

Modeling and experimental study of resistive switching in vertically aligned carbon nanotubes

O A Ageev, Yu F Blinov, M V Ilina, O I Ilin, V A Smirnov

Southern Federal University, Institute of Nanotechnologies, Electronics and Electronic Equipment Engineering, Taganrog, st. Shevchenko, 2, 347928, Russia

ageev@sfedu.ru, mailina@sfedu.ru

Abstract. Model of the resistive switching in vertically aligned carbon nanotube (VA CNT) taking into account the processes of deformation, polarization and piezoelectric charge accumulation have been developed. Origin of hysteresis in VA CNT-based structure is described. Based on modeling results the VACNTs-based structure has been created. The ration resistance of high-resistance to low-resistance states of the VACNTs-based structure amounts 48. The correlation the modeling results with experimental studies is shown. The results can be used in the development nanoelectronics devices based on VA CNTs, including the nonvolatile resistive random-access memory.

1. Introduction

The development of nonvolatile high-access resistive random-access memory (RRAM) is one of the priority trends in the development of present nanoelectronics [1-4]. Vertically aligned carbon nanotubes (VA CNTs) are of special interest for advanced memory applications due to high scalability and possibility the locally growth nanotubes by plasma-enhanced chemical vapor deposition (PECVD) compatible with the silicon technology [5-7].

We have previously established by scanning tunnel microscopy (STM) that structures based on VA CNTs exhibit resistive switching with a resistance ratio in high-resistance (R_{HR}) to low-resistance (R_{LR}) states more 25 [8, 9]. Experimental studies have shown that the ratio of R_{HR}/R_{LR} increases with increasing applied between the STM probe and VA CNT voltage and depends on the form of the voltage pulse [9]. The mechanism of resistive switching based on deformation, polarization and piezoelectric charge accumulation of the VA CNT was proposed [9-11]. However there is no theoretical description of the resistive switching in VA CNTs. This fact limits application of the VA CNTs for the design and creation of RRAM based on them.

The aim of this work is to develop the resistive switching model of VA CNT-based structure taking into account the processes of deformation, polarization and the piezoelectric charge accumulation of nanotube.

2. Modeling description

The voltage pulse $U(t)$ applied to the VA CNT-based structure results in the polarization of the nanotube [12, 13], which gives rise to the surface attractive force $F_{at}(x,t)$ occurring between the VACNT and the upper electrode (Figure 1). This force is directed at the area of maximum field intensity $E(x,t)$ [9, 12]:



$$F_{at}(x,t) = 0.5\epsilon\epsilon_0 E(x,t)^2 S, \quad (1)$$

where $0 \leq x \leq L$; ϵ_0 is the electric constant; ϵ is the relative permittivity of the medium between the top of the VACNT and the upper electrode; S is the cross-section of the VA CNT.

The attraction force causes the elongating of the VACNT by $\Delta L(x,t)$, which gives rise to the elastic force $F_{el}(x,t)$. The elongation of the VACNT $\Delta L(x,t)$ can be determined by the solution of a hyperbolic differential equation with the following initial and boundary conditions:

$$\rho \frac{\partial^2 \Delta L(x,t)}{\partial t^2} = \frac{F_{at}(x,t)}{V} - Y \frac{\partial^2 \Delta L(x,t)}{\partial x^2}, \quad (2)$$

where $0 \leq x \leq L$; ρ is the density of the VA CNT; V is volume of the VACNT; Y is Young's modulus of VA CNT determined using the technique in [14]. Figure 2 shows the results of the solution of (2) at $x = L$ and $t = t_0$ (t_0 is a point in time corresponding the maximum amplitude of the sawtooth voltage pulse) for VACNT with diameter $D = 90$ nm, length $L = 2$ μ m and $Y = 1$ TPa and the following distances between the tip of the nanotube and the upper electrode d : 0.5, 1.0, 1.5 and 2.0 nm.

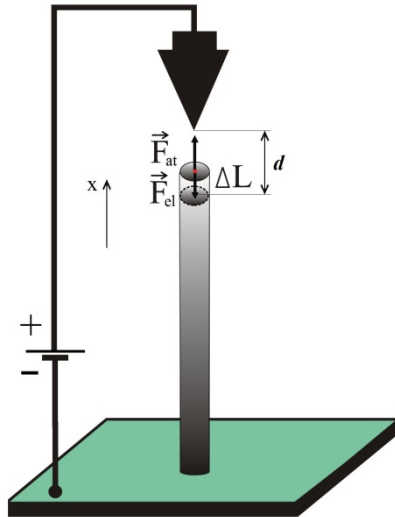


Figure 1. The representation of VA CNT-based structure by applying a local external electric field.

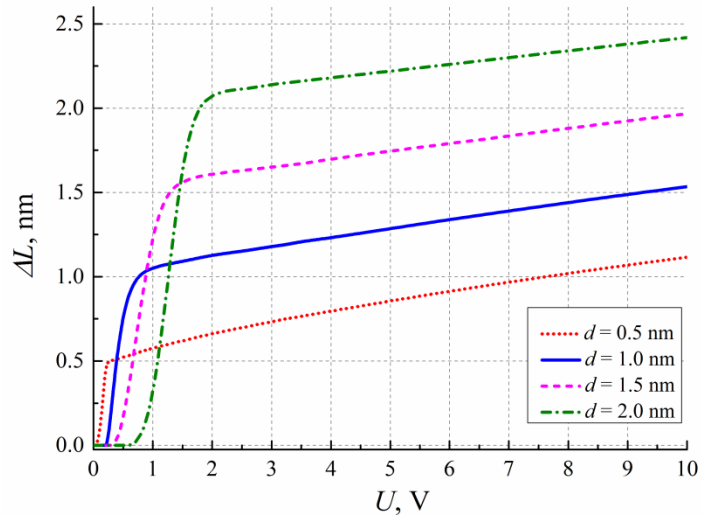


Figure 2. The deformation of VACNT ($D = 90$ nm, $L = 2$ μ m, $Y = 1$ TPa) by applying the voltage.

Figure 2 shows that at the initial segment of $\Delta L(U)$ dependency, where $E(x,t) < 10^9$ V/m, the deformation of nanotubes is close to zero. When the threshold value ($E(x,t) = 10^9$ V/m) is achieved, there is a jump of the deformation curve and the nanotube touches the upper electrode. Then the deformation curves $\Delta L(U)$ go into saturation due to the fact that the maximum value of the external electric field is concentrated in the tip area of the upper electrode and the nanotube comes into contact with the electrode within the bounds of this area. The jump of $\Delta L(U)$ dependencies is connected with a non-linear increase in the external electric field $E(x,t) = U(t)/(d - \Delta L(x,t))$ which takes place in the process of VACNT elongation.

According to the power balance equation, the energy W , which is expended on the processes of deformation $\Delta L(x,t)$, polarization, accumulation of piezoelectric charge Q_{cnt} and conduction current creation in the VA CNT-based structure, is equal to the consumed energy of the external electric field:

$$\frac{dW(x,t)}{dt} = vF_{at}(x,t), \quad v = \frac{\tau}{m} F_0(x,t), \quad (3)$$

where v is the charge carrier transport speed; τ is the relaxation time of the charge in the VACNT; m is the mass of the charge carriers; $F_0(x,t)$ is the resultant force arising in the nanotube under the influence

of the external electric field $E(x,t)$ and equal to the vector sum of the forces of surface attraction $F_{at}(x,t)$ and elasticity $F_{el}(x,t)$.

When $W=U(t) \cdot Q(t)$, the current which flows in the VACNT-based structure (prior to contact with the upper electrode) is equal to:

$$\frac{dQ_1}{dt} = \frac{\tau \varepsilon_0 SE^2(x,t)}{2mU(t)} F_0(x,t) - \frac{Q_{cnt}}{U(t)} \frac{dU}{dt}. \quad (4)$$

When the VA CNT touches the upper electrode conductivity current is inversely proportional to the resistance $R(t)$ of the VACNT arises in the memristor structure. The $R(t)$ is the sum of the intrinsic resistance of the nanotube R_0 which depends on its resistivity and the additional resistance $R_{def}(t)$ which is associated with the deformation and piezoelectric charge:

$$\frac{dQ_2}{dt} = U(t) / (R_0 + R_{def}(t)). \quad (5)$$

According to the power balance and the equations of the piezoelectric theory the $R_{def}(t)$ of the VACNT with length L and longitudinal permittivity $\varepsilon_{||}$ is:

$$\frac{1}{R_{def}(t)} = \frac{dQ_{cnt}(t)}{dt} \frac{1}{U(t)} + \frac{Q_{cnt}(t)}{U^2(t)} \frac{dU}{dt}, \quad (6)$$

$$\frac{dQ_{cnt}(t)}{dt} \frac{1}{U(t)} = \left[\frac{dE(L,t)}{dt} \Delta L(t) - \frac{d\Delta L(t)}{dt} E(L,t) \right] \frac{SL\varepsilon_0 \varepsilon_{||}}{\Delta L^2(t)U(t)}.$$

Despite the fact that the VACNT is held on the upper electrode and cannot be deformed, the external electric field $E(L,t)=U(t)/L$ creates an additional mechanical tension $\sigma'(t)=bE(L,t)$, where b is the piezoelectric coefficient of VACNT. Then the total deformation of the VACNT $\Delta L(t)$ will be the vector sum of the elongation of the nanotube $\Delta L_0(t)$ which corresponds to the recording voltage and the deformation $\Delta L'(t)$ which corresponds to the additional mechanical tension $\sigma'(t)$. At $dU/dt > 0$ we have the additional nanotube tensile stress $\sigma'(t)$ with $\Delta L'(t) > 0$; at $dU/dt < 0$ – additional compressive stress $\sigma'(t)$ with $\Delta L' < 0$. Thus, if we apply sawtooth voltage pulses to the VACNT-based structure, there will be a hysteresis in the current-voltage characteristic (CVC), which is associated with redistribution of stress and their corresponding piezoelectric charge of the VACNT.

3. Experimental studies

As the experimental sample we used a VA CNTs array grown by PECVD at the multifunctional complex NANOFAB NTC-9 (NT-MDT, Russia). As the substrate, we used a silicon plate with a bilayer structure consisting of a 20-nm-thick titanium film and a 10-nm-thick nickel film formed on its surface. The reaction gas was acetylene. The studies of the array of the VA CNTs on a Nova NanoLab 600 scanning electron microscope (SEM) (FEI, the Netherlands) and on Ntegra probe nanolaboratory (NT-MDT, Russia) made it possible to estimate $D = 108 \pm 39$ nm, $L = 2.23 \pm 0.37$ μ m and $Y = 1.05 \pm 0.21$ of VA CNTs in the array.

For study of individual VA CNTs resistive switching the two nanotubes were extracted by mechanical atomic force lithography from the experimental sample using a Solver P47 Pro scanning probe microscope (NT-MDT, Russia). Diameters of the VA CNTs are 88 and 76 nm, length is 2.1 μ m (Figure 3). The role of the lower electrode in the VA CNTs-based structure was played by the conducting layer formed on the silicon substrate surface after the growth of the carbon nanotubes, while the upper electrode was the tungsten STM probe 146 nm in radius sharpened by electrochemical etching (Figure 4). The resistive switching of the vertically aligned carbon nanotubes were determined by scanning tunneling microscopy (STM) in spectroscopy mode at $d = 1$ nm using the Solver P47 Pro.

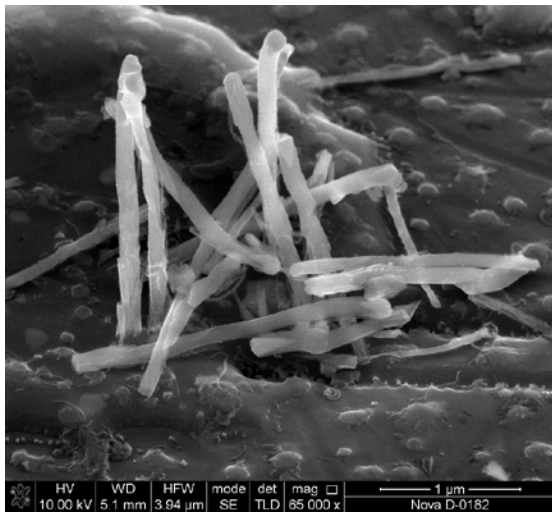


Figure 3. SEM image of the vertically aligned carbon nanotubes.

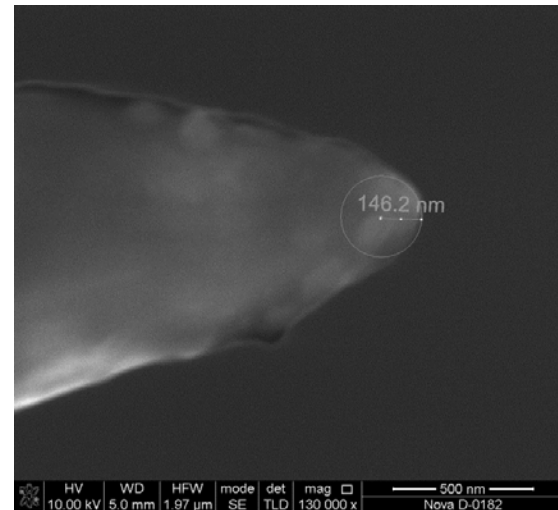


Figure 4. SEM image of the the upper electrode.

The CVC of the VA CNTs-based structure measured in the case of applying the sawtooth voltage pulse of 1.5 V shown in Figure 5. The CVC shows that the structure resistance is changed from the high-resistance to low-resistance state under action of an external electric field; i.e., the resistive switching effect is observed. The ratio $R_{HR}/R_{LR} = 48$ at reading voltage of ± 0.2 V, recoding voltage of 1.5 V and erasing voltage of -1 V. Thus the results of experimental studies show the correlation with the modeling.

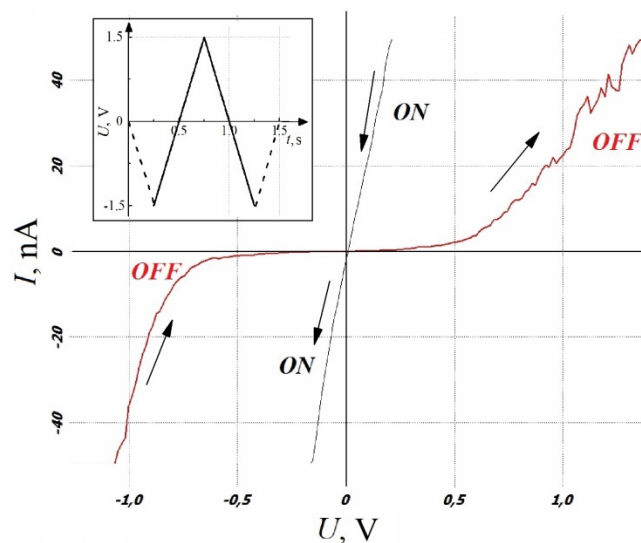


Figure 5. Current-voltage characteristic of the VA CNTs-based structure. In the inset is shown the applied voltage pulse.

Switching time of the VACNT-based structure is estimated based on the analysis of the CVC at $U < 1$ V and equation (4) and amounts 13 ps. The number of switching cycles of this structure theoretically has no limit, as operating principle associated with low elastic deformation (less than 1%) and the electronic polarization of VACNT that does not lead to its degradation.

4. Conclusion

In summary, the developed model taking into account the processes of deformation, polarization and piezoelectric charge accumulation makes it possible to explain the mechanism of the resistive

switching in vertically aligned carbon nanotubes. Origin of hysteresis in VA CNT-based structure is redistribution of stress and their corresponding piezoelectric charge of the nanotube under the influence of an external electric field.

The results of experimental study of VA CNTs-based structure show that the ratio of resistance of the high-resistance to low-resistance states amounts 48 at reading voltage of ± 0.2 V, recoding voltage of 1.5 V and erasing voltage of -1 V. Switching time of this is 13 ps. The obtained results can be used in the development nanoelectronics devices based on VA CNTs, including the nonvolatile resistive random-access memory with ultra-high speed and density.

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