

Fabrication technology of CNT-Nickel Oxide based planar pseudocapacitor for MEMS and NEMS

E.A. Lebedev², E.P. Kitsyuk¹, I.M. Gavrilin², D.G. Gromov², N.E. Gruzdev², S.A. Gavrilov², A.A. Dronov², A.A. Pavlov³

¹Scientific Manufacturing Complex “Technological Centre”, 124498, Russia, Moscow, Zelenograd, Bld. 5, Pas. 4806

²National Research University of Electronic Technology, 124498, Russia, Moscow, Zelenograd, Bld. 5, Pas. 4806

³Institute of Nanotechnologies of Microelectronics Russian Academy of Sciences, 119991, Russia, Moscow, Leninsky Prospekt, 32A

E-mail: dr.beefheart@gmail.com

Abstract. Fabrication technology of planar pseudocapacitor (PsC) based on carbon nanotube (CNT) forest, synthesized using plasma enhanced chemical vapor deposition (PECVD) method, covered with thin nickel oxide layer deposited by successive ionic layer adsorption and reaction (SILAR) method, is demonstrated. Dependences of deposited oxide layers thickness on device specific capacities is studied. It is shown that pseudocapacity of nickel oxide thin layer increases specific capacity of the CNT's based device up to 2.5 times.

1. Introduction

A rapid development of miniature electronics devices such as micro- and nanoelectromechanical systems, robots and implantable medical devices has significantly increased the demand for effective micro-sized energy storage devices. Electrochemical capacitors and batteries are the most popular solutions for these purposes in the “macro world” today, which are fundamentally different from each other in accumulation and energy storage mechanisms. With one hand, in the electrical double layer capacitors (EDLC) the charge accumulation occurs due to the formation of the electric double layer at the electrode-electrolyte interface. On the other hand, electric energy accumulation in batteries occurs as a result of ion intercalation into bulk electrode material. The mechanism of charge accumulation and storage determines the physical properties of the device – electrochemical capacitors are powerful and capable for rapid recharging, and batteries are high capacity sources [1].

However, in recent years a growing interest have been confined to pseudocapacitors (PsC) or supercapacitors. These devices accumulate and store energy using a reversible redox reactions (Faradaic process) in thin surface layer of the electrode, have a higher capacity compared to EDLC and demonstrate a much higher power density compared to batteries, combining the advantages of these two types of energy storage devices.

Transition metal oxides (Co_3O_4 , RuO_2 and NiO) have significant specific pseudocapacitance (3560, 2200 and 2584 F/g respectively [2]) compared to the values for carbon (about 150 F/g [3]). To create the PsC an electrodes with a high specific surface area are covered with thin metal oxide layers using various methods. From this point of view methods of layer-by-layer deposition, such as atomic layer deposition from gas-phase (ALD) [4], are of the greatest interest. Such approaches provide the most



effective usage of the entire electrode area due to the conformal deposition, and allow to control the deposited layers thickness with high precision. Another promising method is SILAR [5] (successive ion layer adsorption and reaction) - a stepwise chemical deposition technique based on immersion of the substrate into separately placed cationic and anionic precursors and rinsing after every immersion cycle with deionized water to avoid homogeneous precipitation. The possibility of growing good quality thin films at room temperatures and normal pressure is the main advantage of SILAR as compared with the gas-phase techniques. Moreover, SILAR deposition equipment is simple and inexpensive, since vacuum systems are not required.

In this work we report on the planar pseudocapacitor based on CNT forest covered by nickel oxide using SILAR method - promising electrochemical energy storage device, which are in one hand combines significant energy and power density and long life cycle, and on the other hand the integral fabrication technology allows to implement on-chip energy sources directly on substrates for “micro world” applications.

2. Experimental data

Planar PsC based on the structure which consists of two metal combs nested into each other on the substrate surface. This structure allows to place two electrodes in the same planar surface and do not use separator. All experimental samples were prepared using standard integral technology and equipment.

The fabrication process schematically presented on Figure 1 and starts with wet cleaning and thermal oxidation of a bare silicon wafer to isolate the substrate from the electrodes (1). After that, Ti, TiN and Ni layers were evaporated onto the substrate using magnetron sputtering system with a thickness of 300 nm, 25 nm and 5 nm, respectively (2). Ti acts as the current collector material, TiN as the diffusion-barrier layer and Ni as the common catalyst for CNT forest growth. Then deposited layers were covered by photoresist (3) and lithography was made to pattern two comb-like electrodes and pads (4). Wet metal etching (5) and photoresist lift-off (6) followed to remove the metals on unwanted areas and photoresist mask.

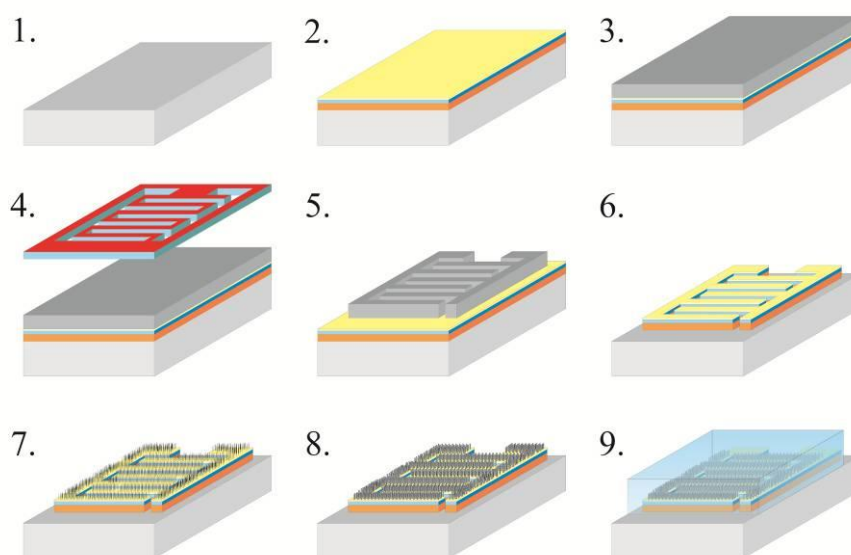


Figure 1. Basic steps of planar PsC fabrication.

Vertically-aligned multi-wall carbon nanotubes were directly synthesized on the substrate surface by PECVD method (7) on Oxford PlasmaLabSystem 100 (Nanofab 800 Agile) according to the author's described procedure [6]. For CNT arrays growing it was needed to form a catalyst

nanoclusters, that was performed by thermal oxidizing of samples at 280°C in oxygen environment and subsequent annealing at 450°C in H₂ atmosphere. Synthesis of multi-wall carbon nanotubes was carried out in gas mixture of C₂H₂, H₂ and NH₃ at 2 Torr operating pressure. Additional plasma assistance allow to reduce process temperature down to 500°C. Temperature of substrate holder was controlled by heat sensor. Plasma energy generator creates the radio frequency (RF) – 13,56 MHz radiation with power of 20 W and low frequency (LF) – 500 Hz radiation with power of 30 W. The growth rate of CNT arrays was 600 nm per minute.

To increase the PsC specific capacity CNT arrays were covered with a nickel oxide thin layer (8). Prior to the NiO deposition the CNTs surface was preliminary functionalized in Ar-O₂ plasma at low incident power of 50 W for 120 seconds on NIITM MVU TM Plasma RIT-T. The deposition of NiO onto the aligned CNT forest was done using the SILAR method. The cationic precursor for this study was a mixture of 0.01 M Ni(NO₃)₂*6H₂O and aqueous ammonia. Initially, precipitate of Ni(OH)₂ was formed from 0.01 M Ni(NO₃)₂*6H₂O, which was dissolved upon addition of ammonia to adjust the pH to 12, thereby forming hexaamminonickel (II) complex. The anionic precursor source was a hot water bath. When the substrate was immersed in the precursor solution (0.01 M Ni(NO₃)₂*6H₂O) at room temperature for 30 s, nickel ions were adsorbed onto the substrate surface. The substrate was transferred to the hot water bath at a temperature of 90°C for another 30 s to convert it into NiO, after which it was rinsed in deionized water for 30 s to remove the loosely bound or excess nickel hydroxyl ions. The SILAR steps were repeated for different number of cycles. After deposition, the samples were heat treated at 250 °C for 2 h in air. In the last step 1 M aqueous solution of KOH was used as the electrolyte (9).

Study of the deposited NiO layer thickness influence on the PsC capacity was performed using bulk samples consisting of two stainless steel electrodes on which surface the CNT arrays were synthesized and covered with NiO layer using SILAR method; porous polypropylene separator impregnated with electrolyte was placed between the electrodes.

Testing and measurement of electro-physical charge-discharge characteristics and cyclic voltammetry curves using potentiostat Elins P-30J were made. Charge and discharge current varied from 0.5 to 2 mA, and the voltage changed from 0 to 2 V. The scan rate during cyclic voltammetry ranged from 10 to 50 mV/sec.

CNT arrays structure and morphology were investigated and controlled using scanning electron microscope Agilent 8500 FE-SEM.

3. Results and discussion

During the research it was found that the synthesized CNT arrays after a short-term air exposure lose their hydrophilic properties and cease to be water wettable. This become a serious problem because SILAR method uses aqueous solutions and hydrophobic means the inability of the layer deposition. However, several methods of carbon nanotubes surface activation are referred to in earlier publications [7]. We chose plasma method, which uses a gas mixture of argon and oxygen – each component provides respectively the physical and chemical activation mechanism. Experiments with different values of incident power and the process duration were conducted and low power (50W) and short process duration (maximum 120 seconds) were selected. The increase of the incident power causes significant etching of nanotubes – arrays become sparse and lower in height. Before plasma treatment the water formed droplets on the array surface and no CNT wetting was observed. But after the treatment the water is promptly went into the arrays and wetted carbon nanotube surface.

The CNT arrays height varied in the range from 3 to 5 µm. Such heights interval was determined by the depth of nickel oxide depth deposition. At higher arrays altitudes the delivery of cationic and anionic solutions to the reaction zone becomes difficult, because of limited depth of plasma functionalization, and, therefore, large CNT surface area will not be involved in the charge accumulation and storage process.

Figure 2 shows SEM images of the morphological features of clean CNT (2a) arrays and NiO/CNT (2b) composite after 15 SILAR cycles (NCc-15).

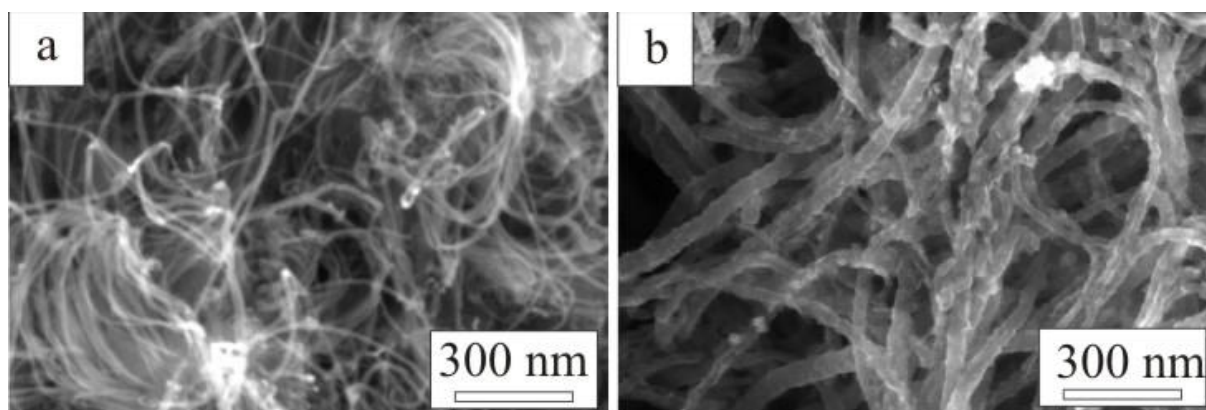


Figure 2. SEM images of clean CNT arrays (a) and NCc-15 (b).

The SEM image of NCc (fig. 2 b) show that the walls of CNT are uniformly coated by NiO nanoparticles with the average size of less than 10 nm. It was observed that with number of SILAR cycles increasing the total deposited layer thickness also increased, what can be proven by carbon nanotube diameter growth.

Scale photo and SEM image of electrode structure of the planar PsC manufactured according to the described technology are presented in Figure 3 and 4 respectively.



Figure 3. Scale image of planar PsC.



Figure 4. SEM image of planar PsC electrode.

The study of the SILAR layer thickness influence on the device capacity was performed using bulk samples, prepared according to described technique. For electrical test measurements the set of samples based on pure CNT arrays and CNT/NiO composites with different amount of SILAR cycles (5, 10, 15 and 20 cycles) was prepared. The charge-discharge characteristics measurements were made and subsequent analysis of the obtained curves was produce to determine the samples capacity. Figure 5a shows the capacity dependence on the SILAR cycles number. Figure 5b shows typical charge-discharge characteristics for samples based on pure CNTs (blue line) and CNT/NiO composite (black line).

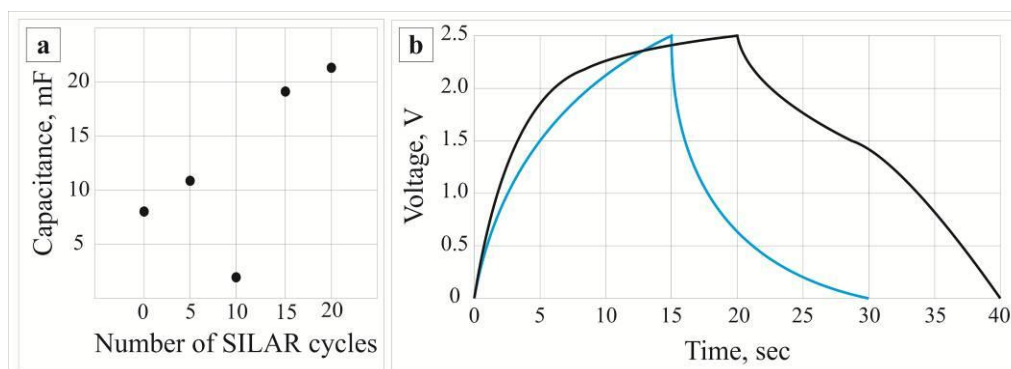


Figure 5. “a” – capacitance dependence on number of SILAR cycles and “b” - character of charge-discharge curves for clean CNT and CNT/NiO composite samples.

As can be seen in Figure 5a linear capacity dependence on SILAR cycles number was detected. Obviously, that point № 3 for NCc-10 is an experimental error. The greatest capacitance value was observed for NCc-20 and it exceeds the value for pure CNT at 2.5 times. Estimated value of the maximum nickel oxide layer thickness for NCc-20 was about 20 nm. It is necessary to conduct additional experiments with thicker layers and, most likely, the capacitance line reaches a maximum and then there will be a recession that is easily explained by gradually decreasing of the effective surface area of the electrode as a result of overgrowing of free space between the individual nanotubes. Figure 5b shows typical charge-discharge curves for pure carbon nanotubes and the NCc. In the first case (blue line), the curve has a “classic” character for EDLCs – rapid voltage lowering over time is observed. In the second case (black line), the clear inflection at a voltage value of 1.5 V on the curve is detected. This kink indicates the presence of pseudocapacitance, i.e. the appearance of an additional mechanism of accumulation and storage of energy.

4. Conclusions

We introduced the integral fabrication technology of planar PsC based on CNT arrays and nickel oxide thin layers deposition SILAR method. The influence of CNT’s pre-treatment operations on the quality and morphology of the deposited layers was investigated.

The study of the PsC capacity dependence on the deposited nickel oxide layer thickness was produced. For these purposes the bulk experimental samples based on CNT’s and oxide layers were made. Nickel oxide layer thickness was determined by the number of SILAR cycles. It was shown that with layers thickness increasing the device capacitance also increased. Capacitance value for the thickest oxide layer (20 SILAR cycles) was 2.5 times greater than that of devices based on pure CNT.

Further research and development should be directed towards to optimize the PC geometric dimensions, determine the oxide layers optimum thickness and to develop suitable the solid-state electrolyte.

Acknowledgments

This work was supported by the Ministry of education and science of the RF (№ 11.2551.2014/K).

References

- [1] Conway B E 1991 *J. Electrochem. Soc.* **138** 6 pp 1539-1548
- [2] Zhi M *et al* 2013 *Nanoscale* **5** pp 72-88
- [3] Stoller M D *et al* 2011 *Energy Environ. Sci.* **4** pp 4685-4689
- [4] Galperin V A *et al* 2014 *J. of Nano- and Microsystem technique* **6** 16
- [5] Gavrilov S A *et al* 2010 *J. Semiconductor* **44** 13 pp 1649-11653
- [6] Kitsyuk E P *et al* 2012 *Proc. Of SPIE – The Int. Soc. For Optic. Eng.* **8700** 87000A-2
- [7] Conway B E 1999 *N.-Y.: Kluwer Academic Plenum Publishers*