PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **2**No 1, 01PCSI28(4pp) (2013)

Field Emission from an Array of Free-standing Copper Nanowires Grown in PET Ion-track Membranes

A.Zh. Zhanbotin[1,*], A.S.Yessenbekov[2] M.M.Saifulin[2], V.V. Saiko[2]

[1] *Institute of Nuclear Physics, Astana branch, 2/1, Abylai-khana Str., 010008Astana, Republic of Kazakhstan*
[2] *L.N.GumilyovEurasianNationalUniversity, 2, Mirzoyana Str., 010008Astana, Republic of Kazakhstan*

(Received 29 June 2013; published online 03 September 2013)

There is a description of field emission from an array of free-standing copper nanowires grown in ion-beamed PET polymer films.Highly oriented, free standing cylindrical and conical copper nanowires were electrochemically grown in the pores of track etched PET films with pore density $1 \times 10^6 cm^{-2}$, $2 \times 10^6 cm^{-2}$ and $4x10^7 cm^{-2}$. Copper nanowires were observed using scanning electron microscope, atomic force and electro-force methods of scanning probe microscope. All of the nanowires showed high efficiency tunneling current (up to ~ -1uA) from metal samples to positive charged SPM cantilever.

Keywords: Copper Nanowires, Template Method, PET Film, Track Etched Membrane, Electro Deposition, Field Emission.

PACS number: 73.25._i,79.70._q, 81.15.Pq

1. INTRODUCTION

Quasi-one-dimensional nanostructures with high aspect ratio (length over diameter) such as nanowires, nanofibers or nanotubes are expected to provide extraordinary physical properties. At the tip of such an electrically conductive object an external applied electric field can be microscopically enhanced by several orders of magnitude. Therefore, field electron emission (FE) by tunneling through the surface potential occurs already at a few V/um. Since no elevated temperatures are required, such nanostructures could act as cold electron sources with many potential applications for vacuum nanoelectronics.

It is well known that the FE strength of randomly distributed nanostructures strongly depends on the mean distance between neighboring emitters due to mutual electrostatic shielding [1, 2]. The field enhancement factor ß is influenced by the length and the diameter of the emitter, as was verified for single carbon nanotubes [3, 4]. Compared to nanotubes, FE properties of metallic [5, 6] and semiconducting [7] nanowires have been studied less systematically with respect to their geometry.

Ensembles of numerous (10^3–10^9 cm^{-2}) metallic nanowires can be fabricated by electrochemical deposition of the respective matter into the hollow structures of a nanoporous template [8]. Two types of material are most common for templates: anodized aluminum-oxide (AAO) and polymeric ion-track membranes.

In contrast to AAO, the ion-track density in polymeric ion-track membranes (TM) can easily be varied over several orders of magnitude by adjusting the fluence of the heavy-ion beam. Subsequent to irradiation, the ion tracks are chemically etched into cylindrical pores. The diameter of the electrochemically deposited wires depends on the pore size which is controlled by the etching process, and the wire length is only limited by the thickness of the polymer membrane.

Maurer and others [9] presented field emission properties of randomly distributed copper nanowires. The wires were potentiostatically deposited into the pores of polycarbonate membranes produced by the ion-track etch technique. By means of field emission scanning microscopy, emission site densities between 0.4×10^5 cm^{-2} and 1.4×10^5 cm^{-2} were obtained for nA currents at 6 V/um. Two-thirds of the nanowire emitters showed Fowler–Nordheim behavior with an average field enhancement factor of β = 245, which is about three times higher than expected for a cylindrical wire geometry with a half-sphere tip.

Azarian A. and others fabricated field emitter arrays of cobalt nanowires by electrodeposition on polycarbonate template (PC) [10]. The field emission properties of the samples showed low turn on electric field (E_{to}) with values varying between 2.9 and 11.3 V/µm showing a minimum value for R = 20 (E_{to}< 3 V/µm). Field emission data using the Fowler–Nordheim theory showed nearly straight-line nature confirming cold field emission of electrons. The fabricated field emitter arrays of cobalt nanowires in the PC templates opens the possibility of fabricating flexible flat panel displays.

2. EXPERIMENTAL DETAILS

2.1 Irradiation of polymer films

Hostaphan® PET film produced by the company «Mitsubishi Polyester Film» (Germany) with thickness of 12, 19, 23 microns was exposed to heavy ion accelerator DC-60 and beamed by ^{84}Kr ions, accelerated to an energy of 1,75 MeV/nucleon with a density of 1×10^6 cm^{-2}, $2 \times$ cm^{-2}, 4×10^7 cm^{-2}.

*gr.armani@gmail.com

2.2 Chemical etching of PET films

Beamed PET films were held 30 minutes on each side by 320nm UV light for sensibilization then etched on one or both sides in 3MNaOH for different time at room temperature for cylindrical and 85?C for conical pores. The procedure we have used to prepare conical pores is based on the work of Apelet all. [12]. After stopping etching the membrane was placed in a 1M HCOOH solution to neutralize sodium hydroxide for 30 min and washed in 18 MOhm deionized water for 30 minutes. Pore diameter of 0,2 - 1,2 um were archived (Table 1).

2.3 Electrochemical deposition of copper into PET membrane

It was produced electrochemical deposition of copper into the channels of TM. Potentiostatic deposition of copper ions into the pores of the track etched membranes produced from a solution of $Cu_2SO_4 \times 5H_2O$ (238 g/l) and H_2SO_4 (21 g/l). The membrane pores were partially filled with copper nanowires whose length was controlled by current between anode and cathode in galvanic cell. The copper substrate was grown for 15 minutes at a voltage of 0.5 V.

To form conical shape nanowires electrochemical deposition for a sample with a density of 1×10^6 pores/cm^2 has been carried out for 770 sec. (sample #2), 550 sec. (sample #4), 170 sec. (sample #3).

To form cylindrical nanowires, electrochemical deposition for a sample with a density of 1×10^6 pores/cm^2 has been carried out within 370 sec. (sample #1), for a sample with a density of 2×10^6 pores/cm^2 has been performed during the 1000 sec. (sample #5), for a sample with a density of 4×10^7 pores/cm^2 performed during the 1000 sec. (sample #6) (Table 1).

3. RESULTS AND DISCUSSION

3.1 SPM, SEM measurements

According to etching of TM and electrodeposition of copper into TM conditions we got an array of free standing copper nanowires with massive copper base.Scanning probe microscope (Smart SPM, AIST-NT Ltd.) was used to characterize the topology of nanowires. Electrodeposition of copper ions into the pores for all samples produced without filling the pores, and up to lengths suitable for SPM scanning methods, i.e. their heightsare lower than the cantilever length (10 um). 3D images for samples #1-6 shown in Figure 1.

Wires density is equal to the pores density of the etched PET films. Heights of the wires were found smaller than measured by SEM method. We assume, this happens with sample #6 because of small distance between wires, so cantilever cannot reach base and sounding out the top of the wires.

Scanning electron microscope (Jeol 7500F) was used to determine height and geometry form of copper nanowires (Figure 2).

It is obviously that nanowires fabricated using conical shape etched membranes have conical geometry, as well as cylindrical shape etched membranes gives cylindrical nanowires. Tips of conical nanowires have diameters ten times smaller than diameter of base.It is also seen that cylindrical nanowires have flat end and length smaller than thickness of the membranes in contrast with conical nanowires which have length very same as a thickness of membranes.

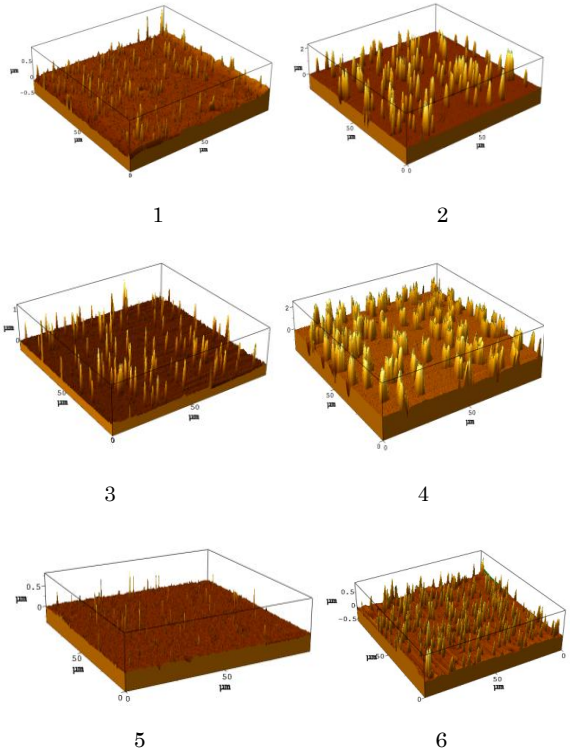

Fig. 1 – 3D images of copper nanowires with copper base (samples # 1-6 are indicated in Table 1)

Table 1 – Terms of chemical etching of TM and electrochemical deposition of copper into the pores of TM

№	**Density** pore/cm^2	**Film thickness**	**Etching time**	**Pore diameter (nm)**		**Deposition time (sec.)**	**Pores form**
				face	**back**		
1	1×10^6	12 um	45 sec.(2)	198,6	180	370	cylindrical
2	1×10^6		90 min + 30 min (1+2)	1166		770	conical
3	1×10^6		30 min + 180 sec. (1+2)	784		370	conical
4	1×10^6		180 min +60 min (1+2)	2404		550	conical
5	2×10^6	19 um	80 sec.(2)	215,9	90,2	1000	cylindrical
6	4×10^7	23 um	90 sec.(2)	147,7	141,4	1000	cylindrical
1 – one-side etching, 2 – two-side etching							

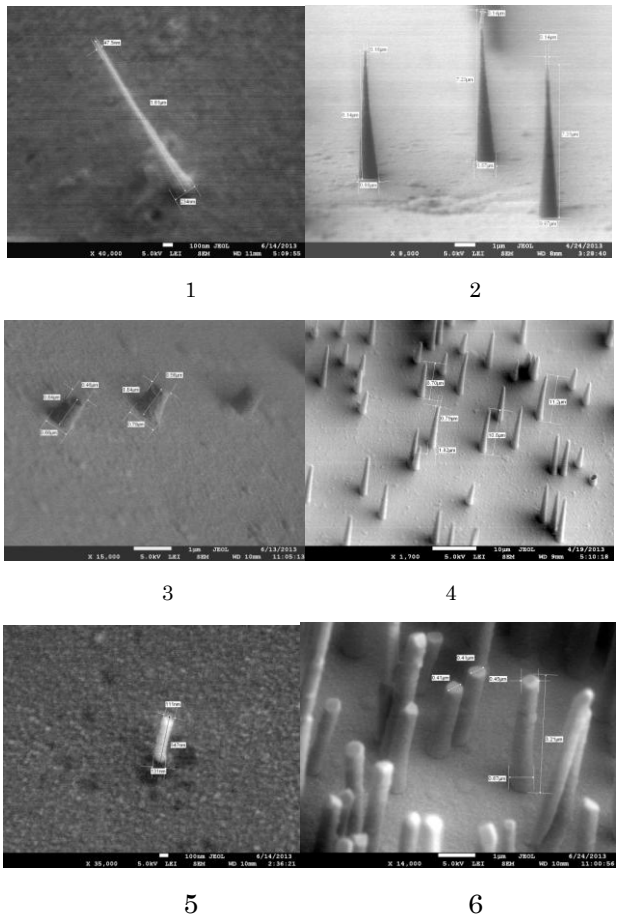

Fig. 2–SEM images of conical and cylindrical nanowires (samples # 1-6)

3.2 Field emitting from copper nanowires

The field emission measurements were performed by electric force microscopy method of SPM (Jeol-5400), whose vacuum degree was maintained at 2.8×10^{-4} Pa. Local conductivity of all copper nanowires samples were measured using electrically conductive platinum cantilever. The distance between the sample and the cantilever was set to 10 nm, the voltage was set to +1V on the cantilever to create a directional electrons tunneling from sample to the cantilever. Figure 3 shows the topology (a) and map of the conductivity (b) for a sample # 6.

Conductivity map for the samples of copper nanowires corresponds to the physical topology of the sample, i.e. upland areas (white dots, Figure 3a) on the surface of the sample correspond to the highest values of tunneling current (dark area, Figure 3b). Upland area corresponds to grown nanowires. Analysis of the data yields values of the tunneling current up to ~ -1uA for nanowires and up to ~ -50-100pA for a flat base. The dark areas in the image correspond to the maximum current in the negative region.

Samples # 1-5 show very same current from nanowires. Current value reaches -1 uA for nanowires and for the base area it is around 50-100pA (Figure 4).Samples # 1, 2 show high current peaks not only for the wires but also for the base, we assume it is because of small sharp dots on base surface, which also can create high electric field around that peaks.

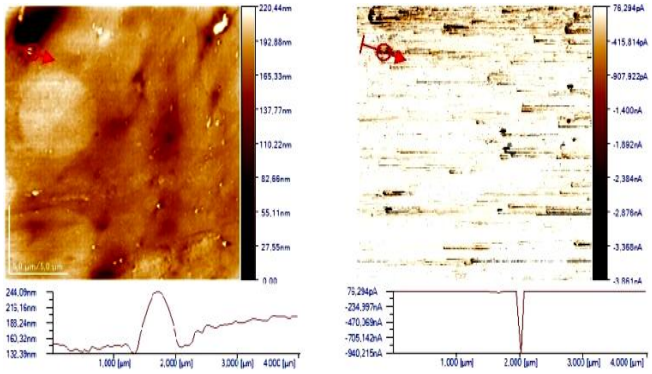

Fig. 3 – Topology and map of the conductivity for the sample # 6. Position of cursor is on a single wire

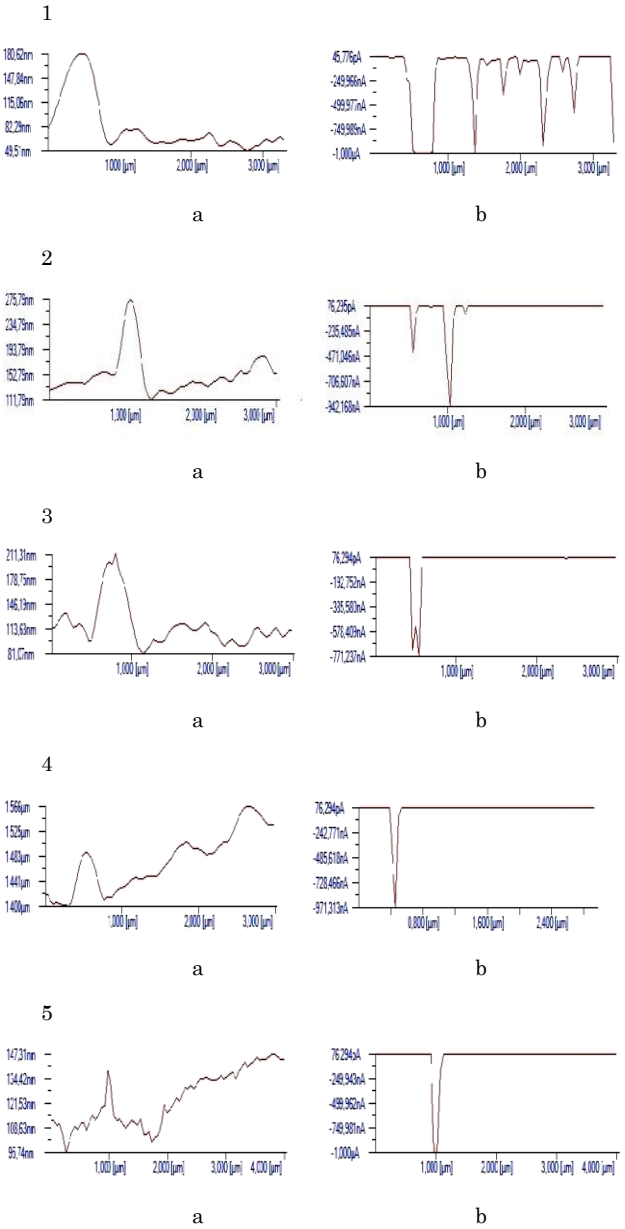

Fig. 4 –Topology profile (a) and conductivity profile (b) for the samples #1-5

In conclusion we can say that highly oriented, free standing cylindrical and conical copper nanowires were electrochemically grown in the pores of track etched PET film with pore density $1 \times 10^6 cm^{-2}$, $2 \times 10^6 cm^{-2}$ and $4x10^7 cm^{-2}$. Copper nanowires were observed using scanning electron microscope, atomic force and electro-force methods of scanning probe microscope. All of the nanowires showed high efficiency tunneling current (up to ~ -1uA) from metal samples to positive charged SPM cantilever. It is obviously that future investigation of copper nanowires current density per unit area is necessary to determine the possibility of using nanowires as cathode emitters in electronic devices.

AKNOWLEDGEMENTS

This work has been made within the Sub-project «Creating of filtration material and metal nanostructures based on track membranes» which is funded under the Technology Commercialization Project JRG#053, supported by the World Bank and the Government of the Republic of Kazakhstan.

REFERENCES

1. L. Nilsson, *Appl.Phys. Lett.* **76**, 2071 (2002).
2. K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W.I. Milne, G. Pirio, P. Legagneux, F. Wyczisk, D. Pribat, D.G. Hasko,*Appl. Phys.Lett.* **80**, 2011 (2002).
3. J.-M. Bonard, N. Weiss, H. Kind, T. Stockli, L. Forro, K. Kern, A. Chatelain, *Adv. Mater.* **13**, 184 (2001).
4. J.-M. Bonard, K.A. Dean, B.F. Coll, C. Klinke, *Phys. Rev. Lett.* **89**, 197602 (2002).
5. D.N. Davydov, P.A. Sattari, D.A. Mawlawi, A. Osika, T.L. Haslett, M. Moskovits, *J. Appl. Phys.* **86**, 3983 (1999).
6. G.-M. Zhang, E. Roy, H.-W. Liu, W.-M. Liu, S.-M. Hou, K. Yu-Zhang, Z.-Q. Xue, *Phys. Lett.* **19**, 1016 (2002).
7. F.C.K. Au, K.W. Wong, Y.H. Tang, Y.F. Zhang, I. Bello, S.T. Lee, *Appl. Phys. Lett.* **75**, 1700 (1999).
8. A. Huczko, *Appl. Phys. A* **70**, 365 (2000).
9. F. Maurer, A. Dangwal, D. Lysenkov, G. Muller, M.E. Toimil-Molares, C. Trautmann, J. Brotz, H. Fuess, *Nucl. Instr. Meth. B* **245**, 337 (2006).
10. A. Azarian, A. Irajizad, A. Dolati, S.M. Mahdavi, *Thin Solid Films* **517**, 1736 (2009).
11. P. Scopece, L.A. Baker, P.U. Martin, C.R. Martin, *Nanotechnology* **17**, 3951 (2006).
12. P.Y. Apel, Y.E. Korchev, Z. Siwy, R. Spohr, M. Yoshida, *Nucl. Instrum. Methods Phys. Res. B* **184**, 337 (2001).