ACOUSTIC PROPERTIES OF CARBON NANOTUBE ARRAYS AS CHEMICAL SENSOR ELEMENTS

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Abstract. Prospects of ordered carbon nanotube arrays in sensorics are studied basing on molecular dynamics and finite element method simulations. Mechanical and acoustic properties of such arrays are calculated. Array elastic modules and density dependences on oxygen adsorption value are presented. Mechanical instability of square lattice of nanotubes with respect to the transition to triangular one was demonstrated. Using of carbon nanotube arrays as sensing elements of surface acoustic wave based sensors is shown to increase the sensitivity of such sensors up to dozen and more times with respect to usually obtained values for the acoustic wave frequency range 0,1 – 1,0 GHz. Vibration modes of carbon nanotube arrays are calculated in continual approximation on the basis of LS-DYNA package depending on nanotube lengths and diameters distribution in array. Vibration spectrum of arrays exhibits zone character inherent to sonic crystals. Such type of acoustic excitations makes it possible to generate both regular and chaotic motion of carbon nanotube arrays under the external forces.

1. 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 absorbed to the inter-tubes spaces of array. This leads to high value chemomechanical effect of adsorption in CNT array based nanoelectronic structures which can be used in nanosensorics for the development of chemical sensor elements with acoustic pickup [2].

In this 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 array is discussed. Acoustic properties of such array are studied from the surface acoustic waves (SAW) viewpoint because of their prospects in chemical nanosensor area [3].

2. Chemical sensor element on CNT array

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

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Table 1. Substrate factors in SAW phase velocity sensitivity for various crystallographic orientations.

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

$$\frac{\Delta V}{V} = \frac{kh}{\rho V^2}\left\{C_{11}A\left(\frac{\Delta h}{h}+\frac{\Delta C_{11}}{C_{11}}\right)+\right.$$

$$\left. C_{66}B\left(\frac{\Delta h}{h}+\frac{\Delta C_{66}}{C_{66}}\right)+C_{55}C\left(\frac{\Delta h}{h}+\frac{\Delta C_{55}}{C_{55}}\right)\right\}-$$

$$-\frac{k}{\rho}\left(A+B+C\right)\Delta m + \frac{D}{2\rho V^2}\cdot \qquad (1)$$

$$\left\{\Delta\left(C_{12}-C_{66}\right)\frac{\partial h}{\partial y}+\frac{\partial\left(C_{12}-C_{66}\right)}{\partial y}\Delta h\right\}.$$

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 $A<B<C$.

In the 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

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

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

$$C_{IJ} = C_{IJ}^{vdW}+C_{IJ}^{bond}, \qquad (3)$$

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 (10,10) as as $C_{11}^{tube} = 3.855\cdot10^{10}$ Pa, $C_{12}^{tube}= C_{13}^{tube}= 2.065\cdot10^{10}$ Pa, $C_{33}^{tube}=1.25\cdot10^{12}$ Pa, $C_{44}^{tube}= 0.895\cdot10^{10}$ Pa. From (1) one can see that
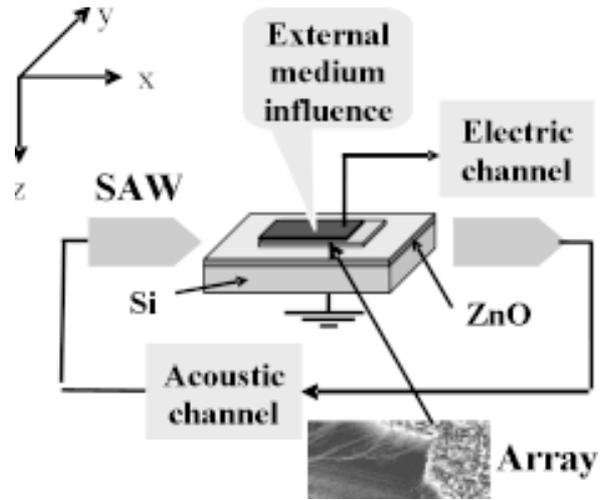

Fig. 1. SAW chemical sensor with CNT array based sensing element and acoustic and electric output signal.

largest module C_{33}^{tube} does not contribute to sensor output.

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

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

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

$$E_{vdW} = -\frac{C_s}{4a^2d^5}\cdot N\cdot z\cdot h\cdot\left(1+\Pi\right), \qquad (5)$$
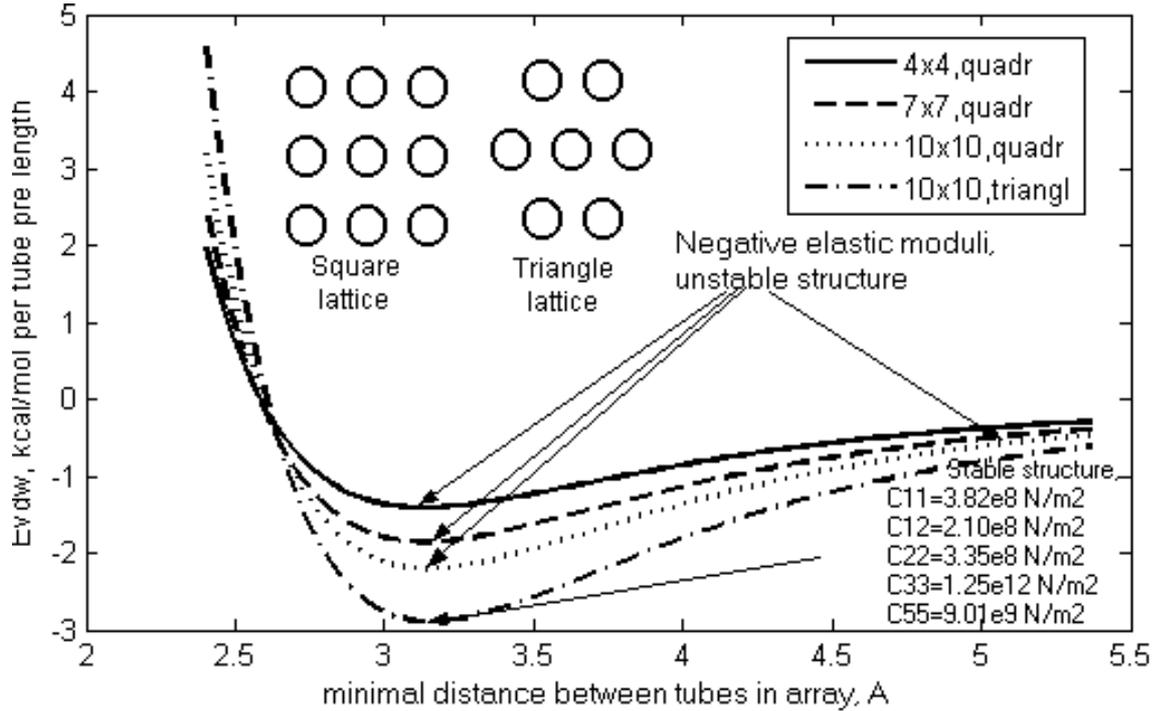
Fig. 2. Energy of van der Waals interaction in CNT arrays.
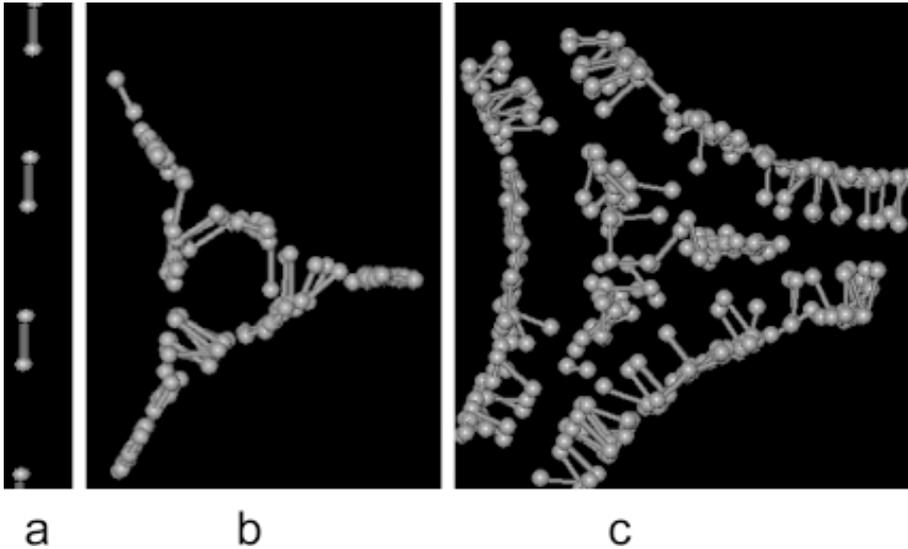
**Fig. 3.** Basic shapes of oxygen filling of (10,10) nanotube array pores: (a) intertube distance *a*<3.5 A, lateral view, linear chain; (b) *a*=6 A, top view, one layer; (c) *a*=10 A, top view, two layers.

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

For "clean" array $\Pi=0$ and C_s was estimated as 1.5-3.0×10³ kCal/mol (all distances in Å).

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

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

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

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

Table 2. Acoustic parameters of (10,10) nanotube array versus oxygen content.

Linear density of O_2, $Å^{-1}$	Intertube distance, Å	Array density, kg/m3	C_{11}, 10^9 N/m²	C_{12}, 10^9 N/m²	C_{13}, 10^9 N/m²	C_{33}, 10^9 N/m²	C_{55}, 10^8 N/m²	C_{66}, 10^9 N/m²
0	3,13	1353.1	0.4464	0.2528	66.804	350.05	66.862	0.0968
0.03	3,15	1349.9	0.4811	0.2705	66.644	349.21	66.702	0.1053
0.07	3,17	1346.7	0.5201	0.2903	66.486	348.37	66.463	0.1149
0.10	3,18	1345.0	0.5787	0.3243	66.406	347.96	66.463	0.1272
0.13	3,20	1341.9	0.6104	0.3398	66.247	347.13	66.305	0.1353
0.20	3,24	1335.5	0.6635	0.3649	65.932	345.47	65.989	0.1493

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

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

$$C_{IJ}^{inter} = \frac{1}{V}\frac{\partial^2}{\partial\varepsilon_I\partial\varepsilon_J}\left(E_{vdW} + E_{bond}\right),\qquad(8)$$

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

3. SIMULATION

Calculation of C_s and P is complex task and demands quantum mechanical approach [4]. It includes analysis of dispersion interactions between elementary blocks of nanotubes, which may consist of dozens and hundreds of atoms.

In the 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.

Variation of elastic moduli is of the same order in magnitude as moduli themselves irrespective of the accounting of possible relaxation in the array. In accordance with (1), using of nanotube arrays as sensitive layer of SAW based gas sensors makes it possible to increase usually realized value of $\Delta V/V \approx 10^{-4}$ up to dozens of times for the SAW frequency range 0.1-3 GHz. This is proved by SAW phase velocities and their changes due oxygen adsorption calculation for SAW structure $Si_{\{001\}<100>}\backslash SiO_2\backslash array$ as function of normalized array thickness kh (k - SAW wave number) using algorithm presented in [6] (Figs. 5 and 6).

The selectivity of SAW base gas sensors with CNT array sensing layer could be refined by introducing additional electrical output, in which changes of electrical impedance of array lead to the changes of electric current throughout it. Acoustic and electric channels interact because the adsorption of molecules on CNT change with applied voltage in electric channel. This effect makes it possible to realize time resolution of adsorption kinetics. The selectivity of sensor can be increased radically by chemical modification of CNT.
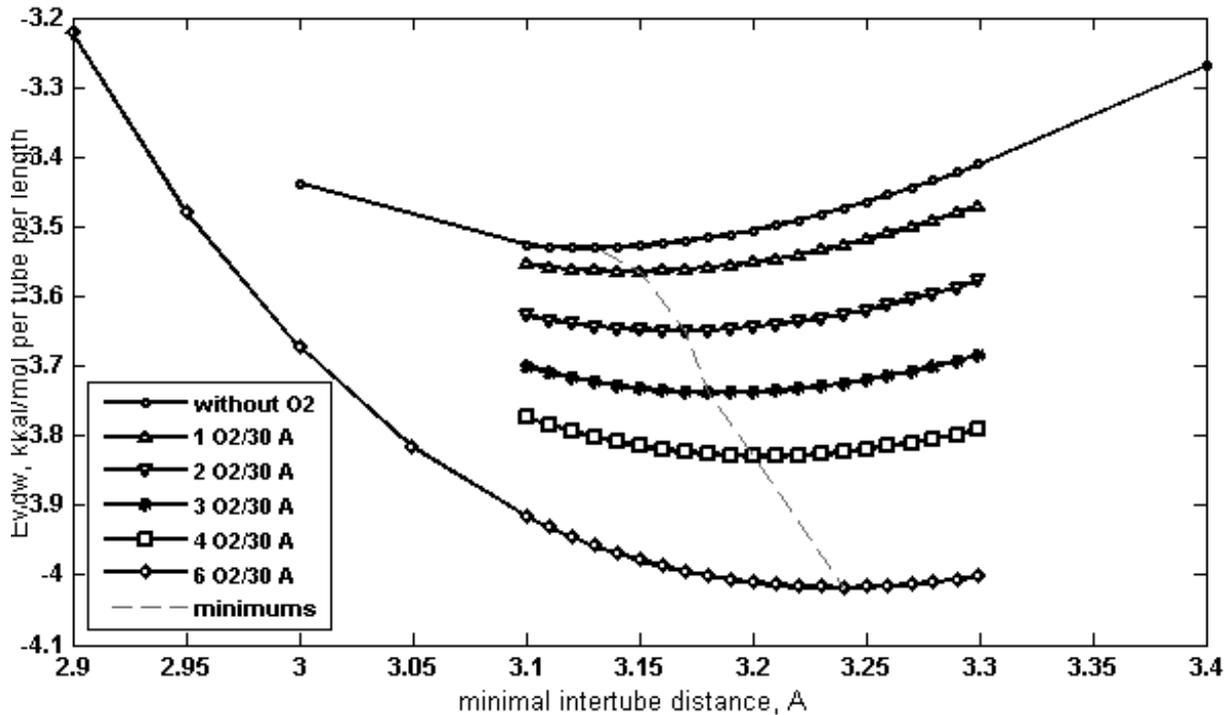
Fig. 4. Van der Waals energy of (10,10) nanotube array near energy minima per tube per tube length for various linear density of oxygen in chains.
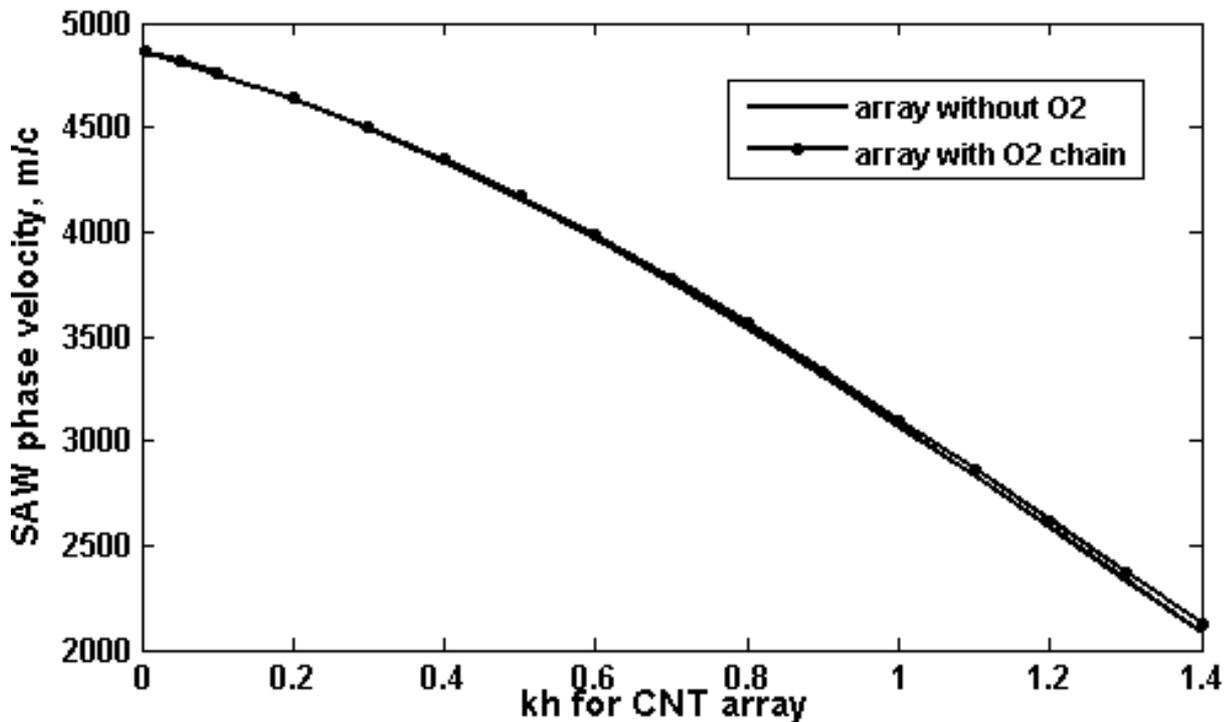

Fig. 5. SAW phase velocity dispersion curve for $Si_{\{001\}<100>}\backslash SiO_2\backslash array$ structure with adsorbed oxygen.

From acoustic point of view CNT array is sharply non-homogeneous medium which could have resonant properties effecting wave propagation. To study this feature we undertake (FEM) simulation of CNT array resonant behavior in continuous approximation. The model consisted on silicon substrate 285nm×285nm×30nm with square CNT array (Fig. 7) on it. Nanotubes were represented by
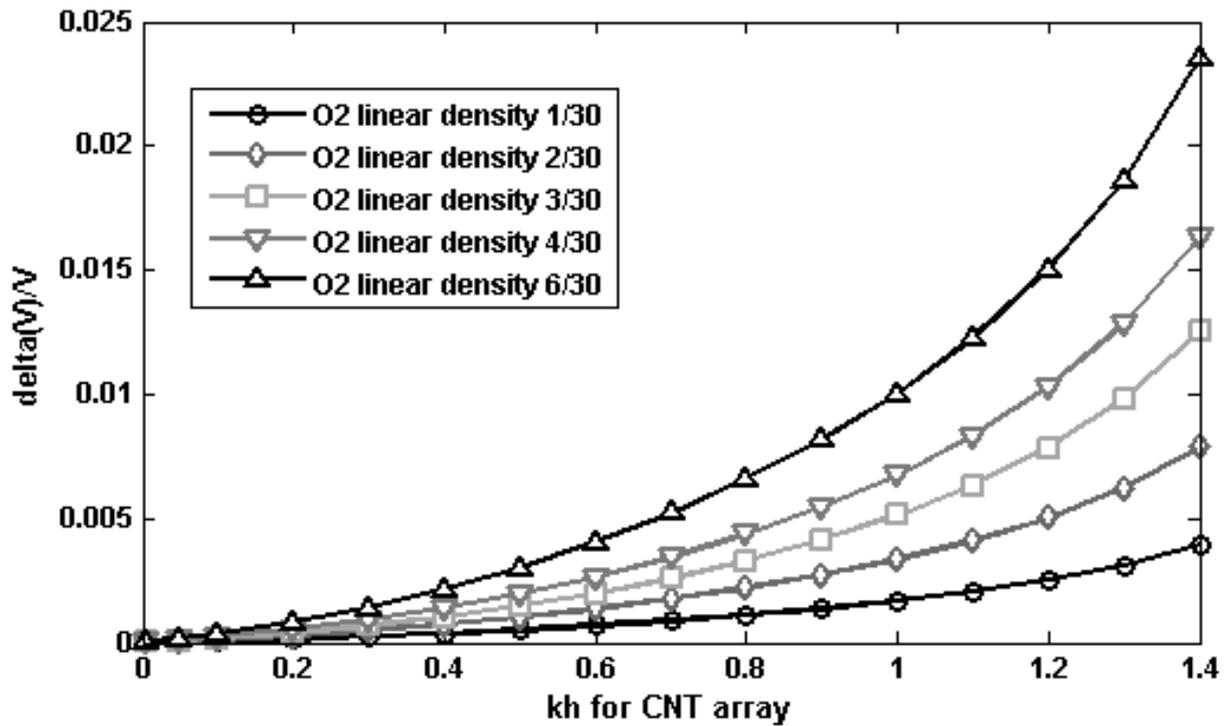
Fig. 6. SAW phase velocity relative change due to oxygen adsorption for $Si_{\{001\}<100>}\backslash SiO_2 \backslash array$ structure.
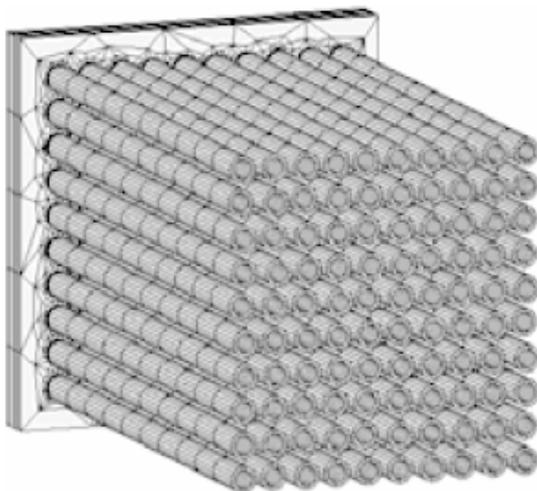
Fig. 7. Initial model.
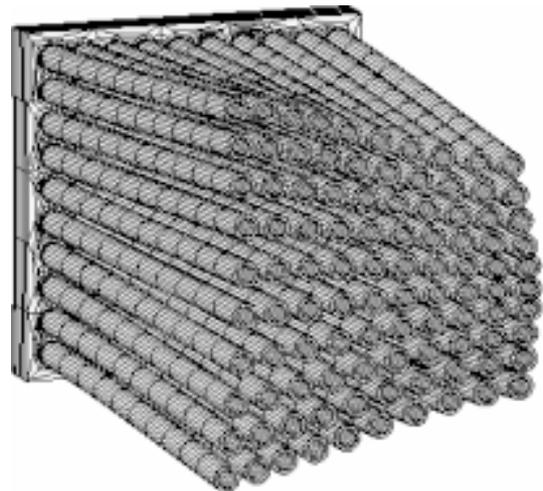
Fig. 9. 357.88 MHz eigenmode.
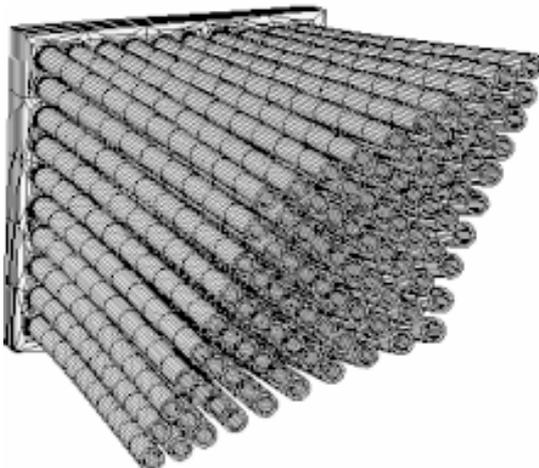

**Fig. 8.** 285.71 MHz eigenmode.
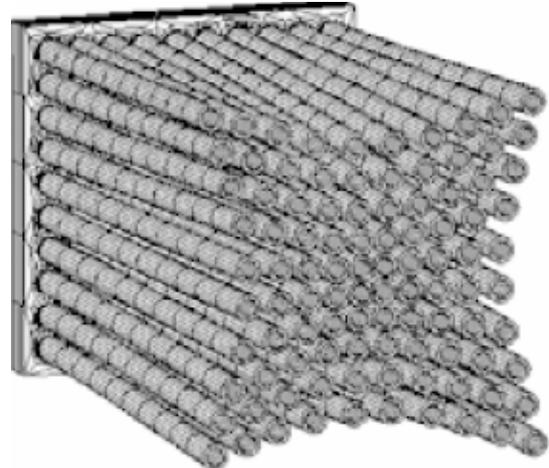
Fig. 10. 396.14 MHz eigenmode.
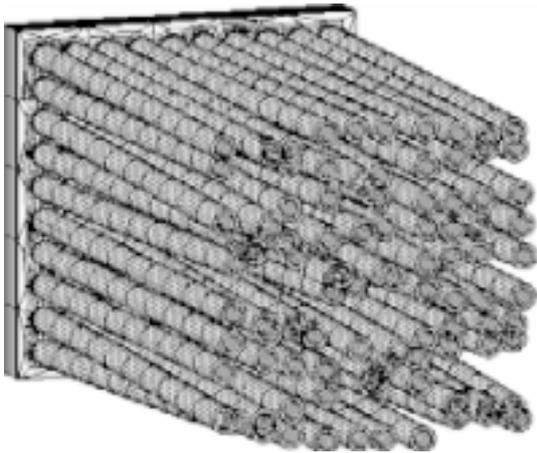
Fig. 11. 426.05 MHz eigenmode.

Fig. 12. 1153.6 MHz eigenmode.

Fig. 13. 1587.2 MHz eigenmode.

Fig. 14. 2012.5 MHz eigenmode.

Fig. 15. 2114.1 MHz eigenmode.

C_{33} = 1210·10^9 N/m^2, C_{44} = 9·10^9 N/m^2 and density 1500 kg/m^3.

Calculations were realized on SKIF K-1000 supercomputer cluster using LS-DYNA package. 501 eigenmodes of vibration were obtained in frequency range 200 – 3000 MHz, some of them are presented in Figs. 8-15. Spectrum of modes and histogram of their frequencies are presented in Fig. 16 which shows the band structure of vibration excitations of array similar to sonic crystal spectrum.

4. 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, where resonant prop-

hollow cylinders with outer diameter 20 nm, inner diameter 14 nm and length (400±10) nm. Substrate parameters were chosen as C_{11} = 166·10^9 N/m^2, C_{12} = 63.9·10^9 N/m^2, C_{13} = 63.9·10^9 N/m^2, C_{33} = 166·10^9 N/m^2, C_{44} = 79.6·10^9 N/m^2 , mass density 2330 kg/m^3; while for CNT effective material C_{11} = 39·10^9 N/m^2, C_{12} = 21·10^9 N/m^2, C_{13} = 31·10^9 N/m^2,

(a)

(b)
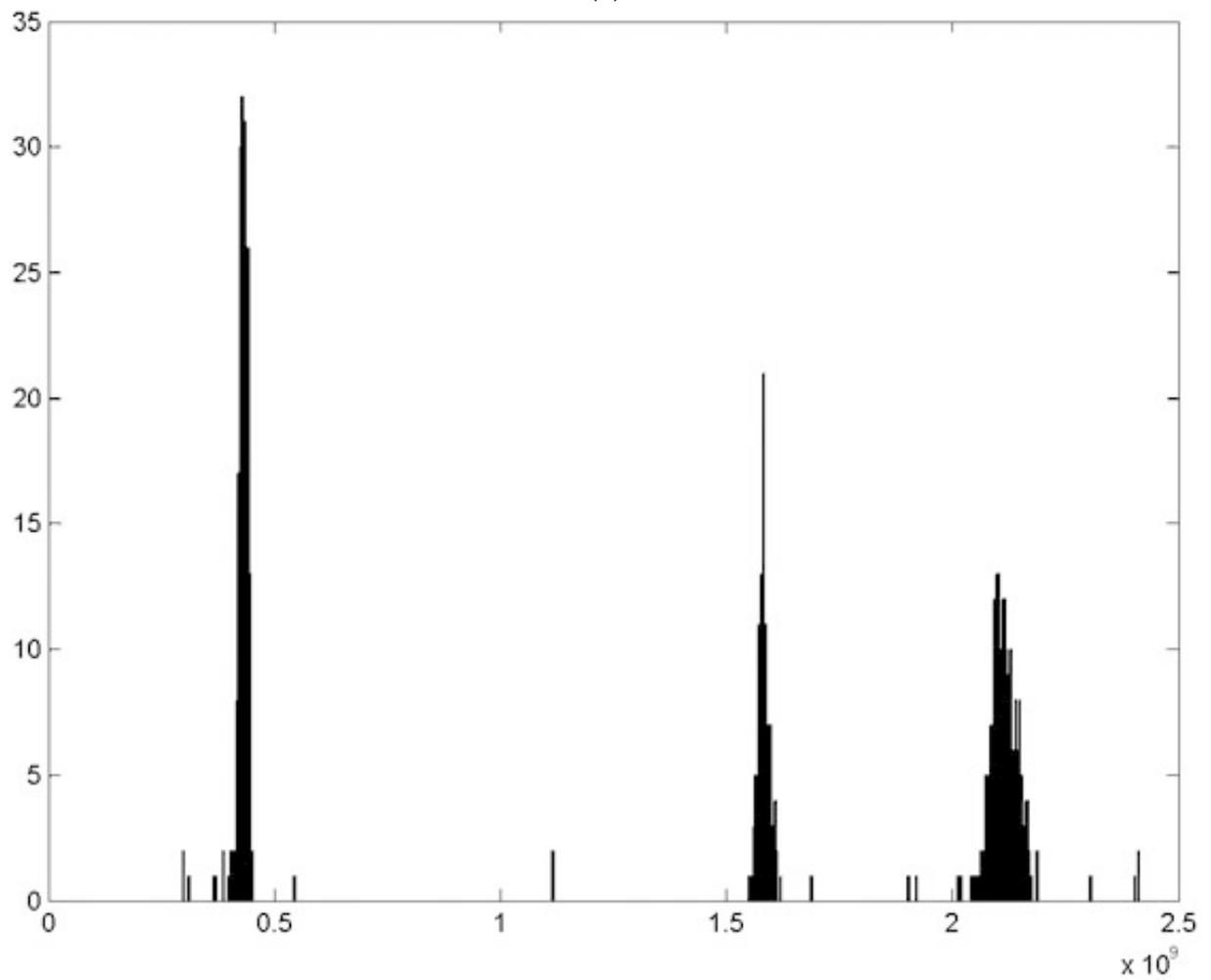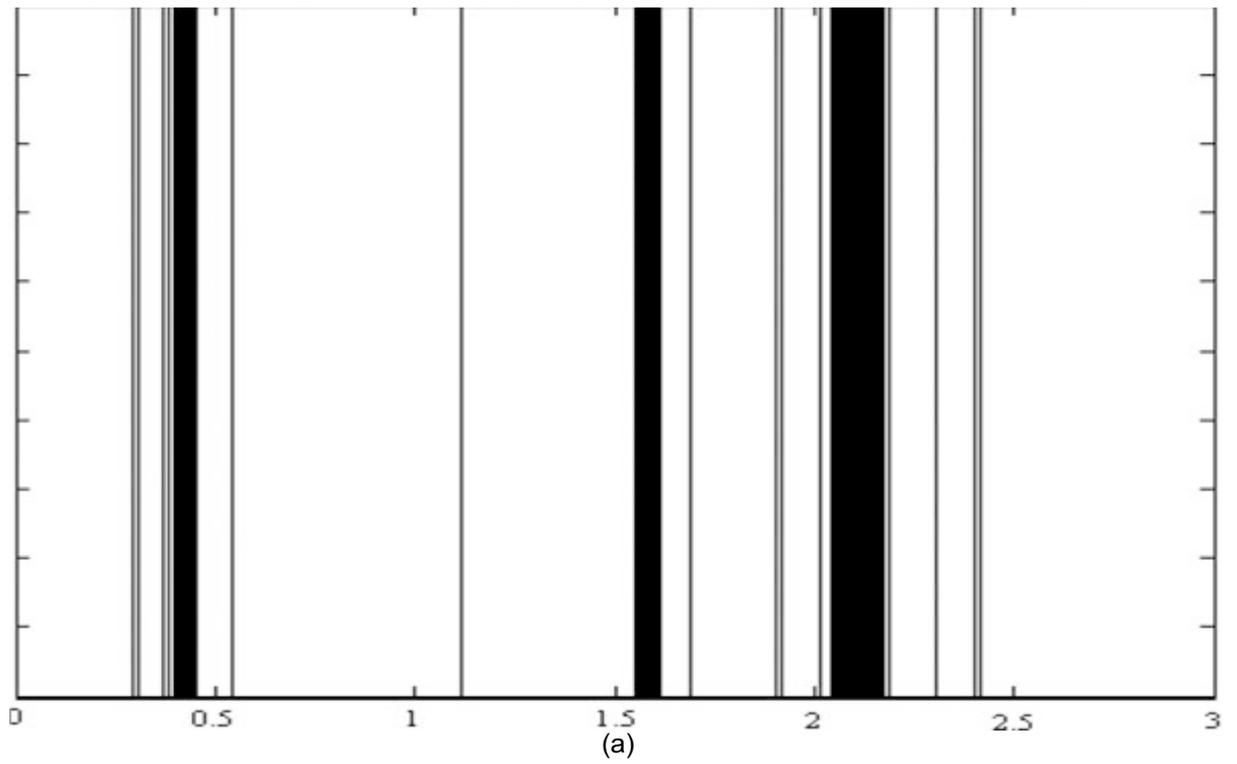
Fig.16. Eigenfrequencies (GHz) a) and number of modes b) in frequency range 10 MHz of CNT array on silicon substrate.

erties of CNT array may be essential for SAW devices too.

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