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# Properties of SiC-based One-dimensional Nanostructures

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This chapter is based around the presentation of the physical properties expected in silicon carbide (SiC)-based one-dimensional (1D) nanostructures. First, the properties of the SiC material will be presented, focusing on the electronic properties of SiC as well as its crystalline properties. Next, a definition of 1D nanostructures and a demonstration of their physical and chemical properties will be put forward.

## 1.1. Intrinsic properties of silicon carbide

### 1.1.1. Crystallographic description

#### 1.1.1.1. *The tetrahedron, base unit of SiC*

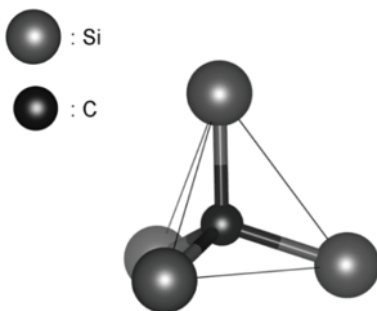
Based on the Si—C bond, with a length of  $d_{\text{Si-C}} = 0.189$  nm, a bond that is both covalent (89%) and ionic (11%), SiC is organized in the form of tetrahedrons (see Figure 1.1<sup>1</sup>) with a carbon atom (or silicon atom) at their center, linked to four silicon (or carbon) atoms. In such a

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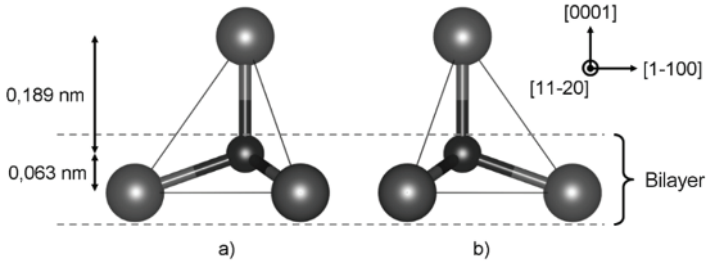
<sup>1</sup> The crystallographic representations were carried out using the Visualization for Electronic and Structural Analysis (VESTA) program [MOM 11].

configuration, the nature of the atoms at the summit of the tetrahedron and in the tetrahedral site is interchangeable. However, for more clarity, all of the explanations will be given with one single configuration: the atom of C in a tetrahedral position. This tetrahedral organization is easily explained if we consider the electronic structures of the silicon and carbon and the hybridization of the atoms in the lattice. These two atoms are part of column IV of the periodic table of elements and have the electronic configurations of  $[\text{Ne}] 3s^2 3p^2$  and  $[\text{He}] 2s^2 2p^2$  for silicon and carbon, respectively. In the SiC lattice, the atoms are hybridized into  $sp^3$  allowing the valence electrons to form four bonds. The angle between two Si—C bonds is then equal to  $\alpha = 70.529^\circ$ . Let us note that in this configuration, the basal plane consisting of three silicon atoms and the next plane of silicon atoms are separated by  $d_{\text{plane Si-plane Si}} = 0.252 \text{ nm}$ , while the plane containing the carbon atom in the tetrahedral interstitial space is  $d_{\text{plane Si-plane C}} = 0.063 \text{ nm}$  from the basal plane.

The tetrahedrons can be orientated in two ways by a  $60^\circ$  rotation around the  $\vec{c}$  axis of the hexagonal system: we talk of “right” or “left” tetrahedrons. The  $\vec{c}$  axis of the hexagonal system corresponds to the axis [111] of the cubic system and axis [0001] of the hexagonal system (see Figure 1.2).



**Figure 1.1.** Representation of the characteristic SiC tetrahedron. The smaller carbon atom has an interstitial position



**Figure 1.2.** Schematic representation in the  $(11\bar{2}0)$  plane of the a) “left” and b) “right” tetrahedrons, along the vertical axis  $[0001]$ . A bilayer, made up of the two first planes of atoms is also represented, as well as the distances  $d_{\text{plane Si-plane C}}$  and  $d_{\text{Si-C}}$

Thus, SiC can be represented as a stack of this tetrahedral unit by their summits. From this stack comes one of the particularities of SiC, called polytypism. Indeed, SiC can be organized into different crystalline networks – the polytypes – according to the manner in which the tetrahedrons are stacked up along the  $\vec{c}$  axis.

#### 1.1.1.2. Polytypism of SiC and Ramsdell notation

The polytypism phenomenon has been particularly studied in the case of SiC, due to the large number of polytypes – more than 200 – which have been recorded up to now. By the middle of the 20th Century, the scientific community had identified four distinct SiC polytypes, and the crystallographic study of these has been the subject of several scientific publications, notably by Baumhauer [BAU 15], who reported for the first time the existence of several SiC polytypes, or even Thibault who in 1944 referenced all of the works carried out on this particularity of SiC [THI 44]; but also Ramsdell [RAM 47] and Shaffer [SHA 69] who contributed to a better understanding of SiC polytypism.

Polytypism is the ability of a substance to crystallize into different crystalline structures. Polytypism is a particular case of 1D polymorphism, since it is limited to the

crystallization possibilities offered by the stacking of a “module” of identical chemical composition. This is referred to as 1D polymorphism, as reported by Schneer in 1955 [SCH 55]. The polytypes thus differ in the manner in which the modules are stacked up, whether by translation or rotation of the next module, along a crystalline direction along the  $\vec{c}$  axis. This means that only the lattice parameter outside of the plane of the module differs between the polytypes.

In the case of SiC, the base “module” is made of a bilayer formed by the basal plane, itself made of Si atoms, and the plane containing the carbon atom in the tetrahedral site (see Figure 1.2). This bilayer can be replaced by the tetrahedron, since the tetrahedrons are joined in their summits. Let us consider the ideal case where the base of a SiC crystal is made of a single type of tetrahedron, the “left” tetrahedrons (see Figure 1.2). The next layer of tetrahedrons, depending on the  $\vec{c}$  axis, can be made either of “right” tetrahedrons or “left” tetrahedrons. The third layer can also be found to be made of these two types of tetrahedron, and so on and so forth until a complete crystal is formed. The result is an infinite amount of possibilities for the SiC to crystallize.

The different polytypes are identifiable using the Bravais lattices. SiC crystallizes mainly as hexagonal, rhombohedral or cubic systems. However, there can be several polytypes associated with one of the Bravais lattices.

Historically, the different polytypes were, therefore, named by number, corresponding to their chronological order of discovery. To be able to offer a more scientific nomenclature, Ramsdell proposed in 1947, in an article called *Studies on silicon carbide* [RAM 47], to use the crystallographic data associated with each polytype. The notation proposed by Ramsdell, and which carries his name today, is the following: the first letter of the Bravais

lattice in which the structure is crystallized (C for cubic, H for hexagonal and R for rhomboidal) is coupled with the number of bilayers needed to entirely describe the structure. The most common polytypes are thus noted:

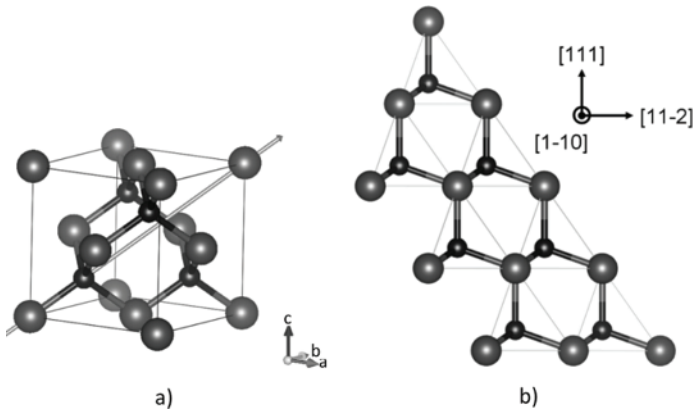
- 3C where all the tetrahedrons are orientated in the same way (see Figure 1.3);

- 2H where the “left” and “right” tetrahedrons alternate (see Figure 1.4);

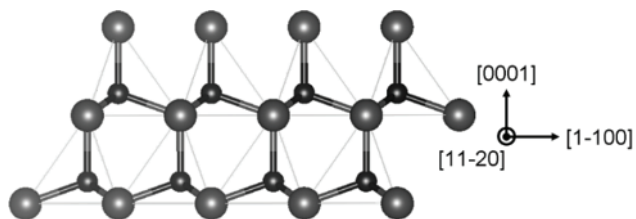
- 4H polytype corresponds to the stacking of two “left” tetrahedrons” followed by two “right” tetrahedrons (see Figure 1.5);

- 6H polytype corresponds to the stacking of three “left” tetrahedrons followed by three “right” tetrahedrons (see Figure 1.6);

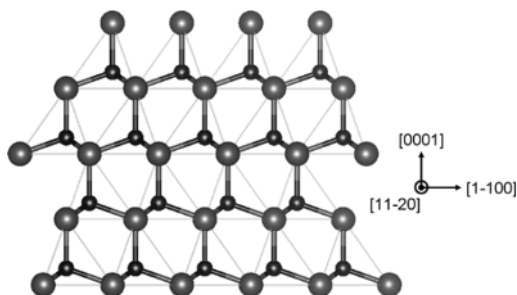
- 15R polytype corresponds to the stacking of three “left” tetrahedrons followed by two “right” tetrahedrons, this pattern being repeated three times (see Figure 1.7).



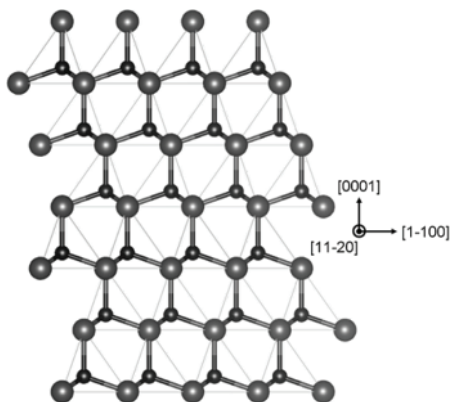
**Figure 1.3.** Schematic representation of the 3C-SiC polytype, which corresponds to the zinc blende structure. a) Primitive cell of 3C-SiC. We can observe the carbon atoms in the interstitial position. [111] axis of the cubic system, which corresponds to [0001] axis in the hexagonal system, is represented by an arrow. b) Stack along axis [111] of the tetrahedrons describing the structure of the 3C-SiC polytype in plane  $(1\bar{1}0)$



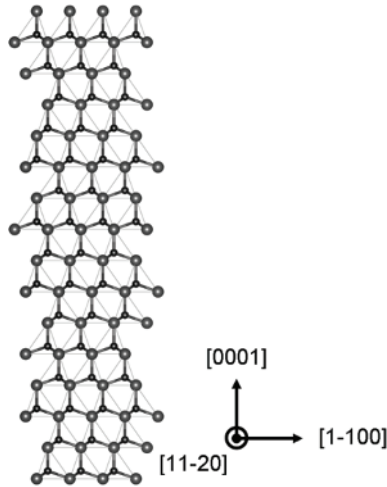
**Figure 1.4.** Schematic representation of stacking along  $[0001]$  axis of the tetrahedrons describing the structure of 2H polytype in  $(1\bar{1}20)$  plane



**Figure 1.5.** Schematic representation of stacking along  $[0001]$  axis of the tetrahedrons describing the structure of polytype 4H-SiC in  $(1\bar{1}20)$  plane



**Figure 1.6.** Schematic representation of stacking along  $[0001]$  axis of the tetrahedrons describing the structure of polytype 6H-SiC in  $(1\bar{1}20)$  plane



**Figure 1.7.** Schematic representation of stacking along the  $[0001]$  axis of the tetrahedrons describing the structure of polytype  $15R$ -SiC in the  $(1\bar{1}20)$  plane

Table 1.1 lists the crystallographic data of the main polytypes of SiC. It must be noted that only one cubic form exists:  $3C$ -SiC. To distinguish it from the other polytypes, it is sometimes written  $\beta$ -SiC, as opposed to other polytypes listed under  $\alpha$ -SiC.

Polytypes		$3C$	$2H$	$4H$	$6H$	$15R$
Space group		$F\bar{4}3m$	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P6_3mc$
Lattice parameters	$a$ (Å)	4.359	3.081	3.081	3.073	3.073
	$c$ (Å)	–	5.031	10.061	15.08	37.70

**Table 1.1.** Crystallographic data of the main polytypes of SiC, from [MOR 94, BEC 97, LAT06]

### 1.1.2. Physical and chemical properties of SiC

The exceptional properties of SiC are the main reason behind the research and development of this material. In this section, first the main physical properties of SiC are

presented, and then the electronic properties of this material are developed, so as to explain how the domain of micro- and nano-electronics is particularly interested in SiC as a semiconductor.

#### 1.1.2.1. *General properties*

As a result of the both covalent and ionic nature of the Si—C bond, as well as its high energy – 5 eV – and the small distance  $d_{\text{Si-C}}$ , SiC possesses good thermal and mechanical properties, and resists well to corrosive agents. Thus, the thermal conductivity of SiC is slightly greater than that of copper (copper =  $3.9 \text{ W}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$ ), the high Young's modulus and the hardness of SiC make it an ideal material for abrasion; finally, it is resistant to ionizing radiation, acid or base etching, and does not oxidize easily<sup>2</sup>. Table 1.2 compares the properties of SiC with other semiconductors: silicon (Si), the diamond form of carbon, aluminum nitride (AlN) and gallium nitride (GaN). This comparison shows that SiC possesses properties close to those of AlN and GaN, better than those of silicon, but not as good as diamond. However, three points must be retained:

- first of all, while diamond is indeed better for mechanical applications (abrasion, material cutting, etc.), it is harder and therefore more expensive to make, as reflected by the fact that synthetic SiC is often used as a diamond imitation;

- the biocompatibility of SiC, coupled with its hemo-compatibility, makes it different from all the other semiconductors and opens up a field of future application [SAD 11a, SAD 11b];

- finally, while many properties are common to all the polytypes, we must remind ourselves that 3C–SiC is the only

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<sup>2</sup> SiC has the same native oxide as Si, which is SiO<sub>2</sub>. This shared point is a definite advantage for microelectronics.



isotropic crystallographic form, and this obviously has consequences with regard to its properties, in the case of a single crystal.

In the end, it appears that SiC possesses good properties of thermomechanical applications when considered as a ceramic. Moreover, its good thermal properties and biocompatibility, coupled with its electronic properties, make it an ideal candidate for micro- and nano-electronics as well as for biotechnology.

Materials	Melting point (F) or non-congruent melting point (S) (°C)	Thermal conductivity $\lambda$ at room temperature ( $W.cm^{-1}.K^{-1}$ )	Isotropy	Young's modulus (GPa)	Density ( $g.cm^{-3}$ )	Resistance to chemical etching	Biocompatibility
3C-SiC	2,200 (S)	4.5	Yes	450	3.21	Very good. Acid and basic	Yes. Bio- and hemo-compatible
2H-SiC			No				
4H-SiC			No				
6H-SiC			No				
15R-SiC			No				
Si	1,414 (F)	1.5	Yes	150	2.33	Moderate for acids, weak for bases	No
C diamond	> 3,800 (S)	20	Yes	1,000	3.51	Excellent	Yes
AlN	> 2,500 (S)	2.5	Depends on the phase	310	3.20	Very good	No
GaN	2,200 (F)	0.8–1.3	Depends on the phase	150–180	6.15	Very good	Yes

**Table 1.2.** Comparison of some physical and chemical properties of SiC with different materials: Si, diamond, GaN and AlN. From [SAD 11a, RAY 07, CAM 98, MER 09, NAL 02]

### 1.1.2.2. *Electronic properties*

As SiC is composed of atoms belonging to column IV of Mendeleev's periodic table, it is itself a semiconductor. It is associated with large bandgap semiconductors, and the value of the energy of the bandgap varies as a function of the polytype between 2.2 and 3.3 eV. Table 1.3 groups the electronic properties of the main polytypes of SiC<sup>3</sup> as well as those of the semiconductors Si, Ge, C (diamond), GaN, AlN, GaAs and InP. The energy of the bandgap  $E_g$ , the saturation velocity of the electron  $v_{sat}$ , the breakdown field  $E_B$ , the mobility of the electrons' and holes' mobility,  $\mu_n$  and  $\mu_p$ , the relative permittivity  $\epsilon_r$ , the thermal conductivity  $\lambda$  and the maximal operating temperature  $T_{max}$  are reported. From this table, it is possible to extract several points that make SiC interesting:

- the indirect bandgap value is high compared to that of silicon, GaAs and Ge. This value, therefore, limits the use of SiC for low-consumption applications, where it is not adapted. However, with such a bandgap, leakage currents at high temperatures are strongly limited. Indeed, the intrinsic carriers will need more energy to pass spontaneously in the conduction band;

- the fact that each polytype possesses a different value of  $E_g$  also allows the consideration of a greater field of application, since it is possible to reach a whole range of  $E_g$ ;

- the indirect nature of the bandgap of SiC – just like for silicon – limits its use in optoelectronics, despite the fact that such applications have already been explored [BRO 93, HU 08, BAI 07]. However, SiC acts as a seed for the epitaxial growth of GaN, a material that is widely developed for

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<sup>3</sup> It must be noted that the electronic properties of 15R-SiC have not yet all been measured, despite the fact that it can be grown.

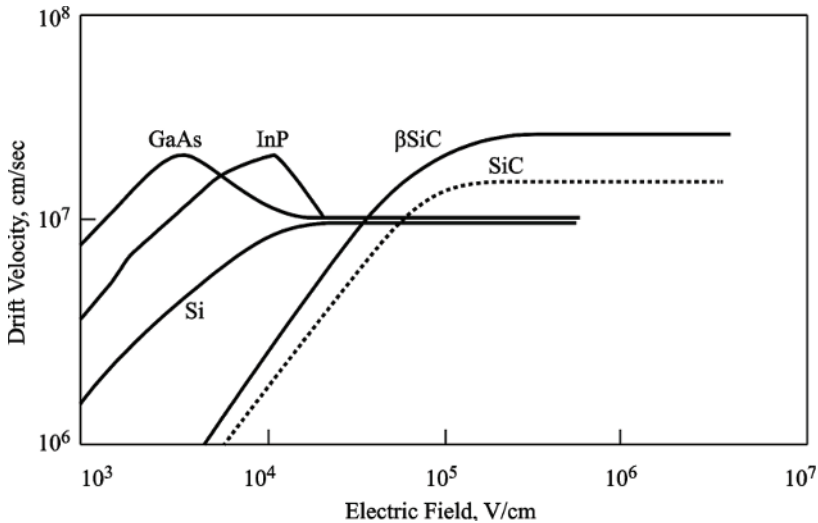
optoelectronics. Indeed, the lattice parameter  $a$  of GaN, crystallizing in a hexagonal system ( $a = 3.186 \text{ \AA}$  and  $c = 5.186 \text{ \AA}$ ) is very close to the parameters  $a$  of the polytypes 4H and 6H of SiC (see Table 1.1);

– the saturation velocity of electrons  $v_{sat}$  corresponds to the maximal speed at which the electrons can move when they are submitted to a strong electric field. This speed is higher in SiC compared to most other semiconductors. Moreover, as reported by Morkoç *et al.* in 1994 [MOR 94], SiC does not experience any decrease in  $v_{sat}$  for strong electric fields, but only a threshold (see Figure 1.8). Moreover, we can note that polytype 3C–SiC possesses a higher  $v_{sat}$  than the other polytypes of SiC, due to a reduced diffusion of the phonons;

– the high values of the breakdown field ( $E_b$ ), as well as the relatively good mobilities, while lower than those of Si, of the electrons ( $\mu_n$ ) and of the holes ( $\mu_p$ ) of the SiC polytypes, explain the use of SiC for high power applications. Indeed, coupled with the correct thermal conductivity of SiC and with its maximal operating temperature, these properties make SiC ideal to allow the flow of a strong current, without overheating the component. These properties have long been exploited to make Schottky diodes functioning at up to 600 V and 60 A (Cree® company [AGA 13]), Junction Field Effect Transistor (JFET) and Metal Oxide Semiconductor Field Effect Transistor (MOSFET) transistors (the Cool SiC™ 1,200 V SiC JFET Family from Infineon® components), as well as thyristors able to withstand up to 6,500 V, for instance.

It would, however, appear that carbon in the diamond form usually possesses better electronic properties than SiC. While this is true, this affirmation meets several difficulties.

There is no complete technological stream based on diamond, due to the current impossibility to obtain good quality and large substrates (substrates greater than 100 mm). Moreover, diamond is easily oxidized when heated to more than 400°C by forming CO<sub>2</sub> and CO, which limits its use for high temperature applications. These two points are resolved in the case of SiC, since commercial substrates are already on the market (4H and 6H), and SiC is difficult to oxidize at high temperatures, due to the formation of a protective layer of SiO<sub>2</sub>. With regard to GaN, it is important to recall the scarcity of global gallium resources compared to silicon and carbon resources, as well as the fact that currently there are no commercial free-standing GaN substrates available.



**Figure 1.8.** Graph representing the saturated electron velocity  $v_{sat}$  as a function of the applied electric field. From Morkoç et al. [MOR 94]

Materials	Indirect bandgap value $E_g$ (eV) direct (d) or indirect (i)	Speed of the electrons at saturation $v_{sat}$ ( $\times 10^7$ cm.s $^{-1}$ )	Breakdown field $E_B$ ( $\times 10^5$ V.cm $^{-1}$ )	Electron mobility $\mu_n$ and hole mobility $\mu_p$ (cm $^2$ .V $^{-1}$ .s $^{-1}$ )	Relative permittivity $\epsilon_r$	Maximal operating temperature $T_{max}$ (°C)	Thermal conductivity $\lambda$ at room temperature (W.cm $^{-1}$ .K $^{-1}$ )
3C-SiC	2.2 (i)	2.5	15	$\mu_n = 1,000$ $\mu_p = 40$	9.6	925	
2H-SiC	3.3 (i)	2.3	?	$\mu_n = 1,500$ $\mu_p = ?$	9.7	?	
4H-SiC	3.2 (i)	2	20	$\mu_n = 1,000$ $\mu_p = 115$	10	1450	4.5
6H-SiC	2.9 (i)	2	22	$\mu_n = 800$ $\mu_p = 90$	9.7	1300	
15R-SiC	3.0 (i)	?	?	?	?	?	
Si	1.12 (i)	1.1	2.5	$\mu_n = 1,400$ $\mu_p = 370$	11.8	325	1.5
Ge	0.66 (i)	0.5	1	$\mu_n = 3,900$ $\mu_p = 1,900$	16	300	0.6
C (diamond)	5.5 (i)	2.7	100	$\mu_n = 2,000$ $\mu_p = 2,100$	5.6	560	20
GaN	3.3 (d)	2.5	14	$\mu_n = 900$ $\mu_p = 150 ?$	11.1	1650	1.3
AlN	6.2 (d)	2.1	12-18	$\mu_n = 300$ $\mu_p = 14$	8.5	?	2.85
GaAs	1.4 (d)	1.0	3	$\mu_n = 8,500$ $\mu_p = 400$	12.8	$T_{melting} = 2200$ 490	0.5
InP	1.34 (d)	1.0	5	$\mu_n = 4,600$ $\mu_p = 150$	12.4	?	0.68

**Table 1.3.** Comparison of some electronic properties of the main SiC polytypes with different semiconductors: Si, Ge, diamond, GaN, AlN, GaAs and InP. From [LAT 06, RAY 07, CAM 98, MER 09, NAL 02, FER 06, MOH 96, NIL 91]

From the exposition of the physical and chemical properties of SiC, it is possible to extract some important information:

- SiC possesses several crystalline forms, called polytypes, coming directly from crystallographic considerations via the stacking of the SiC<sub>4</sub> tetrahedrons (or CSi<sub>4</sub>). Three polytypes do stand out, however, by their possible growth: the cubic 3C–SiC form, and the hexagonal 4H–SiC and 6H–SiC forms;

- the physical properties of SiC come from the Si–C bond, while maintaining the idea of polytypism. The excellent thermal properties of SiC, as well as its high resistance to harsh environments, (irradiation, acidic or basic media and high temperatures) make it an exceptional material;

- the biocompatibility, as well as the hemo-compatibility, of SiC places it in a category of its own among semiconductors and provides new possibilities;

- from an electronic point of view, in the application fields such as power electronics and/or functioning in a harsh medium, SiC appears as the ideal material due to its high resistance, good thermal properties and ability to withstand strong currents and voltage, where silicon is not suitable;

- globally, 3C–SiC is the polytype with the best electronic properties, notably due to its isotropy, greater electronic mobility and the smaller value of its bandgap.

## **1.2. Properties of one-dimensional nanostructures**

### **1.2.1. *Definition and classification***

Before presenting the different physical and chemical properties of 1D nanostructures, it is necessary to define the latter. When looking at nano materials, the legal definition proposed by the European Commission and quoted hereafter provides an initial legal framework, notably in terms of

dimensions: a nano material is “a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm”<sup>4</sup>.

1D nano-objects can, therefore, be defined as:

*One-dimensional nano-objects are any three-dimensional objects for which at least two dimensions are smaller or equal to 100 nm.*

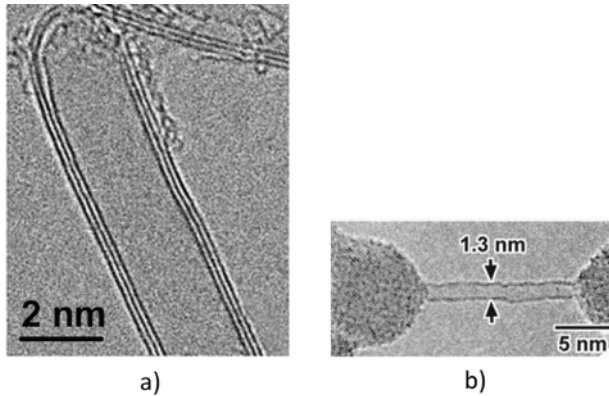
Using this concise definition, it is possible to group a large number of terms that appear gradually as new scientific discoveries are made. However, we can distinguish two large categories of 1D nano-objects: “hollow” 1D nano-objects and “full” 1D nano-objects.

#### 1.2.1.1. “Hollow” 1D nano-objects

Usually called nanotubes, these objects are made of walls surrounding an empty space. The wall can be composed of a single atomic plane: these are single-walled nanotubes; or they can be made of several atomic layers (multi-walled nanotubes). Among these nanotubes, the best known, most studied and most used are without a doubt carbon nanotubes. Discovered by Iijima, who published his work in *Nature* in 1991, carbon nanotubes are made of layers of graphite bent over themselves [IJJ 91, END 97]. Figure 1.9 gives two examples of carbon nanotubes, respectively, single-walled (Figure 1.9(b)) and multi-walled (Figure 1.9(a)). There is a large range of materials that have been developed in the form of nanotubes: semiconductors [PAR 09], metals [MOR 07, FEN 10], as well as oxides [HU 09].

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<sup>4</sup> Recommendation 2011/696/CE of the Commission, JO L 275 from 20.10.2011



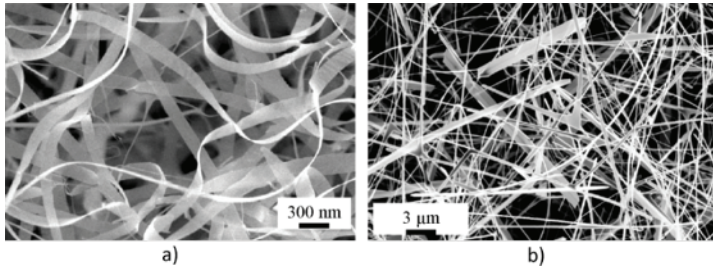
**Figure 1.9.** Images obtained by transmission electron microscopy: a) of two multi-walled carbon nanotubes (from [CAM 08]); b) of a single-walled carbon nanotube linked to two silicon carbide electrodes. From [ZHA 99]

#### 1.2.1.2. “Full” 1D nano-objects

It is possible to distinguish here again two large categories: on the one hand nanoribbons, and on the other hand nanowires. However, this distinction is rarely clear and is usually only made indicatively. Nanoribbons possess a section with one side that is much larger than the other (see Figure 1.10(a)), while nanowires, sometimes called nanorods, nanocables, nanowhiskers or nanopillars, have a roughly circular section, even if in reality the section is sometimes polygonal (see Figure 1.10(b)). Here as well, it is possible to create “full” 1D nano-objects with many materials: metals [SEL 01], oxides [TSA 05] but especially semiconductors such as GaN [JOH 02], ZnO [HUA 01], GaAs [PER 04], InP [ALG 08], SiGe [POT 11] or SiC [CHO 04] or even nano-objects in which the core does not have the same chemical composition as the exterior of the nanowire: these are called core-shell nanowires (for example, Si–SiO<sub>2</sub> core-shell nanowires [LAU 02] or SiC–SiO<sub>2</sub> core-shell nanowires [ZHA 02]). Nevertheless, the Si nanowires have been the most extensively studied for a long time. In 1964, Wagner



and Ellis demonstrated the growth of such nanostructures [WAG 64]. Since then, from the mastering of the growth of Si nanowires [WU 01, SCH 05, SCH 09], to the integration of these nanowires into transistors [HOC 05, LI 06, GOL06], they have been the subject of active research.



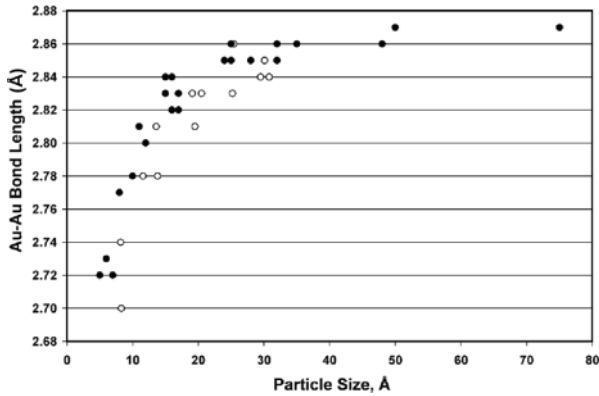
**Figure 1.10.** Images obtained by scanning electron microscopy a) of ZnO nanoribbons (from [WEN 03]; b) of SnO<sub>2</sub> nanowires (from [KAC 07])

1D nanostructures have, therefore, only two dimensions that are smaller than 100 nm, and can be either structurally empty, or structurally full. These 1D nano-objects have been – and still are – the subject of much interest in the research community, especially with regard to semiconducting carbon nanotubes and nanowires in general.

### **1.2.2. High surface/volume ratio and its consequences**

The major advantage of nano-objects in general, and 1D nanostructures in particular, comes from the high surface to volume ratio. Indeed, the higher this ratio is, the greater the place occupied by surface atoms. The atoms of a surface distinguish themselves from the atoms located in the volume in several ways. For example, on the surface of a material there are several dangling bonds that influence the other bonds of the atom, as well as the electronic structure. Moreover, the surface does not only affect the first atomic monolayer in direct contact with the empty space, but also

the first and second neighboring atoms of the surface. Thus, in a conducting material, electric transport at the surface of a nano-object must be taken into account to better describe the total current. Furthermore, the intrinsic phenomena of interfaces are preponderant at a nanometric scale.



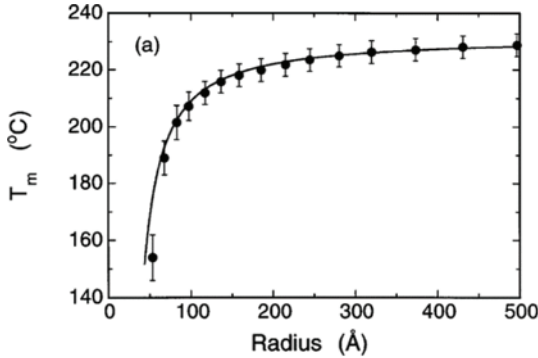
**Figure 1.11.** Evolution of the interatomic distance of Au – Au in gold nanoparticles, as a function of the diameter of the particles. From [MIL 06]

Among the properties that will be affected in this way by the nanometric scale, it is possible to list the following few examples:

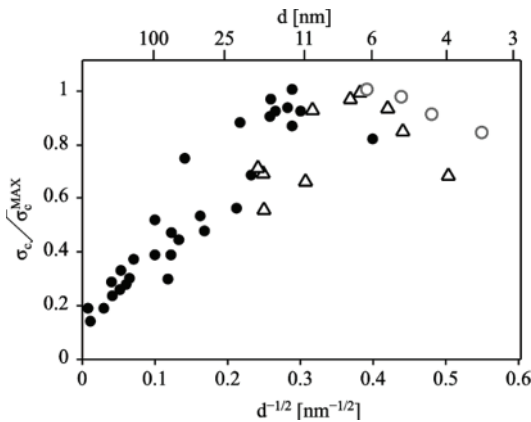
- structural properties: the greater the surface/volume, the greater the value of the surface energy, which leads to changes in interatomic distances. If we take the example of gold nanoparticles, Miller *et al.* have shown that the interatomic distance between gold atoms decreases when the diameter of the nanoparticles decreases [MIL 06], as can be seen in Figure 1.11;

- the thermal properties are also affected by the fact that the surface is preponderant. For example, works by Lai *et al.* [LAI 96] have shown that the melting point of tin nanoparticles decreases as the size of the particles decreases, as can be seen in Figure 1.12;

– finally, mechanical properties are also affected by the effects of the nanometric scale. Nickel and copper nanoparticles have a higher critical stress when the diameter of the nanoparticles is smaller (see Figure 1.13);



**Figure 1.12.** Evolution of the melting point of tin nanoparticles, as a function of the diameter of the particles. From [LAI 96]



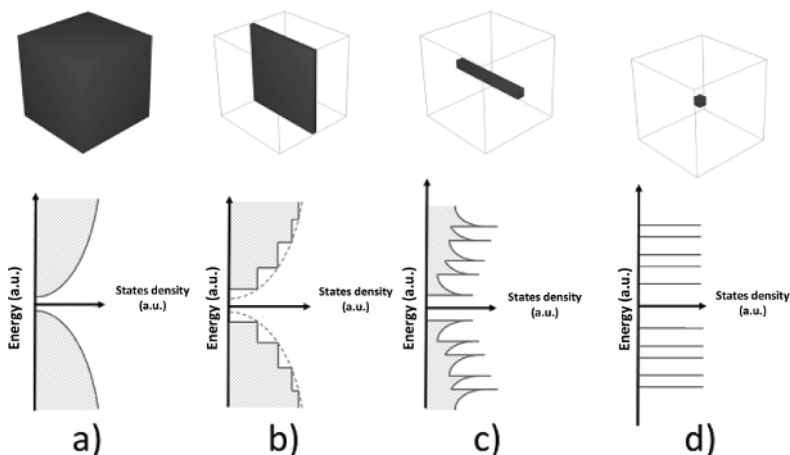
**Figure 1.13.** Evolution of the critical stress of nanoparticles of copper and nickel, as a function of the diameter of the particles. From [KUM 03]

Thus, all the physical properties, as well as the behavior of a material, are impacted when this material is nanometric. This modification comes from the importance of

the surface/volume ratio, as well as from the interfaces in relation to the volume.

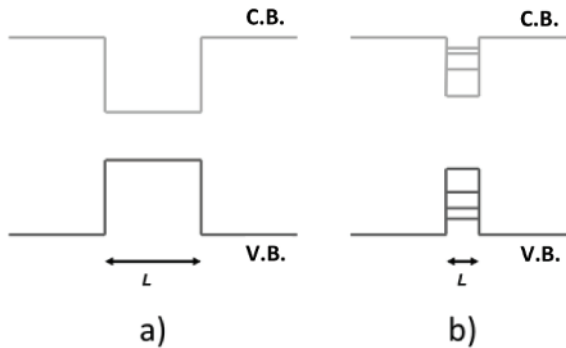
### 1.2.3. *Specific properties at the nano metric scale*

Nano-objects, whether one, two or three-dimensional, have been extensively studied, both theoretically and experimentally, not only because of the effects linked to the high surface/volume ratio, but also because of the new properties unique to the nanometric scale. These specific properties come mainly from the modification of the electronic structure of the conduction and valence bands of the materials at a nanometric scale. If we consider the states' densities as a function of the energy of the particles for a bulk material, it appears that covering of the orbitals leads to the existence of conduction and valence bands. These partially cover themselves up in conducting materials, are very farther apart for isolating materials and are close together but separated by a gap for semiconducting materials.



**Figure 1.14.** Representation of the states density of objects that a) are volumic, meaning they have no nanometric dimensions; b) have a nanometric dimension: very thin films; c) have two nanometric dimensions: nanowires, nanotubes and nanoribbons and; d) have three nanometric dimensions: nanodots

However, when the dimensions of an object get close to nanometric sizes, quantum effects, and notably the wavelike behavior of electrons (respectively, the holes) cannot be ignored. Because of this, it appears that the states densities of the electrons (respectively, the holes) are modified and tend toward a quantification of the energy levels possible for the electrons (respectively, the holes). The states densities of the electrons are represented in Figure 1.14, which are the energy levels that are acceptable for the electrons, for objects that have no nanometric dimensions (see Figure 1.14(a)), those with one nanometric dimension (see Figure 1.14(b)), those with two nanometric dimensions (see Figure 1.14(c)) and finally those with three nanometric dimensions (see Figure 1.14(d)). The greater an object's number of nanometric dimensions, the more the energy states of the electrons are quantified, due to the limitation of the movement of the electrons. This is also the case for the holes. This is referred to as quantum confinement in one, two or three dimensions.



**Figure 1.15.** Illustration of a dimension representing a semi-conducting material trapped between two insulators. If length  $L$  is small enough, the energy levels in the semiconductor are quantified

To better grasp the importance of quantum confinement, let us take the example of quantum wells: a semiconductor surrounded by two insulators. Simply put, it is possible to

represent (Figure 1.15) the conduction and valence bands for a semiconductor with and without the effects of quantum confinement (Figures 1.15(a) and 1.15(b), respectively). In the first case, the energy necessary to make an electron goes from the valence band to the conduction band is equal to the energy of the gap. However, in the second case, the energy allowed for the electrons (respectively, the holes) being quantified, we first observe an increase of the size of the gap, as well as a quantification of the energies needed to pass from the valence band to the conduction band. This quantification, which comes directly from the resolution of the Schrödinger equation, can be expressed in the following manner:

$$E_n = -E_g + \frac{1}{2m} \left( \frac{n\pi\hbar^2}{L} \right) \quad [1.1]$$

where  $E_n$  represents the energy levels allowed in the conduction band,  $E_g$  represents the bandgap energy, taking the top of the valence band as reference,  $m$  is the mass of the electron,  $\hbar$  is the reduced Planck's constant and finally  $L$ , which is defined as the width of the central zone. It is important to note that the dimensions of the quantum wells, and by extension the dimensions of the nano-object, impact directly the effect of quantum confinement.

However, these effects, which are unique to the nanometric dimensions of objects, do not appear for the same dimensions for each material. Indeed, the notion of the exciton Bohr radius, written  $a_0^*$ , must be introduced here. It depends on the intrinsic nature of the material, and will allow us to define the limit from which quantum confinement exists. The exciton is defined as the quasi-particle made of an electron-hole pair linked together by Coulomb forces. The radius of this quasi-particle can be expressed in the following manner:

$$a_0^* = \frac{a_0 \epsilon_r m_e}{m^*} \quad [1.2]$$

with  $\epsilon_r$  being relative permittivity,  $m_e$  is the mass of the electron,  $m^*$  is the reduced mass that can be written like this:

$$m^* = \frac{m_e^* \times m_h^*}{m_e^* + m_h^*} \quad [1.3]$$

Let us remind ourselves that the Bohr radius  $a_0$ , depending on the vacuum permittivity  $\epsilon_0$ , the reduced Planck's constant  $\hbar$  and  $e$  the charge of the electron, among other factors, is equal to:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 52,918 \text{ pm} \quad [1.4]$$

Let us note finally that the effective masses of the electron  $m_e^*$  and of the holes  $m_h^*$ , which allow us to take into account the medium in which these particles evolve, can be calculated as a first approximation and by considering that the effective masses are the same in all directions with equation [1.5], where  $\epsilon$  represents the energy of the electron, which depends on  $\vec{k}$ , the wave vector<sup>5</sup>. Table 1.4 lists the effective masses of several semiconductors:

$$m_e^* = \hbar^2 \times \left[ \frac{d^2 \epsilon}{dk^2} \right]^{-1} \quad [1.5]$$

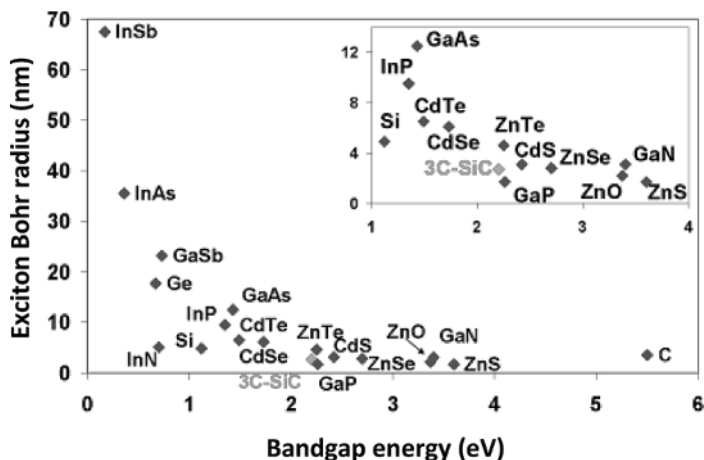
<i>Material</i>	<i>Si</i>	<i>Ge</i>	<i>3C-SiC</i>	<i>GaAs</i>	<i>C (diamond)</i>
$m_e^*$	1.08 $m_e$	0.55 $m_e$	0.34 $m_e$	0.067 $m_e$	1.87 $m_e$
$m_h^*$	0.56 $m_e$	0.37 $m_e$	0.8 $m_e$	0.45 $m_e$	0.92 $m_e$

**Table 1.4.** Summary of the effective masses of electrons and holes for some semi-conducting materials. From [YOS 95, SON 94, SON 95, KAP 85, IOF 13, SAU 04]

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<sup>5</sup> We can also talk of dispersion relation for equation  $\epsilon = f(\vec{k})$ .

Thus, when an object possesses at least 1D smaller than  $a_0^*$ , a quantum confinement appears. This value depends on the material through the effective masses of the electrons and of the holes  $m_h^*$  and of the relative permittivity  $\epsilon_r$ . In the case of 1D nano-objects, the diameter would, therefore, need to be smaller than  $a_0^*$  to be able to obtain quantum confinement. Figure 1.16 represents the value of the exciton Bohr radius for different semiconductors as a function of the bandgap. It appears that few materials possess an exciton Bohr radius greater than 10 nm (see Figure 1.16).



**Figure 1.16.** Representation of the value of the exciton Bohr radius as a function of the bandgap for different semiconductors. From [WU05, YOF 01, NIQ 00, OST 05]

The physical properties unique to nanometric scales, therefore, depend on the nature of the material used. While we refer to them as nano-objects as soon as 1D is smaller than 100 nm, it is clear that quantum effects only appear for dimensions that are much smaller, in the order of 10 nm. This separation between nanometric objects and the properties specific to the nanometric scale allow us to define



two classes of nano-objects: those whose dimensions allow the appearance of quantum effects and those whose dimensions do not. These two classes of nano-objects have not been developed in the same manner: while quantum objects are still in the early stages of fundamental research, larger nano-objects are already being used in industry. From this remark, it must be noted that 3C-SiC is not one of the most interesting materials in terms of the effects of quantum confinement, due to small value of the exciton Bohr radius of this material ( $\approx 2.7$  nm [WU 05]). We will see soon that such dimensions are hard to reach even today, which explain why applications targeted by 1D 3C-SiC nanostructures do not use the properties unique to the nanometric scale. The main advantage of these objects currently resides in the obtaining of large surface/volume ratios so as to benefit from greater sensitivity.

### 1.3. Conclusion

The physical and chemical properties intrinsic to SiC reflect the advantages of developing such a material. Among its remarkable properties, we can list the following:

- the thermal properties of SiC, notably its high operating temperature and the excellent thermal conductivity of SiC, which is better than that of copper;

- the electronic properties of SiC such as the strong breakdown field and the good saturation velocity of the carriers;

- the resistance of SiC in harsh environments: high temperatures, acid and basic media, and oxidizing media;

- SiC is the only semiconductor that is both biocompatible and hemocompatible;

– the polytypism of SiC limits its development to grow zero-defect single crystals. The cubic form of SiC is the only one that has isotropic properties and an indirect bandgap energy less than the other polytypes.

The stakes present in the growth of 1D SiC nanostructures are, therefore, to ally these physical and chemical properties with the effect of nanometric dimensions. As emphasized previously, quantum effects are hard to reach in SiC nano-objects; however, the effects caused by the high surface/volume ratio are promising and warrant the studying of 1D SiC nanostructures.