Annals of the Academy of Romanian Scientists
Series on Science and Technology of Information
ISSN 2066 - 8562 Volume **4**, Number **1**/**2011**

CARBON NANOTUBES AND THEIR NANOCOMPOSITES FOR CARBON DIOXIDE SENSING

Bogdan SERBAN[1], Cornel COBIANU[1,2],
Cazimir-Gabriel BOSTAN[1], Octavian BUIU[1]

Abstract. *In this paper we present some applications of carbon nanotubes and carbon nanotubes-based matrix nanocomposites in sensing of carbon dioxide. The design of surface functionalization of carbon nanotubes in order to improve the sensitivity and selectivity for carbon dioxide sensing is presented. Experimental results of* CO_2 *sensing have proven high sensitivities for the functionalized films. Novel concepts for differential resonant sensors aiming the reduction of base-line drift during long term operation are described. Advantages versus drawbacks regarding the using of carbon nanotubes in gas sensing are presented in the last section of this review.*

Keywords: carbon nanotubes, matrix nanocomposite, surface functionalization, HSAB, carbon dioxide sensing

1. Introduction

Carbon nanotubes (CNT), discovered by Sumio Iijima in 1991 [1] are fullerenes–related structures with the diameter of a few nanometers.

Due to their unique geometry and dimensions, carbon nanotubes exhibit remarkable electrical, thermal, chemical, optical and mechanical properties [2, 3].

In the last decade, the CNTs have become a very important material for a wide range of applications like nanoelectronics, optoelectronics, polymer matrix nanocomposites electrochemical capacitors, sensors (gas sensors and biosensors), field–emission displays, hydrogen storage, nanoscale reactor, photovoltaic devices, transistors, Schottky diodes, electrodes.[4-6].

The CNTs can be classified into two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [7, 8].

Due to the extreme high surface-to-volume ratio, carbon nanotubes have generated huge interest among researchers, focused on exploiting these materials for the development of new gas sensing structures.

In this paper, we review some applications of carbon nanotubes (pristine or functionalized) and their matrix nanocomposites in carbon dioxide sensing.

---

[1] Honeywell Romania, Sensor and Wireless Laboratory Bucharest, Romania.
[2] Corresponding member of the Academy of Romanian Scientists.

2. Carbon dioxide sensing using carbon nanotubes and their matrix nanocomposites

Carbon dioxide detection at room temperature still remains a challenge in the field of chemical sensors. Since carbon dioxide is an almost inert molecule, the design of a sensor with high sensitivity, reversible response time and selectivity is difficult. Recently, many efforts were dedicated to conceive new carbon nanotubes –based sensor for carbon dioxide.

Zribi *et al* fabricated a carbon dioxide sensor using a single–walled carbon nanotubes(CNT) and a microelectromechanical system (MEMS) resonator. Adsorption of the carbon dioxide molecules onto the surface of carbon nanotubes changes the stress state of sensing film, which is then further transmitted to the substrate of the sensor and thus changing its resonant frequency, as it is the case of resonant sensors based on vibrating beams. It is important to emphasize the excellent properties of this type of resonant sensor [9]: (a) sensitivity-300 Hz/% CO_2 (resonance frequency f_0=155 kHz); (b) linearity-93%; (c) hysteresis-less than 2% (c) no cross-sensitivity with moisture or oxygen. Koylothu *et al* developed a surface acoustic wave (SAW) based CO2 sensor using carbon nanotubes as the sensitive layer. Adsorption of carbon dioxide molecule in the sensitive layer changes conductivity of the carbon nanotube. This conductivity change will give a shift in frequency which is correlated with the concentration of carbon dioxide molecule in the examined sample. Carbon nanotube can be used single or in conjunction with $BaTiO_3$, La_2O_3, SnO_2, Sm_2O_3, $CaCO_3$ etc. [10].

Sivaramakrishnan fabricated a resistive carbon nanotube-based sensor fabricated by attaching nanoparticles of calcium carbonate to SWCNTs. The resistance of CNTs film changes due to the reaction between calcium carbonate and carbon dioxide. A major drawback of this type of sensors is its slow response time [11]. Faizah *et al* developed carbon nanotubes – based sensor by measuring the change in electrical resistance upon carbon dioxide adsorption [12].

Ong *et al* fabricated a sensor by depositing a thin layer of a multi-wall carbon nanotube-silicone dioxide composite upon a planar inductor-capacitor resonant circuit. It is demonstrated that permittivity of carbon nanotubes changes to CO_2 concentration, with linear and reversible response [13].

In some cases, pristine CNTs exhibit a low affinity toward analyte molecules. As a consequence of this behavior, this type of sensor shows lack of selectivity, low sensitivity etc. Non-covalent or covalent functionalization of carbon nanotubes could increase the affinity for target molecule, and thus the performance of the sensor.

Serban *et al* proposed that the selection and functionalization of sensing materials (polymers and carbon nanotubes) should be done according to the Hard soft acid bases (HSAB) theory [14-20].

Carbon dioxide, together with RCO^+, SO_3, AlH_3, BF_3, Na^+, Li^+, H^+, $AlCl_3$, $B(OR)_3$, are examples of hard acids. According to the HSAB theory, a hard base is suitable for CO_2 sensing. Examples of hard bases include alcohols , ethers, chloride anion (Cl^-), acetate anion (CH_3COO^-), fluoride anion (F^-), ammonia (NH_3), primary, secondary and tertiary aliphatic amines (RNH_2, R_2NH, R_3N), and amino group functionalized polymers. As a consequence of this theory, it is assumed that the compounds eligible for carbon dioxide detection could be amino groups–based polymers and/or carbon nanotubes functionalized with amino groups and matrix nanocomposites based on these types of compounds. The interaction between carbon dioxide and amino groups is reversible, fast and leads to carbamates [21-23].

Different types of aminocarbon nanotubes were used in detection of carbon dioxide (Figs. 1-4) as component of matrix nanocomposites [24, 25]

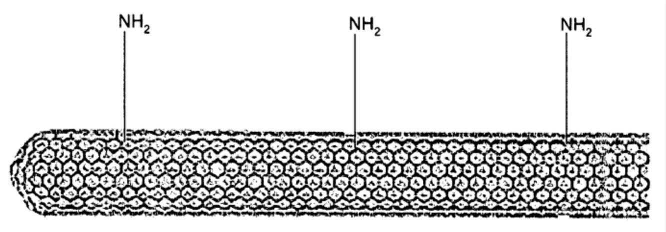

Fig. 1. The structure of aminocarbon nanotubes.

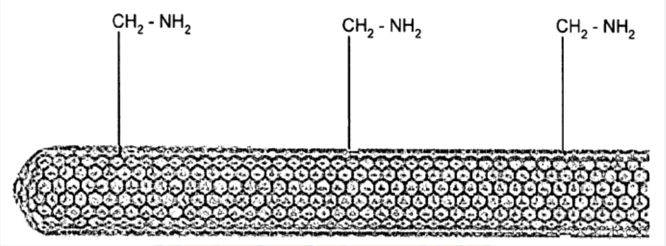

Fig. 2. The structure of aminomethylcarbon nanotubes.

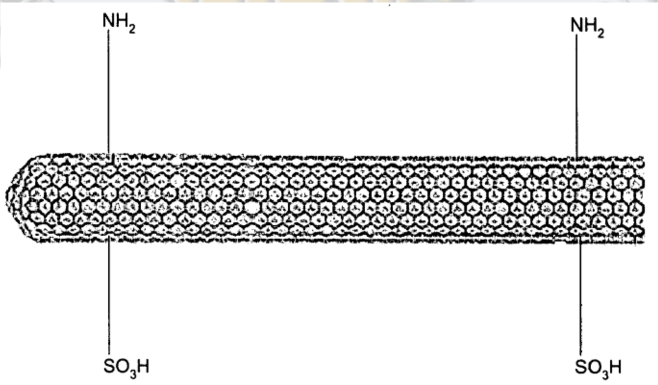

Fig. 3 The structure of aminosulfonic carbon nanotubes.

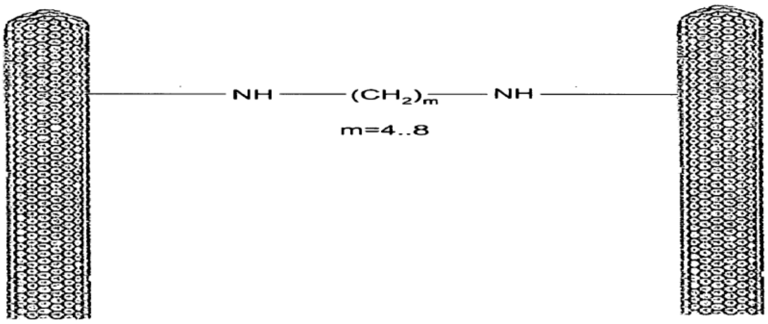

Fig. 4. The structure of carbon nanotubes linked through the spacercontaining amino groups.

Three different procedures for design of polymer–carbon nanotubes matrix nanocomposites were identified.

A. Mixing solution of a aminogroup-based polymers and aminocarbon nanotubes and sonication in ultrasonic bath for twelve hours

Among the used amino-groups based polymers in detection of carbon dioxide are: polyethyleneimine, polyllylamine, polyvinylamine, Versamid 900, BMBT etc. [26-29]. The used amino carbon nanotubes are presented in Figs. 1, 2 and 4.

Using a surface acoustic wave (SAW) device (Fig. 5.) Serban et al. demonstrated that a matrix nanocomposite based on polyethyleneimine and aminocarbon nanotubes is more effective in sensing than polyethyleneimine [23]. As shown in Fig. 5, the CO_2 sensing layer is located in between the two interdigitated (IDT) structures of a SAW delay line, which is then placed in the feed-back of an electronic oscillator, determining its oscillation frequency. The shift of the central frequency of the oscillator is proportional to the target gas. In our case, an oscillator with the central frequency of 80 MHz was used, and for a CO_2 concentration of 2500 ppm, the frequency shift was equal to 800 Hz for a PEI+amino-CNTs coated (35 nm thickness determined) SAW sensor, whereas for PEI coated SAW sensor the equivalent values calculated from previous reports are between 200 Hz.

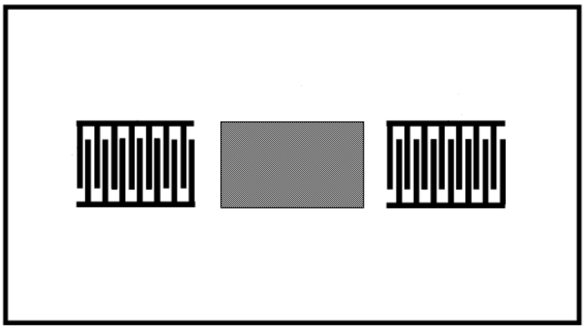

Fig. 5. SAW-based chemical sensor,
where a sensitive layer is positioned between two interdigitated structures.

In Fig. 6, we present a method of direct printing which can be used for the selective, additive and maskless deposition of the sensing layer, in the appropriate region between the two IDT's of the SAW delay line. The liquid state of the sensing layer is atomized and then directed by the computer-controlled nozzle in the desired position.

The thermal treatment of the deposited jelly layer is thermally consolidated for reaching the final solid state of the sensing film.

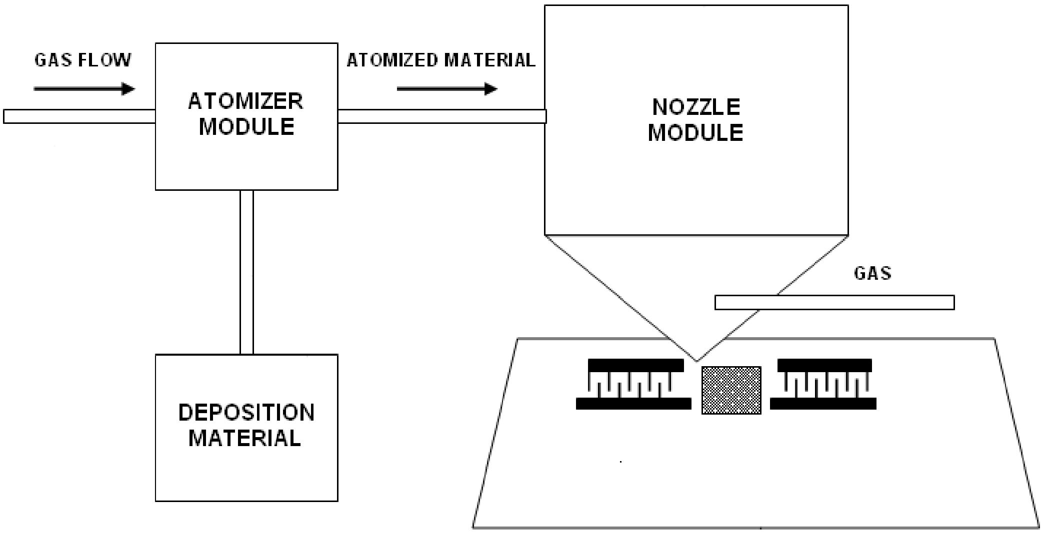

Fig. 6. Schematic presentation of a direct printing tool
for the selective deposition of the sensing layer.

B. Covalent functionalization of polymers with aminocarbon nanotubes

Functionalization of chloromethylated polystyrene with aminomethylcarbon nanotubes and functionalization of brominated polyphenyleneoxide (PPO) with amino carbon nanotubes a are presented in figs. 7 and 8 [28].

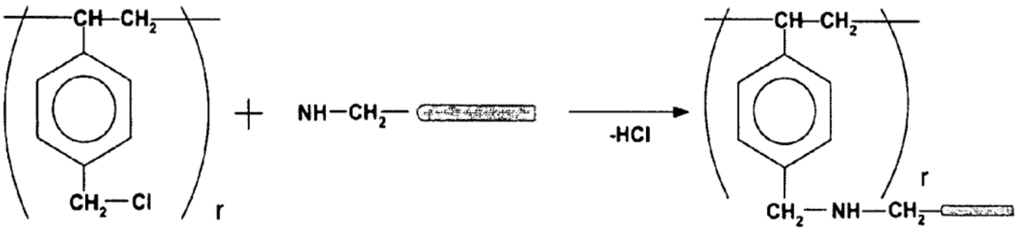

Fig.7. Functionalization of chloromethylated polystyrene
with aminomethylcarbon nanotubes.

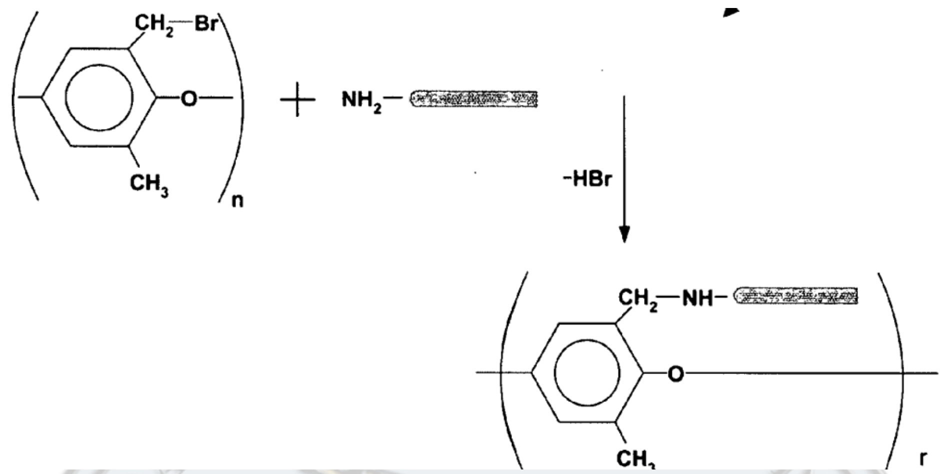

Fig. 8. Functionalization of brominated PPO with amino carbon nanotubes.

C. Incorporation of functionalized carbon nanotubes into the backbone of the polyaniline through doping [28]

A matrix nanocomposite polyaniline/carbon nanotubes can be synthesized through doping (Fig. 9). The doping is ensured by the sulfonic group (which protonates the emeraldine), while sensitivity toward carbon dioxide molecule is ensured by amino groups.

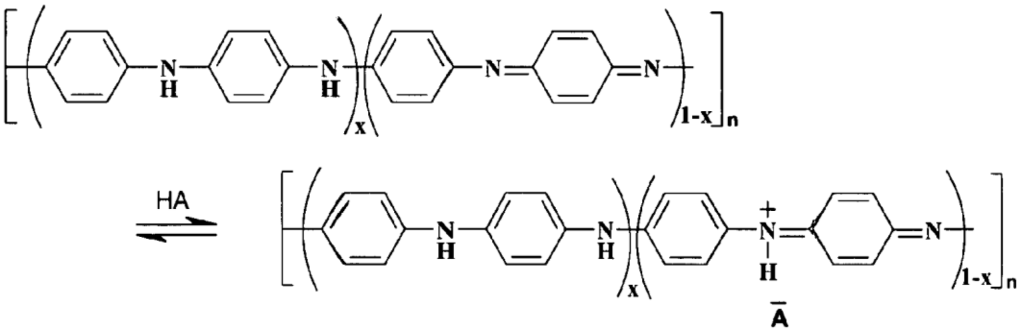

Fig. 9. Doping of emeraldine with HA (HA is aminosulfonic carbon nanotubes from fig. 3).

Despite the fact that, according to the HSAB theory, aminocarbon nanotubes are borderline bases (very much alike aromatic amines), many amino groups are situated at the layer surface (due to the nanometric size of carbon nanotubes) and are able to interact with the carbon dioxide molecules. Carbon nanotubes also possess a good hydrophobicity and thus can limit the cross-sensitivity due to humidity. Finally, the carbon nanotubes improve the mechanical properties of the layer and may increase the lifetime of the polymer due to their antioxidant character [30, 31].

Another approach for carbon dioxide sensing is the use of carbon nanotubes – ionic liquid matrix nanocomposites.

Serban et al conceived a CO_2 gravimetric sensor concept based on sensing silicon nanocantilever and reference silicon nanocantilever, each of them being functionalized with the appropriate sensing and reference layer, respectively [32-34]. The sensing layer contains ionic liquid with amino group (which, according to the HSAB theory, are more susceptible to react with carbon dioxide and thus yielding to mass loading). Ionic liquid used are 1-(4-amino butyl)-3 methylimidazolium hexafluorophosphate, 1-(2-amino ethyl)-3 methylimidazolium tetrafluoroborate. Carbon nanotubes used are functionalized with amino groups, also.

The reference layer contains the same compounds, the only difference being in the fact that all amino groups are in form of hydrochloride. Thus, all these amino hydrochloride groups are insensitive toward carbon dioxide. In Fig. 10, we show an example of such an differential resonator containing both a vibrating sensing beam (where the terminal sensing amino groups are exhibited) and vibrating reference beam (where the sensing amino groups have been poisoned with hydrogen chloride, thus becoming un-sensitive).

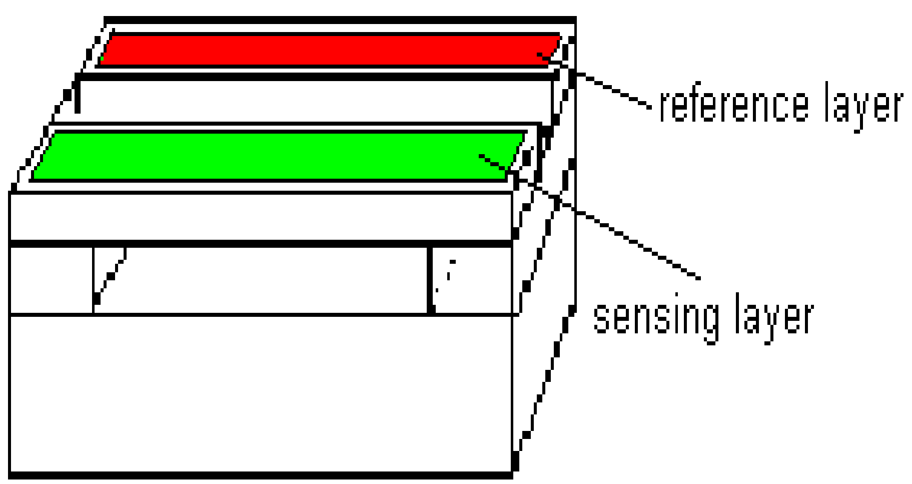

Fig. 10. Simplified schematics of a differential resonant CO_2 sensor with functionalized sensing and reference layer located above two suspended beams vibrating at their natural resonance frequencies.

Such a novel all-differential resonant sensing concept has the advantage of a smaller drift of the baseline of the sensor response with respect to prior art, where not only temperature compensation occurs, but also the effects of the sensing film ageing and its humidity response are minimized due to the fact that the sensing layer and the reference layer have similar visco-elastic properties and humidity response [35].

3. Limitations and concerns regarding the carbon dioxide sensing with carbon nanotubes and their matrix nanocomposites

Despite the high number of carbon nanotubes–based gas sensors, there are still several drawbacks remaining before the real–world application. Among these, we can mention:

- Synthesis of pure and defect-free carbon nanotubes is difficult and costly.
- Synthesis of identical and reproducible carbon nanotubes is challenging.
- Low selectivity, mainly for pristine carbon nanotubes.
- Slow response [2.8].

Intensive research is performed all-over the world for reducing the effect of the above challenges and bringing faster these nanotechnology enabled sensors to the application field.

4. Conclusions

Some applications of carbon nanotubes (pristine or functionalized) in carbon dioxide sensing were reviewed.

Appropriate functionalization of carbon nanotubes increases sensitivity and selectivity toward carbon dioxide molecules.

HSAB (hard soft acid bases) theory was reviewed as useful tool for functionalization of pristine carbon nanotubes.

Different types of carbon nanotubes- based matrix nanocomposite (with polymers, metal oxides, calcium carbonate, ionic liquid) were proven useful in carbon dioxide detection.

Experimental results obtained on SAW delay line sensors have shown sensitivity of our CO_2 sensors, beyond state of the art.

Novel resonant sensing principles were proposed for further improving the performances of the resonant differential sensors in terms of sensor drift reduction.

Acknowledgments

A part of this paper was performed during the work at the EU-FP-7 NEMSIC project. The authors express their gratitude to Honeywell International and EU-FP-7 NEMSIC project for their support with the development of this research.

REFERENCES

[1] S. Iijima, *Helical microtubules of graphitic carbon*, Nature, Vol. **354**, No. 3648, pp. 56-58, 1991.

[2] T. Zhang, S Mubeen, N. V. Myung, and M. A. Deshusses, *Recent progress in carbon nanotube-based gas sensors*, Nanotechnology 19, 2008.

[3] P. M. Ajayan and O. Z. Zhou, *Carbon Nanotubes*, **391**, 425, 2001.

[4] M. Burghard and K. Balasubramanian, *Chemically functionalized carbon nanotubes*, Small, 2005, **1**, No 2, 180-192.

[5] V. N. Khabashesku, W. E. Billups, J. L: Margrave, Acc. Chem Res, 2002, **35**, p. 1087.

[6] J. L. Stevens, A.Y. Huang, H. Q. Peng, L. W. Chiang, V. N. Khabashesku, J. L. Margrave, *Sidewall Amino-Functionalization of Single-Walled Carbon Nanotubes through Fluorination and Subsequent Reactions with Terminal Diamines*, Nano Lett, 2003, **3**, 331.

[7] S. Niyogi, M. A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M. E: Itkis, and R. C. Haddon, *Chemistry of single-walled carbon nanotubes*, Acc. Chem. Res. 2002, **35**, pp. 1105-1113.

[8] Y. Wang and J. T. Yeow, *A review of carbon nanotubes -based gas sensors*, Journal of Sensors, 2009, Article ID 493904, 24 pages.

[9] A. Zribi, A. Knobloch, R. Rao, CO_2 *detection using carbon nanotube networks and micromachined resonant transducers*, Appl. Phys. Lett. **86**, 2031112, 2005.

[10] S. A. Koyilothu, R. A. Raghurama, *SAW based* CO_2 *sensor using carbon nanotubes as the sensitive layer*, U.S. Patent Application Publication, Pub. No.: US 2008/0216558A1, Pub. Date: Septembr, 11, 2008.

[11] S. Sivaramakrishnan, *Carbon Nanotube Based Carbon Dioxide Gas Sensors for Respiratory Monitoring,* A dissertation submitted to the faculty of the Graduate school of the University of Minnesota.

[12] Y. Faizah, *Room temperature multi gas detection using carbon nanotubes*, European Journal of Scientific research, Vol. **35**, No. 1 (2009), pp. 142-149.

[13] K. G. Ong, P. D. Kichambare, C. A. Grimes, *A carbon nanotube-based sensor for* CO_2 *monitoring*, Sensors, 2001, **1**, pp. 193-205.

[14] J. March, *Advanced organic chemistry*, 3rd edition, pp. 227-229.

[15] R. G. Pearson, *Hard and soft acids and bases*, J. Am. Chem. Soc., **85** (**22**), pp. 3533-3539.

[16] B. Serban, M. Mihaila, S. Costea, O. Buiu, *New ligand selection rule for quantum dot functionalization*, Proceedings of the International Semiconductor Conference CAS 2009, pp. 81-84.

[17] B. Serban, A. K. Sarin Kumar, C. Cobianu, O. Buiu, S. Costea, C. Bostan, N. Varachiu, *Selection of gas sensing materials using the hard soft acid base theory. Application to surface acoustic wave* CO_2 *detection*, Proceedings of the International Semiconductor Conference, CAS 2010, pp. 247-250.

[18] C. Cobianu, B. Serban, V. Petrescu, J. Pettine, D. Karabacak, P. Offerman, S. Brongersma, V. Cherman, S. Armini, F. A. Hassani, M. A. Ghiass, Y. Tsuchiya, H. Mizuta, C. Dupre, L. Durrafourg, A. Koumela, D. Mercier, E. Ollier, D. Tsamados, and A. Ionescu, *Towards nano-scale resonant gas sensors,* Annals of the Academy of Romanian Scientists, Series on Science and Technology of Information, Vol. **3**, No. 2, 2010, pp. 39-60.

[19] B. Serban, M. Mihaila, O. Buiu, S. Costea, *A new approach for quantum dot-polymer nanocomposite design*, Nanomeasure 3-4 June 2010, Krakow, p. 12

[20] O. Buiu, B. Serban, M. Mihaila, M. Brezeanu and S. Costea, *New design approach for quantum dot solar cell* , Second workshop on Size-dependent Effects in Materials for environmental protection, Nessebar, Bulgaria, September 19-21, 2010, p. 22

[21] J. C. Gabriel, G. Gruner, A. Star, *Carbon dioxide nanoelectronic sensor*, WO 2005/026694 A2.

[22] K. Korsah, C. L. Ma, B. Dress, *Harmonic frequency analysis of SAW resonator chemical sensors: application to the detection of carbon dioxide and humidity*, Sensors and actuators B 50 (1998) pp. 110-116.

[23] M. S. Nieuwenhuizen, A. J. Nederlof, *A SAW Gas Sensor for Carbon Dioxide and Water. Preliminary Experiments*, Sensors and actuators B 2 (1990) pp. 97-101.

[24] A. Gromov, S. Dittmer, J. Svensson, O. A. Nerushev, S. A. Perez-Garcia, L. Licea-Jimenez, R. Rychwalski, and E. B. Campbell, *Covalent amino functionalization of single –wall carbon nanotubes*, J. Mater. Chem., 2005, **15**, pp. 3334-3339.

[25] T. Ramanathan, F. T. Fischer, R. S. Ruoff, and L. C. Brinson, Chem. Mater., 2005, 17, 1290.

[26] B. Serban, A. K. Sarin Kumar, S. Costea, M. Mihaila, O. Buiu, M. Brezeanu, N. Varachiu, C. Cobianu, *Surface acoustic wave* CO_2 *sensing with polymer-amino carbon nanotube composites*, Proceedings of the International Semiconductor Conference CAS 2008, pp. 73-76.

[27] B. Serban, A. K. Sarin Kumar, S. Costea, M. Mihaila, O. Buiu, M. Brezeanu, N. Varachiu, C. Cobianu, *Polymer–amino carbon nanotubes nanocomposites for surface acoustic wave* CO_2 *detection*, Romanian Journal of Information Science and Technology, Volume **12**, Number 3, 2009, pp. 376.

[28] B. Serban, C. Cobianu, M. Bercu, N. Varachiu, M. Mihaila, C. Bostan, S. Voicu, *Matrix nano-composite containing aminocarbon nanotubes for carbon dioxide sensor detection*, Pub. No.: US 2008/0264147 A1, Pub. Date: Oct. 30, 2008

[29] V. Avramescu, C. Bostan, B. Serban, I. Georgescu, S. Costea, N. Varachiu, C. Cobianu, *Surface acoustic wave devices and their sensing capabilities,* Proceedings of the International Semiconductor Conference CAS 2009, pp. 27-36.

[30] P. C. P. Watts, P. K. Fearon, W. K. Hsu, N. C. Billingham, H. W. Kroto, D. R. M. Walton, *Carbon nanotubes as polymer antioxidants*, Journal of Material chemistry, 2003, **13**, pp. 491-495.

[31] P. Ajayan, C. Y. Ryu, N. Chakrapani, G. Viswanathan, S. Curran, *Nanotube polymer composite and methods of making same*, US 2006/0252853 A1.

[32] B. Serban, C. Cobianu, M. Mihaila, V. Dumitru, O. Buiu, U.S Patent Application No. 10196990.5 Filing Date: December 24, 2010.

[33] C. Cobianu, B. Serban, I. Georgescu, S. Costea, C. Bostan, *A novel concept for low drift chemical sensing at micro and nano scale*, Proceedings of the International Semiconductor Conference, CAS 2010, pp. 217-220.

[34] B. Serban and C. Cobianu, *Novel concepts for* NO_2 *detection by differential resonant nanosensing*, Nano-Electro-Mechanical Devices for Integrated Sensing and Switching Satellite workshop to ESSDERC/ESSCIRC 2010.

[35] C. Cobianu and B. Serban, *All-differential resonant nanosensor apparatus and method*, U.S. patent application, Application number: 12/617, 893, Filing date: 11/13/09.