Virtual Potentiostat

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Abstract - In recent years, nanowires have attracted considerable attention because of their expected extraordinary physical properties and large number of possible applications in research and technology. There are different techniques to get nanowires, like electrodeposition from aqueous solutions or growth from vapors, each one characterized by special conditions and limitations. The electrodeposition process asks for a potentiostat This article presents such a device realized around a PC with data acquisition board allowing the remote control and data recording over long time periods.

I. Introduction

Studies on the nanowires structures and properties last since 35 years, but they increased steadily during the last decade. Several alternate techniques for producing nanowires exist, each characterized by special opportunities and limitations [1]. Track etching technique is based on the irradiation of polymer materials with energetic heavy ions leading to the formation of linear damaged tracks across the irradiated polymeric layer or film. These tracks are then revealed into pores using a well-chosen wet chemical etching. The etching process and the electrodeposition can be performed in the same electrochemical two-compartment cell, the polymer foil being positioned between them. A potentiostat is used to control the potential of the counter electrode regard to the reference electrode. The potentiostat has two working modes: constant current and constant voltage [2]. Ion track technology opens a new route to micro and nanotechnology realizing high aspect ratio structures with minimum diameters down to the range of 10 nm [3]. This technology is used for industrial production of filters, printed circuit boards, heat exchangers and anti-fraud coding.

II. Standard Potentiostat

A potentiostat circuit combined with an electrochemical cell form a potentiostatic system. The potentiostatic system consists of a circuit which accurately maintain a preset potential between the working and reference electrodes of an electrochemical cell. Often included in the potentiostatic system is the ability to measure the current flowing thru the electrochemical cell [4]. The standard potentiostat circuit consists of a differential input amplifier used to compare the potential between the counter and reference electrodes to a required working bias potential. This is done by adding to the desired potential the reference voltage (OA1). Any changes in the impedance between the counter and reference electrodes will cause a change in the voltage applied between the electrodes. In order to maintain the constant voltage between working and reference electrodes, an operational amplifier is used (Fig. 1). The working electrode is held at virtual ground by a current to voltage converter (OA2).

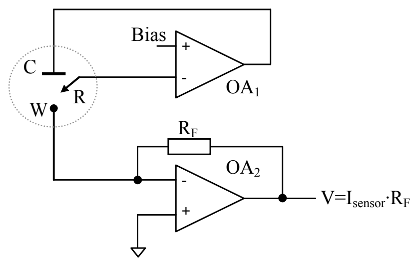

Figure 1. Conventional Potentiostatic System (W=Working, C=Counter, R=Reference)

The potentiostat will compare the reference voltage to the desired bias potential and adjust the voltage at the counter electrode to maintain the proper working-to-reference voltage. This method can lead to instability due to the increase in the input impedance of the current follower at higher frequencies.

III. Diagram of the potentiostat

Around the potentiostat, an electrochemical cell and a data acquisition board driven by a computer are used (Fig.1). 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 electrochemical cell is made from two chambers, in between being placed the irradiated foil. 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, for the electrodeposition configuration. The voltage is applied by mean of two gold electrodes, inserted one in each chamber (figure 2). The voltage is applied on one electrode, referred to the other, that is practically connected to the system ground [1].

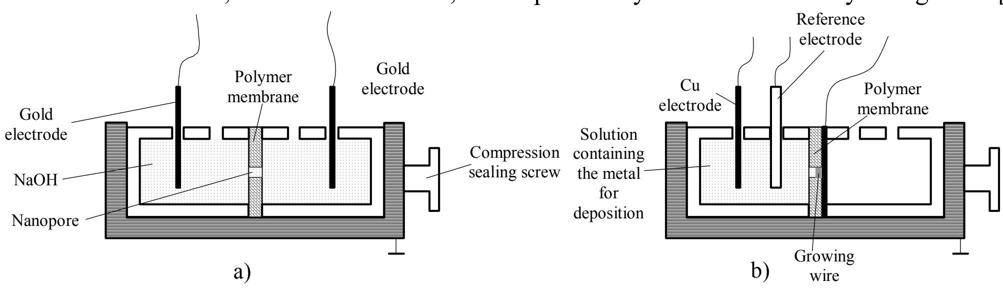

Figure 2. The electric setup: a) the etching configuration; b) the electrochemical deposition configuration

A personal computer with an acquisition board (National Instruments PCI-6036E) [5] is used to control the voltages applied to the electrochemical cell and to measure the current flowing through the cell. Another function accomplished is the digital control of the output and input scale. The important data are recorded together with the time for further processing and analyzing.

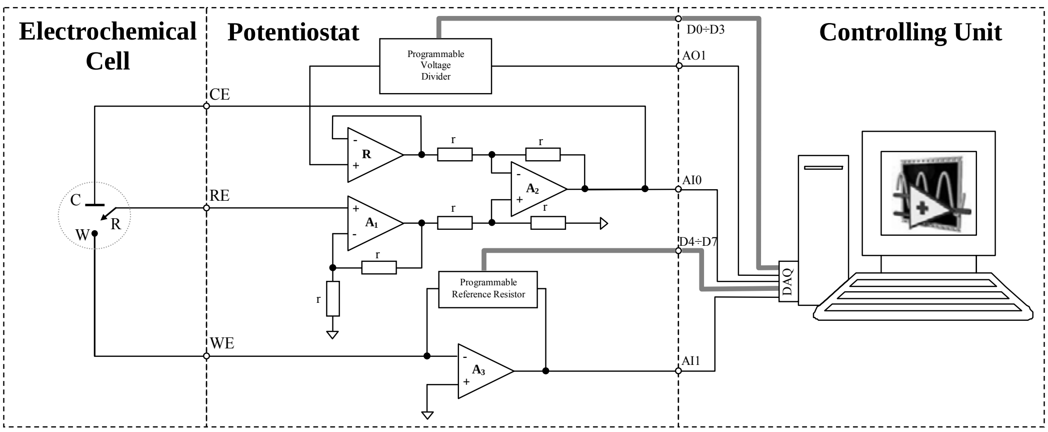

Figure 3. Electrical setup for the Potentiostat System

Two sections (digital and analog) form the potentiostat circuit (figure 3). The digital section is used to drive the measuring ranges and the voltage divider. Because usual voltages are less than 1V, and the output voltage of the DAQ ranges between -10V an 10V, a voltage divider is necessary to achieve the full resolution. The measuring ranges are established via relays. They introduce in the feedback of an operational amplifier resistors of well known values. In order to ensure small leakage currents, relays with high R_{off} (10GΩ) resistance were used. The analog part is mainly formed by four operational amplifiers: a repeater (R), a non-inverting amplifier (A_1), a summing stage (A_2) and a current to voltage converter (A_3) which measures the current of working electrode. A voltage level is generated by the analog output of the data acquisition board depending on the desired potential at the cell level via $AnalogOut_1$ line. The signal is divided with the Programmable Voltage Divider (PVD). A repeater stage R is used to keep a low resistance source for the next stage. Then the voltage is summed with

reference potential read from the reference electrode by the summing stage (A_2). The programmable voltage divider allows five divide factors ($^1/_1$, ½, $^1/_5$, $^1/_{10}$, $^1/_{20}$) and 3 digital lines are used to drive it.
The picoamperemeter is realized with an LMC6001 low noise [6], low input current operational amplifier which has bias input currents as low as 25 fA and ultra-low input noise current of 0.13 fA/√Hz. Because of these properties the LMC6001 can provide almost noiseless amplification of high resistance signal sources. Since input referred noise is only 22nV/√Hz, the operational amplifier can achieve higher signal to noise ratio than JFET input type electrometer amplifiers. This type of circuit it is used also for picking up the reference voltage from RE.
Switching the resistances in the feedback of the A_3 different measuring ranges are achieved. Using resistances from 1GΩ down to 100Ω, eight current scales can be obtained (2nA, 20nA, 200nA, 2μA, 20μA, 200μA, 2mA and 20mA). Because the resistors are not calibrated, software correction for measured values are performed.

IV. 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, Pscale.vi, Acquisition.vi and ElDepGen.vi. When running, all 4 are active (figure 4).

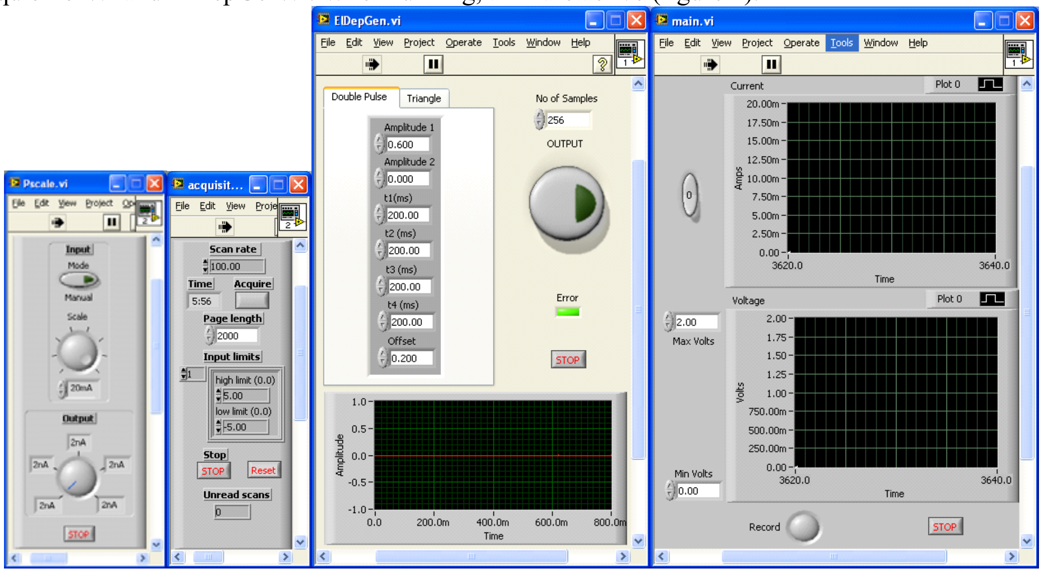

Figure 4. The virtual instrument: the front panel

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 4) there are two graphs, one for the measured 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) Pscale.vi
This instrument is used to drive the picoamperemeter via the the digital port of the data acquisition board. The operator can program the instrument on automatic scale or on manual scale (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.
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 4) the length of data stream kept in memory and displayed. This has been introduced because working time is sometimes very long (hours) 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

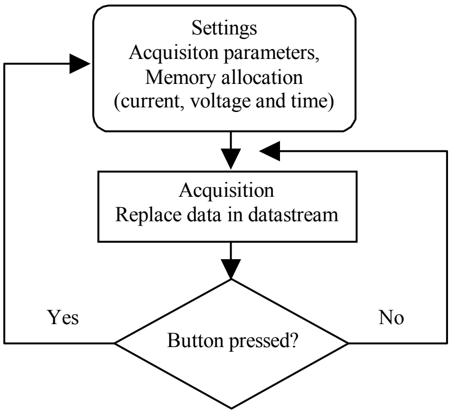

Figure 5. Acquision.vi flow diagram

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.

V. Experimental Results

The picoamperemeter has been tested using a voltage generator (Keithley 6487) [7] and resistors to create the reference current. The resistors have been measured with a Keithey 200 multimeter. All the scales were tested in 20 points for both polarities. For every point 500 measurements were performed and the dispersion has been computed. The relative error determined from experiment is plotted in figure 6.

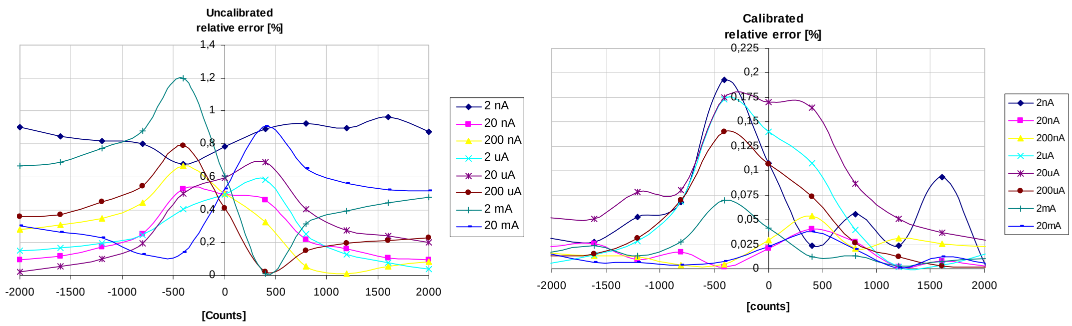

Figure 6. Picoamperemeter's errors characteristics

Because the resistors used in the feedback of the current to voltage converter are not calibrated a software calibration is necessary. Even the system is not calibrated the error is less than 1% except one value. After calibration the maximum error is reduced under 0.2%. The computed dispersion shows a type A uncertainty much less than the type B uncertainty (0.0013). Thus the type A error can be neglected.

Measured data can be stored on the harddisk for long time. Various waveforms can be generated in order to obtain deposited layers or gradients of the deposited materials. The instrument can be used, by modifying the software, for impedance spectroscopy of the electrochemical system formed in the electrochemical cell from the solution, the membrane and the electrodes.

VI. Conclusions

A potentiostatic system for controlling the etching and the electrodeposition process into an electrochemical cell was presented. Some of the advantages are the those brought by the virtual instrumentation (versatility, data storage), low measured currents and low errors (less than 0.2%).

Acknoledgements

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