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半导体异质结构与 纳米结构表征

Characterization of Semiconductor Heterostructures and Nanostructures

Carlo Lamberti



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Carlo Lamberti

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by Carlo Lamberti

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导 读

本书是由意大利 Torino 大学材料系 Carlo Lamberti 教授主编的，以意大利的大学教授为主体，包括欧洲其他国家：英国（第 8 章）、法国（第 10、11 章）、西班牙（第 11 章）、瑞士（第 12 章）及比利时（第 13 章）学者共同编写的。全书共 13 章，内容是介绍表征异质结构，包括半导体异质结、超晶格，以及低维结构如 III-V 族化合物纳米线、量子点等——的结构性质与电子性质的分析手段和方法。这些性质主要是指在衬底上生长的异质表面层或异质材料间的界面、界面层（interlayer）特性。

具体来说，结构参数包括生长出来的层中的材料组分、掺杂及应变等；界面特性则有材料跨越界面的原子互混（inter-mixing）、共价键的键长变化等。固体的电子结构则是指 $E-k$ 关系（即能带、能级），包括通常在异质结能带图中最为关注的导带底与价带顶的偏差。另一类与载流子（电子、空穴）在异质结构中输运十分有关的晶格振动模式（用声子描述），其表征方法在书中也有介绍。

该书十分全面地描述了对上述异质/纳米尺度结构性质进行表征的手段与方法，包括

- ◆ 高分辨率 X 射线衍射技术（XRD）（第 4 章）
- ◆ 透射电子显微镜（TEM）（第 5 章）
- ◆ 光致发光技术（PL）（第 6 章）
- ◆ 与功率大小有关的阴极发光（第 7 章）
- ◆ 拉曼谱技术（第 8 章）
- ◆ X 射线吸收精细结构（XAFS）方法（第 9 章）
- ◆ 采用同步辐射的对表面敏感的 X 射线技术：包括掠入射（GI）及异常散射（第 10 章）
- ◆ 掠入射衍射异常精细结构（GIDAFS）（第 11 章）
- ◆ 光发射谱（第 12 章）
- ◆ 电子自旋谐振（ESR）谱分析（第 13 章）

这种对表征手段的全方位介绍（基本上都是基于各种谱分析原理，包括固体实空间与晶体倒格子空间的变换），可以帮助读者在进行结构的体材料特性、表面特性或界面特性分析时做适当的选择。

除了实验手段，本书的另一个显著特点是用了大量篇幅介绍了计算机分析与辅助设计在异质结构的表征上起到的日益重要的作用。这种计算机模拟方法包括用第一原理（*ab initio*，也称从头开始）对器件电子结构的计算。本书第 3 章专门讨论了采用第一原理计算方法来研究材料的结构与电子性质，以及相应模型的建立。该书提供的这种实验与理论计算相结合的方法是研究与设计高性能的异质结构和纳米结构的强有力的工具，也是目前科学界发展的趋势。

该书在叙述结构安排上也颇具匠心。在每一章的起头都对所叙述的表征与实验方法的物理原理进行了简要而清晰的介绍，使得初学者能很快地掌握与熟悉该方法的历史背景与应用范围、特点，然后介绍使用该方法的具体步骤。各章的后一部分则给出了所描述的方法的具有代表性与应用实例。

需要指出的是，书中介绍的参考文献十分全面（近期与经典的）与准确，这是因为各章的作者都是从事该方面测试方法与技术研究有长的专门学者，对本领域的发展状况与动态十分熟悉。从这个意义上说，本书提供了一个深入了解晶体、异质结构表征研究的捷径或入门向导。

该书对于从事硅 CMOS 大规模集成电路研究与开发的科研、工程人员也有很好的参考价值。

(1) 书中多处讨论了应变对晶体晶格与界面结构的影响，也介绍了多孔（porous）材料（如多孔硅）的原子排列与物理性质。这两个技术（应变硅与多孔介质）都是目前 CMOS 技术进入纳米尺度（即 90nm 及以下工艺节点）后，工业与学术界广泛使用以改善集成电路性能（前端晶体管与后端互连）的主要方法。

(2) 书中涉及的电子自旋效应讨论（第 10 章）也对日趋活跃的半导体自旋电子学研究有很好的回顾与分析。

(3) 全书的讨论多处提及氮化物半导体或合金材料的表征方法。这也十分适合目前研究的热点。以 GaN 为例，其宽禁带与良好的热导率与化学稳定性，使其在光学与电学器件中的应用极有价值。

以上三方面的内容都反映了本书写作有很好的时效性与实际意义。

最后可以提及的是，尽管本书是编著而成的，但依然提供了索引（index），这对检索众多纷繁的表征方法与现象提供了极大的方便。

诚如编著者指出，本书可供从事基于异质结构的器件设计、材料生长，表征

与测试的研究人员与大学研究生（包括本科高年级学生）阅读。笔者更认为，对从事微电子（包括集成电路工艺、器件）与纳电子材料、器件研究的科学、工程人员也极具参考价值。谨此推荐。

余志平

清华大学微电子学研究所

为了那些年代久远的树木，因为它们是我们的起源；但是更重要的是，为了年轻的树木，因为未来属于它们。

在我的内心里，我愿意将知识的传播视为一棵其根深深扎入土地的老树，它的种子被可爱的风吹散在四周。让土地紧裹着老树的根，让微风轻抚它的枝条，直到年轻的树木成长起来并最终取代老树，越长越壮……

(余志平 译)

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(余志平 译)

前 言

在 C. Lamberti 的“采用同步辐射技术对应变半导体异质结构与薄膜的表征”综述文章发表之后，Elsevier 出版社与我联系来协调编写一本有关用于研究半导体异质结构和纳米结构的最常用的表征技术的新书。在最开始的拖延之后，我接受了这个任务。我所接触过的大多数章节作者的迅即又热情的回复使我的工作比起预期的要容易得多。我要对所有这些同事们表示衷心感谢。我也要对那些章节进行校验的能干的同事表示感激，因为他们的辛勤工作对章节的作者和我在改进最后的定稿质量方面帮助极大。在结束这项任务时，回顾最终的成果，我能自豪地在章节作者中数出不少我的好朋友以及在各自领域中的杰出科学家。在这些杰出的科学家中，我更为女科学家在其中起的作用而骄傲：她们共编写了 4 章。

《半导体异质结构与纳米结构表征》一书章节是这样组织的：每个章节介绍了一种用于了解半导体量子阱和超晶格的性质（结构、物理、化学、电磁等）中表征技术。有一章专门介绍了用第一原理进行模拟的建模方法。本书有两个基本目的。第一个是基于教学的考虑。本书提供了可被物理、化学、材料、科学、工程和纳米技术领域的硕士和博士理解的某一特定技术的基本概念。第二个目的是从最新文献中选择一些例子，它们能代表应用某一专门技术来理解半导体异质结构与纳米结构性质的前沿结果。因此每一章有双重结构：第一部分是用来解释基本概念以服务于最大限度的读者；第二部分则用来讨论特别与新颖的例子，使得本书可以在书架上寿命可以更长些。如果发现理解每个章节的第二部分有困难时，不用沮丧。我的建议是集中精力在第一部分；当经验增加时，总是可以在随后几年里回过头来再看第二部分。当然，本书也对学术和工业界中对基于异质结构的器件的设计、生长、表征和测试领域中工作的科学家适用。这些读者可以跳过每个章节的第一部分，直接专注于第二部分。

除了上面谈到的之外，本书还有一个更长远，甚至可以说是雄心勃勃的目的。这是指，本书中有关量子阱、量子线和量子点的内容应该被看作是一个将先进表征技术应用到理解纳米（甚至亚纳米）尺度物质的结构、电子等性质一个前奏。可以这么说，本书的目的是作为更为广阔和极其活跃的纳米技术领域的参考书。

（余志平 译）

To the older trees, because that's from them that we came from but most importantly, to the young trees, because to them belongs the future.

In my naïve mind I like to think of knowledge dissemination as an old tree, with its roots strongly and deeply set in the ground, and with its seeds gently taken by a lovely wind that spreads them all around. Let the ground stick close to the old tree's roots and let the wind caress its branches, as long as possible . . . till new young trees grow up from the ground and become stronger and stronger and can finally replace the old one.

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Preface

After the publication of the review “C. Lamberti, The use of synchrotron radiation techniques in the characterization of strained semiconductor heterostructures and thin films, *Surf. Sci. Rep.*, **53** (2004) 1–197”, Elsevier contacted me for the coordination of a new book collecting the most used characterization techniques for the investigation of semiconductor heterostructures and nanostructures. After an initial inertia from my part, I accepted the task. The immediate enthusiastic replay of most of the contacted chapter coordinators has made my work easier than expected. I would like to express my gratitude to all these colleagues, as well as to all colleagues who have kindly acted as competent reviewers, as their hard work has importantly helped the chapter coordinators and myself to improve the quality of the final product. At the end of the task, looking to the final result, I am proud to count within the chapter coordinators dear friends and eminent scientists that are in the top positions in the ranking lists of the corresponding disciplines. I am even more proud to underline that, among such list of eminent scientists, women play an important role, leading four chapters.

“Characterization of Semiconductor Heterostructures and Nanostructures” is structured in chapters, each one devoted to a specific characterization technique used in the understanding of the properties (structural, physical, chemical, electrical, etc.) of semiconductor quantum wells and superlattices. A chapter is devoted to the *ab initio* modeling. The book has basically a double aim. The first one lies on the educational ground. The book provides the basic concept of each of the selected techniques with an approach understandable by master and Ph.D. students in Physics, Chemistry, Material Science, Engineering, and Nanotechnology. The second aim is to provide a selected set of examples from the recent literature of the TOP results obtained with the specific technique in understanding the properties of semiconductor heterostructures and nanostructures. Each chapter has consequently this double structure: a first part devoted to explain the basic concepts, serving the largest possible audience, and a second one to the discussion of the most peculiar and innovative examples, allowing the book to have the longest possible shelf life. So students should not get frustrated if they find more difficulties in the understanding of the second part of the chapters. My advice is to focus on the first parts; they can always come back to the second parts in the ensuing years, when their experience will be improved. Of course, the book is devoted also to the specialized community of scientists working in the fields of design, growth, characterization, and testing of heterostructures-based devices in both academic and industrial laboratories. Such readers should skip the first parts of the chapters, focusing on the final ones.

On top of this, the book has a further and somewhat even more ambitious goal. In this regard, the topic of quantum wells, wires, and dots should be seen as a pretext of applying top level characterization techniques in understanding the structural, electronic, etc. properties of matter at the nanometer (even sub-nanometer) scale. In this way, it is aimed to become a reference book in the much broader, and extremely hot, field of Nanotechnology.

1

Introduction: the interdisciplinary nature of nanotechnology and its need to exploit frontier characterization techniques

Carlo Lamberti

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Abstract High-performance electronic and optoelectronic devices based on semiconductor heterostructures are required to obtain increasingly strict and well-defined performances, needing a detailed control, at the atomic level, of the structural composition of the buried interfaces. This goal has been achieved by an improvement in the epitaxial growth techniques and by the parallel use of increasingly sophisticated characterization techniques and of increasingly accurate ab initio calculations. This chapter, introducing the book *Characterization of Semi-conductor Heterostructures and Nanostructures*, is divided into five sections. In Section 1, the impact of nanoscience and nanotechnology in our society is described, using the point of view of the articles, the citations and the journals devoted to the field. The multidisciplinary nature of nanotechnology is reported in Section 2, while the dynamic interplay among growth/synthesis techniques, theoretical modeling, and characterization techniques in the design and improvement of semiconductor heterostructure-based devices is discussed in Section 3. Section 4 reports the purposes of the book and the layout of the chapters. Finally, in Section 5, the strength of combined experimental and theoretical investigation of a selected nanomaterial is underlined by an example.

Keywords nanotechnology, nanoscience, heterostructures, nanostructures, characterization techniques, ab initio calculations

1. The scientific and editorial blow up of nanotechnology in the new millennium

The term nanotechnology refers to a branch of applied science and technology whose unifying theme is the control of matter at the atomic and molecular scale, normally 1–100 nm ($1 \text{ nm} = 10^{-9} \text{ m}$), and the fabrication of devices within that size range. The appeal in such approach lies in the fact that the structural, physical, chemical, electronic, optical, etc. properties of nanometer-dimensioned materials differ markedly from those of the corresponding bulk (unconfined) materials. Nanotechnology, among the most advanced frontiers of Science, is certainly showing the higher degree of multidisciplinary, generated from the well-accorded interplay among different fields such as materials science, applied physics, interface and colloid science, device

physics, supramolecular chemistry, surface science, and engineering. Nanotechnology results from a combined extension of such sciences into the nanoscale.

Scientists, politicians, media, and industries have much expectation concerning what new science, technology, and application may result from these lines of research. Such expectations have strongly stimulated the effort made in the previous years by university and industrial laboratories in the field of nanoscience and nanotechnology. A simple way to evaluate such effort is to look to the number of papers published per year that are found using *nanochemistry* OR *nanophysics* OR *nanotechnology* OR *nanoscience* as search keys (Fig. 1(a)), and to the number of citations that such papers have received (Fig. 1(b)). It is evident that such simple and superficial statistical study is far to be comprehensive, as most of the papers that actually report results in this field do not necessarily used one of those four keywords. It is evident from the last row of Table 1 that the 32 journals belonging to the *Subject Category*¹ named “Nanoscience & Nanotechnology” have published 8939 papers in 2006, while only 1125 have been found using those four keywords (Fig. 1(a)). So, the data reported in Fig. 1 are not important as absolute values, which are underestimated by a factor of about 10, but for the trend they are showing. It is evident that this trend shows an impressive acceleration starting from the new millennium.

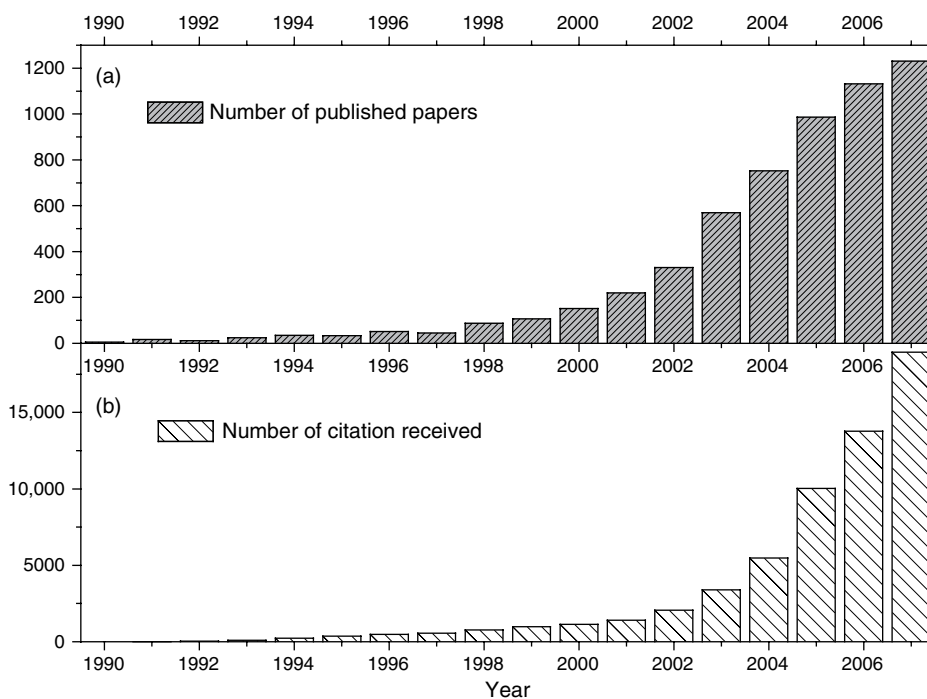


Fig. 1. (a) Number of paper published per year found using nanochemistry OR nanophysics OR nanotechnology OR nanoscience as search keys. Spanned period 1990 to 2007; total number of papers 5788 source ISI web of science. (b) Number of citations received per year by the papers reviewed in (a): total number of citations 59,747.

¹ *Subject Categories* are classes where journals are sorted according to the scientific topic of the published papers.

Table 1

List of a selection of scientific journals belonging to the Subject Category named “Nanoscience & Nanotechnology” sorted by publishing age. The last column refer to the aggregated values obtained by the 32 journals together. Data reported in this line allow to evaluate the impact of the Subject Category and to locate each single journal belonging to the category in a pondered ranking scale

Journal name	Publisher	Published since	Papers published in 2006	Impact factor 2006 ^a	Immediacy index 2006 ^b
<i>Nanotechnology</i>	IoP	1994	1042	3.037	0.534
<i>J. Nanopart. Res.</i>	Kluwer first, now Springer	1999	101	2.156	0.119
<i>Nano Lett.</i>	ACS	2001	555	9.960	1.485
<i>Lab Chip</i>	RSC	2001	190	5.821	1.111
<i>Physica E</i>	Elsevier	2001	503	1.084	0.163
<i>J. Nanosci. Nanotechnol.</i>	American Scientific Publishers	2001	586	2.194	0.309
<i>IEEE Trans. Nanotechnol.</i>	IEEE	2002	111	1.909	0.207
<i>Small</i>	Wiley-VCH	2005	210	6.024	1.152
<i>Curr. Nanosci.</i>	Bentham Science Publ. Ltd	2005	33	2.080	0.242
<i>Nano Today</i>	Elsevier	2006	14	–	1.357
<i>Nature Nanotechnol.</i>	Nature Publishing Group	2006	24	–	0.833
<i>ACS Nano</i>	ACS	2007	0	–	–
Subject Category: 32 journals	–	2005	8939	2.459	0.400

^aThe journal impact factor of year 2006 is the average number of times articles from the journal published in 2005 and 2004 have been cited in 2006. Journals published first in 2006 will have their first impact factor evaluation for year 2007, usually divulgated in spring 2008.

^bThe journal immediacy index of year 2006 is the average number of times an article published in 2006 is cited in 2006. The journal immediacy index indicates how quickly articles in a journal are cited.

This scientific and technological phenomenon has been so significant that the most important publishing companies have decided to create new journals specifically devoted to this topic (see Table 1 for a selection). The Institute of Physics (IoP) has been the first publisher in this field, founded in the early 1990s the journal *Nanotechnology* (impact factor 3.037), which has published more than 4000 papers so far. This number makes *Nanotechnology* the most important journal in the field in terms of published papers. In 1999 Kluwer Academic Publishers founded the journal *J. Nanopart. Res.* Then, in 2001 appeared *Nano Lett.*, from the American Chemical Society (ACS), which probably represents today the most prestigious journal in the field, with more than 2800 published papers and an impressive impact factor that, starting from 5.033 in 2002, progressively increased to almost 10 in 2006. Among the ACS journals, excluding the review journals (*Chem. Rev.* and *Accounts Chem. Res.*), *Nano Lett.* has become the highest impact factor journal, even exceeding the prestigious *J. Am. Chem. Soc.*, first published in 1879. In the same year 2001, the Elsevier journal *Physica E* changed its name into *Physica E-Low-Dimensional Systems & Nanostructures*, while the Royal Society of Chemistry (RSC) launched

the title *Lab Chip* (impact factor as high as 5.821) and also *J. Nanosci. Nanotechnol.* (impact factor 2.194) appeared. An important impact factor (6.024) has been achieved by the title *Small*, published by Wiley-VCH since 2005 (see Table 1). In 2006, Elsevier launched the title *Nano Today*, while the prestigious Nature Publishing Group entered the business with the journal *Nat Nanotechnol.* The success of *Nano Lett.* encouraged ACS to found a second title in the field: *ACSNANO*, whose first articles appeared at the end of 2007.

The American Institute of Physics (AIP) and the American Physical Society (APS) adopted a different strategy. Starting from 2000, they selected the most pertinent papers published on the regular AIP and APS journals (*Phys. Rev. Lett.*, *Phys. Rev. A*, *Phys. Rev. B*, *Appl. Phys. Lett.*, *J. Appl. Phys.*, etc.) in a web collection named *Virtual Journal of Nanoscale Science & Technology* (<http://www.vjnano.org/>). Currently, more than 50 journals (see <http://www.virtualjournals.org/vjs/partpub.jsp> for a complete list), including *Science* and *Nature*, joined this virtual journal.

In 2005 the ISI web of Science (<http://scientific.thomson.com/products/wos/>) has introduced a new subject category (see footnote 1) named “Nanoscience & Nanotechnology.” Twenty-seven journals joined that subject category that year, and they are 32 in 2006. Among them, we count journals that already had a long history, like *J. Vac. Sci. Technol. B* (impact factor 1.597) started in 1983, or *Scripta Materialia* (impact factor 2.161), or *Mater. Sci. Eng. A* (impact factor 1.490), or *Microporous Mesoporous Mater.* (impact factor 2.796), and devoted to zeolites and zeotypes that are crystalline porous materials with regular empty cavities and cages in the nanometer and sub-nanometer regime. The 32 journals belonging to the *Subject Category* “Nanoscience & Nanotechnology” in 2006 have 8939 edited papers, exhibit an aggregate impact factor of 2.459 and an aggregate immediacy index of 0.400 (see last row in Table 1). It is strange to note that the Academic Press/Elsevier journal *Superlattices Microstruct.* did not join this new *Subject Category*.

From the data reported in Fig. 1 and Table 1, the tremendous editorial blowup of nanoscience and nanotechnology in the past few years is evident. The editorial blowup mirrors the efforts produced worldwide in the laboratories. This research is funded with public and private money and represents the expectation that the society has in respect to this new branch of science.

2. Heterostructures and nanostructures: definition and applications, from optoelectronics to catalysis

On a historical ground, the future born of nanotechnology was probably first foreseen by physicist Richard Feynman at the American Physical Society meeting at Caltech on December 29, 1959, with his famous talk “There’s Plenty of Room at the Bottom.”

The first applications of nanotechnology were probably semiconductor heterostructures and nanostructures, also defined as low-dimensional systems, i.e., systems that are confined in one, two, or three spatial dimensions, resulting in 2D, 1D, and 0D systems, respectively [1–8]. In the fields of solid-state physics and optoelectronics, 2D, 1D, and 0D systems are usually labeled as quantum wells, quantum wires, and quantum dots (or boxes), respectively.

However, the interest in low-dimensional systems is not restricted to the fields of solid-state physics [1,7,9–12], interface physics [13–17], and optoelectronics [7,18–21], but examples of application of confined systems can be found also in several fields such as metallurgy [22,23], chemistry [24–54], catalysis [55–65], photocatalysis [66–73], and drug delivery [74–81]. All these systems are generally labeled as nanostructures as the confinement usually lies in the nanometer scale. The ultimate frontier in nanotechnology, the single molecule device, has been reached recently [82–88].

Emblematic among the fields mentioned so far is the case of catalysis. Catalysis is the science that is aimed to increase the speed and the selectivity of a given chemical reaction. A catalyst is a species that allows to reduce the activation barrier of a chemical reaction, and remains unchanged at the end of the process. Two examples of nanostructured catalysts will now be given. The first one concerns gold. Gold in bulk is known to be chemically inert and gold jewels have been passed on through millenaries, still keeping a perfect conservation. However, when gold is small enough, with particle diameters below 10 nm, it turns out to be surprisingly active for many chemical reactions [89–92], for instance, CO oxidation and propylene epoxidation. As a second example, we will mention zeolites and zeotypes: a new class of materials that, starting from the late 1970s, entered aggressively in the market of catalysts used in industrial plants. Zeolites are nanoporous crystalline aluminosilicates constituted by corner-sharing $[TO_4]$ tetrahedra, where $[TO_4]$ represents a silicon or an aluminum atom. The introduction of a trivalent Al(III) atom in a $[TO_4]$ unit (substituting the tetravalent Si(IV) atom) induces a net negative charge to zeolitic framework, which must be compensated by the presence of charge-balancing extra-framework cations. Such cations act as Lewis acid centers, being electron acceptors, but when they are protons, the zeolite becomes a Brønsted solid acid (i.e., a proton donor). Starting from the basic constituents, the framework of any zeolite will be realized by progressively connecting two adjacent $[TO_4]$ units by sharing an oxygen atom, which thus becomes “bridged” between the two T atoms (T–O–T).

The remarkably great flexibility of the T–O–T angle (from $\approx 100^\circ$ up to 180°) allows to realize, using the unique $[TO_4]$ unit as the sole building block, an impressive large number of different zeolites that results in crystalline aluminosilicates with ordered empty cavities in the 0.5–1.5 nm (Fig. 2) range hosting catalytic metal centers or proton donor centers [24,25,27,93–96]. Such materials act as nanoreactors as the chemical reactions occur inside their cavities. The pore opening and the dimension of the internal cavities discriminate the

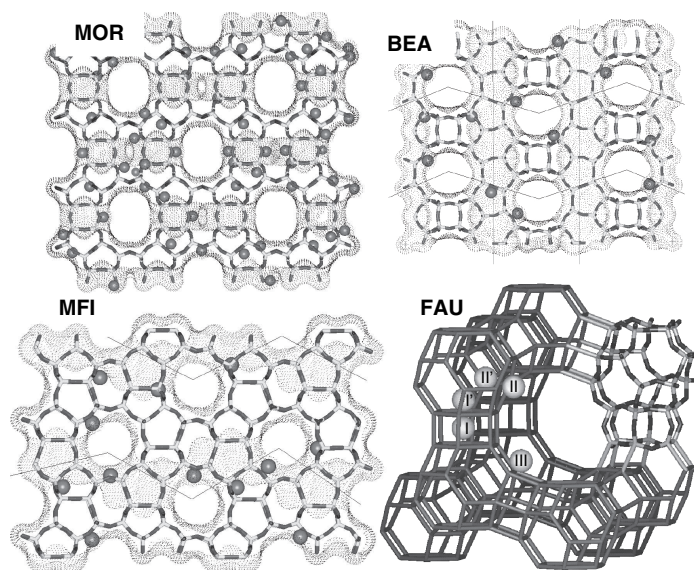


Fig. 2. Sticks representation of four different nanostructured zeolitic frameworks: mordenite (MOR), ZSM-5 (MFI), β (BEA) and Y (FAU). Light gray the tetrahedral coordinated Si or Al atoms; dark gray O atoms. Extra-framework charge-balancing counterions, playing the role of active catalytic centers, are represented as spheres.

reactant molecules that reach the catalytic centers and the product molecules formed. Therefore, we are dealing with shape-selective catalysts, which represent the best artificial attempt to simulate the enzymes created in the nature. Only recently, the scientists involved in the field of catalysis have explicitly used the word “nano” in their articles and books [65], but it is evident that people working in the field of catalysis studied nanoscience since decades.

3. Dynamic interplay among growth/synthesis techniques, theoretical modeling, and characterization techniques in the design and improvement of semiconductor heterostructure-based devices

Great efforts have been made in improving the preparation methods (epitaxial growth [97–113], etching/regrowing [5,114,115], self-organized growth [116–118], Langmuir–Blodgett films [26–27,119,120], nanolithography [50,121–123], scanning tunneling microscopy (STM) tip-assisted deposition [113], surfactant assemblies as supramolecular templates [124], bottom-up self-assembly approaches [50,113,125–131], intrazeolite encapsulation [24,25,27,28,50,132–134],

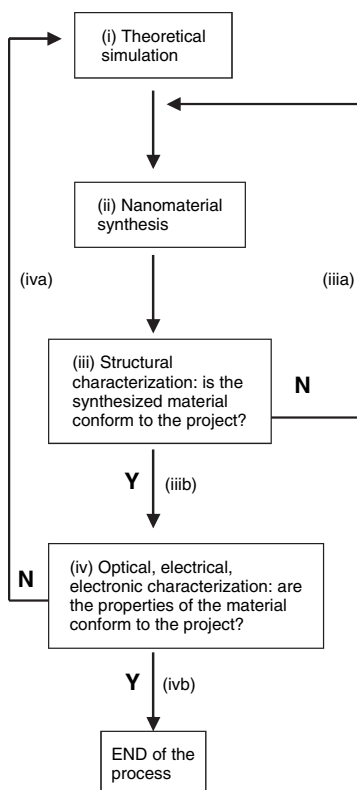


Fig. 3. Flow chart schematizing the strictly interconnected interplay among theoretical calculations (i), synthesis/growth techniques (ii) and characterization techniques (iii and iv) in the improvements in the realization of nanostructures with desired performances.

etc.) of low-dimensional systems to optimize the size control of the confinement regions and of the confined systems, to guarantee a spatial homogeneity, and to optimize the preparation reproducibility. Parallely, important theoretical efforts have been made to predict the properties of low-dimensional systems, and relevant progresses have been achieved in their characterization [21,123,135–143].

Improvements in the realization of nanostructures can be realized by a strict interplay among the progress achieved on these three grounds, as basically schematized in the flow chart in Fig. 3 and described in the following. (i) theoretical calculations predict the physical properties of a given nanostructure; (ii) the preparation techniques try to realize it; (iii) structural characterization techniques check whether the actually realized nanostructure corresponds to the desired one or not; (iiia) if not, the preparation conditions have to be optimized and step (ii) has to be repeated; (iiib) if yes, then optical, electrical, electronic, chemical reactivity, etc. properties are checked to verify whether the desired nanostructure has actually the foreseen properties (iv); (iva) if not, then the level of theory used in step (i) has to be improved and the game has to restart again from the beginning; (ivb) if yes, then end of the process. Point (ivb) represents the final point of the scientific work and the future of the device lies now on an engineering/economical level where the production rate, the realization costs, and the demand of the device are the main driving forces. Of course, the interplay often moves in the opposite direction, i.e., theoretical models help in the interpretation of the previously not understood (or wrongly interpreted) experimental results.

4. Purposes of the book and chapters layout

The book is structured in chapters, each one devoted to a specific characterization technique used in the understanding of the properties (structural, physical, chemical, electrical, etc.) of semiconductor quantum wells, superlattices, and nanostructures in general. A chapter is devoted to the *ab initio* modeling. Basically, the book has two aims. The first one deals with the educational point of view. The first part of each chapter provides the basic concept of each of the selected techniques with an approach understandable by Master and PhD students in Physics, Chemistry, Material Science, Engineering, and Nanotechnology. The second aim is to provide a selected set of examples from the recent literature of the latest results obtained with the specific technique in understanding the properties of semiconductor heterostructures and nanostructures. Each chapter has this dual structure: a first part devoted to explain the basic concepts, providing the larger possible audience, and a second one to the discussion of the most peculiar and innovative examples, allowing the book to have the longer possible shelf life. Of course, the book is devoted to the specialized subset of scientists working in the field design, growth, characterization, and testing of heterostructure-based devices based in both academic and industrial laboratories. But the final goal is somewhat more ambitious, and in this regard, the topic of quantum wells, wires, and dots should be seen as a pretext of applying top level characterization techniques in understanding the structural, electronic, etc. properties of matter at the nanometer (even sub-nanometer) scale. In this way, it is aimed to become a reference book in the much broader, and extremely hot, field of nanotechnology.

Besides growth and synthesis techniques, step (ii) for which we refer the reader to specified books and reviews articles [5,24–28,50,97,110–112,116–120, 122,124,125,127,131,144–149], the remaining three fundamental steps of the flow chart reported in Fig. 3 have been considered in the book. Chapter 2, coordinated by Maria Peressi (University of Trieste, Italy), is devoted to

the study of structural and electronic properties of semiconductor heterostructures and nanostructures by *ab initio* calculations (step (i) in Fig. 3).

The experimental investigation of structural properties (step (iii) in Fig. 3) is provided in the following chapters: Chapter 4 discussing X-ray diffraction (XRD) (coordinated by Claudio Ferrari, IMEM-CNR, Parma, Italy); Chapter 5 presenting transmission electron microscopy (TEM) (coordinated by Laura Lazzarini IMEM-CNR, Parma, Italy); Chapter 9 introducing extended X-ray absorption fine structure (EXAFS) (authored by Federico Boscherini, University of Bologna, Italy); Chapter 10 dealing with surface-sensitive X-ray techniques and anomalous scattering (coordinated by Till Metzger, ESRF, Grenoble, France); and Chapter 11 treating the coupled crystallographic and spectroscopic diffraction anomalous fine structure (DAFS) technique (coordinated by Maria Grazia Proietti, CSIC-Universidad de Zaragoza, Spain and by Hubert Renevier, CEA Grenoble, France).

The characterization of the nanostructures properties (step (iv) in Fig. 3), is explained in the following chapters: Chapter 3 for the electrical properties of nanostructures (coordinated by Anna Cavallini, University of Bologna, Italy); the methods for investigating the radiative recombination channels of semiconductor nanostructures are discussed in Chapter 6 (coordinated by Stefano Sanguinetti, Università Milano II, Italy) and in Chapter 7 (coordinated by Giancarlo Salviati, IMEM-CNR, Parma, Italy) that are devoted to photoluminescence and cathodoluminescence spectroscopies, respectively; phonons in nanostructures are described in Chapter 10 (authored by Daniel Wolverson, University of Bath, UK), describing Raman spectroscopy; the band discontinuities in semiconductor heterojunctions are explained in Chapter 12 (authored by Giorgio Margaritondo, EPFL, Lausanne, Switzerland), where photoelectron spectroscopies are introduced; and last but not the least, Chapter 13 (coordinated by Andre Stesmans, University of Leuven, Belgium) deals with the characterization of interfaces and nanolayers in semiconductor heterostructures by means of electron spin spectroscopy.

By moving from bulk materials down to 2D-, 1D-, and 0D-confined heterostructures, the volume (and thus the number of atoms) forming the active regions in nanostructured devices is reduced by order of magnitudes. This means that the understanding of the structural properties of such nanostructures often requires high photon flux techniques like those exploiting synchrotron radiation sources [150–152]. In fact, synchrotron radiation has distinct advantages as a photon source, notably high brilliance and continuous energy spectrum; by using the latter characteristic atomic selectivity can be obtained and this is of fundamental help to investigate the structural environment of atoms present only in a few angstroms (Å) thick interface layers of heterostructures. The third-generation synchrotron radiation sources have allowed to reach the limit of measuring a monolayer of material, corresponding to about 10^{14} atoms/cm². Chapters 9–12 describe synchrotron radiation techniques.

5. A key example of multidisciplinary in nanotechnology: the atomically defined –O–Ti–O–T–O– quantum wires guested in ETS-10 titanosilicate

The last section of this chapter is devoted do briefly describe an example of a nanoporous titanosilicate material that, as zeotype, belongs to the class of materials for catalysis. It has however become rather famous for its nanostructured nature.

Titanium dioxide colloids have attracted tremendous interest because of their potential utility in photocatalytic [153–157], photovoltaic [158,159], and battery [160] applications; moreover, they exhibit nonlinear optical properties [161]. Also heteroepitaxial technique has been used to grow TiO_2 films (see e.g., Refs [162,163]). These interests have strongly encouraged the study of TiO_2 nanoparticles [154,156,157,164–174]. Among all these studies, we mention the studies of Anpo et al., who combined UV–Vis diffuse reflectance spectroscopy, photoluminescence, X-ray absorption near-edge structure (XANES), and EXAFS to investigate TiO_2 nanoclusters hosted inside zeolite Y [156,157]. A blue shift of the energy gap of the TiO_2 particle hosted inside the zeolite, with respect to bulk titania, has been observed. These studies represent examples of semiconductor quantum dots hosted inside the ordered nanovoids of zeolite materials, acting as inverse template agents. We focus now the attention on the different case of semiconductor nanowires already present inside the zeolitic framework. The two great advantages in obtaining the semiconductor quantum wire directly during the synthesis as part of the framework, with respect to postsynthesis encapsulation inside the voids, are the elimination of the risks of (i) the formation of a bulk semiconductor segregated phase outside the zeolitic crystals and (ii) an incomplete filling of the voids, which could result in inhomogeneity of the size confinement.

Engelhard titanosilicate ETS-10 is a microporous crystalline material belonging to the family of Ti-substituted silicates [175]. Owing to the high degree of disorder, and also due to the presence of two polymorphs, a straightforward structural determination from XRD was not possible; and Anderson et al. have solved the structure using combined high-resolution TEM, XRD, solid-state NMR, and molecular modeling techniques [176–178]. They proposed a model where the ETS-10 framework is composed of corner-sharing $[\text{SiO}_4]$ tetrahedra and $[\text{TiO}_6]$ octahedra (Fig. 4(a)) linked through bridging oxygen atoms, forming 12-membered rings, which give rise to two sets of perpendicular channels having an elliptical cross-section $7.6 \times 4.9 \text{ \AA}$ (Fig. 4(c)). One of the most important characteristics of ETS-10 is that the $[\text{TiO}_6]$ octahedra are linked together with formation of linear $\dots\text{O-Ti-O-Ti-O-Ti-O}\dots$ chains (see Fig. 4(b)). Each Ti atom is also linked, in the perpendicular plane, to four Si atoms through oxygen bridges [176–178] resulting in the 3D structure shown in Fig. 4(c).

As bulk TiO_2 is a wide band gap semiconductor [179], $E_g = 3.02 \text{ eV}$ for rutile (see gray curve in Fig. 4(d)) and 3.18 eV for anatase, the presence of an atomically defined $\dots\text{O-Ti-O-Ti-O-Ti-O}\dots$ chains, embedded inside a highly insulating siliceous matrix, $E_g(\text{SiO}_2) \sim 9 \text{ eV}$ [180], implies that ETS-10 can be considered as a 1D quantum wire of atomic definition. This observation was first in 1997 [33], proving that the confinement of electrons and holes inside the $\dots\text{O-Ti-O-Ti-O-Ti-O}\dots$ wires resulted in a blue shift of the energy gap ($E_g = 4.03 \text{ eV}$, evaluated at the inflection point of the black spectrum in Fig. 4(d)) of ($E_g = 0.85$ and 1.01 eV , when computed from anatase or from rutile, respectively). The experimental blue shift was comparable with that predicted by the simple model of a particle confined along the two directions (xy , in Fig. 4(b)) inside an infinite potential barrier:

$$\Delta E_g = \frac{h^2}{4\mu d^2} = 0.84 \text{ eV} \quad (1)$$

where h is the Planck constant ($6.6256 \times 10^{-34} \text{ J s}$), $\mu \sim 2m_e$ is the reduced effective mass of the electron–hole pairs along the wire direction, and $d \sim 6.7 \text{ \AA}$ is the wire diameter. Equation (1) has

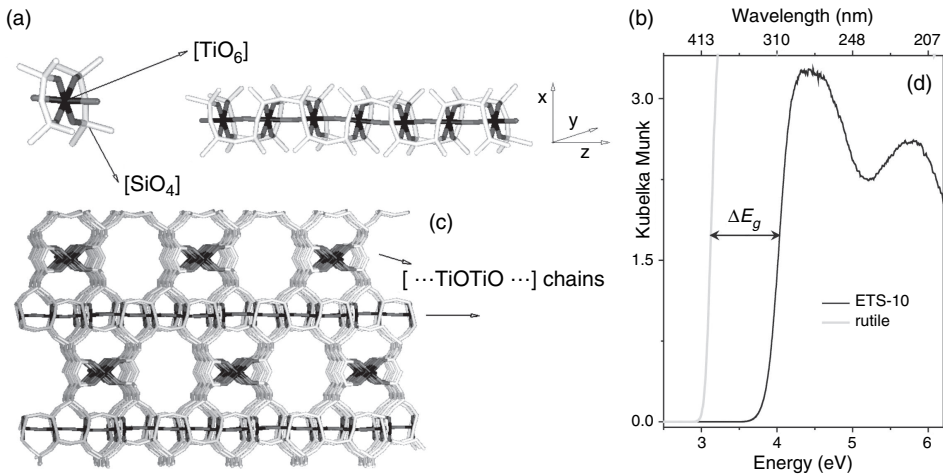


Fig. 4. The framework structure of ETS-10 showing chains of corner-sharing [TiO₆] octahedra which run along two perpendicular directions, and which are isolated by corner-sharing [SiO₄] tetrahedra: (a) single element of the chain; (b) single chain; (c) three-dimensional view. For clarity, extraframework (charge-balancing) cations are omitted. Ti (black), O (dark gray), Si (light gray). Part (d) reports the DRS UV-VIS spectrum of ETS-10 (black curve, reported from [33]) compared with that of rutile bulk (gray curve). The shape of this spectrum reflect the DOS of the unoccupied valence states. The blue shift of the band gap (ΔE_g), with respect to bulk TiO₂, is also evidenced.

been written by considering the potential outside the wire infinite and neglecting the exciton binding energy. Both approximations are well acceptable as the E_g of the host SiO₂ matrix (≈ 9 eV) is much greater than that of TiO₂ (≈ 3 eV), and because of the high dielectric constant of TiO₂ ($\epsilon \approx 180$ [179]): this implies that the exciton binding energy is in the meV range [181]. The oversimplified model that is behind Eq. (1) already gives a qualitative agreement between the predicted energy shift ($\Delta E_g = 0.84$ eV) and the experimental ones ($\Delta E_g = 0.85$ or 1.01 eV). Subsequently, the band structure of the $\dots\text{O-Ti-O-Ti-O-Ti-O}\dots$ quantum wires embedded inside ETS-10 has been computed by ab initio periodic models [37,45].

Recently, Yilmaz et al. [182] reported original I - V experiment on a similar titanosilicate (ETS-4), also characterized by $\dots\text{O-Ti-O-Ti-O-Ti-O}\dots$ linear chains, reporting a non-linear behavior at higher bias voltages. The nonohmic I - V behavior has been explained in terms of space-charge-limited effect due to the fact that the conduction occurs inside an atomically defined $\dots\text{O-Ti-O-Ti-O-Ti-O}\dots$ quantum wire embedded in an highly insulating SiO₂ crystalline hosting matrix.

Till now, one of the most promising application of ETS-10 and ETS-4 materials is in the field of photocatalysis [69,71,183]. The combination of a wide band gap semiconducting oxide with a 3D 12-membered ring microporous framework offers many potential advantages in photocatalysis such as excellent diffusion of reactant molecules, trapping and, in particular, shape selectivity. In the perfect structure, these quantum wires are surrounded by an envelope of SiO₄ groups. These wires are characterized by full (O-based: 2p) valence and empty (Ti-based: 3d_{xy} and 3d_{x₂-y₂}) conduction bands [37,45], separated by a band gap of about 4.03 eV, which is slightly higher than that of TiO₂ (3.2 eV) due to confinement effects. They can act as an antenna-like system able to collect the light and to form electron-hole

pairs in the $-O-Ti-O-Ti-$ chain. Like in TiO_2 , these pairs can recombine or diffuse toward the wire, to its end, originating a photocatalytic activity. In a perfect crystal, this happens where the wires emerge on the external surface, but in the real material this can happen also at internal defects (Ti vacancies). In the cited works [69,183], it has been demonstrated that there are three main features of the degradation process: (i) the photocatalytic active sites are titanols located on the external surfaces where the $-O-Ti-O-Ti-$ chain emerge, exposing a surface $Ti-OH$ titanol group; (ii) the fundamental role in determining the shape selectivity is played by the channels and channel mouth shape; (iii) both activity and selectivity can be improved by controlled defect production [69]. As a high selectivity toward the photodegradation of large aromatic molecules has been observed, it has been concluded that molecules entering the pore system were protected from photodegradation, which occurred on the external surface. The ETS-10 thus displays a peculiar inverse shape selectivity. The interpretation that the active photocatalytic centers are $Ti-OH$ species at defective sites agrees well with the parallel studies by the Howe's group [184,185], who have shown how a highly defective proton exchanged sample of ETS-10 was much more active for the gas-phase photo-oxidation of ethylene than a well-crystalline as-synthesized sample. The local structure of the actually involved $Ti-OH$ sites and the photochemical mechanism are however still a matter of debate.

ETS-10 has presented a severe problem for the characterization techniques. It has already been shown how its structure has been solved by only combining high-resolution TEM, XRD, solid-state NMR, and molecular modeling techniques [176–178]. Also the EXAFS characterization of this material was far from being straightforward. EXAFS spectroscopy (see Chapter 9) is an important tool for the characterization of new materials, particularly when an important degree of disorder in the structure prevents the straightforward use of diffraction techniques, as was the case for ETS-10 [177]. In the first EXAFS results on ETS-10, Davis et al. [186] performed a single scattering study treating all the first shell oxygen as equivalent and finding an averaged $Ti-O$ distance of $2.00 \pm 0.01 \text{ \AA}$. Subsequently, Sankar et al. [187] presented a local model for the Ti environment able to reproduce the whole EXAFS signal, i.e., up to the second Ti and Si shells, whose contributions appear up to about 3.6 \AA in R space. This model is based on the presence of four equivalent $Ti-O-Si$ contributions, perpendicular to the $-Ti-O-Ti-O-$ chain (characterized by a unique $Ti-O$ distance of 2.02 \AA), and two unequivalent $Ti-O$ contributions along the chain, characterized by significantly different first shell $Ti-O$ distances of 1.71 and 2.11 \AA [187]. The presence of a short and a long $Ti-O$ distance along the $-Ti-O-Ti-O-$ chain is not present in the model proposed by Wang and Jacobson [188] based on single-crystal diffraction, or in the computational results of Sankar himself, based on a periodic atomistic approach [187], or in those of Damin et al. [45] based on a periodic ab initio method. In all the cases, two equivalent axial $Ti-O$ distances are found at 1.872 \AA (by Wang and Jacobson [188]), at 1.88 \AA (by Damin et al. [45]) and at 1.90 \AA (atomistic approach by Sankar et al. [187]). Prestipino et al. [189] have been able to analyze EXAFS and XANES spectra of ETS-10 starting from the periodic ab initio investigation by Damin et al. [45], and with the single-crystal data (collected on a single polymorph) by Wang and Jacobson [188].

The example of ETS-10 titanosilicate, chosen to conclude this chapter, is emblematic and tells us that when the structure and the properties of a nanostructured materials become highly complex, the synergic use of different structural and nonstructural characterization techniques properly supported by ad hoc, ab initio simulations becomes a must to fully understand and exploit the synthesized nanomaterial.

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