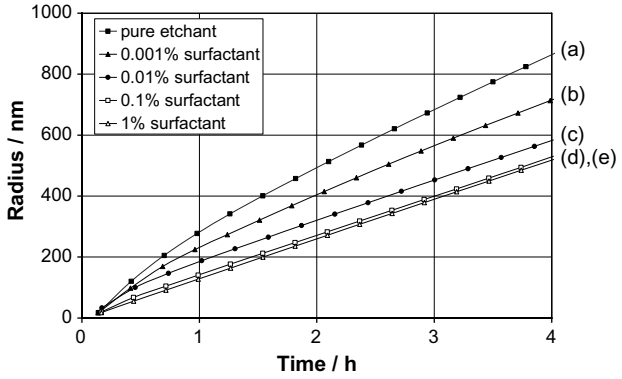

Fig. 4. Radius as function of time. With increasing surfactant concentration, (a) to (e), the radius becomes gradually an almost linear function of time.

tiation of the radius with respect to time, the radial etch rate $V_r(t)$ is determined. Using the inversion of the monotone function $r(t)\rightarrow t(r)$, V_r can be plotted as function of r (Fig. 5). With increasing surfactant concentration the steady-state of radial etching (ca. 0.13 μm/h) is reached faster. At high surfactant concentration ($\geqslant$0.1 vol.%) the radial etch rate becomes rapidly constant except at small radii (30–100 nm). This favours the formation of cylindrical channels.

2.3. Electro replication

To verify the electro conductivity measurement, a single ion track is etched 9.6 h in 5 M NaOH plus 1 vol.% of Dowfax 2A1 surfactant at (41.5 ± 2) °C. For determining the shape of the resulting channel it is electro replicated (Fig. 6) using the following steps.

A gold film is deposited on the rough side of the membrane and pressed against a polished copper cylinder replacing the right cell half. A copper anode is inserted into the left cell half. The left cell half is filled with an acidic copper sulfate solution (220 g $CuSO_4$ penta-hydrate + 36.8 g $H2SO_4$ per liter of etchant). The current is limited by a resistor of 10^8 Ω in series with the electrolytic cell. For a negative dc voltage between cathode and anode

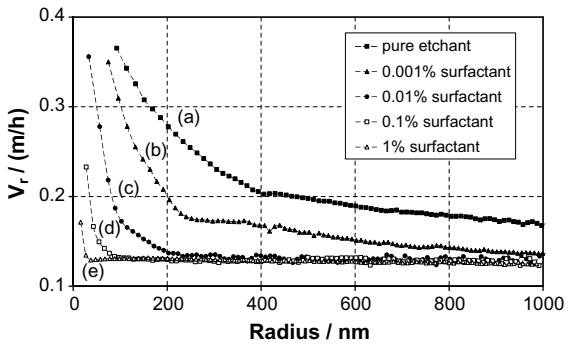

Fig. 5. Radial etch rate V_r as function of radius (derived from Fig. 4). With increasing surfactant concentration, (a) to (e), the steady-state of radial etching (about 0.13 μm/h) is reached faster.

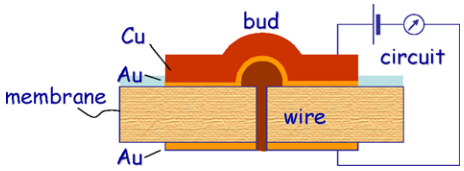

Fig. 6. Contacting a single wire [14].

(ranging between −0.5 and −10 V) the deposition current is limited between 5 and 100 nA. Low deposition currents correspond to the growth of compact cylindrical wires. High deposition currents correspond to the growth of hollow cylinders.

2.4. Manipulating a single wire

After completing the wire, electroplating is continued until a bud of 30 μm diameter is reached. The membrane is dried, the bud is localized under a stereo microscope at

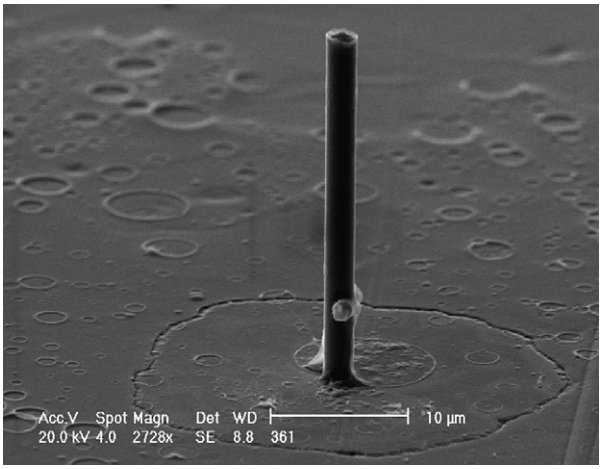

Fig. 7. Compact wire. Copper replica of cylindrical ion track channel electro deposited at 10 nA maximum current. Diameter 2.2 μm, length 25.6 μm, bud diameter 31 ± 3 μm.

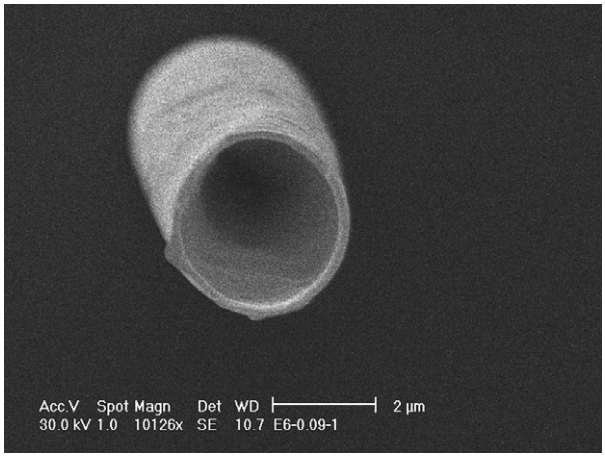

Fig. 8. Hollow wire. Copper replica of cylindrical ion track channel at 100 nA maximum current. Diameter 3.5 μm, length 27.3 μm, bud diameter 31 ± 3 μm.

Table 1
Comparison between electro conduction and SEM measurements

Figure	Type	Surfactant conc.	Etch time/h	Current limit/nA	Pore diam./μm		Pore length/μm		Wall/μm
					Calc.	SEM	Calc.	SEM	SEM
–	–	10^{-2}	9.8	5000	2.38	2.39	27.6	–	–
Fig. 8	hollow	10^{-5}	13.0	100	3.52	3.55	26.4	27.3	0.18
–	–	10^{-4}	12.5	100	1.84	1.91	28.2	–	–
Fig. 7	full	10^{-2}	9.7	10	2.16	2.19	27.8	25.6	–

Agreement of radii is better than 0.1 μm.

grazing illumination, and a circle around the bud marked with a polished needle. A gold film is deposited on the shiny side of the membrane. A copper layer of ca.1 μm thickness is electro-deposited on the gold film keeping the deposition current density $\leqslant 10\ mA/cm^2$. A copper wire of 0.7 mm diameter is soldered to the periphery of the 1 μm copper film. Using the copper wire as handle, the polycarbonate is dissolved in DiChloroMethane. During dissolution the gold film on the bottom side (rough side) of membrane is removed. Using the copper wire as handle the micro wire is transferred to a conductive adhesive tape on a SEM holder.

Electro replication at 10 nA limiting current results in a hard, compact, polycrystalline copper wire (Fig. 7). Electro replication at 100 nA limiting current results in a hard, hollow polycrystalline copper cylinder (Fig. 8).

The agreement of SEM and conductance measurement is verified using 4 wires with diameters between 1.8 and 3.5 μm (Table 1).

3. Discussion

3.1. Pore shape control

The interplay between etch attack and protection by a surfactant, combined with different molecular mobilities, enables to control track shapes [9,4]. The present concept of track shaping is as follows (Fig. 9, [15]).

The hydrophobic tails of the surfactant adsorb on the polymer surface exposing their hydrophilic groups toward the etchant. The adsorbed layer protects the polymer from etch attack. The large molecules of the surfactant diffuse slower into the track lumen than the small molecules of the etchant.

At *high etch rate* (high concentration of the etchant and high temperature) the inner lumen of the etched track remains unprotected and reacts fast with the etchant. A barrel shaped channel is formed (Fig. 9(a)).

At *low etch rate* (low concentration of the etchant and low temperature) the protecting action of the surfactant molecules dominates. The molecules of the surfactant penetrate into the track lumen and organize into a protective sheath along the pore wall before the etchant starts reacting (Fig. 9(b)). Lateral etching is suppressed and longitudinal etching prevails. Large track etch rates (cylindrical pores) result.

Cylindrical channels require a low reactivity of the etching medium. Since the described experiments use modest etchant concentration (5 M NaOH) and temperature (41.5 ± 2) °C, the protective action of the surfactant dominates. Almost cylindrical channels are formed.

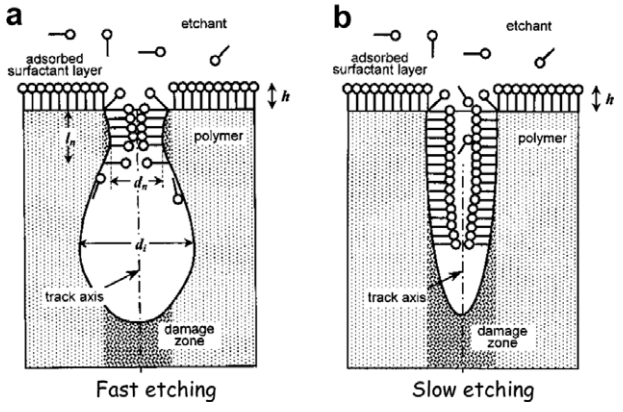

Fig. 9. Influence of surfactant on track etching. (a) Fast etching – barrel shaped pores [4]. (b) Slow etching – cylindrical pores [15].

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