Surface Physics of Semiconducting Nanowires

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Abstract

Semiconducting nanowires (NWs) are firm candidates for novel nanoelectronic
10 devices and a fruitful playground for fundamental physics. Ultra-thin nanowires,
with diameters below 10 nm, presents exotic quantum effects due to the con-
finement of the wave functions, e.g. broadening of the electronic band-gap,
deepening of the dopant states. However, although several reports of sub-10 nm
wires exist to date, the most common NWs have diameters that range from 20
15 to 200 nm, where these quantum effects are absent or play a very minor role.
Yet, the research activity on this field is very intense and these materials still
promise to provide an important paradigm shift for the design of emerging elec-
tronic devices and different kinds of applications. A legitimate question is then:
what makes a nanowire different from bulk systems? The answer is certainly
20 the large surface-to-volume ratio.

In this article we discuss the most salient features of surface physics and
chemistry in group-IV semiconducting nanowires, focusing mostly on Si NWs.
First we review the state-of-the-art of NW growth to achieve a smooth and con-
trolled surface morphology. Next we discuss the importance of a proper surface
25 passivation and its role on the NW electronic properties. Finally, stressing the
importance of a large surface-to-volume ratio and emphasizing the fact that in
a NW the surface is where most of the action takes place, we discuss molecular
sensing and molecular doping.

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1. Introduction

40 Semiconducting nanowires (NWs) are rod-like pieces of semiconductor with a characteristic diameter in the nanometer scale. In a strongly confined regime nanowires exhibit an exotic behavior that reveals their quantum nature: the band-gap can be tuned [1], the density of states is quantized [2], luminescence can be largely increased [3]. As a matter of fact some of the early publications [3,
45 4, 5, 6, 7] even refer to them as *quantum wires*, to highlight the exquisitely quantum nature of these physical effects.

Nowadays, nanowires have become a credible platform on which to build the next generation of electron devices [8]. They are always semiconducting, because of their aspect ratio they can be simultaneously used as the active region
50 of the device, e.g. the channel of a field-effect transistor, or to connect different devices [9], and –most importantly– they can be naturally integrated within the existing Si-based technology. Most of the applications where nanowires have shown superior performances, though, does not rely on those signatures of an

underlying *quantum world* that captivated researchers in the beginning. Indeed,
55 after the *gold rush* to the *thinnest nanowire ever* that yielded diameters in the
1-10 nm range [10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20], nanowires that are
routinely grown today have a characteristic transverse size that typically lies in
the 20-200 nm range where such quantum effects are at most negligible. Yet,
nanowires keep on being an active fertile ground for fundamental research and
60 advanced proof-of-concept devices, some of which outperform their conventional
planar counterparts [21].

In this article we review the surface physics and chemistry of group-IV semi-
conducting nanowires –focusing on Si NWs. We argue that the high surface-to-
volume ratio is one of the reasons for which nanowires are keeping the promise
65 to be nanomaterials that could drive innovation and that are an ideal test-bed
for fundamental research. The paper is organized as follows: in Section 2 we
review the factors that, at growth time, determine the crystallographic orien-
tations of nanowires and, consequently, the facet arrangement; the chemical
passivation of the nanowire surface and its effect on the nanowire properties are
70 discussed in Section 3; molecular doping and sensing are critically examined in
Section 4, where we review how molecular adsorbates can be used to tune the
nanowire conductivity to engineer electronic devices (Section 4.1) or chemical
sensors (Section 4.2); a brief overview of Surface Enhanced Raman Scattering
(SERS) in nanowire is also given in the second part of Section 4.2; we give our
75 conclusions in Section 5.

2. Surface reconstruction and facet arrangement

The most fascinating peculiarity of Si NWs is the possibility to vary their
properties by tailoring the size. As it has been demonstrated in many works
(see Ref. [22] and references therein), the reduction of diameter in Si NWs can
80 induce novel effects that have often a remarkable impact on both basic and ap-
plied research. The same happens with the study of NW surface structure. As
a matter of fact, for such nanoscale systems, the traditional distinction between

morphology –a term associated to a macroscopic property– and *structure* –a term which refers to a microscopic atomistic picture, focusing on the detailed atomic arrangement– cannot be applied anymore. In fact, due to the nanometric size, the two terms overlap and the atomistic structure may often determine the morphology of the wire [23]. When a nanowire is created the charge distribution as well as the atomic forces in play strongly change with respect to the bulk case [23]. Though it is always hard to find general rules for complex nanoscale processes, there are three main questions that one should address to understand the effect of the size on Si NWs structure: **i) Which is the ground state crystal phase of Si NWs?** The answer to this question is not obvious. In fact, while it is well known that bulk Si finds its lowest energetic configuration (at normal experimental conditions) in the diamond form, the organization of atoms at the nanoscale could in principle impose different atomic structures or novel phases (see for example the case of fullerene [24] and carbon nanotubes [25, 26]). **ii) How do surfaces reconstruct in a NW?** As shown by experiments [27], the growth of a NW is a complex process, in which substrates, interfaces and thermodynamics of atoms play a crucial role. This can easily suggest that a simply scaling down properties of bulk surfaces could not be enough to understand surface structure in such kind of materials. **iii) Can diameter affect also the growth direction of Si NWs?** This question is intimately related to the previous two. As a matter of fact, an important consequence of a particular atomic configuration and shape is the associated crystallographic direction (if it is possible to define it).

Crystal phase of Si NWs – The first experimental evidences of Si NWs growth rapidly indicated that these nanostructures are to a large extent crystalline. In particular it was found that they are rod-like structures constructed around a bulk Si single-crystalline core [22, 10, 11, 28, 29, 17, 15, 30]. This finding was mostly independent on the growth method, although it has been demonstrated that the quality of the crystal and the density of defects can depend on it [27]. All these experiments confirmed that, as can be intuitively expected, Si NWs crystallize in the diamond-like cubic structure as in their bulk

counterpart (see Fig 1).

115 It is also worth highlighting the possibility, predicted in 2005 by Kagimura
and co-workers [31] and recently demonstrated by experiments [32, 33, 34, 35,
36], to find evidences of wurtzite-type crystal in Si NWs. In group IV NWs
the formation of different crystal phases is a rather common phenomenon and
most nanowire growth schemes produces a rather random sequence of polytypes,
120 with a high density of various stacking defects. However, recent results go even
further by showing that the presence of hexagonal ordered phases as atomic
stacking in cubic domains (homojunctions) can be controlled [37, 38].

The experimental characterization of Si NWs structure (a bulk diamond core
which has a rod-like shape) was conducted in parallel with several theoretical
125 works –mainly based on ab initio and semi-empirical methods– whose main
objective was to theoretically determine the ground state phase of this class
of nanostructures. In 2005 Kagimura and co-workers [31] studied by means
of Density Functional Theory (DFT) calculations the structural stability of
three different types of phases for Si NWs (with diameter smaller than 2 nm):
130 diamond-type, fullerene-like and high-density structures (like simple cubic or
simple hexagonal lattice). Their results showed that, at subnanometer scale,
though the diamond structure is favored, all the other considered phases were
quite close in energy, pointing out the central role of surface effects. Similar
studies were conducted by Ponomareva *et al.* [39, 40] who, by employing gener-
135 alized Tight-Binding Molecular Dynamics investigated the stability of diamond,
clathrate or polycrystalline phase in Si NWs with diameter between 1 and 5 nm.
While the instability of the polycrystalline phase was clearly assessed, the au-
thors found the total energies of diamond and clathrate Si NWs comparable,
but with the diamond phase still favored, i.e. more stable.

140 ***Shape and surface reconstruction*** – Once it has been established that
the crystal phase of Si NWs is at a large extent diamond-cubic type, one would
like to be able to determine the shape of its cross section and the atomic re-
arrangement of the surface. As previously pointed out, at nanoscale the mor-
phology of the material and its atomic structure almost coincide and the role

145 of edges can be crucial [41]. The concept of free surface energy is hence funda-
 mental in order to understand which will be the ground state shape of the NW.
 In particular, from a strictly theoretical point of view, the equilibrium shape of
 a solid, at fixed volume and chemical potential, is a complex polyhedron which
 minimizes the total free surface energy of the material (also known as Wulff
 150 plot [23]). The first experimental observations with transmission electron mi-
 croscope (TEM) of NWs structures [10, 11, 28, 29, 17, 15, 30] evidenced that
 Si NWs surfaces (grown with both top-down and bottom-up approaches) are
 usually well faceted, with well defined lattice planes that determine specific
 cross sections. In particular, it has been demonstrated [17, 15] that the cross
 155 section of Si NWs grown along the $\langle 110 \rangle$ crystallographic axis is hexagonal with
 well developed facets that correspond to the low free energy (111) and (100)
 planes (which is consistent with equilibrium shape calculated by the Wulff plot
 approach [42] and with the first principles calculations of Chan *et al.* [43]). On
 the other hand $\langle 111 \rangle$ oriented NWs are presented as bounded (110) facets in
 160 the hexagonal shape [44]. It is worth to note that both theoretical calculations
 and experiments indicate that hydrogen passivation of dangling bonds does not
 modify the morphology in a sizable way [45], but can induce sets of dimers with
 SiH species [46, 47].

The effect of diameter and edges on the surface reconstruction and on the
 165 thermodynamic equilibrium shape of NWs has also been the subject of an in-
 tense theoretical investigation from which the difficulty to figure out general
 rules at the ultimate nanoscale limit [22] emerged. In this context the contribu-
 tion of Zhao and Yakobson has been very important [48]. They reformulated the
 Wulff approach for nanowires, shedding light on the fact that while in solids and
 170 nanoparticles the interaction between edges is usually negligible, the same does
 not happen in NWs for which the Wulff energy must include the term deriving
 from the matching of adjacent facets [48]. Within this formalism they found
 that the most stable NW at diameters less than 6 nm is a pentagonal cross
 section wire with a 5-fold symmetry (that is polycrystalline) followed in energy
 175 by a single-crystal hexagonal wire. Although the predominance of pentagonal

cross-section does not coincide with the trend observed in most of the experiments [10, 11, 28, 29, 17, 15, 30], evidences of a pentagonal cross section NWs reported in the experimental work of Furuya and colleagues [49] are worthy of note, although we are not aware of other reports of these structures.

180 In 1998 Ismail and Arias [50], by applying ab initio simulations to $\langle 100 \rangle$ Si NWs, showed that at small diameters NWs facets undergo a size-driven transition from a 2×1 to a $c(2 \times 2)$ reconstruction. This transition results from the balance between bonding along the edges and the surface energy of the facets. In the same direction was the theoretical work of Cao *et al.* [51], who demon-
185 strated that, driven by the combination of surface reconstruction and intercorner interaction, sharp corners structures can exist for NWs. The analysis of $\langle 100 \rangle$ reconstructed NWs has been conducted by Rurali and Lorente [52, 53, 54], who, by employing DFT calculations, demonstrated that in absence of proper passivation the Si NW surface strongly reconstructs forming a series of buckled dimers
190 noticeably affecting the electronic structure (a similar study for the $\langle 110 \rangle$ was conducted by Singh *et al.* [55]). Moreover, the authors showed that for $\langle 100 \rangle$ wires faceting favors the formation of (100) planes instead of (110) ones.

All the above considerations are referred to the *primary faceting* [56] which is the first level of the description of the surface faceting and that represents
195 the overall shape of the wire cross section. The *secondary faceting* or more complex faceting phenomena (like sawtooth faceting [57]) are beyond the scope of this review and we refer the reader to more specific works (see for example Refs. [56, 57, 58, 59]).

Crystallographic orientation – As clearly pointed out by Schmidt *et al.* [27] the reduction of the nanowire diameter has two main effects on its
200 structural properties which are strictly correlated: **i)** first, as is shown in the previous paragraphs, it influences the crystal phase, the final cross section shape and the surface reconstruction, **ii)** secondly, due to thermodynamic stability arguments, it can be responsible of a change of the crystallographic orientation
205 during the growth process. Both these aspects are intimately related and have an enormous importance for the NWs physics because they will affect electronic

and electrical properties [60, 27, 61, 62].

Assuming a vapor-liquid-solid (VLS) mechanism (the most common used method to obtain Si NWs [22]), the effect of the diameter on the growth direction of a NW can be easily explained by looking at the model presented in Figure 2.

As is known, the VLS growth implies that gas silane molecules diffuse into the silicon-gold eutectic droplet, segregate at the liquid-solid interface and precipitate to build the Si NW crystal. Since the process takes place at the solid-liquid interface, then the growth direction will be influenced by interface properties [63]. Roughly speaking, the most preferred direction of growth will be the one that minimizes the total free energy of the interfaces. Among the others, there are two dominant energetic contributions that have to be considered if one approaches the study of the thermodynamics of this process: **i)** the first is the interfacial energy itself, which can be obtained by multiplying the interfacial surface A for the corresponding liquid/solid interfacial tension σ_{1s} , **ii)** the second is the silicon surface tension contribution from the edge of the interface (which is proportional to the circumference L , to the the surface silicon tension σ_s and to the width of the interface on the silicon side Δz (of the order of 1 nm [63]). If one introduces a geometrical parameter a (function of A , L and of the radius of the wire r), the specific free energy f (per unit of circumference L) of a $\langle 111 \rangle$ oriented Si NW can be expressed as:

$$f = \Delta z \cdot \sigma_s + a \cdot \sigma_{1s} \cdot r \quad (1)$$

An analogous expression can be derived for the interface energy of a $\langle 110 \rangle$ oriented Si NW:

$$f' = \Delta z \cdot \sigma'_s + a' \cdot \sigma'_{1s} \cdot r \quad (2)$$

where a' , σ'_s and σ'_{1s} are the corresponding parameters for a $\langle 110 \rangle$ oriented system. All the quantities contained in both the equations can be evaluated by combining experimental results and theoretical approaches [63] (Young's equation and Wulff theorem). Their values are shown in Table 1. One can easily

$\langle 111 \rangle$ orientation	$\langle 110 \rangle$ orientation
$a=0.43$	$a'=0.39$
$\sigma_{1s}=0.62 \text{ J} \cdot \text{m}^{-2}$	$\sigma'_{1s}=0.62 \text{ J} \cdot \text{m}^{-2}$
$\sigma_s=1.53 \text{ J} \cdot \text{m}^{-2}$	$\sigma'_s=1.28 \text{ J} \cdot \text{m}^{-2}$

Table 1: Summary of parameters contained in Eq.1 and Eq. 2 [63].

observe that $\sigma_s > \sigma'_s$ (due to the fact that a $\langle 111 \rangle$ oriented nanowire presents an hexagonal shape with six $\langle 110 \rangle$ surface planes, while for a $\langle 110 \rangle$ oriented NW
235 two of the six surface planes are $\langle 100 \rangle$ and four are $\langle 111 \rangle$ planes [63]) and that
 $a'\sigma'_{1s} > a\sigma_s$.

In Figure 3 the plot of the specific free energy for both $\langle 110 \rangle$ and $\langle 111 \rangle$ is reported.

Looking at the figure one can easily deduce that there is a critical value of
240 the NW radius r_c for which the curves intersect. This critical radius (that is
of the order of 10 nm, but that strongly depends on the ratio of interfacial and
surface tensions) finds its analytic form in the following equation:

$$r_c = \Delta z \frac{\sigma_s - \sigma'_s}{a'\sigma'_{1s} - a\sigma_{1s}} \quad (3)$$

This elegant model figures out which is the role of the diameter on the growth
direction of a Si NW. For small diameters the most preferred crystallographic
245 direction will be the $\langle 110 \rangle$ because the system will have tendency to minimize
the surface energy of the wire (see Eq. 1 and 2 and Table 1). On the other hand,
at larger diameters, the main contribution to the free energy will be represented
by the liquid-solid interfacial energy and so the preferential growth direction will
be the $\langle 111 \rangle$. The origin of this difference is due to the different scaling behavior
250 of distinct energetic contributions: the one of the side faces is proportional to
the diameter d (through the circumference L) while the liquid-solid interface
tension and the Si volume contribution scale with d^2 [27]. These results have
been confirmed by the first-principles calculations of Rurali *et al.* [54] and Migas

et al. [45]. Furthermore, in 2006 Wang and co-workers [64] inserted these free
 255 energies considerations in their nucleation thermodynamic model and confirmed
 that the growth orientation of a Si NW changes from the $\langle 110 \rangle$ to the $\langle 111 \rangle$ be-
 yond a critical diameter of 25 nm. In the same direction and in good agreement
 with previous results, in 2009 [65] an atomistic-scale model that combines that
 of Schmidt *et al.* [63] and the one of Wang and co-workers [64] has been pro-
 260 posed. Moreover, DFT formation energies calculations [46], showed that, for
 diameters smaller than 3 nm, the $\langle 100 \rangle$ growth direction is energetically less
 favorable than the $\langle 110 \rangle$ and the $\langle 111 \rangle$ directions due to the lowest symmetry
 and the greater strain.

The above mentioned models are able to interpret and explain a huge amount
 265 of experimental results on the growth of Si NWs that have been obtained for
 almost fifteen years (see Ref. [22] and references therein).

The most noticeable work in this context is the one of Wu and co-workers [17],
 reporting a structural characterization of a large number of Si NWs grown us-
 ing Chemical Vapor Deposition (CVD) VLS process using gold catalyst. They
 270 considered 10, 5 and 2 nm diameters nanoclusters and $\langle 110 \rangle$, $\langle 111 \rangle$ and $\langle 112 \rangle$
 growth directions as shown by the High Resolution TEM (HRTEM) images of
 Fig. 1.

According to the thermodynamic model developed by Schmidt *et al.* [63],
 they found that wires with diameters between 3 and 10 nm prefer to grow
 275 along the $\langle 110 \rangle$ direction, those with a diameter between 10 and 20 nm show
 a predilection for the $\langle 112 \rangle$ direction while most of the NWs with a diameter
 between 20 and 30 nm are $\langle 111 \rangle$ oriented. The frequency of these observations
 is accurately reported in Fig. 4, in which the distributions of samples with a
 specific growth direction is plotted for the three class of diameters.

280 The authors explained these results with interfacial and surface energy ar-
 guments [17, 66], which have been then formalized in the thermodynamic model
 of Schmidt *et al.* [63]. Interestingly the $\langle 112 \rangle$ growth direction which has been
 found for intermediate diameters (10 and 20 nm) can be considered as 'transi-
 tional' direction between the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions since the (112) plane is

285 a stepped plane between (111) and (110) planes [66, 67].

The strong dependence of VLS growth direction on the diameter in Si NWs does not set, however, which member of the crystallographic family will be favored. In fact even if a growth type is ensured ($\langle 110 \rangle$, $\langle 111 \rangle$ or $\langle 112 \rangle$) some wires might still choose one of the equivalent inclined directions of that crystallographic family (i.e. they will not necessarily grow perpendicularly to the
290 substrate. This topic is beyond the scope of the present review and has been already carefully addressed in several works (see for example Ref. [68]).

3. Surface passivation

Unfortunately, when it comes to device engineering, the high chemical reactivity of a nanowire surface can be detrimental to its performance. Localized
295 defects can easily act as surface traps of free carriers, decreasing dopant efficiency, and the recombination of charge carriers through surface states can reduce diffusion lengths. More in general, a surface with an uncontrolled morphology and electronic structure leads to a device whose properties are, in the
300 best case scenario, uncontrolled, but more likely severely degraded.

Surface passivation [69, 70] –any chemical process aimed at making the surface *passive*, i.e. virtually inert– is an unavoidable fabrication step of any nanowire-based device that has the goal to compete with standard planar CMOS technology. Passivation of a nanowire surface is naturally obtained by oxidation,
305 i.e. the growth of a tiny SiO_2 sheet around the wire, which occurs spontaneously as soon as the nanowire is exposed to air. This basic kind of surface passivation does the job, but there are still margins for improvement. The first, obvious upgrade is having the oxidation process develop under controlled conditions, tuning the temperature and the oxidation time. Yet, this can keep on being
310 challenging because of the small dimension of the nanowire and the different growth rate of the oxide on the different facets. And interface defects are present in non-negligible concentrations. For instance Baumer *et al.* [71] showed that $3.3 \times 10^{16} \text{ cm}^{-3}$ dangling bonds or P_b centers are found at the oxide interface

in a 10-15 nm Si NW.

315 A possible path to increase the quality of the Si NW-oxide interface is carrying out a H_2 ambient annealing, which leads to dangling bond release from the wire surface and stress relaxation [72]. Dan *et al.* [73], on the other hand, reported in situ passivation with a thin a-Si layer, achieving an almost 2 orders of magnitude reduction of surface recombination, which results in an increase of
320 the carrier diffusion length and lifetime by 1 and 2 orders of magnitude, respectively. Hydrogenated amorphous silicon (a-Si:H) was used by Yang *et al.* [74] instead, resulting in an improved open-circuit voltage.

Ozone oxidation has also received some attention for the low temperature, defect-free oxidation of Si NWs. In bulk Si the O_3 -grown oxide exhibits improved
325 interface and electrical characteristics over a conventionally dioxygen-grown oxide [75] and its use is started to be explored in nanowires, like in the work of Fukata *et al.* [20] (see Fig. 5). Interestingly, in this work the oxidation time is also used as a control parameter to obtain sub-10 nm Si NWs.

Due to the improved electrostatic control of the gate, the use of high- κ oxides
330 such as HfO_2 has proven to play a crucial for the engineering of nanoelectronics devices with cutting edge performances, such as the transistor based on a SiGe core-shell NW reported by Xiang *et al.* [21]. Surface passivation with a HfO_2 layer results in a suppression of the non-radiative recombination rates and the sensing stability of Si NW arrays [76].

335 Thanks to its simplicity, reliability and stability, oxide passivation, in its various form, is the standard way to passivate surfaces in virtually all current nanowire applications. Alternative passivation strategies have been explored in an attempt to obtain ultra-clean surfaces, as interface defects are certainly the weakest point of oxidized surfaces. This goal can be fulfilled, at the expense
340 of a long-term stability, with hydrogen passivation. Hydrogen passivation is conceptually the simplest way to passivate a Si surface, where each monovalent passivating agent –a H atom– individually passivate each Si dangling bond. A simple way to obtain H passivation consists in the use of an aqueous HF etching of the oxidized silicon surfaces, which results in the removal of the surface oxide

345 and leaves behind silicon surfaces terminated by atomic hydrogen. This process,
 well reported for planar Si wafers [77, 78] is now routinely applied also to Si
 NWs. Importantly, it leaves the morphology of the semiconducting nanowire
 intact [28], allowing inspection of the underlying atomic-scale structure. Indeed,
 this is what Ma *et al.* [15] did, achieving the first atomically resolved scanning
 350 tunnelling microscope (STM) images of the surfaces of Si NWs as thin as 1.3 nm
 –the thinnest Si NW reported to date. This unprecedented resolution allowed
 them to unambiguously identify the hydrogen-terminated Si(111) 1×1 and
 Si(001) 1×1 surfaces corresponding to SiH₃ on Si(111) and SiH₂ on Si(001),
 respectively.

355 Although these hydrogenated nanowire surfaces have been reported to be
 more stable in air than their planar counterparts [15], they keep on being un-
 suitable for device fabrication where **i)** an oxide layer is often needed by the
 device design and **ii)** much longer stability lifetimes are requested. Yet, this
 approach has been followed by many groups working in fundamental studies of
 360 the physics of semiconducting nanowires and it is a precious tool every time that
 state-of-the-art characterization measurements –whether of structural [17, 57],
 optical [79] or electronic properties [80]– are in order.

An oxide-free route to nanowire passivation would be of great interest [81],
 because it would reduce the interface defect concentration, avoiding the related
 365 interface states that are highly detrimental of any the performances of any de-
 vice with a large surface-to-volume ratio, such as those based on nanowires. As
 we said, freshly prepared H-terminated Si NWs have low surface recombination
 velocities, but are not stable in air [82] or in aqueous solutions [83] for more than
 a few hours. An idea to circumvent the poor stability of hydrogen passivation
 370 would be replacing the Si-H bond with a stronger, more stable bond. The first
 important step in this direction was taken by Haick *et al.* [84], who reported
 CH₃ passivated Si NWs with no intervening oxide, with good atmospheric sta-
 bility, high conductance values, and low surface defect levels. These nanowires
 were then used for the fabrication of air-stable Si NW FETs. Just like in the
 375 case of H termination, passivation of surface states via Si-C bonds decreases the

probability of electron-hole recombination, thus increasing the carrier mobilities. Interestingly, the enhanced oxidation resistance under ambient conditions of methyl terminated Si NWs turns out to be even higher than equivalent 2D Si(100) and Si(111) surfaces with similar coverage [85]. These promising initial efforts were culminated by the work of Bashouti *et al.* [86], where chemical passivation of Si NWs with increasingly long and complex alkyl chains was demonstrated. Successful oxide-free passivated Si NWs were obtained using $\text{CH}_3(\text{CH}_2)_{(x-1)}$ molecules, with $x = 1 - 6$ (see Fig. 6). An instructive walk-through on hydrosilylation, the insertion of an alkene or alkyne into a surface Si-H bond to obtain such Si-C bonds is given by Buriak *et al.* [87].

Some popular choices for planar solar cells, such as a-SiN_x:H [88, 89, 90], Al₂O₃ [91, 92, 93] and the SiO₂/SiN_x bilayer [94] have been recently explored for nanowires in an interesting comparative study by Dalmau Mallorquí *et al.* [95]. They achieved the highest efficiency with the SiO₂/SiN_x stack.

The vast majority of theoretical studies consider hydrogen passivation, mostly because of its simplicity and because it is the passivation that requires the minimum number of atoms, thus making the calculation computationally lighter [22]. Although some studies have approached oxide passivation by terminating the dangling bonds with a OH group [96, 97, 98] or by bridging two Si atoms with dangling bonds on a {100} facet with an oxygen [99], a realistic description of a-SiO₂ is much more challenging, as it requires accounting for the disordered structure of the amorphous oxide. Electronic structure and transport calculations at the first-principles level that include a quasi-amorphous SiO₂ shell were reported by Koleini *et al.* [100]. They combined classical and DFT molecular dynamics calculations to create the Si/SiO_x core-shell structure and found that the conductance of the oxidized wires is lower with respect to the case of crystalline, H-passivated wires. They ascribed such a decrease to the structural distortions induced by the oxidation and to the presence of electronegative sites at the Si/SiO_x interface [100].

A very appealing feature of nanostructures is that is often possible tuning their electronic properties by controlling some of the structural parameters or

the composition. These effects have been widely discussed in nanowires, particularly for what concern the sensitivity of the electronic properties to changes in diameter, growth orientation, and composition [22, 101]. Several theoretical
410 studies showed that a similar effect can be achieved by controlling the chemical properties of the passivating shell. Aradi *et al.* [97] compared H and OH passivation in $\langle 110 \rangle$ and $\langle 112 \rangle$ Si NWs, showing that a higher electronegativity of the passivating agent results in a narrower energy gap. Similar results were obtained by Nolan *et al.* [96], who also considered NH_2 , tracing the origin
415 of the reduced band-gap to the hybridization between the Si 3p and O/N 2p states in the valence band edge. The work by Ng *et al.* [47] studied OH and F passivation, considering both full and partial substitution (in the case of partial substitution some of the dangling bonds are H terminated). Leu *et al.* [102], went a step further and, given a passivating species, also studied the dependence
420 on the relative coverage, with respect to an all-H passivated nanowire. They studied $\langle 111 \rangle$, $\langle 110 \rangle$, $\langle 100 \rangle$, and $\langle 112 \rangle$ Si NWs with a passivating shell made of A_xH_{1-x} atoms, where A is one of the halogens Cl, Br, and I. The sensitivity to the chemical nature of the passivating elements is stronger, as expected, for thin nanowires and for coverages above 50%. They found that the more weakly
425 interacting species led to a larger band gap reduction, as the surface states were not pulled out of the midgap region by a strong binding.

4. Surface physics and chemistry

A surface is what makes a nanowire what it is: a confined quasi-one dimensional system whose properties differ from its bulk counterpart. In this section
430 we will show that the surface is a privileged place for local chemistry, broadly speaking the adsorption of molecules, that can modify in a controlled way the electronic structure and the conductivity of a nanowire.

At the same time, however, even when no external chemical agent enters the picture, the mere existence of the surface alters the properties of the nanowire.
435 Diarra *et al.* [103], for instance, showed that the ionization energies of dopants

are larger than in bulk as a result of the different way electrical charges are screened, even for thick wires where the effects of quantum confinement are weak. It has also been shown that the band offset at an axial interface is different than in planar interfaces and is strongly influenced by the nature of
440 the surfaces and of the dipoles that develop there [104].

These topics have been reviewed elsewhere [22, 101] and we refer the interested reader to the original publications [103, 105, 104]. In this section we focus on the role of adsorbates to tune the electrical conductivity of nanowires for applications in the field of sensor or to achieve electrical doping beyond the
445 conventional use of ionized impurities.

4.1. Molecular doping

A semiconductor is a material which is *about to conduct* and where, therefore, conductivity can be tuned. The well-known way to perform this task is impurity doping [106]. Electronic device design, in the end, relies on the juxtaposition of
450 regions of a semiconductor material with different doping characteristics.

Impurity doping in nanowires can be troublesome. An extensive discussion of the related issues can be found elsewhere [22] and here we limit ourselves to a brief summary of the reasons that can be detrimental to doping efficiency, without entering in details.

- 455 • **Surface segregation**—Impurities prefer surface and subsurface substitutional locations where they can more easily release the strain induced. There, they can be passivated and become electrically inactive [107, 108].
- **Non-uniform dopant concentration**—The competition between catalyzed and non-catalyzed dopant incorporation leads to radial [109] and
460 axial [110] disuniformities in the impurity concentration.
- **Quantum and dielectric confinement**—As is well known, confinement pushes the otherwise shallow dopant levels down into the midgap region where they cannot be thermally activated [103, 111].

- **Variability of the performances**—Achieving typical impurity concentrations often means relying on the addition of very few dopants [112]. This fact, together with the intrinsic variability of the scattering properties of individual dopants [113, 114], has dramatic consequences on the variability of the performances of nanowire-based devices [115, 116, 112].
- **Dopant aggregation**—The energy gain deriving from the formation of a bound state between two nearest-neighbor dopants has to compete with the energy cost that results from the strain accumulated around the dopant-pair defect. As in nanowires strain is more easily released, the formation of dopant-passive complexes is more likely than in bulk [117].

Several of the drawbacks of conventional impurity doping can be in principle circumvented by means of molecular surface doping (sometimes also called transfer doping), which consists in adsorbing a suitable molecular species – either as isolated molecules or as monolayers– on the nanowire surface. If the adsorbed molecule has the tendency to donate or accept charge carriers to/from the nanowire and the nanowire is not too thick, effective doping can be achieved.

Within this doping approach surface segregation is no longer an issue: the nanowire surface is where the molecules are supposed to be at and a molecular species is only considered as dopant if it can transfer charge in that particular configuration. A uniform axial profile is also easier to achieve, because doping is carried out *ex-situ*, after nanowire growth, and dopant aggregation does not necessarily lead to electrical inactive compounds; the best example of these two features is the reported doping efficiency of some molecular monolayers [118, 119]. The sensitivity of the energy of the molecular orbitals with respect to the nanowire band-edges upon confinement is still under scrutiny, though it is likely prone to strong variations just like conventional impurity doping. Finally, the variability deriving from the strong dependence of the impurity scattering cross-section on their local environment is virtually eliminated, because less adsorption configurations exist and the associated scattering in the ballistic regime is almost negligible [120].

Several experimental results concerning the variation in the conductivity
 495 upon gas adsorption in mesoporous Si have been reported in the early 2000s.
 Porous Si, where electrochemical attack of a Si sample yields a disordered net-
 work of single-crystalline Si wires, is a very simple and cheap alternative to
 bottom-up Si nanowires and, due its sponge-like structure, is particularly suited
 for gas adsorption experiments. The donor character of NH_3 was soon pointed
 500 out in many experimental studies [121, 122, 123, 124]. The doping mechanism
 was later revealed by first-principles calculations to simply rely on a shallow
 molecular orbital [125, 126], whose carriers can be thermally activated into the
 nanowire conduction band, analogously to textbook impurity doping. The same
 group worked intensively also on NO_2 adsorption, which at first sight works as
 505 an acceptor [127, 128, 129, 130, 124], but in that case the reason for the observed
 increase in the conductivity was not as clear as it was with ammonia. It turns
 out that NO_2 is not genuinely doping the semiconductor, but rather reactivates
 sub-surface passivated B atoms that remain buried, next to the surface, as a by-
 product of the etching process [131] Therefore, NO_2 is electronegative enough
 510 to take the electron of the surface dangling-bond, reactivating the passive B,
 but not enough to create a hole in the valence band [125].

A more recent study focuses on the different mechanisms behind doping of Si
 nanowires upon molecular adsorption of two paradigmatic Lewis bases: pyridine
 and ethanol. Pyridine injects carriers from a shallow molecular level similarly
 515 to NH_3 . Ethanol, on the other hand, alters the dielectric screening conditions,
 allowing the reactivation of preexisting electrically passive impurities, just like
 NO_2 does with passive sub-surface B atoms. A similar case was discussed by
 Timoshenko *et al.* [132], who used a simple model based on dielectric mismatch
 to show that the activation energy of a boron acceptor decreases from 105 to
 520 30 meV when the media dielectric constant increases from 1 (vacuum) to 25
 (ethanol). Therefore, pyridine and similar molecules, such as ammonia and
 triethylamine ammonia behave like a conventional *n*-type dopant, inducing a
 free carrier concentration proportional to the number of adsorbed molecules.
 Ethanol (acetone or water) can act indirectly as a donor or an acceptor. The

525 nature of the doping –*n*- vs *p*-type– and the carrier concentration upon ethanol
adsorption depend on the type and concentration of the impurities that are
reactivated.

A remarkable demonstration of surface doping was also provided by Guo
et al. [133], who reported hole and electron doping as a results of the adsorp-
530 tion of H₂O and NH₃ molecules and discussed the role of H-termination of
the surface dangling bonds on the NW carrier concentration. The same group
extended this study one year later, proposing an electron-transfer-dominated
surface doping model to rationalize their results with Si NWs, e.g. *p*-type dop-
ing of H-passivated wires, sensitivity to the pH value of an adsorbed aqueous
535 layer [134].

4.2. Chemical sensing with NWs

The extraordinary potential of Si NWs surface properties has been concreted
in a lot of technological applications in which these nanostructures act as back-
bones for sensing devices. In its most general definition a sensor is a device
540 that converts a detection event or a change in the environment into a measur-
able signal. Si NWs, pristine or specifically functionalized, can act as sensing
device or components for the transduction of biological and chemical quanti-
ties into physical signals, mostly electrical or optical. As clearly explained in
Ref. [135, 136, 137], traditional microelectronic sensors, among the other qual-
545 ities they must possess –small dimension, low cost, low power consumption
and compatibility with Si microelectronics– can be characterized by three main
factors: **i)** the receptor function, **ii)** the transducer function and **iii)** the util-
ity [135]. The first factor is related to the capability of the sensor to interact
with the biological or chemical species to be detected. The transducer function
550 is instead related to the easiness of the signal conversion, i.e. how the sensor
material can convert the external signal into a variation of its intrinsic prop-
erties. The utility function takes usually into account kinetic effects related to
the accessibility of molecular or gas species into the sensor surface. Interest-
ingly, since the beginning of 90s several experimental studies (see for example

555 Ref. [138, 139, 140]) demonstrated that all the sensor performances (in particular the sensitivity, that is usually defined as the ratio between a detectable output signal to the input parameter) can be drastically improved by reducing the characteristic size of its component materials. As a consequence, research on materials for sensors has been focused on finding original ways to produce
560 novel sensors based on nanostructures and nanomaterials.

Today Si NWs represent a viable solution to realize high-performance chemical and biological sensors due their unique properties and their potential for fabrication into high density nanoscale devices with low power consumption [141]. In the last years this topic has been the subject of an intense research work [141,
565 142, 143, 144, 145, 146, 147, 148, 135, 149] whose main directions are not easy to be defined. However, the reasons for this huge interest and for the predominance of Si NWs in this field with respect to other nanostructures can be classified as follows: **i)** their large surface-to-volume ratio and their nano-size of the order of the Debye length. As pointed out in the previous sections, NWs
570 have two dimensions that are usually less than 25 nm. This makes surface effects dominate and induces a strong increase in the sensitivity of the material, i.e. in its capacity to convert the interaction with the biological or chemical species into a variation of its electronic/optical properties, **ii)** their excellent structural properties and their easiness of fabrication. Si NWs can be fabri-
575 cated with a lot of different large scale techniques which always produce high crystalline, stable and reproducible semiconductor materials (in contrast to carbon nanotubes) that can be easily integrated into current Si technology, **iii)** the possibility to easily functionalize their oxide surface. As discussed in Section 3, functionalization is an important aspect of Si NWs sensing as chemical or bio-
580 logical modification is often a fundamental requirement for their operation and biocompatibility [141, 142, 143, 144, 145, 146, 150]. Depending on the working principle of the sensor, metallic, covalent or non-covalent functionalization of Si NWs [141, 142, 151] have been proposed always assuming particular importance for the efficiency of the device, **iv)** the cylindrical 1D geometry that together
585 with the small size induces electrical and optical properties that can be strongly

influenced by minor perturbations. Indeed compared to 2D films in which the electrostatic changes due to the detection stay localized on the surface of the device, in Si NWs the modification of the surface potential creates an accumulation or depletion charge space region that covers also the *bulk* of wire (due to the small cross section area).

All things considered, it is clear that Si NWs can provide novel and unexplored sensing modalities. High label-free detection sensitivities of biomolecules, single molecules detection as well as chemical detection of various compounds have been reported [141, 142, 143, 144, 145, 146, 147, 148, 135, 152, 153, 154, 155, 156, 157]. Although, due to the huge amount of articles, it is beyond the scope of this review to describe in detail all the specific works, a simple and straightforward distinction among Si NWs sensing devices can be done by classifying them on the basis of their working principle.

Electrochemical sensors – The basic physical mechanism governing the working principle of electrochemical Si NW based sensors is a standard field-effect as employed in a conventional Field Effect Transistor (FET). As is well known, the mode of operation of a classical planar FET is based on the variation of conductance of the semiconductor (usually p-type silicon) between source and drain by a third gate capacitively coupled by a dielectric layer [158, 144] as illustrated in Fig. 7. This operation concept made such kind of devices ideally suited for the detection of chemical and biological species, as demonstrated by the development of ion sensitive field-effect transistor (ISFET) [159]. Indeed the electric field induced by the binding of the chemical or biological species to the gate dielectric changes the conductance of the Si channel and provides the switching mode operation. However, despite its great potential, this approach was rapidly abandoned because of its low sensitivity.

On the other hand, the same underlying mechanism can be successfully reproduced by developing Si NWs based FETs [160], as illustrated in Fig. 8.

Through the exploitation of the excellent electrical performances characteristics of Si NWs FETs [161, 162, 163, 164, 165, 160, 166] in 2001 the Lieber group paved the way to this new research line by reporting the detection of

different chemical and biological species in solution with extremely high sensitivities. This novel device concept (first realized with carbon nanotubes [167]) is simpler with respect to ISFETs because it is the nanowire itself that can act as
620 conductive channel [147]. By looking at the scheme of Fig. 8 it is clear that the increased surface charge sensing effect occurs because of the reduced dimensions of the wire (that can be as small as 2-3 nm) that generate a large surface/volume ratio [168]. When a molecule or biomolecule links to the NW surface, depending on the surface orientation [169], it causes a variation of the surface potential
625 which induces an accumulation or depletion of charges. This charge spatial variation, due to the reduced size of the system, directly affects the *bulk* properties of the wire, such as its electronic structure and its electrical conductivity. For example, in a p-type Si NWs, positive charge carriers on the surface can cause an electron accumulation in the *bulk* region of the wire hence reducing the electrical current between source and drain. On the other hand, negative charges
630 on the surface can induce hole accumulation [147, 135]. The described physics can be analytically converted in the following formula [135, 152]:

$$\frac{\Delta G}{G} = \frac{\Delta n_s}{n_0} \quad (4)$$

in which the variation of conductance before and upon molecular binding on the surface (ΔG) is proportional to the variation in charge carrier concentration
635 due to the surface carrier variation (Δn_s). Noticeably, it has been demonstrated that reducing the Si NW cross section from 200 nm to 50 nm can give a twenty-fold increase of device sensitivity [170]. However, a word of caution is in order here, because several works [171, 172] have also shown that the most appropriate way to improve device performances, and hence sensitivity, is to optimize the
640 signal-to-noise ratio relative to the size and shape of the sensor.

As mentioned before, the first experimental reports of Si NWs FETs for biological and chemical detection dates back to the work of the Lieber's group in 2001 [143]. By functionalizing B-doped Si NWs surface with 3-aminopropyltriethoxysilane (APTES), antigen, biotin and calmodulin, high sensitivity detection (down to

645 picomolar range) of pH level, streptavidin, antibody and calcium ions respectively was reported [143, 135]. The underlying concept of these experiments relies on the surface functionalization and can be pointed out by describing the case of pH sensing. The functionalization of the oxide Si NW surface with APTES can serve as an optimal substrate for reaction of protonation and de-
650 protonation by exploiting the surface NW potential changes before and upon chemical detection, as illustrated in Fig. 9(A).

The APTES terminating groups -NH_2 and SiOH- have different dissociation constants and can switch the charge accumulation in the NW when the proton concentration is changed. In particular, at low pH, the NH_2 group is protonated
655 to NH_3^+ and acts as a positive gate which depletes hole carriers in the p-type NW thus decreasing the conductance. On the other hand, at high pH levels, SiOH is deprotonated to SiO^- and an increase in the conductance is observed. The resulting linear dependence [shown in Fig. 9(B)] observed was then theoretically explained by the model of Nair and Alam [173]. All the cases studied in the
660 work of Cui *et al.* [143] demonstrated that the sensing mechanism was the result of a field-effect equivalent to applying a voltage using a gate electrode [144] and that the functionalization was responsible for the high selectivity.

Following the same approach, by functionalizing Si NW surface with antibodies, the electrical selective detection of influenza A in solution was observed [174].
665 Again, the basic operation mechanism of the device consists of a switch of the Si NW conductance by the binding and unbinding of the virus particle on the functionalized surface. Interestingly, in this work simultaneous detection was achieved by employing the excellent electrical performances of Si NWs arrays devices [175, 176, 177]. Moreover, in 2004 the use of Si NWs FET as sensors
670 for single-stranded DNA was successfully demonstrated both for top-down [178] and bottom up Si NWs synthesis [179]. Modified Si NWs surface [with appropriate DNA receptors as peptide nucleic acid or 3-mercaptopropyltrimethoxysilane (MPTMS)] can easily bind with DNA sequences inducing a variation in carrier concentration in Si NWs and thus resulting in the changes of the conductance.

675 Si NW FETs were also employed to demonstrate ultra-sensitive detection

of bacterial toxin [Staphylococcus aureus Enterotoxin B (SEB)] with detection limits in the range of 10-35 fM [180].

It is worthwhile noting that in all the above mentioned works the chemical or biological detection was achieved in aqueous solution, a process that can be
680 critical because of the dependence of the Debye screening –i.e. charge carrier’s net electrostatic effect in solution– on sensor response and performances [181].

Equally challenging, but probably less complex, is the use of Si NWs for gas sensing. In this direction, since 2003, noticeable results were obtained by S.T. Lee group (see for example Ref. [182]). By developing a novel method
685 for Si NWs synthesis, the oxide-assisted growth, they were able to fabricate high purity Si NWs in large quantities. These NWs were then HF-etched and installed to set up the device shown in Fig. 10 put in a vacuum chamber.

After evacuating the chamber, the gas species are introduced and then the variation of resistance in the device is measured. The chemical sensitivity to
690 NH_3 and water vapor was reported. In particular they found that both NH_3 and water vapor could act as a molecular chemical gate resulting in hole depletion and resistance reduction (see top panel of Fig. 11). This effect is absent when the oxide is not removed from the surface thus revealing the high reactivity nature of pristine Si NW surfaces.

The same type of Si NWs was used to build a solution glucose bio-sensor
695 by employing COOH-functionalized Si NWs [183, 184]. The main result here was demonstrating that the sensitivity strongly increased (in the range of 0.1-0.15 mM) with the treatment of carboxyl group with respect to HF and pristine NWs thus improving the transduction ability.

SERS sensors – The Surface Enhanced Raman Scattering (SERS) is a
700 molecular spectroscopy technique that has been gaining much momentum since the discover of its basic principle in 1973 [142, 185, 186, 187, 188]. In particular it occupies a special role in the field of chemical and biological sensing since it can provide ultrahigh sensitivity and excellent performances even in aqueous
705 environment [189, 190] as demonstrated for the detection of DNA, pH values, protein or other biological molecules [191]. In the last years with the aim of

improving the performances of SERS based devices –trying to improve the poor stability, the low reproducibility and the lack of homogeneity– many research efforts have been conducted towards the fabrication of SERS sensors in which
710 Si NWs represent one of the backbone constituents. In order to illustrate which is the physical reason of this novel and original research line, the underlying operation mode of a SERS device merits being briefly described.

As elegantly explained in Ref. [191], the SERS process not only involves interactions between light and molecules, but also between light and metal nanostructures. The mechanism is described in Fig. 12(A): an incoming electromagnetic
715 wave of frequency ω_{inc} can excite delocalized electrons in the metal (plasma oscillations) at a resonance frequency that depends on the dielectric functions of the metal and of the surrounding medium [191]. The resonance phenomenon [called Localized Surface Plasmon Resonance (LSPR)] makes electrons of the
720 metal oscillating thus inducing a local electrical dipole which itself behaves as a nanoantenna, emitting radiation at the frequency ω_{inc} (see Fig. 12(A)). On the other hand, in the same way, the local electric field can excite the molecule placed near the metal nanostructure by inducing a dipole. Depending on the vibration frequency ω_{vib} of the molecule, Rayleigh, Stokes Raman and anti-Stokes
725 Raman scattering can occur. The latter (Stokes and anti-Stokes processes) are quantum mechanical effects and concern, respectively, a decrease and an increase of the emitted frequency with respect to the frequency of the incident light. The Stokes Raman scattering (that for molecules in their ground state is much more favored with respect to the anti-Stokes one) can produce an outgoing
730 field of frequency $\omega_{inc} - \omega_{vib}$ itself again exciting and enhancing the LSPR of the metal nanostructure (see Fig. 12(B)).

This electromagnetic enhancement is called Surface Enhanced Raman Scattering (SERS) and has an intensity that depends on both the incoming and outgoing field [191]. As pointed out by Lee and co-workers [192] there are two
735 main effects contributing to the enhancement of the Raman signal: a purely electromagnetic effect associated with the plasmonic resonance on the metal surface and a chemical effect responsible of the scattering process of the incoming wave

due to the interaction between the molecule and the metal. The amplification of the signal (by enhancement factor of 10^{12-14}) enables the detection of chemical and biological species even down to the single molecule level [193, 190].

Recently, it has been demonstrated that the fabrication of hierarchical structures composed by metal nanoparticles (NPs) and large nanosized supports can be essential for the building of highly efficient SERS devices [189, 194, 195, 196, 197]. In particular the use of Si NWs as Ag and Au NPs support has an enormous potential for the design of nanosensors with ultrahigh sensitivity and specificity. In contrast to the electrochemical devices described in the previous paragraph, in this case the Si NWs do not represent the active part of the device (that is instead composed by metal NPs), but they play, however, a crucial role in the detection process. The three reasons of the interest for such kind of systems can be listed as follows: **i)** the ease of functionalizing the Si NWs surface with Ag [189] or Au NPs [198] of different shape and dimensions [151]. Indeed the HF treatment of Si NW surfaces creates a perfect platform for metal ions reduction' reaction hence offering the possibility to easily build metal NPs@SiNW-based SERS substrates with enhancement factor values of 10^6-10^{10} (see Fig. 13). This enhancement is mainly due to the strong coupling of plasmonic oscillations between NPs (electromagnetic enhancement) thanks to their dense and controlled distribution, **ii)** the unique optical properties of Si NWs. Besides the plasmonic resonance occurring in NPs on the NW surface, Si NWs themselves can act as nanoantennas to capture, confine light and further enhance the optical signal [199]. Moreover, the strong interaction between excitons of the Si NWs and plasmons of the NPs (due the absence of spacing layer [189]) can increase further the local surface electric field [189] and increase the absorption in the visible range with respect to standard Si substrates, **iii)** the good reproducibility of the SERS signal and the high stability in solution. The good reproducibility is due to the strong immobilization of metal NPs on the Si NW surface which reduces their agglomeration and guarantees high sensitivity and potential for real applications [193]. Furthermore, due to impregnation of metal NPs at the surface of Si NW and to their resistance

to aggregation process, such kind of substrates show a substantial stability in
770 aqueous environment [189].

A prominent contribution to the development of these novel devices has
been made by the group of S.T. Lee and co-workers. In 2008 [192] they used
large scale uniform Si NWs array functionalized with Ag NPs to detect mouse
immunoglobulin G (mIgG) and goat-anti-mouse immunoglobulin G (gamIgG)
775 and relative immune complexes. They demonstrated that 50 ng of mIgG or
gamIgG in this substrate can give structural dependent Raman bands while
their complexes produce distinct Raman bands for intensity and positions. The
same kind of substrate was also used to detect Rhodamine 6G, crystal violet and
nicotine [200] and, again, in 2010 [201] to study the Raman spectra of five Sudan
780 dyes in detail thanks to enhancement factors of 10^8-10^{10} . Few years later [202]
the same group reported the sensitive, specific and multiplex DNA detection
on AgNPs@SiNWs SERS substrate with a concentration range of nearly 1 fM.
More recently this type of substrate has been noticeably improved by increasing
its reproducibility and selectivity [203].

785 AgNPs@SiNWs SERS single wire substrates were prepared by Han *et al.* [189]
(see Fig. 14(a)) and employed for the detection of carbaryl residues on a cucum-
ber surface and *E. coli* in drinking water. The latter experiment is presented
in Fig.14 [panels (b) and (c)] from which the presence of carbaryl can be easily
recognized looking at the peak at 1378 cm^{-1} appearing after transferring the
790 AgNPs@SiNWs onto the probed surface.

It is important to point out that the research activity in the field of Si NWs
based SERS sensors is very vivid and wide so that it results difficult to cover all
the aspects of the problem. We refer the reader to specific reviews for a more
accurate and detailed discussion [142, 193, 204, 157].

795 Finally, it is worth mentioning another type of *optical* Si NW device which
is based on the fluorescence properties of functionalized Si NWs. By covalently
modifying the Si NW surface with fluorescent ligands it is in fact possible to
realize optical sensors which have a high sensitivity and selectivity, as demon-
strated in the case of Cu(II) [205, 206], DNA [207] and nitric oxide (NO) [208]

800 detection. Though outstanding and innovative as device conception, this re-
search approach has not been followed yet as the previous two, thus we address
the reader to a few specific works [205, 206, 157].

5. Conclusions

Semiconducting nanowires are playing an increasingly important role in
805 defining the new generation electron devices and their interaction with the
existing Si-based microelectronics technology. While in the beginning what
captivated researchers was the possibility to highlight quantum effects of these
systems, slowly a rich, equally interesting physics taking place at the surface
started to emerge. In this article we have reviewed the most salient features
810 deriving from the high surface-to-volume nature of these systems, which is ulti-
mately what makes them what they are. We have first reviewed the morphology
of the surfaces, their faceting, and chemical passivation, then focusing on the
most significant progresses in the field of molecular doping and sensing (a dis-
tinction sometimes fictitious). The future of semiconducting nanowires and the
815 success of the applications based thereupon will critically depend on our ability
to gain a full understanding and control of the surface phenomena here reviewed.

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Figure 1: HRTEM images of Si NWs with diameters of (a) 13.2 nm, (b) 5.7 nm and (c) 3.5 nm. The three wires correspond respectively to $\langle 112 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ crystallographic orientations. Reprinted with permission from ref [17].

Figure 2: Solid-liquid interface region during Vapor-Liquid-Solid (VLS) growth process. Reprinted with permission from ref [63].

Figure 3: Specific free energy plots for $\langle 111 \rangle$ (red line) and $\langle 110 \rangle$ (blue line) oriented nanowires as a function of the radius r . Reprinted with permission from ref [63].

Figure 4: Distribution of samples with a specific growth direction for the three class of diameters: (a) 3 to 10 nm, (b) 10 to 20 nm, (c) 20 to 30 nm. Reprinted with permission from ref [17].

Figure 5: High-resolution images of a SiNWs (a) before oxidation and after (b) ozone oxidation at 600°C and (c) normal oxidation at 600°C. The oxidation times are 180 min. (d) A schematic illustration of thermal oxidation of SiNWs. (e) Dependence of the thickness of the surface oxide layer on oxidation temperature. Reprinted with permission from ref [20].

Figure 6: Sketch of the functionalization of Si NWs through the two step chlorination/alkylation process. Reprinted with permission from ref [86].

Figure 7: Side view of a traditional 2D FET device. Letters S, D and G stand for source, drain and gate. Reprinted with permission from ref [144].

Figure 8: Schematic view of a Si NW cross section, in which the drain (D), the source (S) and the electrical current (I_{DS}) are shown. The graph is not in scale. Reprinted with permission from ref [147].

Figure 9: First Si NW based FET device for chemical and biological detection. (A) The steps of the conversion of a NW FET into NW nanosensors for pH sensing are shown. The NW is contacted with two electrodes, a source (S) and drain (D), for measuring conductance. Zoom of the APTES-modified SiNW surface showing the effect of pH in the surface charge state. (B) The real-time measurements of the conductance for an APTES-modified SiNW for pHs from 2 to 9; the pH values are indicated on the conductance plot. (Inset, top) Plot of the time-dependent conductance of a SiNW FET as a function of the back-gate voltage. (Inset, bottom) Field-emission scanning electron microscopy image of a typical SiNW device. (C) Dependence of the conductance on the pH level; the red points are experimental data, and the dashed green line is a linear fit through this data. (D) The conductance of unmodified SiNW (red) as a function of pH. The dashed green curve is a plot of the surface charge density for silica as a function of pH. Reprinted with permission from ref [143].

Figure 10: Optical micrograph of a Si NW connected to the two Ag electrodes. Reprinted with permission from ref [182].

Figure 11: Resistance measurement of a Si NW exposed to N_2 , a mixture of N_2 and NH_3 and air with a relative humidity of 60 %. Top panel refers to the introduction of the gases into the chamber while bottom report the measurements done when the gas are pumped away. Reprinted with permission from ref [182].

Figure 12: Underlying physics of SERS. (A) The incoming electromagnetic wave of frequency ω_{inc} can excite delocalized electrons in the metal of dielectric function ϵ_{Au} in a surrounding medium with dielectric function ϵ_M . (B) Enhancement of incoming and out coming fields due to the interaction with the LSPR of the metal nanostructures. Reprinted with permission from ref [191].

Figure 13: Schematic of the realization of Ag NPs functionalized Si NWs in solution for SERS substrates. The metal ions reduction' reaction is highlighted. Reprinted with permission from ref [189].

Figure 14: (a) Schematic of an AgNPs@SiNWs SERS single wire substrate. (b) Photograph of the detection of the pesticide residue on a cucumber surface experiment (left) and the microscope image of a single AgNP@SiNW transferred to the rough cucumber surface (right). (c) Recorded Raman spectra for clean cucumber surface (curve I), carbaryl contaminated surface (curve II), SERS spectra of a carbaryl contaminated surface modified by a single AgNP@SiNW (curve III), SERS spectra of pure carbaryl (curve IV). The presence of carbaryl can be easily recognized looking at the peak at 1378 cm^{-1} in curve III and IV appearing after transferring the AgNPs@SiNWs onto the probed surface. Reprinted with permission from ref [189].