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A VISION ON RESONANT NANO-ELECTRO-MECHANICAL SENSORS

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Abstract. *In this paper, we present a possible vision of the resonant nano-electro-mechanical system (NEMS) technology and their sensing applications. The work is briefly describing the major milestones of the nanotechnology progress starting from the moment when it was existing only in the imagination of the science and technology pioneers, until the stage of the first commercial applications. Here, we are focusing on the status and roadmap of the resonant NEMS technology, as the largest technology platform with the highest mass detection capability and huge potential in nanomechanical, chemical and biological sensing, and future computing science applications. Today, there are multiple technological possibilities for the realization of these resonant NEMS systems, all of them being described here in the so-called "top-down"," bottom-up" or the mixed" top-down-bottom-up" approaches. The biggest challenge of today's nanotechnology research on resonant NEMS for gas and biomolecule detection is the transition from the present state of proof of principle for zeptogram detection in ultra-high vacuum and cryogenic temperatures by means of external magnetic actuation and detection to the room temperature operation and atmospheric pressure ,as well as on-chip excitation and readout, as required by real application. Finally, our novel concepts on differential sensing and associated functionalization routes for resonant NEMS gas sensing are described.*

Keywords: NEMS roadmap, resonant NEMS sensors , top-down, bottom-up, chemical NEMS sensors, SO_2 detection

1. Introduction

The early stage of nanotechnology was born more than fifty years ago, in the mind of the visionary scientist, Richard Feynman, who challenged the entire scientific community towards the technology of controlling the atoms, by their identification, visualization, manipulation, and finally chemically binding them one-by-one in order to build new structures and devices. Thanks to his famous talk, "There is plenty of room at the bottom" [1], from 1959, Feynman is considered the father of nanotechnology. In 1965, Gordon Moore was envisioning the twofold increase of integrated circuits complexity, each twelve months [2], and this statement became 'Moore's law", which, with small rate changes is still valid today, when the electronics is already living the nanoelectronics era, with the "line" width of the integrated circuits of about 32 nm. The term of "nanotechnology" was coined by Norio Taniguchi, in 1974, while he was doing basic research in the field of high precision machining of the hard coatings and materials [3]. Finally, it is worth to

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mention here, Eric Drexler's contribution, who has founded the term of "molecular nanotechnology" [4]. In 1986, his nanotechnology vision was described in the book called "Engines of Creation: The Coming Era of Nanotechnology", where Drexler extended Feynman's vision on nanorobots travelling inside the human body (swallowing doctor) by defining the "nanoscale assembler", who would be able to 'clone" itself. The above pioneers have triggered the nanotechnology "golden rush" of the entire scientific community, and the results started to appear after 1981, when the scanning tunnelling microscopy was invented, followed by other discoveries at material level, like fullerene, in 1985.

An exhaustive presentation of the major stages of the nanoscience and nanotechnology is described in the paper [5], while an evolution from 2D electronics to 3D-MEMS is presented in reference [6], where it is has been shown the vision of Moore in other electronics field, beyond his famous law.

The development of the nanotechnology by such revolutionary experimental achievements has created the critical mass for the governmental research planning in this field, generating in the same time high expectations from this technology, perceived as the foundation of the next generation of products in all domains of the society's evolution. In this idea, we can mention here the "USA's National Nanotechnology Initiative", the European Framework Projects FP-6-7-8, which are now, accompanied by the EU Future and Emerging Technologies (FET) Research Flagship Initiatives (2011-2020), and the Japan's Fourth Science and Technology Basic Plan (2011-2015).

The major role of the nanotechnology in the future development of our society can be generically understood, if we look at some of the important megatrends, like ageing population, globalization, health and environmental awareness, urbanization with its smart-eco cities, and network organizing, which have been predominantly triggered by the unprecedented progress of technology in general, and microelectronics and microtechnologies, in special. It is therefore expected that the nanotechnology will not only address the society's needs coming from these megatrands, but also may generate new megatrends. Professor Mihail C. Roco, of Romanian origin, who has architected the "USA National Nanotechnology Initiative" has defined the states of the generic nanotechnology roadmap, envisioning that the commercial applications would come on the market in the following sequence: 1. Passive Nanostructures, 2. Active Nanodevices and Circuits, 3. Complex Nanomachines, and 4. Productive Nanosystems. Indeed, firstly, the nanotechnology material research has created its commercial outcomes, if we think about the use of Ag-nanoink for many commercial bulk applications, or the TiO2/ZnO for sunscreens, or even the giant magneto-resistance (GMR) sensors for sensing the magnetic field in the hard-disk drives. Secondly, as predicted by Mihail C. Roco, the active nanodevices and circuits came into play after 2004, when the nanoelectronic integrated circuits with lay-out “line” width below 0.1 micrometers entered the market. In line with the above predictions, in the coming years, the complex nanomachines are expected to come, and this is one of the targets in EU-FET flagship research initiatives. Important building blocks of these future complex nanomachines are the resonant Nano-Electro-Mechanical Systems (NEMS), which are nano-scale functional interfaces able to convert mechanical, chemical, optical and biological signals into electrical signals providing thus real-time information about the outside physical world, as shown in reference [7]. The resonant NEMS realization and their use in a large applications platform is one the most important drivers of the nanotechnology, today.

Within this paper we shall briefly describe the transition from Micro-Electro-Mechanical Systems (MEMS) to NEMS, while the entire focus will be given to resonant NEMS sensors and their roadmap, due to their huge expectations for ultra-high sensitivities at low power/size/cost for replacing existing MEMS sensors and actuators and generating new “killer” applications in the field of large areas distributed wireless sensor networks (WSN), real-time detection and communication, and personal assistance applications.

The roadmap of the resonant NEMS sensors and their applications will be treated as a function of their realization (nano) technologies, starting with the so-called “top-down” approach, and then continuing with the “bottom-up”, and finally the mixed “top-down bottom-up” approaches.

2. From MEMS to resonant NEMS sensing systems

The MEMS systems are micrometer-scale transducing interfaces which are integrating the electrical and mechanical signals for the realization of a large applications platform in the field of mechanical, chemical, optical and biological sensing and actuation, with an output in the form of an electrical signal in the case of sensors, or a mechanical movement in the case of actuators. The MEMS structures contain a mechanical part which is deflecting as a result of the interaction with the external environment (pressure, acceleration rotation rate, force, mass loading) and an electrical part for reading the effect of the input mechanical-chemo-biological signal.

The MEMS technology is mainly built upon the strong foundation of the silicon integrated circuit (IC) technology, at which specific processes like 3D anisotropic silicon etching, wafer bonding and sacrificial layers etchings are added. This microtechnology is essentially a top-down approach, which means that the final structure is obtained by removing a certain amount of material from the initial volume in order to obtain the final microstructure shape as required by the functional requirements. There are two major MEMS technologies called “bulk micromachining” and “surface micromachining”, where the first one is based on the 3D anisotropic or plasma etching of the back side of the substrate for the creation of the suspended membrane, while the second one is based on the isotropic etching of a sacrificial layer in order to obtain a suspended membrane, which will respond to above external stimuli.

The integrated MEMS technology is the result of the on-chip integration of both MEMS microstructure and electronic circuit for the excitation and/or the detection of the electrical response of the deflecting membrane.

The discovery of the piezoresistive effect in silicon and germanium in 1954 by Charles Smith, as shown in his reference paper [8] from 1954 may be considered the birth year of the MEMS field and its sensing applications. In 1965, Nathanson and Wickstrom have made the first resonant movable gate MOSFET transistor [9] and proved for the first time the capability of surface micromachining technology for creating MEMS devices by wafer batch processing.

Based on the above discoveries and the conjugated effort of the academic and industrial research, the family of commercial MEMS products started to appear. Here we shall simply enumerate the most relevant MEMS products, now on the market, as follows: piezoresistive pressure sensor, inkjet head, 3 axis accelerometer, 3 axis gyroscope, microphone, microbolometer, digital light processors, MEMS-based oscillators. As can be seen from this list of successful MEMS products, they are all operating in the field of MEMS mechanical sensing or mechano-optical sensing and actuators domain, but there is a lack of commercial integrated MEMS chemical gas sensors, and this is due to the difficulties in preserving the long-term functional stability of the sensing thin films. The only commercial MEMS-based chemical gas sensor is done by microhot plate technology on which thick sensing films of SnO_2 are deposited for the detection of volatile organic compounds [10]. So, “there is plenty of room” for low power integrated chemical gas sensors, which may need to replace the existing gas sensors, which are consuming much more electric power than the portable application may request.

On this arena of commercial MEMS technologies there will be a change from single sensors to MEMS-based sensing solutions thanks to new business models, where sensors fusion seems to be the key approach for stacking multiple sensors in the same package, like in the case of “Accelerometer/Magnetometer Combo” MEMS system developed by ST (accelerometer) and Honeywell (magnetometer) [11].

In parallel with MEMS research and product development, the continuous decrease in the size of the MEMS components has moved the shrinkage process beyond the threshold of 0.1 micrometer, where the NEMS technology is starting. Therefore, NEMS realization has already started to emerge, and this happened by different technology approaches, like “top-down”, “bottom-up”, or what we called mixed “top-down-bottom-up”. Here, it is useful to mention how the three approaches differentiate one from the other, when the resonant NEMS is the final target, for all of them. Thus, for the “top-down” approach, the entire resonant NEMS technology is performed by using the deposition processes followed by lithographic processes and corresponding selective etchings of the material or sacrificial layers till the suspended nanobeams are obtained, by the so-called subtractive processing. Such nanobeams will be able to vibrate at their mechanical resonance frequency when the suitable actuation scheme is used. The “bottom-up” approach for the realization of NEMS resonant sensors means that only additive processing is used for obtaining the final nanosystem, made of molecular building blocks which will be interconnected one to the others, till the functional resonant NEMS is structure is obtained without any subtractive process. Today, this genuine “bottom–up” approach is emerging for nanomotors, but we do not have any experimental demonstrator of a pure “bottom-up” macromolecular architecture for a resonant NEMS. Finally, the mixed “top-down-bottom-up” approach for processing the resonant NEMS sensors means that both subtractive and additive steps are used at the technology level. There is an important question for us: Why resonant NEMS for detection?. The answer has come very explicitly more than 10 years ago from Michael Roukes [12]. Such resonant NEMS nanomachines have ultra-small mass and size, and this feature will trigger ultra high mechanical natural resonance frequencies, which will then determine ultra high sensitivities for forces (zepto Newton), displacements (femtometers), additional mass loadings (zepto grams) at low power consumption and ultra fast response time [12]. In addition, these resonant nanomachines can be ultimately used not only for single molecule chemical and bio detection [13] but also for nano-mechanical computing applications and front-end passive resonant RF electronics performing active functions like amplification, modulation-demodulation [14]. Finally, the resonant NEMS systems represent a powerful tool for novel experimental discoveries in the field of quantum physics, where a possible quantum of mechanical displacement to be evidenced at ultra-low cryogenic temperatures? [12]. Such high mass sensing performances, at the level of 1 Hz/zg have been proven in the case of ultrahigh vacuum operation and cryogenic temperatures, for the actuation schemes based on the application of a high magnetic field followed by electromotive force (EMF) detection principle [15]. These operating conditions and actuation/detection principle cannot be used in the case of practical, low-cost gas sensing approaches, where low power consumption, low sensor size are all required by future commercial applications. Therefore, there is a strong need for room temperature and atmospheric pressure operation, as well as on-chip actuation and readout circuitry so that the whole resonant NEMS system to be compatible with real gas/bio sensing applications. At the technology level, there is an expected challenge of nanolithography processes for generating width of the vibrating nanobeams below 100 nm, as well selective deposition of functionalization layer over the surface of the nanobeam.

From the description of different approaches, as well as expectations and challenges, one can easily understand that the objectives of all these technologies are the same: the development of electro-mechanical-bio sensing nanomachines reaching ultimate quantum limits of the detection, and realization of NEMS based sensor able to operate under conditions dictated by the real applications. Now, we shall enter the details of the three approaches.

3. Top-down resonant NEMS sensing systems

This approach takes the technology benefits from the well-established MEMS technology pushing their size limits below 100 nm for reaching the high resonance frequencies and associated high sensitivities of the resonant NEMS systems. The huge mass sensing capabilities of these resonant NEMS sensors have started to be shown. Thus, a resonant NEMS having a clamped-clamped SiC suspended nanobeam, with a resonance frequency of 133 MHz has shown a mass resolution of 7 zeptograms (1 zg=10^{-21} grams), when the resonator was exposed in ultrahigh vacuum and cryogenic temperatures of 37 K [15]. Such mass detection resolutions, under ultrahigh vacuum and cryogenic temperatures have been used for proof of principle of a resonant NEMS-based mass spectrometer [13], which, nowadays is able to detect molecules with minimum mass of 100 Da (1 Da = 1 AMU). Here, the detection principle is based on the mass loading increase due to adsorbed molecule on the surface of the vibrating nanobeam. The NEMS resonator is located in ultra-high vacuum (10^{-8} Torr) and cryogenic temperatures (40 K) at the end of about 2 meter-long channel where the electrospray ionization, ion optics and the two vacuum stages are located. The mass loading principle is also used for the gas sensing, where a functionalized nano beam is used for selective adsorption of the gas species of interest, while the mass loading created by these adsorbed molecule will give a shift in the resonance frequency, which is proportional with the amount of gas from the ambient to be monitored. Actually, this gas sensing application is a major challenge for entire scientific community, as in this case, the resonant device needs to vibrate at room temperature and atmospheric pressure, conditions for which the quality factor of the resonant beam is decreasing due to viscous damping of the beam vibration in the air. In addition, the frequency shift can be much decreased due to an additional mass of the resonator coming from the viscous air which is moving due to nanobeam vibration, not to mention the increase in the background noise due to increased surface adsorbate fluctuations at atmospheric pressure. An important step forward on this direction of gas sensing at atmospheric pressure and room temperature was done by the work of Li et al [16], who have shown for the first time that a mass resolution of about 25 zg was reached at room temperature and atmospheric pressure operation. In addition, in that paper, the authors have proven that on-chip piezoresistive detection can replace the magnetic detection principle, while the magnetic actuation was replaced by piezoceramic actuator transferring its vibration to the NEMS resonator. Also, a quality factor of more than 400 at atmospheric pressure was obtained for an operation frequency of 127 MHz, for the suspended SiC nanocantilever with a small size $(0.6\times0.4\times0.07)$ μm. The SiC nanocantilever was functionalized with a thin layer of polymethyl methacrylate (PMMA) for the detection of 1,1 difluoroethane (DFE) gas . The reversible mass loading of the nanocantilever in the presence of the DFE pulses has proved both the reversible adsorption of the DFE, as well as the high accuracies of mass detection in the range of 1 attogram, at room temperature and atmospheric pressure. Unfortunately, for the moment, there is no gas calibrated detection, so that to be able to make a correlation between the gas concentration in the ambient, the adsorbed gas on the small surface of the cantilever sensing surface, and the corresponding resonance frequency shift measured.

Starting from the above state of the art results in the field of resonant NEMS sensor technology, and transducer principles, where the most important mass detection results were obtained from SiC nanobeam epitaxially grown on silicon substrates, it is important to see what are the major trends in the future developments of the top-down NEMS resonators and their applications. From the point of view of the technology for NEMS sensor realization, the most important direction is the use of the integrated SOI-CMOSFET technology for the realization of both resonator and excitation/detection circuitry on the same chip. Such an integration of sensing and electronics will open the way to major breakthrough in the use of resonant NEMS for gas and biosensing applications. This SOI-CMOSFET “top-down” technology approach is in progress, today. It appears that the electrostatic actuation combined with piezoresistive detection is a possible integrated resonant nanodevice solution.

As an alternative, the use of NEMS resonators in the feed-back loop of the on-chip oscillators may be a major breakthrough in the field of NEMS resonators, as this approach, which is “imported” from the classical SAW-based electronic oscillators has the advantage of eliminating both the existing actuation circuitry as well as reading technologies. The resonance frequency of the vibrating nanobeam will determine the oscillation frequency of the NEMS-based oscillator, and its variation with external analytes will provided the sensing function. If the selective functionalization of each sensing nanobeam can be done, and its reading is performed as described above, then the next step would be the realization of the resonant NEMS-based gas sensing array. We anticipate that electron beam writing combined with maskless dip pen nanolithography will be required for selective functionalization of the nanobeams or cantilevers, depending on the chemistry used for functionalization. From this point of view, it may be possible that the “top-down” approach to be slightly moved in the direction of “bottom-up” technologies, where additive processing is done, as described above.

Additional on-chip electronics will generate the wireless capabilities for such integrated systems, which will make them suitable for the future portable applications. There are good expectations for the use of the same SOI technology for the next generations of low dimensions mass spectrometers, where the present electrospray ionization (ESI) system and ion optical guidance (which require a channel of about 2 m in length) to be replaced by microfluidic processor chip, and thus, ultimately, miniaturized, maybe even portable mass spectrometers would be done one day [17].

Taking into consideration, the state of the art in the “top-down” NEMS resonator technology, briefly described above, and their potential applications, below, we try to envision a possible roadmap of the top-down technology and its products, as shown in Table 1.

Table 1. A possible roadmap for the top-down technology of the resonant NEMS systems, acting on a timeline of about 10-15 years

Society needs	Low cost/size/power, high sensitivity/selectivity gas sensors for air monitoring. High sensitivity biodetection for rapid response at low sampling volume Real-time-detection-analysis-computing-wireless communication and feed-back
Potential Future Products	Wireless NEMS based gas and bio sensing array operating at room temperature and atmospheric pressure Hybrid miniaturized mass spectrometer with novel analyte transportation principle. Novel mechanical sensors (acceleration, gyro, pressure) based on resonant NEMS Resonant NEMS based nanomechanics computing and RF front-end electronics
Components	On chip actuator and detector of the resonant frequency Self-sustaining oscillators Microfluidic processor chip for mass spectrometer
Technologies	SOI-CMOSFET for both NEMS resonator and electronics Electron beam lithography Dip Pen Nanolithography
Enablers	Governmental support for high risk research Science and Technology of MEMS-NEMS resonator Low cost applications required by the market

4. Bottom-up resonant NEMS sensing systems

As briefly described above, the “bottom-up” approach is the realization of the molecular architectures and devices/systems by means of additive atom-by-atom construction, based on supramolecular chemistry foundation and molecular self-assembly and molecular recognition specific processes. Within the molecular self-assembly, the molecules are arranging themselves, without external support, in a certain conformation, by means of non-covalent chemical bonds (like hydrogen bonds, van der Waals forces, etc.).

Molecular recognition, which is at the heart of many chemical bio-sensing processes and future molecular sensors means the non-covalent bonding between a host and a guest molecule, based on molecular complementarity. The molecular recognition can be static, which means that the guest molecule will fit perfectly in the “open” structure of the host, like the key and the keyhole, and thus it will be recognized. In a more complex case of the dynamic molecular recognition, the host could be thought as having two “holes” in his open structure, and filling one of the holes by the first guest molecules will affect in a certain way the reaction rate of filling the second hole in the host by the second guest molecule fitting in the remaining hole of the host molecule.

These fundamental notions of the “bottom-up” approach are at the origin of the molecular electronics, containing single-molecule based devices and more complex molecular architectures, as well as the molecular machines and ultimately the molecular nanotechnology, the last being a yet speculative field envisioning the technology of doing future “nano-products” by means of productive nanosystems like molecular assembler, as initially described by Drexler [4]. This concept of productive nanosystem was also promoted by Mihail C. Roco, in the “US National Nanotechnology Initiative” as later stage of nanotechnology penetration in the application domain, where such systems of nanosystems will be used in the factories of the future for the production of the atomically precise parts of commercial nanosystems.

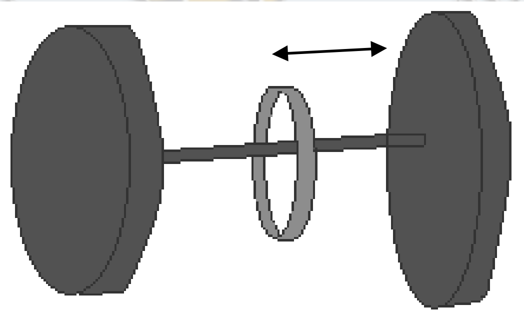

Fig.1. Schematic diagram of a rotaxane organic molecule looking like a dumbbell with a ring-like macrocycle sliding along the axle.

There is a legitimate question: *why molecular electronics and machines?* The answer would be, yes, we need to go to that direction, because the molecule is the place where the electronic processes take place, if we think about signal transduction or photosynthesis processes [18].

Beyond this fundamental motivation, there are practical advantages of molecular electronics in terms of small size of molecules (1 nm up to 100 nm), excellent support from molecular processing of self-assembly and molecular recognition for “bottom-up” chemical design and fabrication, to which, other well-developed knowledge like dynamical stereochemistry and synthetic tailorability are added for the molecular design of the electrical, optical, and mechanical properties [18]. The molecular electronics has been able to prove the principle operation of the molecular devices like switches, rectifiers, computational circuits and even the memory circuits.

At the level of proof of principle for molecular electronic circuits, a memory of 256 bits of RAM performed in a cross bar architecture has been already proven, as shown in the reference [18]. As an example, in Fig. 1, a molecular switch is shown, which is obtained from the mechanically interlocked molecular architecture (MIMA) called rotaxane. The rotaxane is a dumbbell like organic molecule containing a ring-like macrocycle sliding on the axle of the dumbbell, which is limiting the macrocycle movement at both ends by stoppers of a larger diameter.

The rotaxane based switch is operating like this: when the sliding macrocycle is at one end, the rotaxane is in an electrically conducting state, while when the macrocycle is at the other end, the rotaxane is in an electrically not-conductive state. Solid state rotaxane-based memories in thin films of Langmuir-Blodgett have been already reported, where the switching of the macrocycle between two different conductive states is the core of operating principle. The writing of the nano-recording dot was done by applying locally a positive voltage with the tip of the scanning tunneling microscope [19].

The family of the MIMA architectures is larger, and is containing other organic components of the future molecular machines like knotane, acting as a mechanical junction between two machine components, as well as catenane, acting as a chain made of interconnected rings.

Such MIMA building blocks represent the starting point of the future complex nanomachines. An initial approach of the rotaxane based molecular motors has been already published, where the macrocycle of the rotaxane architecture can rotate around the axle [20]. The rotaxane machines are actuated by chemical or photochemical input signals, and thus muscle functions have been also reported [21]. Recent efforts in molecular NEMS are considering biomimetics technologies, where the forces developed by biological and artificial molecular machines are controlled at this molecular level, in solid environments, for getting macroscopic effect, like in the case of skeletal muscles [22].

It is just a matter of time before the molecular electronics will make a ‘junction” with the molecular machines for defining the future integrated “molecular intelligence”, where both sensing and actuation and signal processing to be done at molecular level, in the integrated molecular nano-machine.

In order to reach such level, important milestones of further understanding the fundamental aspects of electric conduction, sensing and actuation in such molecular structures and their interfacing with the outside world followed by reliable and reproducible fabrication of such molecular building blocks of molecular electronics and their interconnection need to be passed .

As a summary of the above discussions, below, in Table 2, we present a possible roadmap of the bottom–up molecular electronics and machines.

Table 2. *A possible roadmap of molecular electronics and machines*

Society's needs	Ultimate, molecular-level miniaturized nanosystems and nanorobots for portable applications and health enhancement, and tools (productive nanosystems) for their large scale production
Potential Future Products	Productive nanosystem for large scale fabrication of nanorobot Molecular systems for nanorobot application Molecular systems for computing and sensing applications
Components	Molecular NEMS building blocs, sensors and actuators Molecular Memories and Computing and Outside Interfaces Single electron molecular transistor and gear Molecular Junction and Rectifier Molecular Switches Resistive molecular wires
Technologies	Molecular biotechnology Molecular recognition Molecular self-assembly and recognition, nanomanipulation techniques IC based interfacing technology
Enablers	Quantum Physics and Chemistry Supramolecular Chemistry Material science Top down NEMS technology Classical top-down nanoelectronics, Molecular electronics

5. Mixed “top-down-bottom-up” resonant NEMS sensors

As described by its name, this approach consists of a mix and match of “top-down” subtractive resonant NEMS technologies and “bottom-up” additive processes like silicon nanowires growth and carbon based technologies (carbon nanotube (CNT) or graphene (G)).

The silicon nanowires (SiNW) to be used as suspended vibrating elements in the resonant NEMS were grown atom-by-atom by the so-called vapor-liquid-solid epitaxy, ending-up with a SiNW bridge, as the heart of the resonator [23].

The carbon technologies (CNT or G) for nanodevices fabrication has been developed on two directions: on-chip selective growth or separate growth followed by nanomanipulation of the CNT or G “foil” to the specific place on the chip surface.

Today, there are already well established technologies for growing on-chip self-assembled carbon structures to be used for the realization of active devices and sensors. This is the case of vertical CNT’s obtained selectively and directly on specific areas of the silicon substrates, where metallic catalysts are previously deposited, or the case of epitaxial graphene obtained directly on SiC substrate by the sublimation of the silicon atoms from the surface of the SiC material. The nano-manipulation of the CNT’s or G-foils to the required position on the chip surface is a labor-intensive process requiring very advanced 3 axis piezoelectric nanomanipulators tools for transferring the carbon material (CNT or graphene foil) to the right place on the chip.

Adding the SiNW and carbon technologies to the existing “top-down” resonant NEMS, previously described has opened the way to improved technologies, which did not further require the need for SiC suspended nanobeams to be used for the fabrication of high frequency resonators, and such results will be briefly mentioned here.

For example, in the reference [23], self-transducing resonant SiNW-NEMS operating at room temperature and moderate vacuum (1 mTorr) were obtained. In ref. [23], it is for the first time, when on-chip electrostatic actuation and piezoresistive detection (R = 100 kΩ) for an excitation frequency of 40 MHz is reported. In addition, a quality factor of 800 (1200 at high stress in SiNW, but non-linear response!) is obtained at 300 K and 1 mTorr vacuum. Such a resonant NEMS would generate a mass detection of 500 yg (10^{-24}) [0.6 Da] for 30 nm SiNW, at an operation frequency of 75 MHz !

Reference [23] is the first paper proving the possibility to have on-chip actuation and detection for the resonant NEMS, and this was possible for the case of SiNW resonant nanobeam.

The “carbon” based technologies and their possible integration with IC technology have been of huge interest in the last decades. Since 1991, when the CNT’s applications were triggered by the work of Sumio Iijima from NEC, there has been a major interest in controlling CNT’s fabrication technology and their integration in IC technology as well as in NEMS-based sensing technology, making the CNT’s a major player for both “Beyond CMOS” technology and “More than Moore” technologies. CNT is a material of high surface to volume ratio, with hollow structure and excellent mechanical optical and thermal properties, and a strong candidate for gas sensing. CNT is used either as “it is” (pristine) or functionalized, or as a component of matrix nanocomposite. CNT based chemical sensors are using different principles, like change in the electrical resistance or in the local density of states as a function of gas to be detected. CNT has been functionalized for detection of different gases, like CO, CO_2, H_2S, SO_2, NO_2, NH_3, humidity, methanol, ethanol, 1-propanol, 2-propanol, 1-buthanol, tertiary-buthanol 1-penthanol, 1-octanol.

Challenges with CNT based sensing remains in terms of still being a costly material and the variation of physical and chemical properties as a function of preparation process. Related to CNT-based NEMS system, it is worth to mention here the use of the CNT’s in advanced applications like CNT-based switches, memories and nanomotors [24].

Resonant NEMS based on CNT and their excitation and detection by coupling them in the feed-back loop of an oscillator has been already reported [25]. CNT applications are doing rapid steps towards industrial applications, these days.

The same interest, if not higher has been created by the discovery of the graphene and its applications, by Andre Geim and Konstantin Novoselov [26]. Graphene is one atom-thick sheet of carbon atoms arranged in honeycomb lattice. Therefore, graphene is the 2D unit cell of graphite, where many such graphene “foils” are stacked one over the other.

Graphene has unparalleled strength, stiffness and low mass per unit area. It is a zero-gap material with high mobility limited by defect scattering. The holes and electron mobility is equal and, for free standing graphene, it can have a value of about 40000 cm^2/Vs, while the electrical resistivity of graphene can be about 10^{-6} Ω cm. Its compatibility with 2D IC technology and lithographically patterning capability, as well as good signal-to-noise ratio in integrated readout make the graphene an excellent candidate for mixed “top-down-bottom-up” NEMS resonator technology.

The graphene can be prepared either by mechanical exfoliation method [26] (which remains the best method, for the moment) or by chemical vapor deposition method from heterogeneous surface reaction between CH_4 and H_2 on the copper substrate, which is subsequently etched away, while the graphene layer is embedded in PMMA for its further transfer on the functional substrate. Such a method was used in the ref [27], where the graphene was fixed on the perimeter of a perforated Si_3N_4 membrane, and the quality factor for such a vibrating membrane, under tensile stress was very high.

Actually, the highest ever product between the surface/volume ratio and the quality factor ($R\times Q$) was obtained: $R\times Q$=14000 nm^{-1}, while a quality factor of 2400 at 300 K and 6 mTorr, for a graphene membrane diameter of 22.5 μm was obtained, in the case of photothermal actuation and interferometric detection. This result shows that the graphene is an ideal material for future NEMS resonators.

An important step forward in the integration of the carbon technology with silicon technology has been recently published [28], where graphene is used as a suspended gate of a FET transistor, while the field effect is generated in a single wall CNT (SWCNT) located on the surface of the SiO_2/Si substrate.

This is the first electron device combining the CNT and the graphene technology for the realization of a suspended gate graphene and CNT-based FET device. The CVD-SWCNT is manipulated by SEM to the right position above SiO_2/Si. The electron beam lithography is used for contacting the Pd/Ti metalization to the SWCNT semiconductor tube.

Graphene is mechanically exfoliated from graphite and suspended above SWCNT. The electrical characterization of the device was performed in vacuum at 100 K. The CNT-FET has an on/off ratio equal to 10^4 and a minimum resistance of 90 kΩ.

The 2.1 μm wide graphene gate has maximum resistance (4.7 kΩ) at Dirac point, while the subthreshold slope of CNT FET transistor at 100 K is 20 mV, i.e. higher than the ideal value at this temperature, thanks to the technology which is used. In the same time, the graphene suspended gate FET can be considered as a NEMS resonator, which could work with *electrostatic* actuated graphene, as a movable gate for double gate CNT-FET.

A major advantage of this NEMS resonator could be its electronic-tunable resonance frequency by driving a varying strain in the graphene gate. In addition, non-linear multimode graphene vibrations would allow mass and position sensing, while the FET used a readout circuit with its built-in amplification will simplify the resonance frequency detection, in a sensing application. Therefore, these devices are promising candidate for future mixed "top-down-bottom-up" NEMS sensors.

Based on all these technology and device advances, one can imagine a possible roadmap for this mixed "top-down bottom-up" resonant NEMS sensors, as shown in Table 3, from next.

Table 3. A possible roadmap for mixed "top-down bottom-up" resonant NEMS sensors.

Society's needs	Low cost/size/power-High sensitivity/selectivity gas sensors for air monitoring High sensitivity biodetection for rapid response (<10 min) at nL sampling volume Real-time detection-analysis-computing-wireless communication and feed-back
Potential Future Products	Portable nanorobots with NEMS for sensing and RF Front End. Wireless, on-chip NEMS resonant chemical sensor array, accelerometers, gyro NEMS resonant chemical sensors operating at 300K and 1 atm. Mass Spectrometers for simultaneously mass and position detection. NEMS resonators for on-chip clock, mechanical filtering in Front End RF, GHz (cell phone).
Components	Actuation and detection building blocks for resonant NEMS sensing systems. Functionalized graphene nanobeams and or cantilever used as chemical sensors NEMS resonators based on suspended Graphene-gate SWCNT MOSFET as readout. SWCNT FET transistor, Graphene Schottky diode and Graphene MOSFET transistor. Pristine SiNW piezoresistor, Metallized SiNW, Graphene ultracapacitor.
Technologies	Nanoscale functionalization processes (SAM) and tools (DPN) for chemical sensors. SWCNT and Graphene manipulation tools (SEM, nanopiezoelectric probes, STM). CVD for Fe-catalyzed SWCNT selective deposition and Graphene Transfer Technologies of CNT and graphene to the final chip. SOI-CMOSFET based on Electron Beam Lithography, SLV epitaxy, graphene epitaxy.
Enablers	Governmental support. Carbon Allotrope Chemistry. Material science, Quantum Physics and Chemistry. Present and future bottom-up silicon, silicon carbide and carbon technology. Classical top-down nanoelectronics and NEMS technologies.

6. Novel concepts for differential chemical resonant NEMS sensors

As described above, the present MEMS-NEMS chemical sensors based on thin sensing films are not yet on the market, due to the unstable sensor operation on a long term, which is simply called sensor "drift issue". One of the classical approaches for reducing the baseline drift of chemical sensors is the use of a differential approach containing a sensing loop and a reference loop, where the sensing loop contains the sensing layer, while the reference loop does not contain a sensing layer, but a naked surface of the same structure as used for sensing loop. In the case of the resonant MEMS-NEMS sensor, the sensor response is as a frequency shift as a function of the analyte to be detected (gas or biomolecule). The response of the reference loop is subtracted from that of the sensing loop for reducing the above issues, but unfortunately, such subtraction is far from being ideal, as long as the ageing of the sensing layer cannot be eliminated, and this is because in the reference loop, on the reference device there is no similar layer. In addition, it is possible that the humidity response of the sensing layer to differ from the humidity response of the naked surface of reference device. Therefore, one can understand the need for an improved differential approach in resonant MEMS-NEMS sensor. Such an improved differential approach was disclosed recently [29].

The new differential sensing concept, called "All-Differential" is introducing a reference layer on the surface of the reference, which is having similar physical and compositional properties, excepting the fact that it has no sensing properties with respect to sensing layer. Under such circumstances, the common mode signals like ageing, humidity response, which were not canceled before in the traditional differential schemes, are subtracted in the all-differential approach. In figure 2, the schematic presentation of the all differential principle is shown.

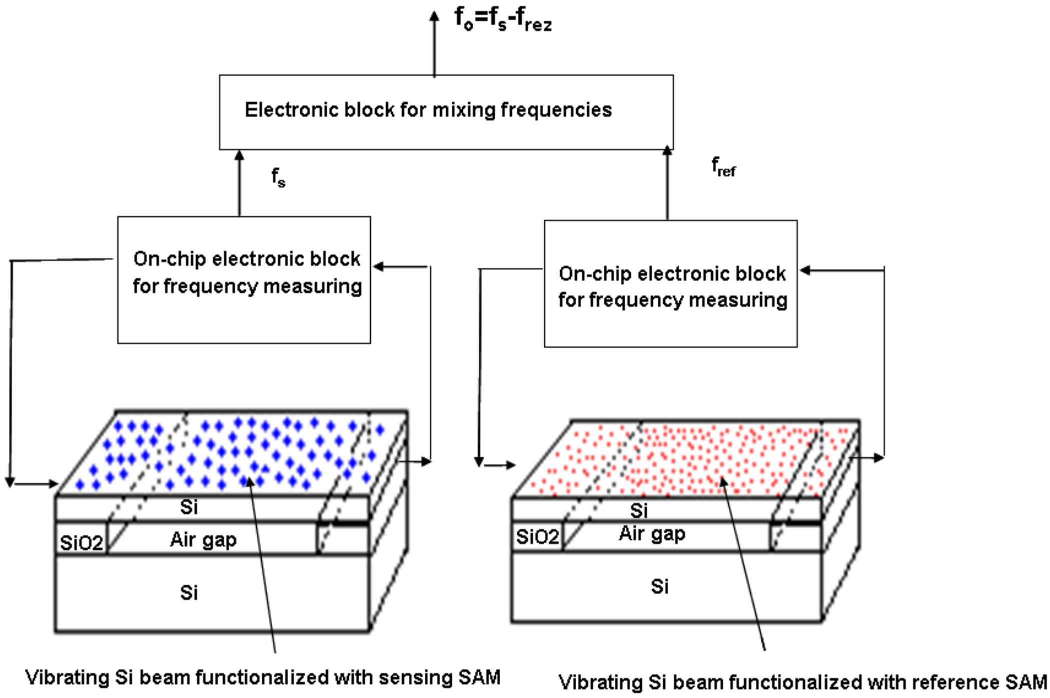

Fig. 2. Schematic blocks of an-all differential resonant NEMS chemical sensor showing a sensing layer in the sensing loop and the reference layer in the reference loop.

As an example of the above approach, the detection of the SO_2 by the all-differential concept is described below. The selection of polymers with sensitive moieties (responsible for the gas sensing properties) 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. A borderline base tends to interact with borderline acid.

According to Pearson theory, sulfur dioxide is borderline acid and has preference for borderline bases. Among the borderline base, we can remind here aromatic amines, pyridine, azide, bromide and nitrite ions. Pyridine units-based polymers, as shown in figures 3-6 were used as sensitive moiety for SO_2 detection:

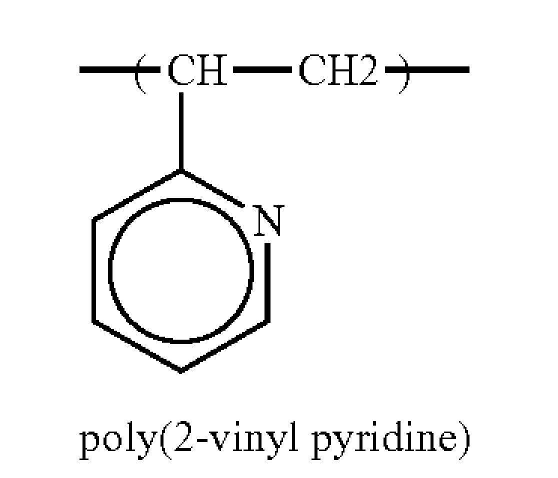

Fig. 3. Chemical formula of poly(2-vinyl pyridine).

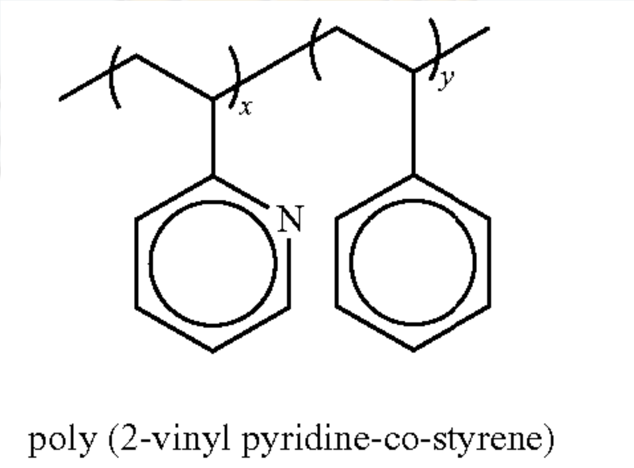

Fig. 4. Chemical formula of poly (2-vinyl pyridine-co-styrene).

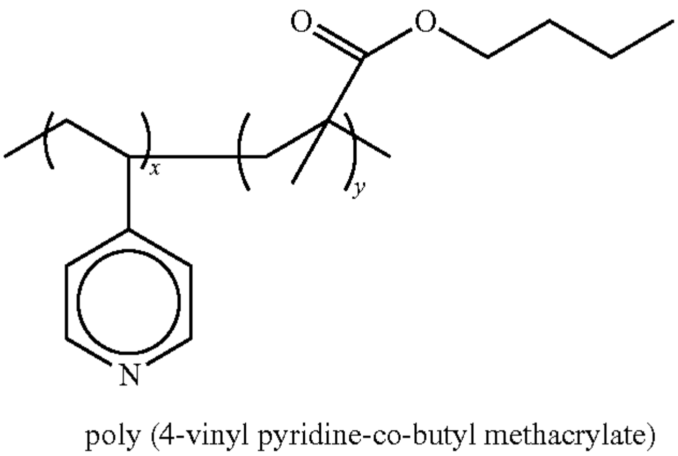

Fig. 5. Chemical formula for poly(4-vinyl pyridine-co-butyl methacrylate).

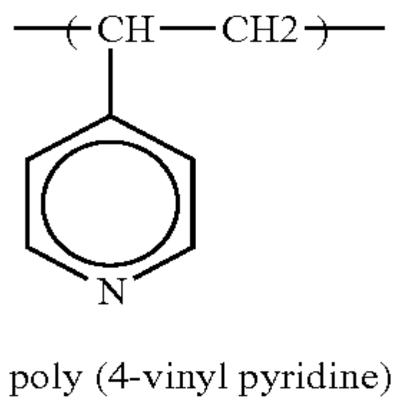

Fig. 6. Chemical formula for poly(4 vynyl pyridine).

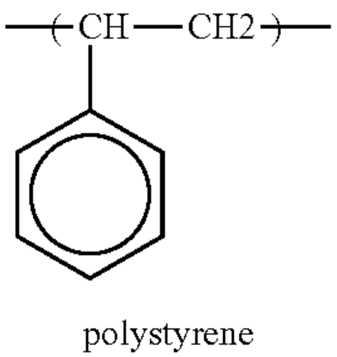

Fig. 7. Chemical formula of polystyrene.

As reference layer polystyrene can be used (Fig. 7).

7. Conclusions

From the vision of Feynman to the present state, the nanotechnology has made major steps thanks to its important theoretical and experimental achievements, culminating with the commercial scanning probe microscopy instrumentation, giant magneto resistance nanodevices, the use of the nanomaterials in many bulk applications, or the discovery of new nanomaterials like carbon nanotube and graphene.

Now, there is a common understanding that the 21st century will belong to the nanotechnology which is going to address our present society's megatrends and may be creating new ones.

During this century, the MEMS technology, which has already reached the commercial status in many application domains will be shifted to its ultraminiaturized NEMS technology, with a few tens nanometers "line" width and a few monolayers in film thickness.

It is envisioned that the resonant NEMS is going to become the biggest technology platform for multiple sensing applications, in the mechanical, chemical and biological domains, thanks to its ultra-high mass detection capabilities, targeting ultimate Dalton level in mass or single-molecule in sensing.

Simultaneous "top-down", "bottom-up" and "mixed top-down-bottom-up" approaches will be tried in order to ultimately reach the on-chip integration of the sensing and signal processing functions, which will assure the extreme 3D miniaturization, at low power consumption, high operation frequencies, as required by wireless, portable applications.

Major milestones of proving ultrahigh sensitivities of resonant NEMS for mass detection have been successfully passed by actuation schemes based on high magnetic field and detection schemes based on electromotive force, keeping the resonator at cryogenic temperatures and ultra-high vacuum, but these approaches cannot be easily miniaturized or on-chip integrated. Therefore, at commercial application level in chemical and biosensing, the major challenges for all these approaches come from the requirement that the NEMS resonator to operate at room temperature and atmospheric pressure, where the quality factor is much reduced with respect to high vacuum condition, and the background noise is high, while the detection limit is deteriorated by the viscous damping generated by the surrounding air.

Highly stressed vibrating beams seem to be the key technological design concept for increasing the quality factor at room temperature operation.

The future emerging applications of resonant NEMS will be in the field of gas and biosening nanoanalyzers, with a major focus on next generations of miniaturized mass spectrometers for single-biomolecule detection, at low sampling volume.

On a timescale, the nanomechanical sensing applications will be the first to reach the commercial level, as in these ones, the packaged NEMS resonators can be easily technologically designed to operate in vacuum conditions.

The “top-down” resonant NEMS approach will extend the MEMS technologies below 0.1 μm size and try to exploit its well established subtractive processes, to which specific nanotechnology steps, like electron beam lithography for patterning ultra-small “line” width, or dip pen nanolithography for chemical functionalization will be added.

The “bottom-up” additive NEMS approach, which is based on supramolecular chemistry principles, molecular self-assembly and recognition is in the very early stage, today. The molecular electronics is growing from single-molecule device to molecular computational circuitry, while novel concepts of the rotaxane-based bio-mimetic nanomachines are proving the capability for future artificial muscle applications. The resonant vibration of the molecular architectures is still to come.

The mixed “top-down-bottom-up” approach is combining the above two approaches, and thus both subtractive and additive processes are mixed and matched for the realization of the resonant structure.

The resonant beam is either built atom-by-atom from silicon by vapor-liquid-solid epitaxy, or by carbon technology, where CNT or graphene are selectively grown or transferred to the required position on the chip.

Recently, novel differential concepts and functionalization routes for self-assembled sensing monolayers and ultrathin sensing layers are expected to improve the long term stability of the solid state IC-based chemical sensing, and hopefully open the way to commercialization.

Deep understanding of the fundamental science and technology principles is the foundation of the future innovative developments, which may bring disruptive discoveries in the field of material-process-device, changing the present vision and bringing unforeseen evolutions in the field of future nanotechnology and applications.

So, even today, there is still “plenty of room” for nanotechnology innovation, and young generations have enough space to play and bring their contribution to the future of nanotechnology.

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