

Carbon Nanotube Array Based Surface Acoustic Wave Gas Sensor Simulation

Viatcheslav Barkaline and Alexander Chashinski
System Dynamics & Material Mechanics Laboratory
Belarussian National Technical University
Minsk, Belarus
barkaline@yahoo.com

Abstract— Oxygen adsorption effect on the Van der Waals interaction contribution to the elastic moduli of ordered carbon nanotube arrays was estimated. Mechanical instability of square lattice of nanotubes with respect to the transition to triangular one was demonstrated. Variation of the elastic moduli due to the adsorption was shown to be of the same order of magnitude as the moduli themselves. This leads to variation of phase velocities of acoustic waves propagating across the array which proved to be dozens of times greater then mass loading by adsorbate for the acoustic wave frequency range 0,1 – 1,0 GHz.

I. INTRODUCTION

The development of the processes of creation of ordered arrays of carbon nanotubes (CNT) on various substrates [1] seems to be one of the most promising achievements of current nanotechnology. Individual tubes in such arrays are bonded by strong Van der Waals interactions which can be effected significantly by external molecules adsorbed to the inter-nanotubes spaces of array. This leads to high value chemomechanical effect of adsorption in CNT array based nanoelectronic structures which can be used in nanosensors for the development of chemical sensor elements with acoustic pickup [2].

At the paper we present the results of molecular dynamics simulation of oxygen adsorption in CNT arrays and calculation of transversal elastic moduli of them. The mechanical stability of the arrays is discussed. Acoustic properties of such array is studied from the surface acoustic waves (SAW) viewpoint because of their prospects in chemical nanosensor area [2].

II. THEORETICAL BACKGROUND OF SIMULATION

SAW chemical sensors are based on the effects of adsorbed molecules on geometrical, elastic and electric properties of gas-sensing layer and corresponding mass-loading of the working surface of the substrate carrying SAW (Fig.1).

These effects lead to SAW phase velocity local changes determining sensor output. For SAW propagating along x axis,

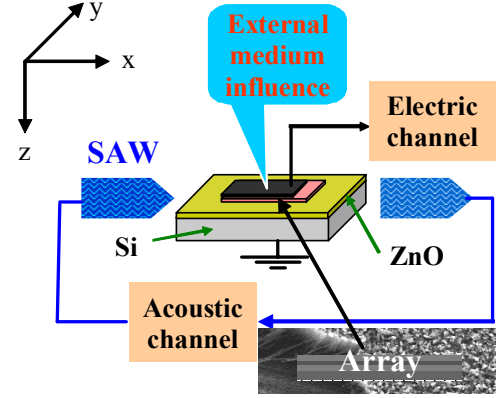


Figure 1. SAW chemical sensor with CNT array based sensing element and acoustic and electric output signal.

the relationship between SAW phase velocity V relative changes and changes of the layer acoustic properties is [2]

$$\begin{aligned} \frac{\Delta V}{V} = & \frac{kh}{\rho V^2} \left\{ C_{11} A \left(\frac{\Delta h}{h} + \frac{\Delta C_{11}}{C_{11}} \right) + \right. \\ & + C_{66} B \left(\frac{\Delta h}{h} + \frac{\Delta C_{66}}{C_{66}} \right) + C_{55} C \left(\frac{\Delta h}{h} + \frac{\Delta C_{55}}{C_{55}} \right) \left. \right\} - \\ & - \frac{k}{\rho} (A + B + C) \Delta m + \\ & + \frac{D}{2\rho V^2} \left\{ \Delta(C_{12} - C_{66}) \frac{\partial h}{\partial y} + \frac{\partial(C_{12} - C_{66})}{\partial y} \Delta h \right\} \end{aligned} \quad (1)$$

Here h , C_{11} , C_{12} , C_{55} , C_{66} - thickness and elastic modules of layer, m - mass of layer per unit square, ρ - density of substrate, A , B , C , D - parameters characterizing SAW energy distribution across the substrate thickness, k - SAW wave number. A , B , C , D values for various silicon substrates are presented in Table 1. For all cases one has $A < B < C$. Usually obtained $\Delta V/V$ values for continuous layer materials is 10^{-4} .

TABLE 1. SUBSTRATE FACTORS IN SAW PHASE VELOCITY SENSITIVITY FOR VARIOUS CRYSTALLOGRAPHIC ORIENTATIONS OF SUBSTRATE

Euler angles, deg.			100 A	100 C	100 B	100 D
λ	μ	θ				
45	90	0	4.1	12.2	0	0
45	54.74	0	3.1	9.3	1.6	-2.2
0	0	45	10.2	18.5	0	0
0	0	0	11.6	17.4	0	0

At present paper we study the behavior of sensing layer composed from ordered array of carbon nanotubes. Volume part of nanotubes in sensing layer will be denoted as ξ . Surface mass density of layer can be represented as

$$m = m^{ad} \cdot (1 - \xi) + m^{tube} \cdot \xi, \quad (2)$$

where m^{ad} and m^{tube} are squared mass densities of adsorbate and nanotubes, respectively. Effective elastic modules of layer are defined as:

$$C_{IJ} = C_{IJ}^{inter} \cdot (1 - \xi) + C_{IJ}^{tube} \cdot \xi, \quad (3)$$

where C_{IJ}^{inter} , C_{IJ}^{tube} are effective elastic modules of inter-tubes medium and tubes correspondingly. Regular method of calculation of C_{IJ}^{tube} on the basis of molecular dynamics was developed by Odegard et al [3]. Using this method we estimated effective elastic modules of single wall carbon nanotubes with chirality (10x10) as $C_{11}^{tube} = 3.855 \cdot 10^{10}$ Pa, $C_{12}^{tube} = C_{13}^{tube} = 2.065 \cdot 10^{10}$ Pa, $C_{33}^{tube} = 1.25 \cdot 10^{12}$ Pa, $C_{44}^{tube} = 0.895 \cdot 10^{10}$ Pa. From (1) one can see that largest module C_{33}^{tube} does not contribute to sensor output.

C_{IJ}^{inter} can be represented as:

$$C_{IJ}^{inter} = C_{IJ}^{vdW} + C_{IJ}^{bond}, \quad (4)$$

where C_{IJ}^{vdW} denotes contribution of van der Waals interactions while C_{IJ}^{bond} accounts for contribution of chemical bonds between nanotubes due to chemically adsorbed large molecules.

Van der Waals contribution to elastic modules in [2] was estimated from general theory of intermolecular interaction [4]. For semiconductor tubes when distances between them are large sufficiently with respect to tubes' diameters but less then characteristic electromagnetic wavelength of nanotubes λ_c , van der Waals energy of array can be represented as

$$E_{vdW} = -\frac{C_s}{4a^2 d^5} \cdot N \cdot z \cdot h \cdot (1 + \Pi), \quad (5)$$

where N is the number of nanotubes in array, z is the number of closest neighbors of nanotube, Π is modulating contribution of external molecules and complexes embedded into array.

For "clean" array $\Pi=0$ and C_s was estimated as $1.5 \cdot 3.0 \cdot 10^3$ kCal/mol (all distances in Å).

For metal-type tubes interaction is determined by delocalized π -orbitals of tubes and one obtains

$$E_{vdW} = -\frac{C_m}{d^p} \cdot N \cdot z \cdot h^5 \cdot (1 + \Pi), \quad p=6+3. \quad (6)$$

Chemical bonds' energy of array is determined by chemical nature of adsorbed molecules:

$$E_{bond} = 0.5 \cdot N \cdot z \cdot \alpha \cdot Q \cdot (d - d_0)^2, \quad (7)$$

where α - probability of bond creation between two nearest tubes, Q - force constant, d_0 - equilibrium bond length.

For C_{IJ}^{inter} one has:

$$C_{IJ}^{inter} = \frac{1}{V} \frac{\partial^2}{\partial \epsilon_I \partial \epsilon_J} (E_{vdW} + E_{bond}), \quad (8)$$

where V is array volume, ϵ_I , $I=1, \dots, 6$ - corresponding component of deformation tensor in matrix notation.

III. SIMULATION

Calculation of C_s and Π is complex task and demands quantum mechanical approach [4]. It includes analysis of dispersion interactions between elementary blocks of nanotubes with certain length a, which may consist of dozens and hundreds of atoms (Fig.3).

At present paper effective modules C_{IJ}^{inter} are estimated on the basis of molecular dynamics method. We used MM+ potential field [5] in which Van der Waals interactions combine an exponential repulsion with an attractive $1/R^6$ interaction.

Dependences of Van der Waals energy from the distance between CNT in array both for square and triangle lattices are presented at Fig.2. Square lattice is unstable with respect to spontaneous transition to triangle lattice with minimal distance between tubes $a \approx 0.3$ nm due to negative value of C_{12} module. For $a > 0.4$ nm triangle lattice become unstable too and plastic flow of array could arise without any resistance.

Array instabilities and low moduli values make one to suppose that adsorption of gases into intertube gaps of array leads to significant change of them. This is illustrated by the calculation of oxygen adsorption influence on acoustic properties of (10,10) nanotube array. Adsorption capacity of array depends on intertube distance a (Fig.3). When $a < 3.5$ Å oxygen molecules build linear chains along nanotubes at centres of array pores, while for larger a oxygen layers are created along outer surfaces of nanotubes. As oxygen content rises van der Waals minima for oxygen molecules became deeper and corresponding intertube distances rise too and array "swells". For the case of linear oxygen chains it is shown on Fig.4. Maximal oxygen content for this case is nearly 320 carbon atoms per one oxygen molecule.

In accordance with (8) elastic modules of array was calculated in dependence of oxygen content resulting in Table 2.

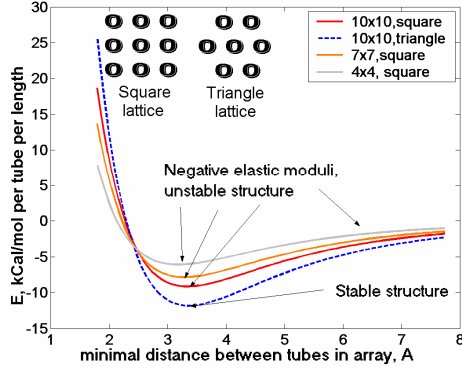


Figure 2. Energy of Van der Waals interaction in CNT arrays.

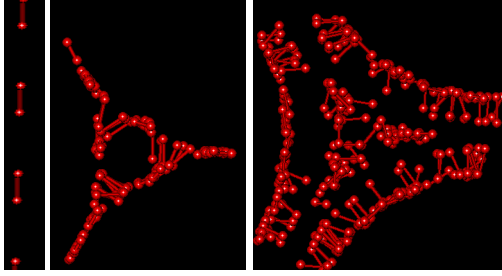


Figure 3. Basic shapes of oxygen filling of (10,10) nanotube array pores: a) intertube distance $a < 3.5$ Å, lateral view, linear chain; b) $a = 6$ Å, top view, one layer; c) $a = 10$ Å, top view, two layers.

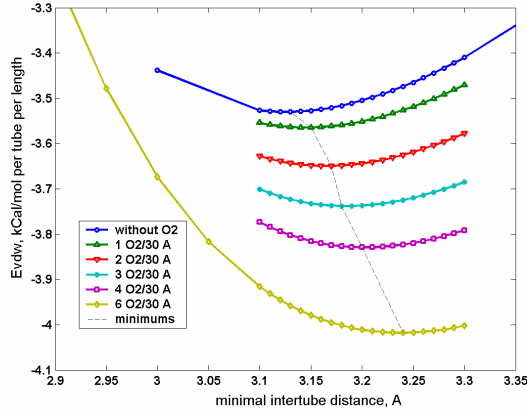


Figure 4. Van der Waals energy of (10,10) nanotube array near energy minima per tube per tube length for various linear density of oxygen in chains

Then SAW phase velocities and their changes due oxygen adsorption for SAW structure $\text{Si}_{\{001\} < 100 \rangle} \backslash \text{SiO}_2$ array were calculated as function of normalized array thickness kh (k - SAW wave number) using algorithm presented in [6] (Fig 5,6).

IV. CONCLUSION

Using of nanotube arrays as sensitive layer of SAW based gas sensors makes it possible to increase their sensitivities up to dozens of times for the SAW frequency range 0.1-3 GHz.

TABLE II. ACOUSTIC PARAMETERS OF (10,10) NANOTUBE ARRAY VERSYS ON OXYGEN CONTENT

Linear density of O_2 , Å^{-1}	Intertube distance, Å	Array density, kg/m^3	C_{11} , 10^8 N/m^2	C_{22} , 10^8 N/m^2	C_{12} , 10^8 N/m^2
0	3,13	1353.1	4.758	4.170	2.528
1/30	3,15	1349.9	4.300	3.764	2.220
2/30	3,17	1346.7	3.868	3.380	1.931
4/30	3,20	1341.9	3.265	2.844	1.529
6/30	3,24	1335.5	2.538	2.200	1.048

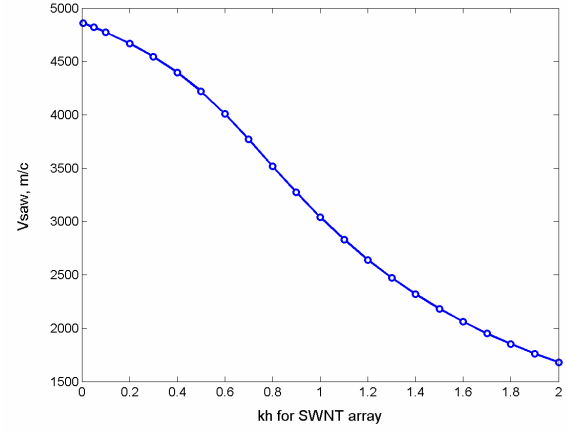


Figure 5. SAW phase velocity dispersion curve for $\text{Si}_{\{001\} < 100 \rangle} \backslash \text{SiO}_2$ array structure without adsorbed oxygen

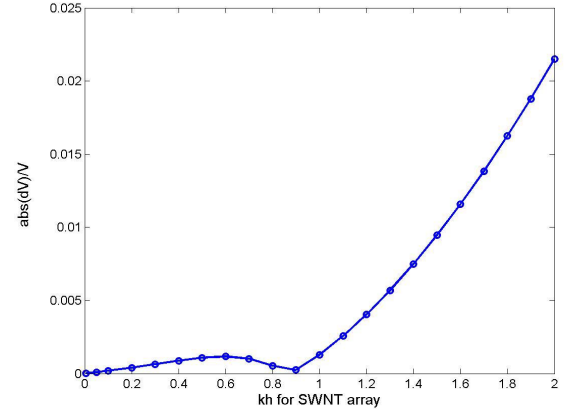


Figure 6. SAW phase velocity relative change due to maximal oxygen adsorption for $\text{Si}_{\{001\} < 100 \rangle} \backslash \text{SiO}_2$ array structure

REFERENCES

- [1] V.A.Labunov. *Metall, installation, tools*, May-Aug. 2005, p.20-22.
- [2] V.Barkaline. Proc. Eurosensors XIX Int.Conf., Sept. 11-14, 2005, Barcelona, Spain. 2 p.
- [3] G.M.Odegard et al. NASA/TM-2002-211454, 2002.
- [4] I.G.Kaplan, Introduction to intermolecular interaction theory, Nauka, Moscow, 1982.
- [5] N.L. Allinger. Hypercube, Inc., Publication HC70-00-01-00, 2002.
- [6] V.M.Koleshko, V.V.Barkaline. Thin Solid Films 298 (1997) 1-8.