Electronic Setup for Etching Ion Tracks and Electrochemical Deposition of Materials Inside Nanopores

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Abstract- During last years, ion track technology has attracted considerable attention. This technology uses as support polymer foils irradiated with ion beams produced by heavy ions accelerators. Accelerated ions passing through these foils produce latent ion tracks by breaking the polymer chains [1]. Latent ion tracks can be selectively removed by chemical etching and obtain nanopores with diameters going down to 10nm. Nanopores can be used as they are or can be filled with metals to obtain nanowires [2]. Both, the etching process and the electrodeposition can be performed in the same electrochemical two-compartment cell, the polymer foil being positioned between them. To control the etching or the deposition process an electric setup must be arranged. The cell configuration is different for etching or growing, but the setup is very similar. It includes a computer with data acquisition board, a picoamperemeter and the electrolytical cell. This configuration is equivalent with a potentiostat but with the possibility to apply different waveforms and to store large amount of data without overloading the computer.

I. Introduction

Studies on the nanowires structures and properties last since 35 years, but they increased steadily during the last decade. Ion track technology opens a new route in micro an nanotechnology [1], [2], [3] allowing to realize high aspect ratio structures with minimum diameters going down to the range of 10 nm. Etched single ion tracks can be used as counting and sizing apertures [4], as bio-mimicking devices [5] and as templates for the electro deposition of metal wires [6]. Multiple ion tracks arrays can be used to prepare textured materials with highly anisotropic properties depending on pH, temperature or electromagnetic fields.

First measurements were performed on arrays of nanowires prepared by the template method. In those works, the nanopores of etched-ion track or anodic alumina membranes were filled with metals [1], [2]. The large number of nanowires (typically 10^8-10^{10} cm^{-2}) embedded in the membrane is then contacted in parallel to characterize them. In order to improve the experimental trust degree, single ion track or single nanowire must be contacted and studied. Several attempts to contact a single nanowire out of an array have been reported in literature. For example, after deposition of an array of nanowires, one or few of them were selectively contacted by fabricating very small and localized metal electrodes on the polymer surface by means of electron beam lithography [7]. In other experiments, a floating electrode (metal layer deposited on the membrane surface) was employed for contacting the first wire protruding the membrane surface during deposition. However, none of these methods do guarantee that single wires are contacted (and not two or more), and good statistics is needed for obtaining a reliable absolute resistance value. Moreover due to the fact that the deposition is interrupted immediately after the first wire touches the surface, the contact between the wire and the floating electrode is relatively fragile. This makes the method suitable enough for measurements taking place at a short time after the preparation step, but longer storage or transport from one laboratory to another are difficult. Moreover in this case due to contact fragility only low current densities or pulsed voltages can be employed during measurements. In an alternative method for characterizing metal or semiconductor nanowires, randomly distributed [8] or flow-aligned nanowires [9] were placed onto a substrate, individual wires being subsequently contacted by optical or electron-beam lithography. This technique does enable to measure the absolute resistance of single wires, but is time consuming and requires lithography techniques, special caution being needed in order to avoid bad contacts due to oxidation of the external surface of the nanowires.

The method developed in GSI, uses single ion irradiated polymer foils, etched until desired diameter is reached. Later on, inside the pore, different metals or semiconductors can be deposited. The method is simple because it asks for one copper layer on one side, than the wire can be grown from solution and in the end, after the cap is big enough on the other side, a gold sputtered layer will be the second contact. The contacts are big enough, the contact resistances are small comparing with the wire resistance and last for long time. In order to make this, an electrolytic cell [10] together with an electronic setup, which is the main subject of this paper, must be used. Problems related on the measurements of very small currents and acquisition, storage and display of large quantity of data must be solved.

II. Electrical setup

Around the electrolytical cell, a picoamperemeter and a data acquisition board driven by a computer is used. According to the desired action, two configurations are available. They are presented in figure 1.

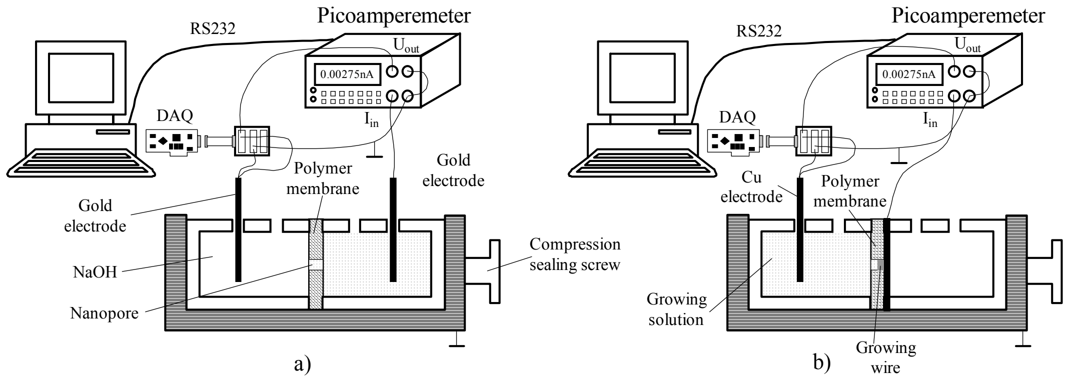

Figure 1. The electric setup: a) the etching configuration; b) the electrochemical deposition configuration

This is a potentiostatic configuration, in which the data acquisition board is generating the controlled voltage and measuring the voltage and the current (converted into voltage), and the picoamperemeter is used only as current to voltage converter. Through the RS232 interface the picoamperemeter can be driven for the appropriate scale, or its display can be read into the computer.

A. The electrochemical cell

The electrochemical cell is made from two chambers, in between being placed the irradiated foil. The part of the foil that separates the chambers must contain the ion track. For sealing the chambers, a dynamometric screw is used. The two chambers are filled with the proper etchant, for example NaOH for polycarbonate or HF for polyimide, for etching configuration, or just the left one with the solution containing the material for deposition, on the back side of the foil being deposited a gold or copper layer for contacting the second electrode. The voltage is applied by mean of two gold electrodes, inserted one in each chamber (fig. 1). The voltage is applied on one electrode, referred to the other, that is practically connected to the system ground through the picoampermeter.

B. The electrical configuration

Depending on the purpose, there are two electrical configurations available (figure 2). The main differences are the replacement the active electrode with one from the metal is being deposited and of the second gold electrode with a copper back-layer. The voltage is applied on circuit from the analog output 0 (DAC0out) of the data acquisition board. The circuit is formed from the solution path, the ion track and the picoamperemeter. The voltage drop introduced by the picoamperemeter (burden voltage) is around 180μV, negligible against the total voltage applied (200mV for Cu deposition). The applied voltage is measured on analog channel 1 (Ach1in) in order to know the exact applied voltage (DAC offset or voltage drop due to current limitations). The picoamperemeter converts the small current flowing in the circuit into a voltage (0 – 2V). The conversion ratio depends on the scale of the instrument. This voltage is measured with the data acquisition board on channel 0 (ACh0in) from the instrument analog output. Because this output is referred to the ground, the picoamperemeter low input must connected at the system ground. Using the serial or GPIB interface, the current meter is driven for remote range shifting. This is necessary for the correct computation of the current from the measured voltage.

Because the main quantity is usually a very small current, shielding and noise precautions must be taken. The electrochemical cell is surrounded with a thick metallic shield connected to the ground. The used cables are coaxial type on Teflon support with silver-plated copper wires. This way, reduced triboelectric and piezoelectric effects are achieved [11].

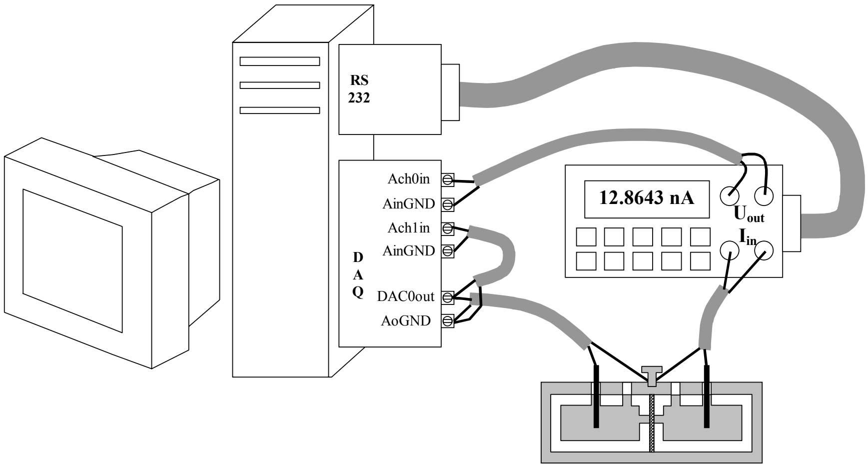

Figure 2. The electrical circuit

III. The virtual instrument

The hardware is driven from computer by a virtual instrument developed in National Instrument's LabView. In order to make it more versatile and easy to debug, it contains 4 VI's: Main.vi, Kscale.vi, Acquisition.vi and ElDepGen.vi. When running, all 4 are active (figure 3).

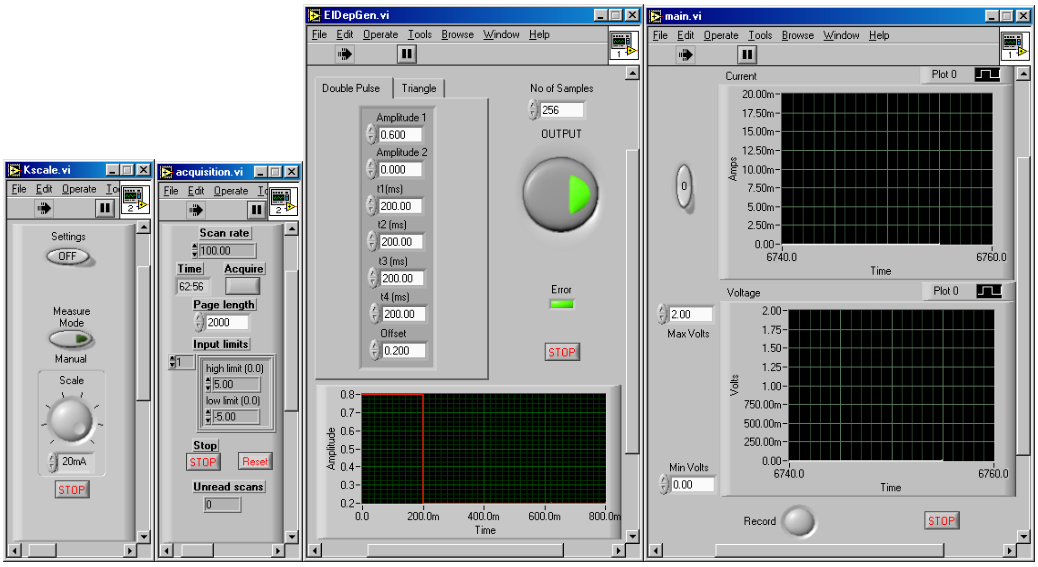

Figure 3. The virtual instrument: the front panel

When starting Main.vi, it opens first the other three, one by one, and it closes them down when Stop button is pressed. Main.vi and Acquisition.vi communicate via global variable (global.vi). Thus, acquired data and acquisition parameters are transferred to Main.vi.

a) Main.vi

This is a very simple instrument that opens the other vi's, display the acquired data and closes the auxiliary vi's when Stop is pressed. On its panel (figure 3) there are two graphs, one for the current and the second for the applied voltage, two controllers for the limits of the displayed voltage, one button for unipolar or bipolar for the current and one indicator for recording data.

b) Kscale.vi

This instrument is used to drive the picoamperemeter via the RS232 serial interface. The operator can program the instrument on automatic scale or on manual scale (Measure mode button). In order to get the proper current to voltage conversion ratio, the manual scaling must be used. The scale value (Scale knob) is made available for other vi's via global.vi. The panel has another button for setting the serial communication parameters (baud rate, parity, start and stop bits). This gives access to the settings panel (figure 4 b).

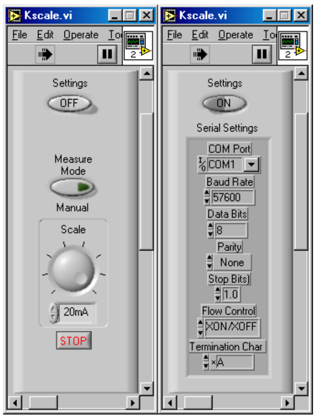

Figure 4 Kscale.vi front panel

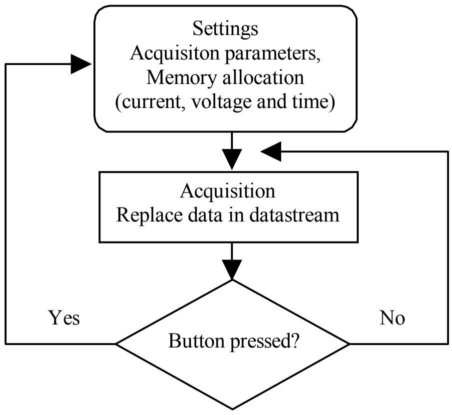

Figure 5 Acquision.vi flow diagram

c) Acquisition.vi

This is the most important VI. It is responsible for the acquisition parameters: scan rate and input limits. The operator can choose from "Page length" controller (figure 3) the length of data stream kept in memory and displayed. This has been introduced because working time is sometimes very long and large amount of data will stuck the computer or when the sampling frequency is high, the data will accumulate very fast and buffer overflow will occur. This way, the memory allocated for storing the data is constant. Usually 2000 sample length is enough to follow the process. If data is necessary to be stored, the "Acquire" button will start saving the data into a file. After the data page is completed the data is flushed on the hard-disk, and a new page is started. Starting from sampling frequency, time and unread scans are displayed. The acquisition is continuous buffered, and no sample is lost. Another trick for minimizing the computer load was to keep the memory allocation functions outside the main loop, and to keep inside just the necessary operations (figure 5). Even acquisition parameters are programmed outside the main loop, and will take effect after "Reset" button is pressed. Files as long as 140Mb have been recorded without any interruptions.

d) ElDepGen.vi

This is an independent VI. It can generate pulse or triangular waveform by choosing one of the two tabs. On pulse waveform, DC and bipolar or unipolar train pulses with different amplitudes can be generated. The operator can program the amplitudes of pulses, pulse length and offset. If amplitudes are zero, DC voltage is generated. For triangular waveform, only frequency and amplitude are available. The number of samples per period can be chosen from the "No of samples" controller, and the waveform shape is displayed on a graph. The output is zero until "Output" is pressed.

IV. Experimental testing

The system has been used to fabricate nanopores and to deposit metals inside them. Polymer foils were irradiated, normal to surface, with single ion, using Xe, Au, and U ion beams of energy higher than 7.8MeV/nucleon. As polymer, polycarbonate has been used because no special or toxic etchants were necessary. To achieve cylindrical pores, prior to etching, foils were irradiated with UV light, in order to increase the track etch selectivity. The foil is inserted between the two chambers of the cell. The chambers are filled with aqueous 2M NaOH solutions kept at 40°C. A DC voltage of about 400mV has been applied between the gold electrodes placed one in each chamber. After about 40 minutes, the break-through occurs (figure 6) [12].

For conical pores one side of the membrane is covered with Cu, and the etching solution is on the other side of the membrane. The voltage is applied between one gold electrode and the copper back layer. The voltage must be pulsed, bipolar, 0.2Vpp because the process is going faster. The current spikes that can be seen at the transitions are generated by the foil capacitance, but only the pulse itself

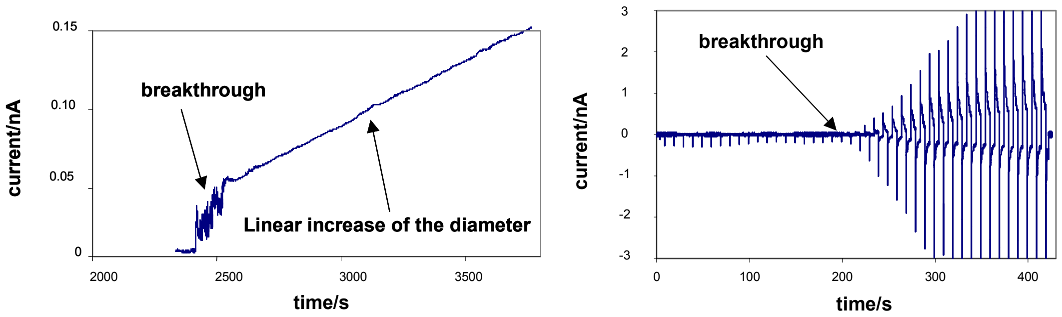

Figure 6. Typical etching curve: a) cylindrical pore; b) conical pore

is useful to determine the pore diameter.

When growing pure metallic nanowires, DC voltage must be applied corresponding to the electrochemical potential of the metal. For example, for copper the voltage is 200mV, and a typical growing curve is shown in figure 7 a, and for Co the typical voltage is around 800mV and the growing curve is shown in figure 7 b [13]. Four phases can be distinguished: 1. the polarization phase, 2. the current plateau, 3. the growth of nanowire, 4. the growth of cap after completely filling the pore. For layered wires, pulsed voltage is necessary, but the whole graph is not suggestive and it is very hard to get because of very large amount of data.

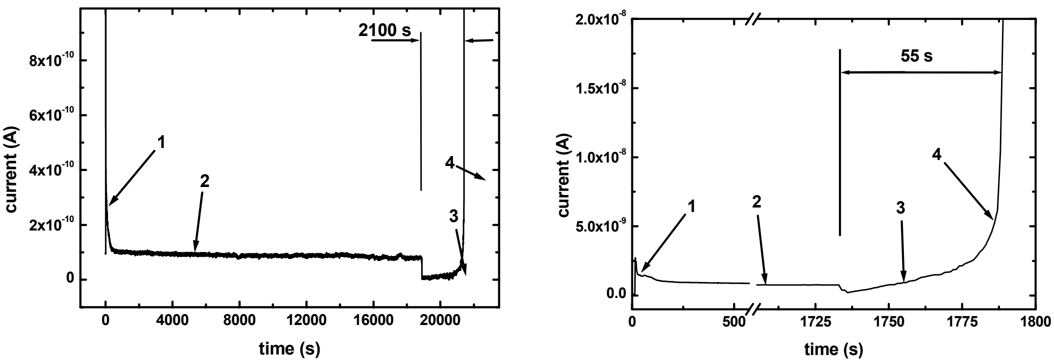

Figure 7 Typical deposition curves: a) growth of copper nanowire; b) growth of Co rich nanowire

IV. Conclusions and results

Interest and applications of the nanopores and nanowires keep the attention of researchers around the world. In order to produce and study them, an electronic setup has been developed. Problems, related on picoamperes current measurements (minimizing triboelectric and piezoelectric effects), and large amount of data recording, at relative high speed, over long time periods, have been solved.

The setup has been used with success to obtain nanopores with various shapes (cilyndrical, conical, etc) and nanowires from various metals (copper, bismuth, nickel) or layered nanowires (copper/cobalt). Figure 8 left shows the SEM image of a conical nanowire from Cu/Co alloy (1:32). Its length is around 30μm and the diameter varies from 100nm down to 15nm. Layered nanowires were grown from $CuSo_4/CoSO_4$ solution (figure 8 right). About 600 bilayers (28nm Co/14nm Cu) occupying 80% of nanowire's length (30μm) were deposited with pulsed voltage (100ms/800ms) as in figure 9.

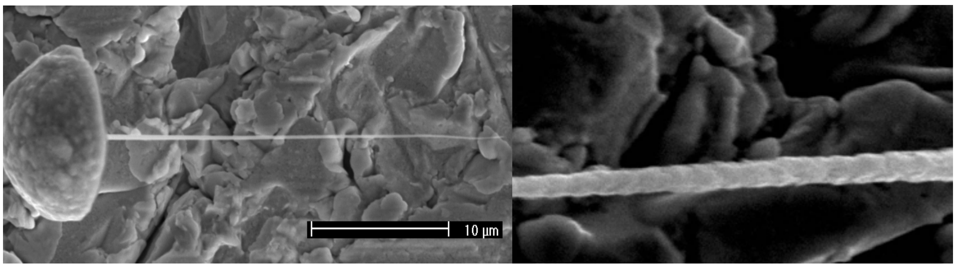

Figure 8. Cu/Co alloy nanowire (left) and Cu/Co layered nanowire (right) – SEM images

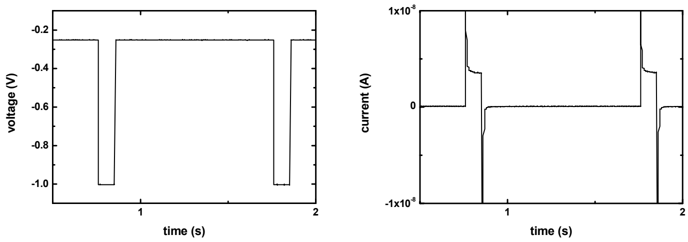

Figure 9 Pulsed voltage and current during growth of layered nanowire

The setup provides a simple and efficient way to develop nanostructures and to control their dimensions and geometry. Fast data acquisition and storage allows the surveillance and later study of the process.

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