

# Novel Concepts for CO<sub>2</sub> Detection by Differential Resonant Nanosensing

Bogdan Serban, Cornel Cobianu, Cazimir Bostan

Sensors & Wireless Laboratory Bucharest, 169A  
Floreasca Street, Building A, 014459, Honeywell Romania, Bucharest, Romania

bogdan.serban@honeywell.com

## Abstract

In this paper we present two general approaches for silicon surface functionalization to be used in carbon dioxide detection by means of MEMS/NEMS nano-cantilever based resonant sensors.

In the first chemical route, the synthesis of sensing layer can be performed using 1,8 diazabicyclo[5,4,0] undec-7-ene (DBU) or 1,5 diaza [3,4,0]-non-5-ene (DBN), as sensing terminal groups. This functionalization is according to Bronsted –Lowry theory.

In the second chemical route, the functionalized monolayer involves amino groups as sensitive pendant groups, according to HSAB theory. A comparison between both types of functionalization in terms of sensing mechanism, reversibility, response time, temperature operation, cross sensitivity, versatility of synthesis is presented.

We propose novel resonant differential sensing principles aiming at further improving the performances of the resonant differential sensors in terms of drift reduction.

## 1. INTRODUCTION

Low cost detection and monitoring of carbon dioxide (CO<sub>2</sub>) has a crucial importance in the area of gas sensors, considering the huge impact of CO<sub>2</sub> emissions to the global warming and the need to survey large ground where the greenhouse gas is generated and even the underground areas, where it is sequestered.

Chemical CO<sub>2</sub> gas sensors with sensitive layers based on polymers or small molecules exhibit some advantages in comparison with spectroscopic sensors, e.g. low energy consumption, simplicity, small size. In the last decade, much attention has been paid to find or design new CO<sub>2</sub> sensitive compounds which could ensure specificity, ambient conditions operations, fast and reversible response, high sensitivity[1].

Among the many organic and inorganic compounds known to have carbon dioxide sensing properties, amino group-based polymers and small molecules containing nitrogen atoms has been extensively studied[1-3].

Synthesis and selection of these CO<sub>2</sub> sensitive compounds were performed using two different approaches.

Hard soft acid bases (HSAB) theory has been introduced as useful tool for design/selection of different carbon dioxide sensing layers.

A lot of older proposed solutions such as polyethyleneimine, Versamid 900, BMBT, monoethanolamine (MEA), diethanolamine(DEA), diisopropylamine(DIPA), triethanolamine(TEA), n-methyldiethanolamine(MDEA) polyallylamine, polyvinylamine, polyethyleneimine –amino carbon nanotubes matrix nanocomposites,

polyallylamine –aminocarbon nanotubes matrix nanocomposites, ionic liquid with amino groups can be understood in the view of this principle [4-13].

Acid-bases Bronsted-Lowry theory is another useful method to select potential carbon dioxide sensitive layers. Taking into account the basicity of nitrogen atoms – based organic compounds[14] several compounds has been tested: 1,8 diazabicyclo[5,4,0] undec-7-ene (DBU) or 1,5 diaza [3,4,0]-non-5-ene (DBN), polyguanidines, polyamidines, DBU- methyl phenylsilica, polyether DBU, etc [15-20]

In this paper we report the functionalization of silicon surface of vibrating nanobeams of resonant sensors for CO<sub>2</sub> detection. Design of this functionalization can be performed according to Bronsted –Lowry theory (as it will be shown in section 3A) and HSAB theory (as it will be shown in section 3B).

In addition, we describe our concept of all-differential resonant gas sensing, aiming at an increased accuracy of sensing by minimizing the baseline drift of the detector, and thus preserving long term operation stability [21-27]. Our functionalization method based on HSAB theory is in agreement with the results shown in Ref. [28].

## 2. RESONANT MEMS/NEMS GAS SENSING

After more than three decades of research, the Micro (Nano)-Electro-Mechanical Systems (MEMS/NEMS) for resonant sensing are becoming a mature principle, with high expectations in the field of chemical detection for biomolecules and gases monitoring [29-32]. The resonant chemical detection principle consists in the shift of the natural resonance frequency of a vibrating beam as a function of the mass loading created by the analyte which has to be selectively adsorbed on the functionalized sensing surface. With the increasing demand for very highly sensitive and selective sensors, the emerging Nano-Electro-Mechanical Systems (NEMS) are pushing the gas sensing limits much beyond the state of the art, and where the mass of the adsorbed gases on the sensing surface is below 1 zeptogram [32]. As this detection is performed at room temperature, the loading effect of humidity should be eliminated, as well as any influence of ambient temperature variation on the resonance frequency. Traditionally, these “common mode” signals, like temperature and humidity, with deleterious effect on sensor accuracy and its baseline drift have been rejected by using a differential resonant approach, as shown in Fig. 1. In this figure, one can see a sensing loop containing an electronic oscillator and the coated MEMS/NEMS vibrating beam in the feed-back, and an “identical” reference loop, which is containing an identical oscillator and an uncoated vibrating beam. The resonance frequency of the vibrating beam is determining the frequency of the oscillator. The two loops are tuned so that to have the same resonance frequency in the absence of the analyte to be detected, but they will become different in the presence of the gas to be detected, as shown in Fig.1. Subtraction of the two resonance frequencies, at the level of the mixer, will provide a frequency difference which will be proportional to the gas to be measured. Such a classical differential approach is using only one functionalized layer on the vibrating sensing beam, while the uncoated surface of a similar vibrating beam is performing the reference function. Unfortunately, this approach does not compensate the sensor response for the sensing layer ageing; moreover, it is limited in compensating the humidity effect, when the uncoated surface has a different humidity response compared to the surface of the functionalized sensing layer. In order to solve these drawbacks of the

classical differential resonant chemical sensors, we have proposed a novel differential resonant concept, as shown in Fig. 2, where a reference layer is added on the reference vibrating beam. This layer is designed to have a humidity and visco-elastic behavior similar to that of the sensing layer, but no sensing properties.

The novelty of our approach comes from the chemical functionalization of the silicon surface of nanoresonator and by the use of the reference sensing monolayer, which will have the same physical properties as the sensing layer, but no sensing capabilities. Such an all differential sensing principle, where a reference layer is added on the surface is solving the prior-art drift issues specific to differential resonant chemical sensors, where the reference loop had only an uncoated surface, which could not eliminate the humidity and aging effects of sensing layer from the sensor response.

The good thing is that such reference layers have almost similar physical response to temperature, humidity and aging in general, which make them very suitable for the differential sensing where the above “common mode signals” can be eliminated, while the differential signal (containing only CO<sub>2</sub> response) may be accurate and drift-free.

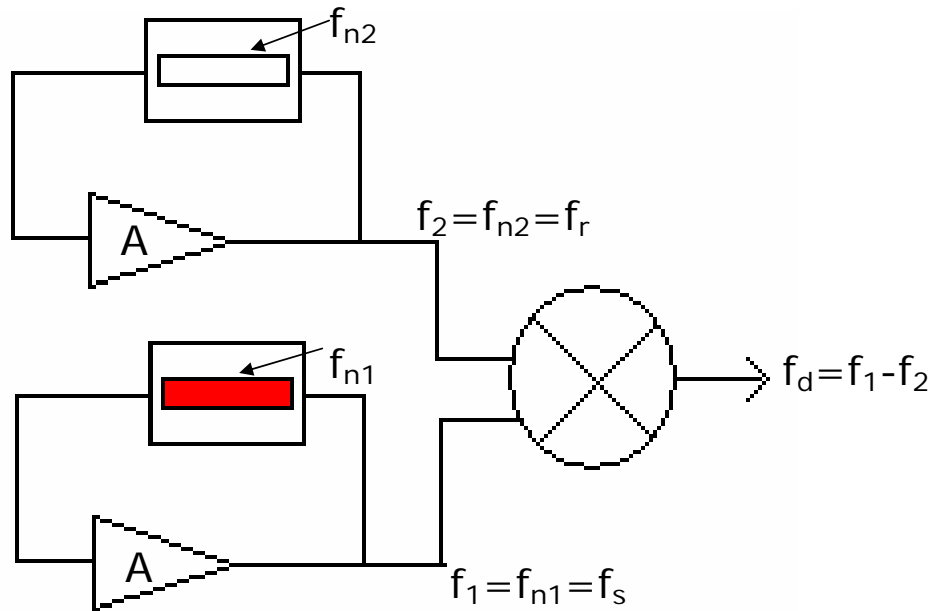


Fig.1 Differential resonant MEMS/NEMS gas sensor with uncoated reference beam

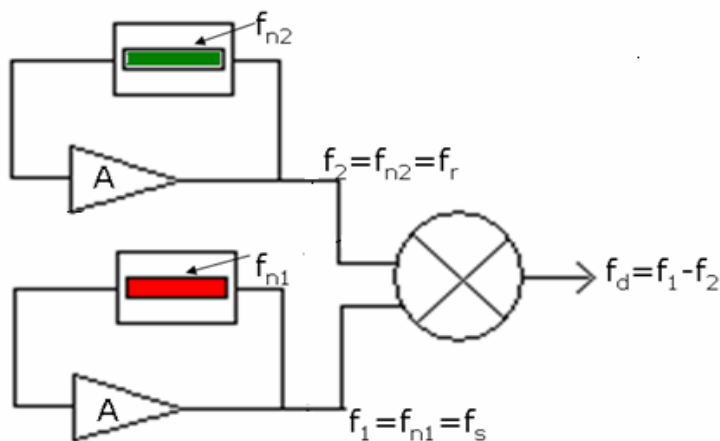


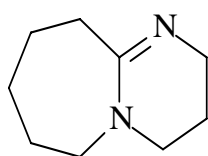
Fig.2 Differential resonant MEMS/NEMS gas sensor with coated reference beam

### 3. RESULTS AND DISCUSSIONS

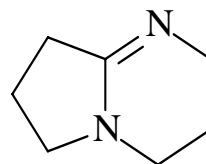
Self-assembled monolayers (SAMs) have been the subject of an intense study because of their potential in chemical sensing applications. Such a sensing monolayer is made of molecules that have a terminal group which is attached to the suspended silicon beam and the other which is functionalized for CO<sub>2</sub> recognition and detection.

#### A. Functionalization of silicon resonant nanosensor according to Bronsted-Lowry theory.

The chemical design of the sensing monolayer with main focus on the functional sensing group was based on Bronsted–Lowry theory. The proposed sensing layers contain CO<sub>2</sub> sensitive pendant groups such as 1,8 diazabicyclo [5,4,0] undec-7-ene (DBU) or 1,5 diaza [3,4,0]-non-5-ene (DBN)[21-26], which are presented in Fig.3 from below.



DBU



DBN

Fig.3 The structure of DBU and DBN

Both DBU and DBN are highly basic (high pKa values) and are able to react at room temperature simultaneously with carbon dioxide and water according to the following equations, from Figs. 4 and 5.

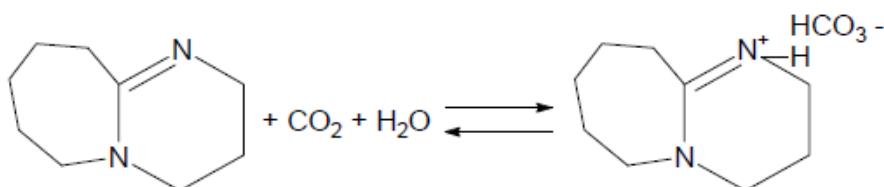


Fig.4 The reaction of DBU with carbon dioxide and water at room temperature

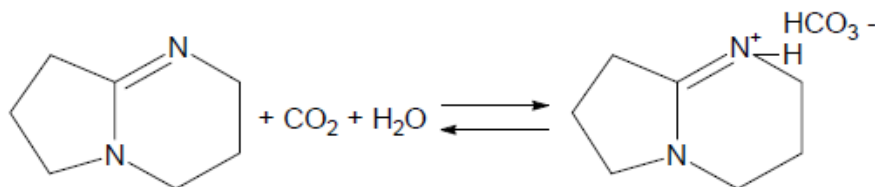


Fig.5. The reaction of DBN with carbon dioxide and water at room temperature

The DBU and DBN sensing moieties are covalently bonded to the Si surface by means of either alkyl chain groups (route I) or styrene moiety (route II).

The sequence of DBU functionalization processes by route I is as follows:

- 1) Wafer cleaning avoiding sticking of the suspended membrane to the substrate.
- 2) Native oxide removal from suspended Si beam in 1% HF in order to create hydrogen -terminated Si beam surface (Fig. 6a).
- 3) Immersion of the wafers containing suspended beam having its hydrogen-terminated surface in a flask containing unsaturated alkyl halide such as alkyl chloride and toluene followed by heating the sealed flask for formation of alkyl monolayer on the Si surface (Fig. 6b).
- 4) Rinsing the wafers in isopropyl alcohol, followed by their cleaning and drying so as to avoid suspended beam sticking to the substrate.
- 5) Deprotonation of the DBU at low temperatures, in the presence of butyl lithium (Fig. 6c).
- 6) Reaction of deprotonated DBU with alkyl chloride monolayer from the silicon surface in order to obtain the CO<sub>2</sub> sensing layer (Fig. 6d).

The scheme of this synthesis is shown below in Figs.6 a-d:

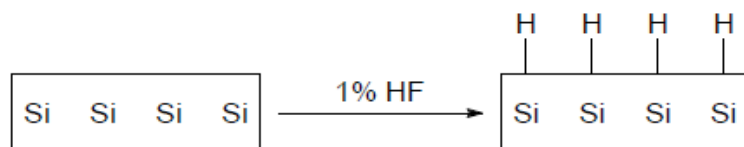


Fig.6 a. Hydrogenation of the silicon surface

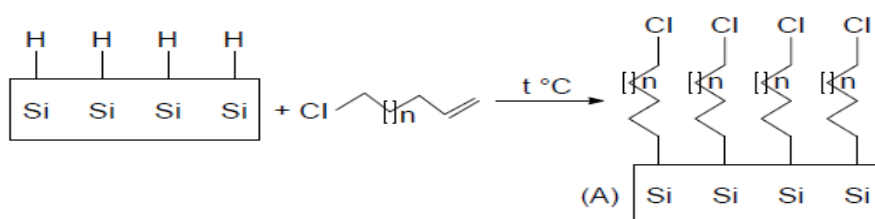


Fig.6 b. Formation of alkyl monolayer on the Si surface

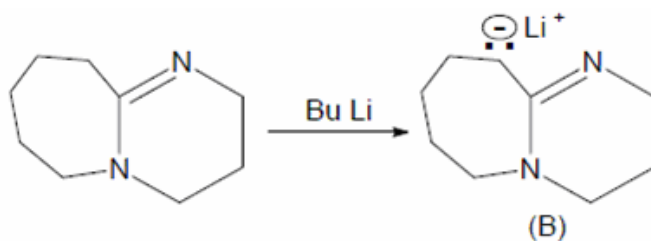


Fig. 6.c. Deprotonation of DBU in butyl lithium in order to obtain the compound B (deprotonated DBU)

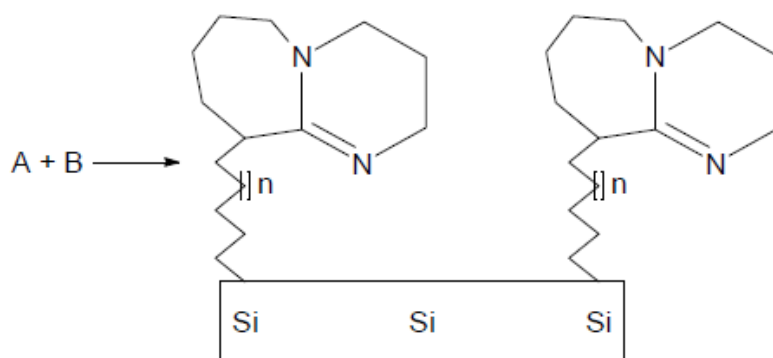


Fig.6 d Attachment of DBU sensing moieties from the silicon surface through covalent bonding

A similar approach is followed for the DBN functionalization process where deprotonated DBN (Fig. 7a) is reacting with alkyl chloride monolayer from Si surface in order to obtain a surface with DBN moiety (Fig.7b), which is sensitive to the CO<sub>2</sub> gas.

Deleted: are

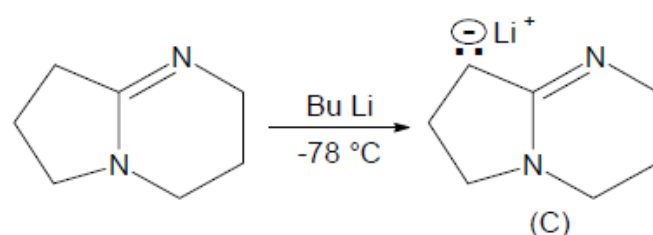


Fig.7a. Deprotonation of DBN

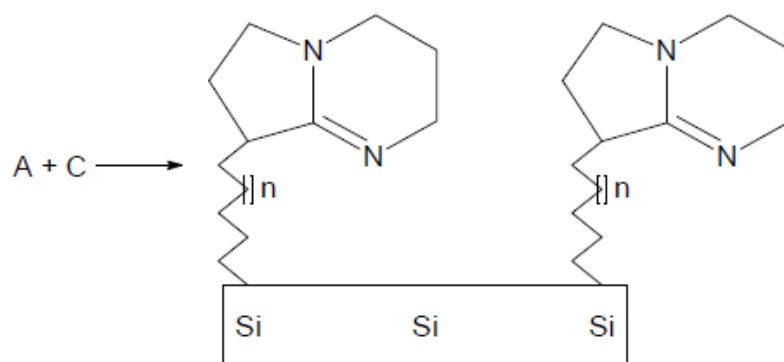


Fig.7b Attachment of DBN sensing moieties from the silicon surface through covalent bonding

Deleted:

The reference layers have almost similar nature like the above DBN and BDU, because they originate from the above sensing layer but in this case, the amidine moieties are converted into hydrochlorides, and thus, we get no sensitivity to CO<sub>2</sub> on the reference channel.

The sequence of DBU functionalization process by route II (Figs. 8a-c) is as follows:

- 1) Wafer cleaning avoiding sticking of the suspended membrane to the substrate.
- 2) Native oxide removal from suspended Si beam in 1% HF for getting H-terminated Si beam surface
- 3) Immersion of the wafers containing suspended beam having its hydrogen-terminated surface in flask containing chloromethylated styrene and toluene followed by heating the sealed flask for getting a monolayer of chloromethylated styrene connected to the Si surface by styrene moiety (Fig. 8a).
- 4) Rinsing the wafers in isopropyl alcohol, followed by their cleaning and drying so as to avoid suspended beam sticking to the substrate.
- 5) Deprotonation of the DBU at low temperature, in the presence of butyl lithium

Deleted:

- 6) Reaction of deprotonated DBU with compound A' in order to synthesize the DBU based sensing layer connected by styrene moiety to the Si surface (Fig. 8b).

The reference layer for the DBU based sensing layer connected by styrene moiety to Si surface is obtained by the reaction of the above DBU based sensing layer with HCl, by selectively printing liquid HCl only on the surface of the future reference beams.

A similar approach is followed by the DBN functionalization process by the route II (Fig. 8c)

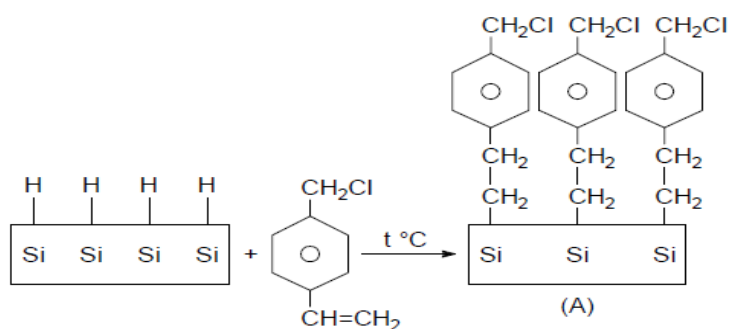


Fig.8a Formation of a monolayer of chloromethylated styrene on Si surface

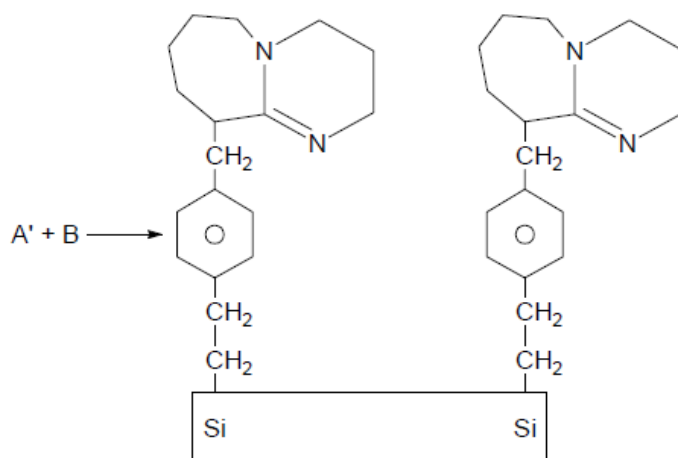


Fig. 8 b. DBU based layer connected to Si surface by styrene moiety



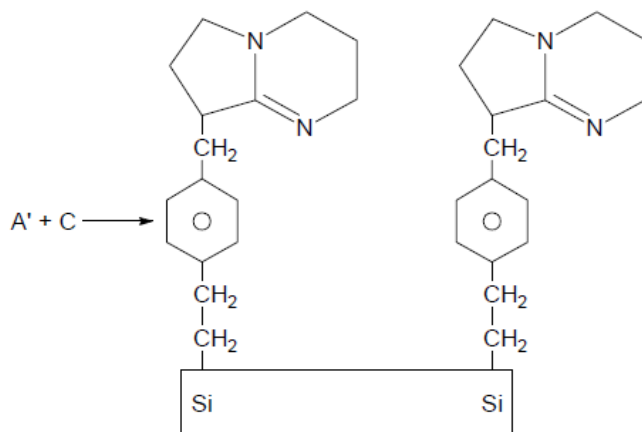


Fig.8c.Attachment of DBN sensing moieties from the silicon surface through covalent bonding

#### B. Functionalization of silicon resonant nanosensor according to HSAB theory[27-28]

The selection and design of sensitive terminal groups which are incorporated in the SAMs was based on the Hard Soft Acid Base (HSAB) rule. According to this theory, a hard Lewis base prefers to bond to a hard Lewis acid, and a soft Lewis base prefer to bond to a soft Lewis acid. Carbon dioxide is a hard acid, and, according to HSAB rule, it can interact with amino groups, which are hard bases. This interaction is an acid-base equilibrium, which is reversible and it leads to the formation of carbamates. Thus, we obtain the CO<sub>2</sub> sensing SAM which is functionalized with amino-terminated groups to be used as anchors for CO<sub>2</sub> detection. We have also chemically designed the molecular composition of the reference SAM, so that this will not respond to CO<sub>2</sub> but will have the same response to humidity and similar ageing properties, as the sensing SAM.

The whole process is following the steps presented in Figs.9a-c.

- 1) Cleaning of processed silicon wafers (samples) containing suspended Si nano-beam and AuCr metallization for 1 h in isopropyl alcohol.
- 2) Rinsing with deionized water.
- 3) Immersion in 2% HF in DI water for five minutes in order to remove the native SiO<sub>2</sub> from the Si surface and to generate Si-H bonds on the Si surface (Fig. 9a).
- 4) Exposure to a flow of ozone for a short period of time in order to obtain a hydroxyl terminated surface (Fig. 9b).
- 5) Immersion of the hydroxyl terminated samples in a sealed flask containing one of the possible amino alcohols (4 amino- 1 butanol, 4- N-methyl amino- 1 – butanol, 5 amino 1- pentanol, 5 N-methyl amino- 1 pentanol, 6 amino- 1 hexanol, 6 methylamino-1 hexanol, ethanol amine, diethanolamine, 1, 3 diamino 2-propanol) heated in dry nitrogen, in order to allow the polycondensation reaction

to happen (Fig. 9c) and a CO<sub>2</sub> sensing SAM monolayer to be formed on the Si surface.

6) Rinsing with isopropyl alcohol, DI water and drying in N<sub>2</sub> stream.

If all the amino groups react at room temperature with hydrochloric acid, the obtained hydrochloride possess the same properties, except the sensing toward carbon dioxide molecules ( Fig.10)



Fig.9a Hydrogenation of silicon surface

Deleted: .

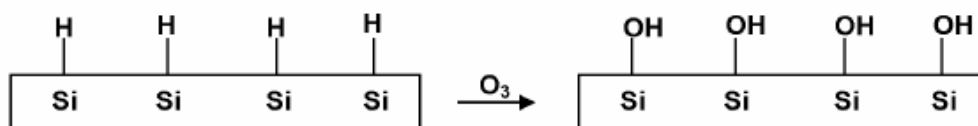


Fig.9b. Formation of hydroxyl terminated silicon surface

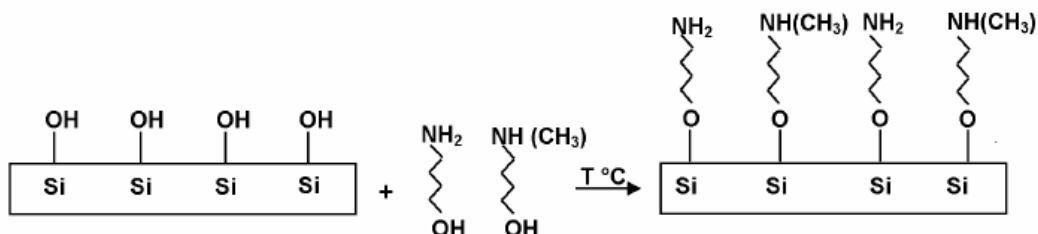


Fig.9c. Functionalization of CO<sub>2</sub> sensing silicon surface with pendant amino groups

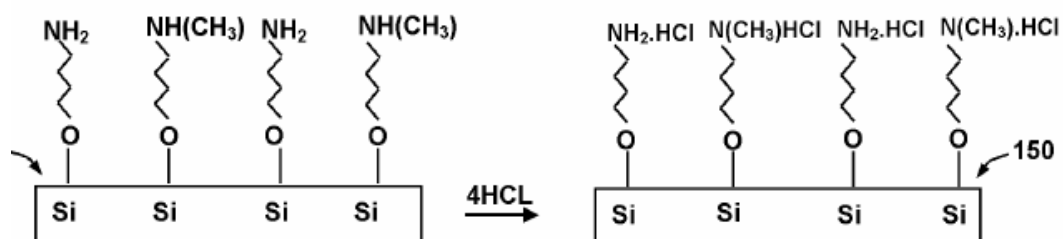


Fig.10.Synthesis of reference layer by conversion of all amino groups into hydrochloride

Deleted: .

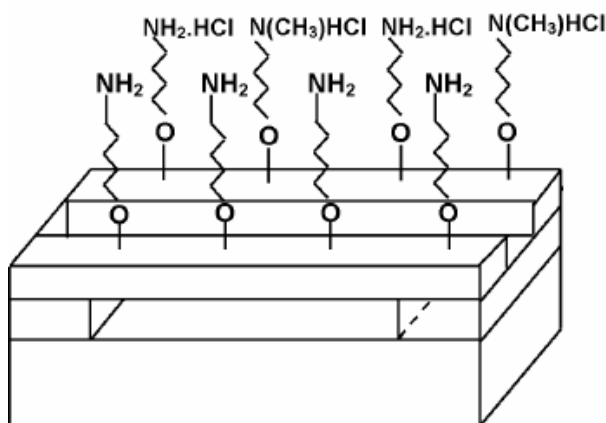


Fig.11. Silicon suspended beam with sensing layer (which contains terminal amino groups) and reference layer (in which all amino groups are converted into hydrochloride)

In order to increase the number of available amino groups, polycondensation can be performed with 1, 3 diamino-2-propanol (Fig.12).

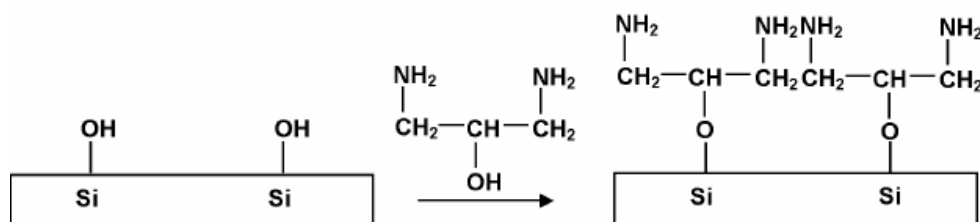


Fig.12. Polycondensation of OH-terminated silicon surface with 1,3 diamino-2 propanol

Functionalization with amidines moieties (according to Bronsted–Lowry theory) and functionalization with amino groups (according to HSAB theory) exhibit some differences, which will be analyzed, below in terms of sensing properties .

	DBU and DBN functionalization based on Bronsted–Lowry theory	Amino groups Functionalization based on HSAB theory
<b>Sensing mechanism</b>	Reaction of DBU and DBN with CO <sub>2</sub>	Reaction of amino groups with

	and H <sub>2</sub> O with the formation of bicarbonate salt; Molar ratio DBU ( or DBN):CO <sub>2</sub> : H <sub>2</sub> O is 1:1:1.	CO <sub>2</sub> with formation of carbamates The molar ratio NH <sub>2</sub> : CO <sub>2</sub> is 2:1
<b>Reversibility</b>	Both reactions are reversible, the trapped CO <sub>2</sub> molecules being released by heating or flowing the inert gas such as N <sub>2</sub>	
<b>Response time</b>	Few seconds - in the case of functionalization with amidine moieties	Few seconds - in the case of functionalization with amino groups
<b>Operating Temperature</b>	Both types of sensors at room temperature	
<b>Cross sensitivity</b>	Possible interferences with other acidic gases, such as CS <sub>2</sub> , SO <sub>2</sub> , COS	Possible interferences with other acidic gases, such as H <sub>2</sub> S, SO <sub>2</sub>
<b>Versatility of synthesis</b>	Sophisticated and costly synthesis. The manipulation of amidines and organometallic compounds must be performed with caution.	more versatile synthesis

DBU and DBN are bases with low pK<sub>b</sub>.

1. Aliphatic amino groups are hard bases, according to HSAB theory and can react with carbon dioxide which is hard acid.

Deleted: .

#### 4. CONCLUSIONS

Two general approaches for functionalization of silicon surface to be used for carbon dioxide silicon detection by resonant nanosensors were presented.

Synthesis of sensing layer can be performed using 1,8 diazabicyclo[5,4,0] undec-7-ene (DBU) or 1,5 diaza [3,4,0]-non-5-ene (DBN), as sensing terminal groups. This functionalization is according to Bronsted –Lowry theory.

Other functionalization of silicon surface involves amino groups as sensitive pendant groups, according to HSAB theory.

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

A comparison between both type of functionalization in terms of sensing mechanism, reversibility, response time, temperature operation, cross sensitivity, versatility of synthesis was made.

#### Acknowledgement

The authors are expressing their gratitude to EU-FP-7-NEMSIC project and Honeywell International for their support with developing this research.

## REFERENCES

- [1] 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, 110-116, 1998.
- [2] M. S. NIEUWENHUIZEN, A. J. NEDERLOF, *A SAW Gas Sensor for Carbon Dioxide and Water. Preliminary Experiments*", Sensors and actuators B 2, 97-101, 1990
- [3] J.C. GABRIEL, G. GRUNER, A. STAR, *Carbon dioxide nanoelectronic sensor*, WO 2005/026694, A2
- [4] R.G. PEARSON, *Hard and soft acids and bases*, J.Am. Chem. Soc., 85 (22), 3533-3539, 1963
- [5] B. SERBAN, M.MIHAILA, S. COSTEA, O. BUIU, *New ligand selection rule for quantum dot functionalization*, Proceedings of the International Semiconductor Conference CAS , pg 81-84, 2009
- [6] 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<sub>2</sub> detection*", Proceedings of the International Semiconductor Conference CAS, 247-250, 2010
- [7] 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, pages 39-50.
- [8] B. SERBAN, M. MIHAILA, O. BUIU, S. COSTEA, *A new approach for quantum dot-polymer nanocomposite design*, Nanomeasure 3-4 June 2010, Krakow, pg.12
- [9] 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, 22, September 19-21, 2010
- [10] B. SERBAN, A. K. SARIN KUMAR, S.. COSTEA, M. MIHAILA, O. BUIU, M. BREZEANU, N. VARACHIU, C. COBIANU, *Surface acoustic wave CO<sub>2</sub> sensing with polymer-amino carbon nanotube composites*, Proceedings of the International Semiconductor Conference CAS, 73-76, 2008,

[11] 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<sub>2</sub> detection*, Romanian Journal of Information science and technology, Volume 12, Number 3, 376, 2009

[12] B. SERBAN, C. COBIANU, M. BERCU, N. VARACHIU, M. MIHAILA C. BOSTAN, S. VOICU, *Matrix nanocomposite containing aminocarbon nanotubes for carbon dioxide sensor detection*", Pub.No.: US 2008/0264147 A1, Pub. Date: Oct.30, 2008

[13] 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 ,27-36, 2009

[14]. [http://evans.harvard.edu/pdf/evans\\_pKa\\_table.pdf](http://evans.harvard.edu/pdf/evans_pKa_table.pdf)

[15] D.J. HELDEBRANT, P.G.JESSOP, C.A.THOMAS, C.A.ECKERT and C.L.LIOTTA, *The reaction of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with carbon dioxide*, J.Org.Chem.70, 5335-5338, 2005

[16] B.OCHIAI, K.YOKOTA, A.FUJII, D.NAGAI, T.ENDO, *Reversible trap-release of CO<sub>2</sub> by polymers bearing DBU and DBN moieties*, Macromolecules, 41, 1229-1236, 2008

[17] S.A.GATTUSO, *Carbon dioxide capture by tertiary amidine functional adsorbents*, PhD Thesis, University of Pittsburg, 2007

[18] M.TOMOI, Y.KATO, H.KAKIUCHI, *Polystyrene-supported 1,8-diazabicyclo[5,4,0]undec-7-ene as reagent in organic synthesis*, Macromol.Chem.185, 2117-2124, 1984

[19] F. BOHME, C.KLINGER, C. BELMANN, *Surface properties of polyamidines. Colloids and surfaces A*.189, 21-279, 2001

[20] R. J. LITTLE, W.P.M van SWAAIJ, G.F.VERSTEEG, *Kinetics of carbon dioxide with tertiary amines in aqueous solutions*, AIChEJ.36, 1633-1640, 1990

[21] C.COBIANU, B.SERBAN, *Novel concepts for CO<sub>2</sub> detection by differential resonant nanosensing*"(invited paper), a 9-a editie a seminarului national de nanostiinta si nanotehnologie, 16 martie 2010, biblioteca Academiei Romane.

Abstract:[http://www.romnet.net/ro/seminar16martie2010/brosura%20final%2018%20martie\\_c1f.pdf](http://www.romnet.net/ro/seminar16martie2010/brosura%20final%2018%20martie_c1f.pdf)

[22] B. SERBAN, C. COBIANU, M. MIHAILA, V. DUMITRU, US Patent Application, *Carbon Dioxide Sensor With Functionalized Resonating Beams*,

[23] 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.

[24] B.SERBAN, C. COBIANU, M. MIHAILA, V. DUMITRU, O. BUIU, U.S Patent Application, *Carbon Dioxide Sensor*, No.: 10196990.5 Filing Date: December 24, 2010

Formatted: Left

Deleted: ¶

[25] 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, pg 217-220

[26] B. SERBAN and C. COBIANU “Novel concepts for NO<sub>2</sub> detection by differential resonant nanosensing” Nano-Electro-Mechanical Devices for Integrated Sensing and Switching Satellite workshop to ESSDERC/ESSCIRC 2010

[27] B. SERBAN, C. COBIANU, M. MIHAILA, V.G. DUMITRU US Patent Application No. 12/856891, Filed on 16 August, 2010, Functionalized Monolayers For Carbon Dioxide Detection by a Resonant Nanosensor,

[28] M. ROCCHIA, E.GARRONE, F. GEOBALDO, L.BOARINO, M.J.SAILOR, Sensing CO<sub>2</sub> in a chemically modified porous silicon film., Phys.stat.sol . (a), 197, No, 2, 365-369(2003).

[29] T.P. BURG, M. GODIN, S.M. KNUDSEN, W. SHEN, G. CARLSON, J.S. FOSTER, K. BABCOCK, S.R. MANALIS, [Weighing of biomolecules, single cells and single nanoparticles in fluid](#), Nature, Vol. 446, 26 April 2007, pp.1066-1069.

Deleted: Weighing

[30] X.M.H. HUANG, M. MANOLIDIS, S.C. JUN and J. HONE, Nanomechanical Hydrogen Sensing, Applied Physical Letters, vol. 86, 143104 (2005).

[31] L.A. PINNADDUWAGE, V. BOIADJIEV, J.E. HAWK, and T. THUNDAT, Sensitive Detection of Plastic Explosives with Self-assembled Monolayer-Coated Microcantilevers, Applied Physics Letters, Vol. 83, Number 7, 18 August 2003, pp. 1471-1473.

[32] Mo LI, H.X. TANG and M.L. ROUKES, Ultra-sensitive NEMS based Cantilevers for Sensing, Scanned Probe, and very High-Frequency Applications, Nature Nanotechnology, 2, pp. 114-120, 2007.