Carbon Nanotube- and Graphene Based Devices, Circuits and Sensors for VLSI Design

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1. Introduction

With the reduction in power consumption and size chip, the electronic industry has been searching novel strategies to overcome these constraints with an optimal performance. Carbon nanotubes (CNTs) due to their extremely desirable electrical and thermal properties have been considered for their applicability in VLSI Design. CNTs are defined as sheets of graphene rolled up as hollow cylinders. They can basically be classified into two groups: single-walled (SWNTs) and multi-walled (MWNTs) as shown in Figure 1. SWNTs have one shell or wall and whose diameter ranging from 0.4 to 4 nm, while MWNTs contain several concentric shells and their diameter ranging from several nanometers to tens of nanometers.

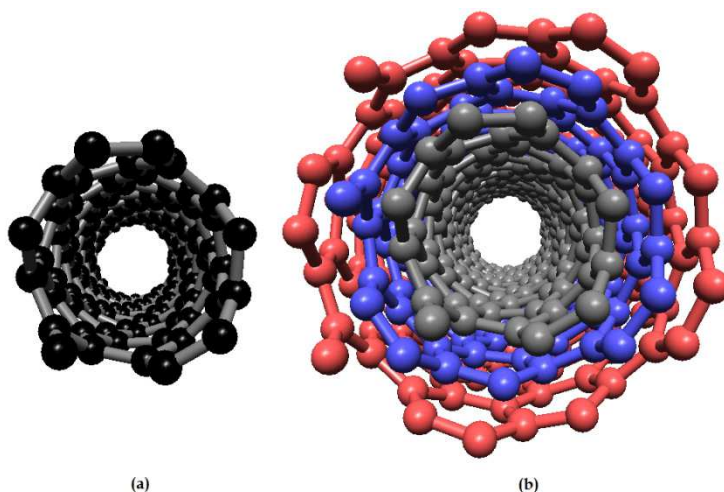(a)   (b)

Fig. 1. Types of carbon nanotubes: single-walled nanotube (SWNT) and multiple-walled nanotube (MWNT).

The electrical properties the SWNTs can be either of metallic or semiconducting materials depending on their chirality, that is, the direction in which they get rolled up. However, MWNTs are always metallic materials. The main applications of carbon nanotubes in

electronics are biochemical sensors, data storage, RF applications, logic circuits and/or semiconductor materials (Xu et al., 2008). Nowadays, graphene nanoribbons (GNRs) or carbon nanotubes unrolled are presented as attractive candidate for next-generation of integrated circuit applications derived of the anomalous quantum Hall effects and massless Dirac electronic behavior (Lu & Lieber, 2007).

The main objective of this review related with carbon nanotubes and graphene nanoribbons is assessing the current status in VLSI design and provides a vision of the future requirements for electrical subsystems based on carbon nanotubes: technology, products and applications. This chapter presents a comprehensive study of the applicability of carbon nanotubes and graphene nanoribbons as base materials, with special emphasis into the advantages and limitations, in the design of elements for VLSI design such as interconnects, electronic devices such field-effect transistors, diodes and supercapacitors; optoelectronic devices such as solar cells and organic light-emitting diodes; electronic circuits such as logic gates, and digital modulators; and bio/chemical sensors such as biosensors and gas sensors.

2. Electrical properties of carbon nanotubes

One promising direction for the VLSI Design is the use of carbon nanotubes as the active part of the device, circuit or sensor. Carbon nanotubes (CNTs) are macromolecular one-dimensional systems with unique physical and chemical properties (Zhou et al., 2007). Such properties are derived of that all chemical bonds are satisfied and they are very strong, which also leads to total mechanical, thermal and chemical stability (Baughman et al., 2002). The electronic structure and electrical properties of CNTs are derived from those of a layer of graphite (graphene sheet). The specific electrical properties of the carbon nanotubes are obtained as result of their particular band structure and the hexagonal shape of its first Brillouin zone. CNTs can carry out high electrical current densities at low electron energies. When high electron energies are used, this quantity of energy destroys the CNT structure, which is not desirable from any point of view (Mamalis et al., 2004; Terrones, 2003, 2004).

This section analyzes the electrical characteristics of carbon nanotubes and graphene nanoribbons through their physical structure with the aim of presenting the attractive interest for using them in VLSI Design. The advantages and drawbacks of the use of CNTs and graphene nanoribbons as active part of an electrical device are studied.

Among physical variables of the carbon nanotube related with the electrical performance are diameter, chirality, length, position, and orientation. Each graphene sheet is wrapped in accordance with a pair of indices (n, m), which represents the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If m = 0, the nanotubes are called zigzag nanotubes, if n = m, the nanotubes are called armchair nanotubes and otherwise, they are called chiral nanotubes (see Figure 2) (Hayden & Nielsch, 2011; Hetch et al., 2007; Marulanda, 2010).

Two physical properties of the graphene modify its electrical properties: symmetry and electronic structure. There are three types of electrical behavior as shown in Figure 3: 1) if n = m, the nanotube is metallic; 2) if n-m is equal to $3j$, where j is a positive integer ("$3j$" rule), then the nanotube is semiconducting with a very small band gap, and 3) otherwise, the nanotube is a moderate semiconducting. The $3j$ rule has exceptions due to the curvature

effects in carbon nanotubes with small diameter, which can influence in the electrical properties. A metallic carbon nanotube can present semiconducting behavior and vice versa (Avouris, 2002).
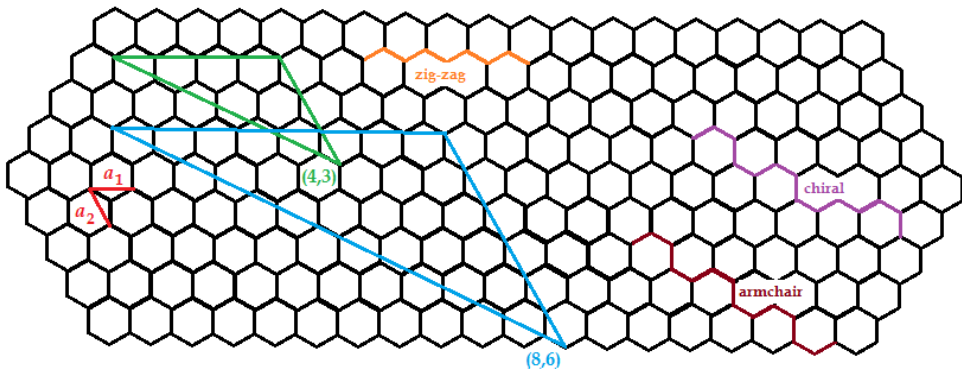

Fig. 2. Classification of carbon nanotubes by chiral indices: zig-zag, chiral, and armchair.
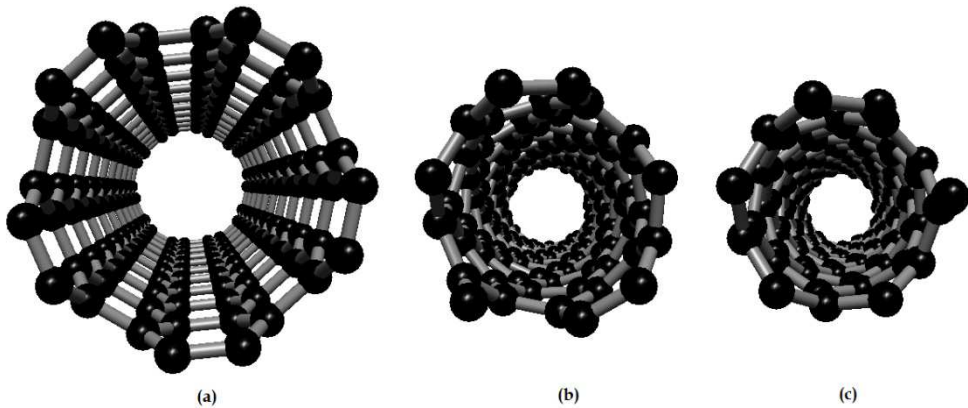

Fig. 3. Classification of carbon nanotubes by electrical properties: (a) metallic nanotube, (b) semiconducting nanotube, and (c) moderate semiconducting nanotube.

The interaction among electrons in an one-dimensional conductor such as a carbon nanotube can be modeled as a Tomonaga-Luttinger liquid, since electronic properties are derived of the collective excitations of charge and spin waves with a bosonic nature, that is, mass-less current flow (Danilchenko et al., 2010). Carbon nanotubes show two different electrical behaviors depending of the range of temperature: ballistic current transport at room temperature and Coulomb blockade phenomena at low temperatures. Ballistic transport is presented when the effective distance between contacts, where voltage is applied, is shorter than the mean free path. Coulomb blockade occurs when electrons hop on to and off from a single atom between two contacts due to a high contact electrical resistance (Hierold, 2008; Léonard, 2009).

In particular, metallic carbon nanotubes allow that very large electrical currents can be used to design high speed nanoscale electronic devices due to its wide band gap. Metallic multiwall CNT can carry a current density on the order of 10^8 A/cm^2 and have the capacity of dissipated power of 1.82 mW (Shacham-Diamand et al., 2009). Individual carbon nanotubes can be considered as quasi-one-dimensional (1D) conductors. Multi-walled nanotubes (MWNTs) are considered two-dimensional (2D) conductors due to their coaxial distribution of SWNTs with intertube spacing of ~ 3.4 Å. Metallic carbon nanotubes present high dielectric constant, while semiconducting carbon nanotubes have low dielectric constant (Joachim et al., 2000; Kang et al., 2007; Krompiewski, 2005).

One of the most promising applications of the electrical properties of carbon nanotubes is the use of them in the fabrication of electronic devices. Special interest is given to the use of soft and ductile matrices to portable, light, and flexible electronics. In the design of electronic devices, the precise and tunable control of the electronic properties is essential to the high performance VLSI circuits. During the synthesis of carbon nanotubes, both metallic and semiconducting carbon nanotubes are obtained (Kanungo et al., 2010), forming sets of carbon nanotubes called bundles. A bundle containing tens to hundreds of tubes is denominated a rope; in this structure, the carbon nanotubes are separated ~ 3.2 Å forming a close-packed triangular lattice where the diameters are almost identical (see Figure 4) (Hou et al., 2008).
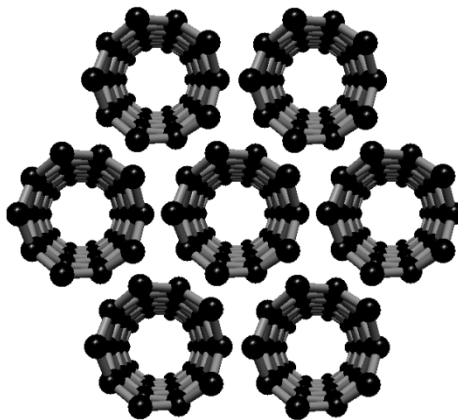

Fig. 4. An ideal bundle of carbon nanotubes.

A bundle of carbon nanotubes is formed by van der Waals interactions among neighboring nanotubes. It is waited that cooperative effects among nanotubes be originated in a bundle (Kim et al., 2010). The presence of multiple carbon nanotubes can substantially reduce the electrical resistance to the electrical current carried out by them, if this is compared with the electrical resistance of an individual nanotube. It is true, only when the bundles have direct physical contact, non electrical, with any material in the device with the aim of reducing the temperature generated by the current carried out. The electrical transport in a bundle has interesting electrical properties such as single electron transport (Coulomb blockade allow us control the number of electrons in the electrical conduction one by one) and metallic resistivity (increased with the temperature). Additionally, the electronic transport in a

bundle is modified by the direction and magnitude of the applied electrical field and the electrostatic screening produced by the carbon nanotubes surrounding to a specific carbon nanotube, as shown in Figure 5. Such electrostatic screening leads to a tunable switching behavior which is induced by electric field perpendicular or transverse to the bundle axis. In the case of semiconducting nanotubes, the applied electrical field produces band gap closure; while for metallic nanotubes, it produces a band gap opening. In this way, only for metallic nanotubes it is possible to modulate the conductivity of the bundle through of the applied field and splitting of the valance and conduction bands thanks to the symmetry breaking of the electrostatic screening between adjacent nanotubes due to a weak electrical interaction presented in the intertube region between them. It is necessary to remember that the level of electrostatic screening inversely determines the electrostatic field and Coulomb potential of the ions in the nanotubes. For semiconducting nanotubes, the band gap is reduced thanks to the increase of size of valence and conduction bands generated by the Stark effect derived of the applied electrical field to the nanotubes (Haruehanroengra & Wang, 2007).
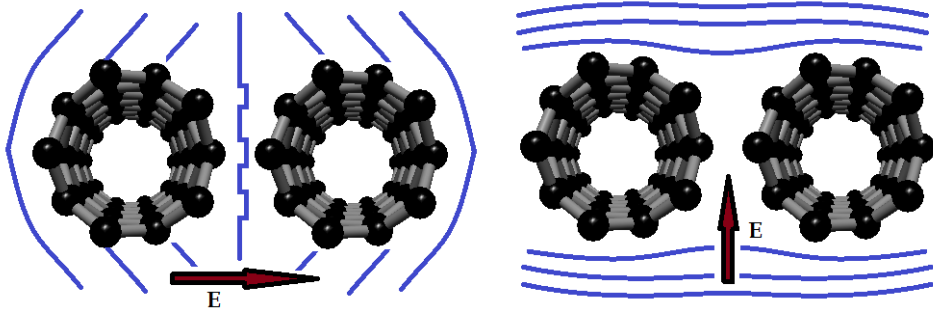

Fig. 5. Electrical field applied in a bundle of carbon nanotubes. Red arrow indicates the direction of the field.

Arrays of carbon nanotubes have electrical properties which can be controlled by means of its length, diameter, and chirality (Jain et al., 2011). A uniformity of the properties can be achieved when performance characteristics such as high yield, reproducibility, sensitivity, and specificity are guaranteed. This is obtained through synthesis procedures, dispersion procedures, and deposition processes whose quality allows us the integration of the carbon nanotubes with the same physical properties before and after of the dispersion of bundles (Hong et al., 2010).

Due to the presence of bundles of nanotubes, it is necessary the development of methods which allow us to separate nanotubes for extending their use in electronic applications. Several methods to separate bundles based on monovalent side wall functionalization have been developed even with the aim of improving solubility, purification and exfoliation. Unfortunately, these methods can lead to disrupts π transitions, generate changes in electrical resistance, and can even produce the tube fragmentation due to the formation of impurity states near the Fermi level. New strategies based on the use of mixtures of metallic and semiconducting nanotubes are producing high mobility semiconducting combinations without laborious separation requirements to use all carbon nanotubes obtained during the

synthesis. The use of divalent functionalizations which produce impurity states far away from the Fermi level, can even lead to generate high performance semiconducting inks of low cost which can be applied in printable VLSI electronics. In addition, divalent functionalization offers a different strategy to control the electrical properties slightly taking into account tube type, size, and chirality. Adequate addends used in the functionalization allow us to transform metallic nanotubes into semiconducting nanotubes (Javey, 2008).

In 2004, graphene arose as a product of exfoliation of graphite, with the form of a two-dimensional sheet of sp^2-hybridized carbon (Novoselov et al., 2004). In the same manner that carbon nanotubes, it has unique electrical, mechanical and thermal properties. Such properties have been exploited in the development of energy-storage materials, transparent conducting electrodes (Alkire et al., 2009; Hu et al., 2007), field-effect transistors, digital and analog integrated circuits, integrated circuit interconnects, solar cells, ultracapacitors, and electrochemical sensors such as single molecule gas detectors and biosensors. High electron mobility at room temperature, low electrical resistivity, and symmetry of carrier mobilities between electrons and holes, are the electrical properties attractive to apply graphene in the design of electronic devices of high-performance. A similar classification to the carbon nanotubes with respect to the electrical behavior of the graphene is illustrated in Figure 6.
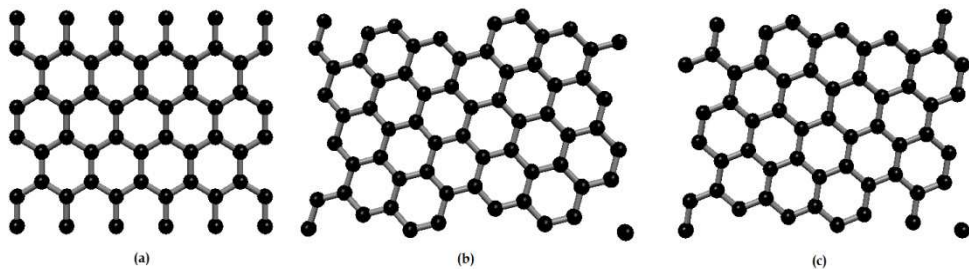

Fig. 6. Classification of graphene by electrical properties: (a) metallic graphene, (b) semiconducting graphene, and (c) moderate semiconducting graphene.

Graphene nanoribbons (GNRs) can be defined as rectangles made from graphene sheets with widths going from a few nanometers to tens of nanometers and lengths from nanometers to micrometers. They are considered as quasi-1D nanomaterials and can have metallic (zigzag) or semiconducting (armchair (AGNR) or zigzag (ZGNR)) behavior depending of its chirality and orientation. Both types are denoted in accordance with the number of chains either, armchair or zigzag, found in its width. High electrical and thermal conductivity, low noise and bidimensional structure are properties which can be useful to produce integrated circuit interconnects with GNRs. The size of GNRs allows us to control the band gap of the material to be electrically manipulated in an electronic device generating a wide versatility of design (Ferry et al., 2009; Guildi & Martín, 2010).

GNRs possess a richer energy band structure than the graphene, since an external electric field can be used to tune a specific bandgap (Chen, X. et al., 2011). Semiconducting AGNRs have electrical behavior as semiconductor material of indistinct manner with respect to the carbon chain position, and metallic AGNRs present both metallic as semiconducting behavior which is related with the change of chain associated with the "3*j* rule" in carbon chain position (Law et al., 2004; Philip-Wong, 2011).

Graphene has interesting electrical properties such as electron-hole symmetric band structure, high carrier mobilities, ballistic transport, and absence of band gap (Reddy et al., 2011). But also, some disadvantages associated with its use in field-effect transistors such as lack of gate control, high off-state leakage current and saturation not controlled by drain voltage. Different methodologies are being developed to overcome, adapt to, and even use these electrical characteristics for its application in electronic devices. The use of graphene as electronic material resides in the reduction of energy consumption, linear energy dispersion, carriers with zero mass, linear current-voltage characteristic, high Fermi velocities, very low channel electrical resistance, mobilities and saturation velocities for a high current-carrying capability (6 orders higher than copper), low density of states, and the increase of frequency operation of the devices based on these qualities (Geim & Novoselov, 2007). Depending of the bias voltage, the sheet of graphene can present electrical resistance in the range of Kilo-ohms to ohms for low voltages and high voltages, respectively. OFF-state leakage currents in field-effect transistors based on graphene are detrimental for digital circuits, but these are very useful to analog circuits where ON-state modulating small voltages and current signals are a common case. For applications as high performance RF circuits, the graphene offers an alternative material given that its cut-off frequency is very high, and it has high compatibility with VLSI systems based on silicon. Due to its nature structurally malleable, the electrical properties of the graphene can be favorably modified by mechanical strain and stress (Geim, 2009). Graphene can also be used in interconnects and optoelectronics.

3. Carbon nanotube interconnects

The interconnects distribute a large quantity of signals used for the diverse elements of a VLSI design such as clock signals, power, or ground in an integrated circuit (IC), and also to various circuits on a chip. Local, intermediate and global interconnects are the levels of operation of such interconnections. The use of Cu as material for interconnects represents a current paradigm for high-performance integrated circuits due to that line dimensions, and grain size become comparable to the bulk mean free path (MFP) of electrons (~ 40 nm). In addition, higher RC delays reduce the operation speed of ICs. When a new proposal in VLSI design is done, the main characteristic must be the compatibility with current IC manufacturing. The two most promising potential candidates that can be used as material for interconnects are optical and carbon-nanotube (CNT) based interconnects (Cho et al., 2008; Koo et al., 2007; Kreupl et al., 2002).

This section provides a summary of the novel challenges that are being realized in nanometer-scale on-chip interconnects. Special topics associated with the operational effects such as performance and reliability are analyzed, with the aim of identifying the electrical characteristics that can be obtained in resistivity, interconnect delay, and current-carrying capability. Finally, the prospective applications of GNRs for interconnects are discussed.

Carbon nanotubes can be integrated into multilevel interconnects to meet emerging needs: delay, lifetime, parasitic resistance, inductive effects, bandwidth density, electromigration (Hosseini & Shabro, 2010), energy efficiency, power dissipation, and lowering temperature of the interconnection. Additionally, the use of carbon nanotubes makes possible the development of three-dimensional hyper-integration architectures with a high performance: versatility, scalability, adaptability, high-density interconnects, and a reduced number of

defects, (Ahn et al., 2006; Bakir & Meindl, 2009; Papanikolau et al., 2011; Shacham-Diamand et al., 2009; Xie et al., 2010; Zhou & Wang, 2011).

Electrical transport in MWNTs presents three different cases. When a MWNT operates at conditions of low energy (thermal and electrical), electrical current in carried by the outermost shell of it. At intermediate energy, only metallic shells contribute to the electrical transport of current. Finally, at high energy all shells of the MWNT carry electrical current. In this manner, is complicated to adjust the operation of MWNTs with the aim of that these can be used in interconnections of VLSI systems (Srivastava, 2004, 2009; Tan et al., 2008).

Since inherently carbon nanotubes can provide high electrical current density, numerous applications, including interconnects for VLSI design, have been suggested as a novel way of reducing physical spaces with an optimal performance. The electrical resistance for CNTs, as large as 1 µm with perfect contacts, is about of 6.45 KΩ. This value is high to be used in interconnects, therefore, carbon nanotubes are placed in parallel in large numbers (a bundle) with the aim of reducing the total electrical resistance. A CNT bundle is generally a mixture of single-walled CNTs, multi-walled CNTs or single-walled CNTs and multi-walled CNTs. CNTs bundle offers a promising alternative to place metallic contacts and vias at the local level for VLSI circuits, with the advantage that they can be grown with low or high indexes when lower or higher current densities are needed, respectively. In particular, the length-to-diameter ratio of the CNT interconnects have significant implications for the design of on-chip capacitors and inductors (Nojeh & Ivanov, 2010).

Due to the very high frequencies used to carry signals in the integrated circuits, the ballistic transport presented by carbon nanotubes and graphene allow us to design advanced interconnect networks (see Figure 7). Since metallic carbon nanotubes are almost insensitive to the disorder, they are considered as perfect 1D electrical conductors. In a similar way, tube-tube connections, junctions and even tube-metal contacts that also are used in the interconnection of VLSI systems must work reliably with minimal electrical losses in the contact points. By nature, nanotube-metal interface presents a tunneling barrier. The research associated with these phenomena has searched solutions based on fabrication methods to modulate the electrical characteristics of the interface (Li, J. et al, 2003).

Tube-tube junctions involve physical contact, with small structural deformation, between two tubes and these are not chemically bonded. This type of junction is found in interconnections between ropes, MWNTs, and crossed-over tubes (Andriotis et al., 2001, 2002). The electrical transport is realized by means of tunneling transport between tubes, producing an alteration in electrical transport of the individual tubes involved in the junction, due to the weak electrical coupling. When specific junctions called "X", "Y" or "T" are been used in the connections, these have proved to be stable and therefore, these can be useful when it is required to joint multi-terminal electronic devices by means of carbon nanotubes or in the case of wiring interconnection (Chen & Wang, 2009; Li, H. et al., 2008, 2009).

Plating a hollow structure inside used as via or trench in circuits VLSI by means of carbon nanotubes have not been reasonable due to high hydrophobicity of graphene sheets, which hinder the entry of solvent and dissolved species (Shacham-Diamand et al., 2009). This problem is emphasized for carbon nanotubes with diameters less than 50 nm.
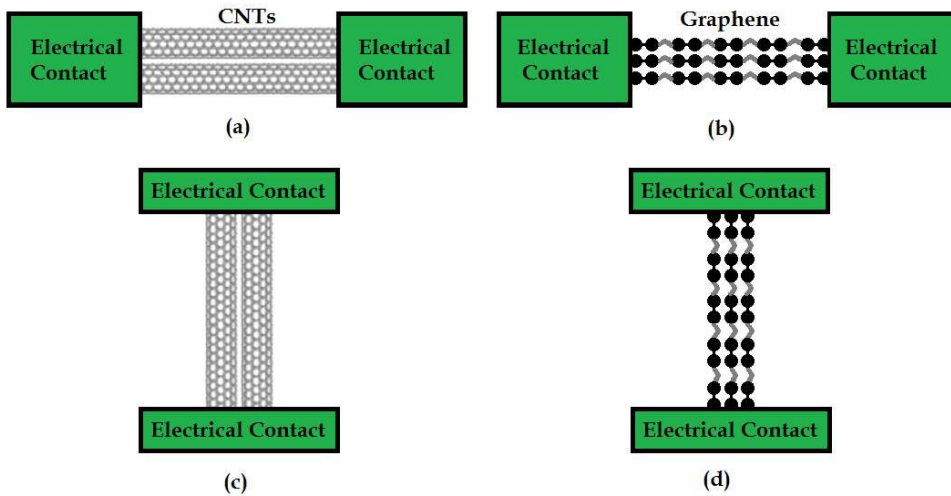
Fig. 7. Electrical connections in VLSI circuits: (a) interconnects based on carbon nanotubes, (b) interconnects based on graphene, (c) vias based on carbon nanotubes, and (d) vias based on graphene.

The graphene presents a higher conductance with respect to Cu for interconnects in the range of nanometers. Among the properties exploited of the graphene for interconnects are: high carrier mobility at room temperature, thermal conductivity, higher mechanical strength, reduced capacitance coupling between adjacent wires, width-dependent transport gap, temperature coefficient, and ballistic transport. When line widths of the graphene nanoribbons are reduced below 8 nm, the resistivity of GNRs is insignificant. Additionally, the use of graphene in interconnects extends the life of high performance for silicon-based integrated circuit technology. In thermal characteristics, the graphene interconnects allow us to cool heat flux, to remove hot-spots, and to spread lateral heat (Goel, 2007).

Additionally to the electrical properties, the mechanical and thermal properties of CNTs and graphene nanoribbons must be taking into account in the design of interconnects. Mechanical properties such as strength, stability and minimal elastic deformation can be achieved thanks to its topology and low density. By another side, carbon nanotubes exhibit good thermal conductivity and high thermal stability, which are necessary to support high current densities (Giustiniani et al., 2011).

Within of the novelties to come in this sector are the scaling of the ordinary interconnects by means of an accurate and reproducible patterning of nanoscale structures based on carbon nanotubes and/or graphene nanoribbons. The use of self-assembly is more and more feasible given the advancements in the development of supermolecular networks. These changes will allow the perfect alignment and optimal charge transport among the elements interconnected in a VLSI system. Additionally, these techniques increase the yield given place to a massive fabrication and lower costs, which are essential in a VLSI system.

4. Carbon nanotube based devices

As active part of electronic devices, the CNTs have been used to control their electrical properties. In this manner, carbon nanotubes can implement electronic devices such as diodes, transistors, Schottky rectifiers (Behman et al., 2008), supercapacitors (Chen, P.-C. et al, 2009), solar cells (Jia et al., 2011; Nogueira et al., 2007), and organic light-emitting diodes, by combining semiconductor and metallic behaviors (Terrones, 2003, 2004; Tseng et al., 2004). Different strategies and topologies have been proposed with the aim of improving their performance. Transistors and Schottky rectifiers can be obtained by means of metallic-semiconducting junctions (Hur et al., 2004).

This section analyses the performance characteristics, topologies, and applications of the electronic devices fabricated by means of carbon nanotubes with emphasis to VLSI Design. It is explained as the choice of material is critical for a successful application with high performance in electronic devices such as field-effect transistors, *p-n* diodes, supercapacitors, solar cells, and organic-light-emitting diodes.

The development of the carbon nanotube field-effect transistors (CNFETs) was due to the historical motivation of reducing or make insignificant short-channel effects, and to improve performance of transistors in these length scales (Burke, 2004). The use of semiconducting carbon nanotubes is strategic given that metallic nanotubes cannot be fully switched off. The main advantages of this type of transistors are: ballistic electron transport over its lengths (Hasan et al., 2006), higher current density, lower power consumption with respect to silicon versions, and faster operation speed (Burghard et al., 2009). There are four main topologies to design CNT field-effect transistors: 1) back-gated CNTFETs, 2) top-gated CNTFETs, 3) wrap-around gate CNTFETs, and 4) suspended CNTFETs, as shown in Figure 8.
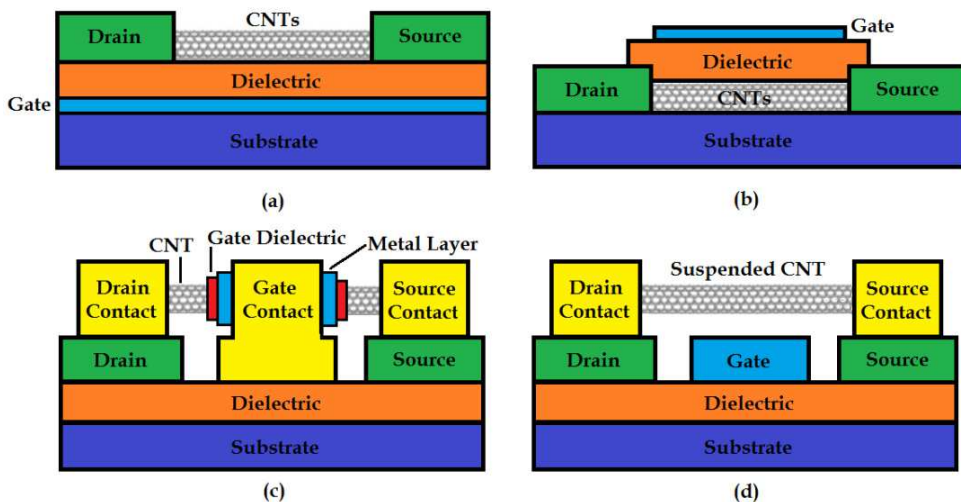

Fig. 8. Cross sections of different geometries of carbon nanotube field-effect transistors: (a) back-gated CNTFETs, (b) top-gated CNTFETs, (c) wrap-around gate CNTFETs, and (d) suspended CNTFETs.

In the case of back-gated CNTFETs, the main disadvantages found for its use are a poor contact between the gate dielectric and CNT, difficult switching between ON and OFF states when low-voltages are applied, and a Schottky barrier between CNTs and drain and source regions. In the case of top-gated CNTFETs, these offer several advantages over back-gated CNTFETs, but it fabrication process is more complicated (Singh et al., 2004). In wrap-around gate CNTFETs, the entire circumference of the nanotube is gated and therefore, electrical performance is enormously improved, reducing leakage current and increases the device ON/OFF ratio. Finally, in the case of suspended CNTFETs is searched the reduction of the contact between the substrate and gate oxide, and therefore, it decreases scattering at the CNT-substrate interface with the drawback of limiting its use in applications where high ON/OFF ratio are required (Kocabas et al., 2005, 2006).

The CNTFETs can be classified in two types: 1) *n*-type CNTFETs, when electrons are majority carriers for positive gate voltages, and 2) *p*-type CNTFETs, when holes are majority carriers for negative gate voltages. An ohmic contact is found when a current-voltage relationship is linear and symmetric (electrons and holes are transported in the same time), while a Schottky-barrier is presented when current-voltage relationship is non-linear and asymmetric (a unique type of electrical carrier is transported) (Lin, A. et al., 2009).

Four electrical transport regimes can be found in transistors based on carbon nanotubes, which are distinguished in accordance with the length of the nanotube compared with their mean free path, and by the type of contact between the nanotubes and the source/drain metals: 1) *ohmic-contact ballistic,* when charge injection is realized by the source and drain contacts into the carbon nanotubes and vice versa, producing a high current flow; 2) *ohmic-contact diffusive,* when bidirectional charge transport suffers scattering between source and drain contacts and carbon nanotubes with a limited current flow; 3) *Schottky-barrier ballistic*, when the gate voltage controls the thickness of the barrier and drain voltage can lower the barrier producing bidirectional high current flow: in ON-state, electrons tunneling from the source, and in OFF-state, holes tunneling form the drain; and 4) *Schottky-barrier diffusive*, when the combination of gate and drain voltages reduces the Schottky barrier and the charge transport suffers scattering producing a reduced current flow (Appenzeller et al., 2005; Cao et al., 2007).

With the introduction of graphene as active material for electronic devices, new field-effect transistors were introduced, namely these are called GFETs. A GFET uses as active material, graphene, for ballistic transport of carriers. As it was illustrated for carbon nanotube, also can be built four types of GFETs: 1) back-gated GFETs, 2) top-gated GFETs, 3) wrap-around gate GFETs, and 4) suspended GFETs. Last two topologies are not available now, but these will be fabricated in a pair of years. Back-gated GFETs present large parasitic capacitances and poor gate control. However, when smooth edges of the graphene nanoribbons are achieved, ON/OFF ratios as high as 10^6 are obtained, which is attractive for digital applications. Top-gated GFETs are the preferred option for analogical practical applications. In wrap-around gate GFETs, the entire rectangle of the graphene nanoribbon will be gated (see Figure 9).

Nowadays, carbon nanotube-based field-effect transistors (FETs) have operating characteristics that are comparable with those devices based on silicon. The active part in field-effect transistors is the electrical channel established by means of the carbon nanotube

in the substrate connecting source and drain terminals. SWNTs have been the ideal candidates as semiconducting materials due to that them can be doped to address the type of conductivity either *n*-type or *p*-type and, in this way, to manipulate the level of electrical conduction. The carbon nanotube based FETs can achieve high gain (> 10), a large on-off ratio (>10[5]), and room-temperature operation (Lefenfeld, et al., 2003).

Carbon nanotubes and graphene nanoribbons are very sensitive to their environments including charges, vacuum levels, and environment chemical components, due to their ultrasmall diameters and large surface-to-volume ratios. Carrier mobility in carbon nanotubes is very susceptible to charge fluctuations derived of the defects located at the ambient surrounding the CNTs and graphene nanoribbons. The mobility fluctuation is the dominant $1/f$ noise mechanism for the narrow channel carbon nanotubes operating in strong inversion region with a small source-drain bias.
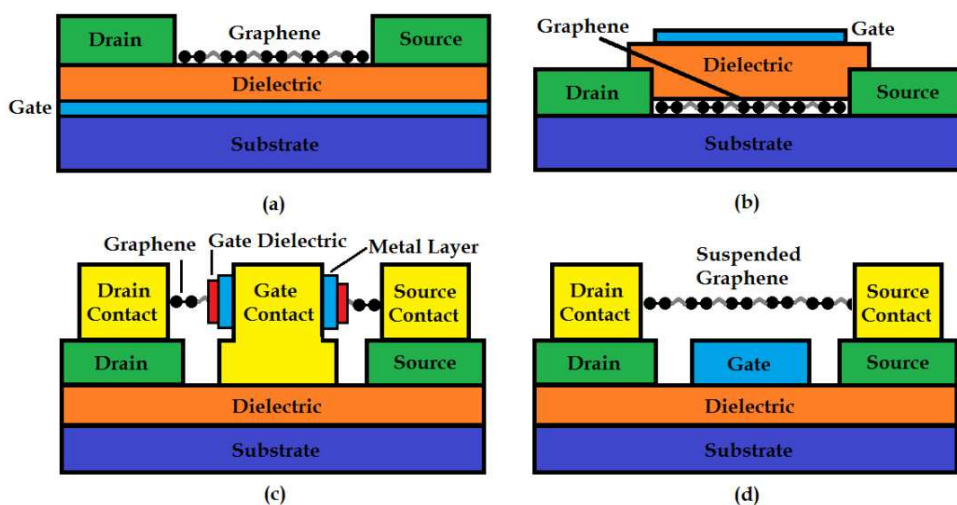

Fig. 9. Cross sections of different geometries of graphene field-effect transistors: (a) back-gated GFETs, (b) top-gated GFETs, (c) wrap-around gate GFETs, and (d) suspended GFETs.

At ambient temperature, semiconducting SWNTs generally show unipolar *p*-type behavior. By doping with potassium, the unipolar *p*-type behavior can be switched to unipolar *n*-type behavior. *p-n* Diodes can be designed by covering one-half of the gate of a single channel field-effect transistor with polymers such as polyethylenimine (PEI) and poly(methyl methacrylate) (PMMA) (Mallick et al., 2010; Zhou, Y. et al., 2004).

Those field-effect transistors that have been fabricated with functionalized nanotubes exhibit high electron mobilities, high on-current, and very high on/off ratios which are necessary in high-speed transistors, single- and few-electron memories, and chemical/biochemical sensors. Studies on scaling resistivity are being realized with the aim of identifying the influence of device parameters in the on/off ratio (Sangwan et al., 2010).

A supercapacitor is an electrochemical capacitor with relatively high energy density of small size and lightweight (hundreds of times greater than those of electrolytic capacitors).

Carbon nanotubes together with ceramic materials can be used to design supercapacitors by means of heterogeneous films. The use of ceramic materials allows increasing their electrical energy accumulated as voltage, while carbon nanotubes offer the properties of flexibility and transparence. Among the optimized properties are specific capacitance, power density, energy density, and long operation cycles. Supercapacitors require electrodes with large surface area, which can be obtained by means of sets of carbon nanotubes operating as electrical conductive networks (Lekakou et al., 2011). These electrodes must be capable of supporting high power and energy density, with reduced internal electrical resistance and produced with lower cost.

Flexible electronics is now a reality thanks to the successful development of the organic electronics working to low-temperature (Lin, C.-T. et al., 2011). Devices such as organic thin film transistors (OTFTs), large-area displays (Wang, C., 2009), solar cells (Rowell et al., 2006), organic light-emitting diodes (OLEDs), and sensors can be implemented based on carbon nanotubes. The electrical properties improved with the use of carbon nanotubes are transistor on-off ratio, threshold voltage, and transistor transconductance. Additionally to the electrical properties, this type of devices can be fabricated to low-cost. Carbon nanotubes can be used to fabricate transparent conductive thin films (Facchetti & Marks, 2010; Ginley, 2010) which are exploited as hole-injection electrodes for organic light-emitting diodes (OLEDs) either for rigid glass or flexible substrates (Wang, 2010; Wiederrecht, 2010; Zhang et al., 2006). The incorporation of CNTs in polymer matrices used to design OLEDs allow changing electrical characteristics of the polymer due to that the CNTs operate as doping materials. Carbon nanotubes introduce additional energy levels or forming carrier traps in the host polymers, therefore, the CNTs facilitate and block the transport of charge carrier and improving the performance at specific dopant concentrations. Such concentrations must be controlled by percolation and functionalization of the carbon nanotubes with the polymer.

The integration of hybrid materials forming heterojunctions has allowed improving the efficiency of solar cells by means of the reduction of internal resistance, which is directly associated with the fill factor, transport and separation of charges that are useful for an optimal performance. Additionally, the use of carbon nanotubes provides the possibility of tailoring the electrical and structural properties to increase the optical efficiency of the light applied to the solar cell. Two great operative advantages of carbon nanotubes are being exploited in organic photovoltaics: higher electrical charge transport properties and elevated number of exciton dissociation centers (Nismy et al., 2010). Such dissociation makes that holes are transported by a hopping mechanism and the electrons are transferred through the nanotube. The ballistic transport of the electrons in carbon nanotubes produces very high carrier mobility in the active layer. Through a well-distributed percolation and careful functionalization of carbon nanotubes it is possible increase the charge transported thanks to the multiple transfer pathways among nanotubes. If carbon nanotubes are used as transparent electrodes in solar cells, then they collect electrical charge carriers (Hatakeyama et al., 2010, Liu, X et al., 2005).

The main strategy to come is the use of multiple nanotubes operating in parallel either individually or forming well-defined bundles with the aim of controlling the on-current in a wide range of electrical current going from micro-amperes to mili-amperes. In this manner,

it is very useful to develop methodologies to produce arrays of nanotubes with well-characterized characteristics with the aim of obtaining high-performance applications.

5. Carbon nanotube based circuits

Carbon nanotubes can be exploited as molecular device elements and molecular wires. Each device element is based on a suspended, crossed nanotube geometry that leads to bistable, electrostatically switchable ON/OFF states. Such device elements can be addressed by means of control elements to manipulate large arrays (10^{12} elements or more) using carbon nanotube interconnects (Ishikawa et al., 2009; Tulevski et al., 2007).

This section discusses circuits based on carbon nanotubes that have been proposed in the last decade for VLSI Design. The necessary steps to leading to the carbon nanotubes based circuits toward integrated circuits are analyzed in detail. Different realizations of analog and digital circuits are studied, which can be used for integrated circuits in VLSI Design. The advantages and limitations of the performance of such circuits in their analog and digital versions are summarized.

The electrical properties of carbon nanotubes are making possible the complete design of VLSI systems under a unique active material (Hosseini & Shabro, 2010). Semiconducting carbon nanotubes can be used to build transistors, devices and circuits, while metallic carbon nanotubes are used to build interconnects and vias. Circuits such as ring oscillators (Pesetski et al., 2008), inverter pair (Nouchi et al., 2008), NOR gate, nonvolatile random access memory, etc. can be designed with field-effect transistors based on carbon nanotubes. Nowadays, simulation software has shown that CNT transistor circuits can operate at upper GHz frequencies (Vasileska & Goodnick, 2010).

The integration of multiple field-effect transistors can be realized to build digital logic circuits. In circuits where back-gated transistors are used, the same gate voltage is applied to all transistors associated with the circuit. Therefore, to increase the potentially of such circuits different strategies are being developed with the aim of applying different voltages to the gates in each transistor associated with the circuit. In digital circuits, the transistors must have electrical characteristics that can favor high performance such as: high gain, high ON/OFF ratio, excellent capacitive coupling between the gate and nanotube, and room-temperature operation (Cao et al, 2006; Jamaa, 2011). Until now, one-, two-, and three-transistor circuits have showed digital logic operations, giving place to logic inverters, NOR gates, static random-access memory cells, and AC ring oscillators (Wang, C., 2008).

Logic inverters are logical devices with one input and one output (see Figure 10 (a)). A logic inverter converts a logical "0" into a logical "1", and vice versa (Bachtold et al., 2001). Therefore, an inverter circuit operates as a basic logic gate to swap between two logical voltage levels "0" and "1". NOR gates are logical devices with two or more inputs and one output. A NOR gate of two inputs operates as follows: an output "1" is obtained when both inputs are "0", and an output "0" is achieved when one or both inputs are "1". A static random-access memory (SRAM) cell is built as a latch by feeding the output of two serial logical inverters together, that is, a bistable circuit generated to store each bit (Rueckes et al., 2000). Each cell has three different states: standby (the circuit is idle, both logic inverters are blocked to be used), reading (the data has been requested, first logic inverter is used) and

writing (updating the contents, second logic inverter is used). An AC ring oscillator produces an oscillating AC voltage signal by means of the connection of three logical inverters in a ring, that is, the output of the last inverter is fed to the input of the first inverter. Such circuit has not statically stable solution, since the output voltage of each inverter oscillates as a function of time.

Digital circuits based on carbon nanotubes depends of the diameter of them, because it is directly proportional to the Schottky barrier height formed by the carbon nanotube and metal contacts of the source and drain terminals (Andriotis et al., 2006, 2007, 2008; Javey & Kong, 2009). In addition, larger diameters reduce the I_{ON}/I_{OFF} ratio and voltage swing, which is the key to achieve very high speed operation and high definition of the output signal, respectively. In the same way, diameters in the range of 1 to 1.5 nm have the highest performance in current drive, which allow us to reduce the delay and increase the short circuit power that are used during switching (Cao & Rogers, 2008). Given the demand of driving large capacitive loads, the carbon nanotube based transistors must be designed with complex architectures to support high current densities. This last implies the use of efficient methodologies for controlled dispersion of carbon nanotubes or the design of bundles with high-uniformity in diameter, chirality, and orientation. The first logic inverter based on graphene (Traversi et al., 2009) was operated to low power consumption and presents inability to the direct connection in cascade configuration due to the different output logic voltage levels.
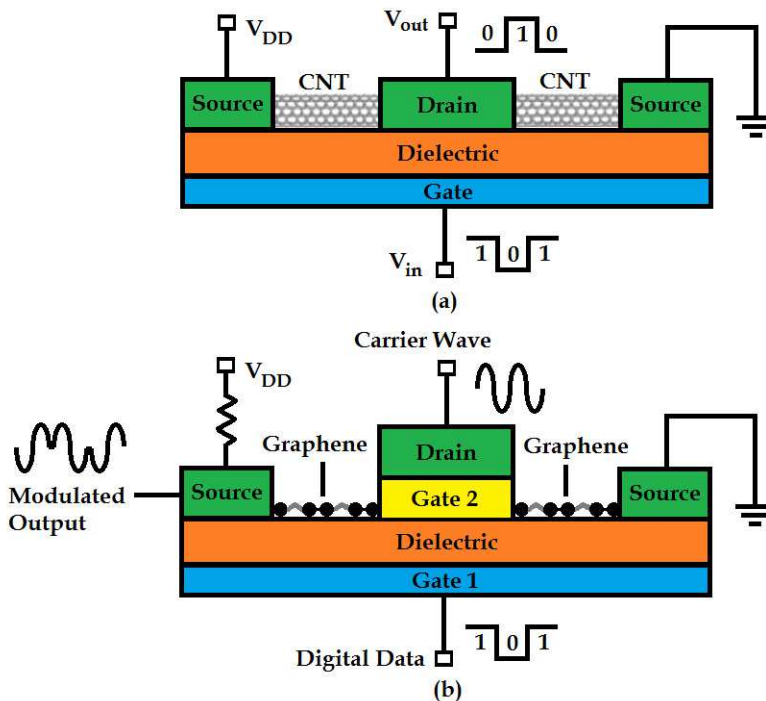

Fig. 10. VLSI circuits: (a) Carbon nanotube-based logic inverter, and (b) graphene-based digital modulator.

CNTs can be used to yield radio-frequency analog electronic devices such as narrow band amplifiers operating in the VHF frequency band with power gains as high as 14 dB. Examples of advanced analog circuits based on carbon nanotubes are resonant antennas, fixed RF amplifiers, RF mixers, and audio amplifiers. Hundred of devices, interconnected into desired planar layouts on commercial substrates are possible; thereby such systems can achieve complex functionality (Kocabas et al., 2008).

In RF applications, GFETs achieve high carrier mobility and saturation velocity (Lin et al., 2011). Mixers are RF circuits that are used to create new frequencies from two electrical signals applied to it. These signals have different frequency and when they are applied to the mixer, then are obtained two new signals corresponding to the sum and difference of the original frequencies. They are used to shift signals from one frequency range to another, for its transmission in RF systems such as radio transmitters. The radio frequency mixer based on graphene can produce frequencies up to 10 GHz, therefore, secure applications such as cell phones and military communications are feasible (Lin et al., 2011). Any limitations can be found for the use to full scale of graphene in VLSI circuits: different ohmic contact between materials, poor adhesion between metals and oxides, and high vulnerability to damage in the integration processes.

Among the main characteristics that graphene offers for VLSI Design are flexible, transparent material, and it operates to room temperature. Thanks to their electrical properties, the graphene is an ideal material to build more energy-efficient computers and other nanoelectronic devices. Nowadays, it is necessary to develop methods that allow us to separate graphene nanoribbons by a thin nonconductive material. Among the proposals that have been made are the use of one-atom-thick sheets of alloys of boron and nitrogen whose electrical behavior is nonconductive, and whose physical appearance is similar to graphene. The contents of such alloy must be controlled due to the geometrical arrangements that can be obtained.

Due to the ambipolarity (conduction of holes and electrons with equal efficiency), it is possible to design electronic devices (Vaillancourt et al., 2008; Xu et al., 2008). In Figure 10 (b), a digital modulator for communications circuits based on graphene is illustrated. This circuit is based on a graphene transistor including two gates: gate 1 controls the magnitude of current flowing through the transistor, and gate 2 controls the polarity of this current. The electrical operation of this circuit is similar to an electronic inverter, where gate 1 delivers a digital data stream as input, and it modulates such signal with the carrier wave applied to the drain to mix both signals, given place to a modulated signal.

6. Carbon nanotube based biosensors and gas sensors

Chemical sensors include a class of devices capable of detecting gas molecules or chemical signals in biological cells. Significant progress has been achieved in the detection of explosives, nerve agents, toxic gases and nontoxic gases due to the threat of terrorism and the need for homeland security. The biosensors and gas sensors based on one-dimensional nanostructures are very attractive, because they present high sensitivity and fastest response to the surrounding environment, thanks to their reduced dimensions and large surface-to-volume ratio (Sinha et al., 2006; Star et al., 2004; Wong et al., 2010).

Carbon nanotubes are promising candidates for designing gas sensors due to their excellent chemical and superficial properties derived of their chemical composition and high-aspect-ratio between its length and diameter, respectively. Levels as low as ppt (parts per trillion) or ppb (parts per billion) can be detected in comparison with their predecessors based on microsystems (MEMS) which could detect only ppm (parts per million). The basic structures used to design gas sensors are based on chemoresistors and FETs with one-dimensional nanostructures. An excellent biosensor or gas sensor is obtained when an appropriate control of the chemical and physical variables associated with the detection is presented. Therefore, the use of one-dimensional nanostructures improves the sensitivity, selectivity, stability, and response time (Balasubramanian & Burghard, 2006; Rivas et al., 2009).

This section analyses the different proposes of carbon nanotube based biosensors and carbon nanotube based gas sensors that were published in the last decade. This review discusses various design methodologies for CNT-based biosensors and CNT-based gas sensors as well as their application for the detection of specific biomolecules and gases. Recent developments associated with the topologies to design CNT-based chemiresistors and CNT-based field-effect transistors are highlighted.

Carbon nanotubes and graphene are technologically attractive to develop sensors due to four great characteristics: 1) each atom in its structure is physically accessible under any environment condition; 2) any perturbation in atoms can be electrically measured; 3) structural stability; 4) superior sensing performance at room temperature; and 5) tunable electrical properties (Wong et al., 2010). These characteristics have allowed the development of chemical, molecular and biological sensors (Oliveira & Mascaro, 2011; Wang, 2009).

Traditionally, pristine high-quality nanotubes are functionalized with functional groups to produce chemical or biochemical coatings (Wang, J., 2005; Zourob, 2010) or sites where very high sensitivity and selectivity to specific gases or to biochemical species is presented. Such gases or biochemical species can be detected by means of a change in electrical resistivity or capacitance presented in individual carbon nanotubes or bundles of them with the presence of this species. The change presented can be an increase or a reduction with respect to the value of the electrical parameter without the chemical or biochemical specie before mentioned (Chen, P.-C. et al., 2010). The chemical and biochemical sensors based on carbon nanotubes have even achieved sensitivities in the order of parts per billion to parts per million for specific gases or biochemical species depending of the molecule size and physicochemical properties (Bradley et al., 2003). Therefore, in any occasions it is necessary to add catalysts to improve the chemical activity during the chemical or biochemical detection (Cao & Rogers, 2009). In particular, the functionalization required by the biosensors regularly needs to favor the biocompatibility with the biological environment and realize the monitoring of information related with biological events and processes (Gruner, 2006; Ishikawa et al., 2009, 2010). In this manner, the biological species must be not affected by the biochemical interaction between the biosensor and the associated biological subject (Dong et al., 2008; Jia et al., 2008).

The basic construction blocks to design chemical or biochemical sensors based on carbon nanotubes can be divided into two different configurations: two-terminal CNT devices or three-terminal transistor-like structures. In the case of two-terminals devices, these can be modeled by an electrical resistor or an electrical capacitor (see Figure 11). In the case of

three-terminals, they are modeled by a bipolar junction transistor (BJT) or a metal-oxide-semiconductor field effect transistor (MOSFET), the latter being the most common for VLSI systems (Zhao et al., 2008).
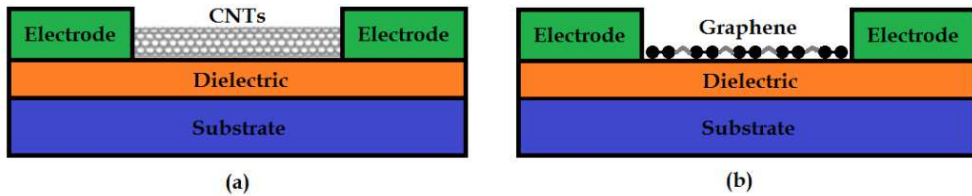

Fig. 11. Cross section of resistive gas sensors and biosensors: (a) sensors based on carbon nanotubes, and (b) sensors based on graphene.

The use of complex morphologies and structures based on composites containing carbon nanotubes and polymers in the design of gas sensors, has allowed the detection of polar and nonpolar gases making use of the change of dielectric constant to enhance sensitivity to minute quantities of gas molecules (Jesse et al., 2006; Mahar et al., 2007).

Graphene is exploited due to its inexhaustible structural defects and functional groups. These are advantageous in electroanalysis and electrocatalysis for electrochemical applications such as gas sensors and biosensors. Physisorbed ambient impurities by graphene such as water and oxygen can produce an effect similar to hole-doping and therefore a behavior similar to a *p*-type material (Traversi et al., 2009). Then, the graphene can be exploited as a sensing material for the design of chemical and/or biochemical sensors. When graphene is doped, well-identified localized states are added and band gap is introduced to the electrical properties generating an interesting alternative to design sensors (Barrios-Vargas et al., 2011).

The main changes to be realized in the optimization of performance of gas sensors are the search of methods which allow us to synthesize identical and reproducible CNTs will give place to gas sensors with high quality and high performance, independently of the type of chemical functionalization required for the detection.

7. Conclusions

In accordance with the review proposed here, CNTs are very attractive as base material to the design of components for VLSI Design. Chemical modifications of CNTs allow to the designer improve the selectivity of the electrical properties for the different applications. In the future, the use of hybrid materials where carbon nanotubes are involved will be a priority, given that the use of composite materials to design electronic devices, circuits and sensors requires multiple physical and chemical properties that a unique material cannot provide by itself. In the search for reducing electrical resistance presented by carbon nanotubes, different strategies have been developed to improve the efficiency of interconnection between devices based on carbon nanotubes and metallic electrodes used to lead the electrical bias to them. The implementation of digital and analog circuits with CNFETs or graphene nanoribbons will produce a great advance toward VLSI design using nanoelectronics. Still, hurdles remain as it was described in each section of the chapter.

8. Acknowledgement

9. References

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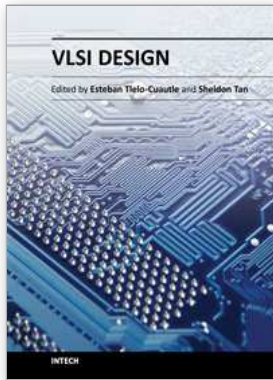
VLSI Design

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