Progress in Surface Science 91 (2016) 1–28

Contents lists available at ScienceDirect

Progress in Surface Science

journal homepage: www.elsevier.com/locate/progsurf

Review

Surface physics of semiconducting nanowires

Michele Amato [a], Riccardo Rurali [b,*]

[a] Institut d'Électronique Fondamentale, UMR 8622, CNRS, Université Paris-Sud, 91405 Orsay, France
[b] Institut de Ciència de Materiales de Barcelona (ICMAB–CSIC), Campus de Bellaterra, 08193 Bellaterra (Barcelona), Spain

A R T I C L E I N F O

Commissioning Editor: Nicolas Lorente

Keywords:
Semiconducting nanowires
Surface physics
Molecular doping
Chemical sensors
Biological detection

A B S T R A C T

Semiconducting nanowires (NWs) are firm candidates for novel nanoelectronic devices and a fruitful playground for fundamental physics.

Ultra-thin nanowires, with diameters below 10 nm, present exotic quantum effects due to the confinement of the wave functions, e.g. widening 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 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 electronic devices and different kinds of applications. A legitimate question is then: what makes a nanowire different from bulk systems? The answer is certainly 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 controlled surface morphology. Next we discuss the importance of a proper surface 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.

* Corresponding author.
E-mail address: rrurali@icmab.es (R. Rurali).

http://dx.doi.org/10.1016/j.progsurf.2015.11.001

Contents

1. Introduction

Semiconducting nanowires (NWs) are rod-like pieces of semiconductor with a characteristic diameter in the nanometer scale [1,2]. In a strongly confined regime nanowires exhibit an exotic behavior that reveals their quantum nature: the band-gap can be tuned [3], the density of states is quantized [4], luminescence can be largely increased [5]. As a matter of fact some of the early publications [5–9] 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 electronic devices [10]. They are always semiconducting, because of their aspect ratio they can be simultaneously used as the active region of the device, e.g. the channel of a field-effect transistor, or to connect different devices [11], 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, after the *gold rush* to the *thinnest nanowire ever* that yielded diameters in the 1–10 nm range [12–22], 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 advanced proof-of-concept devices, some of which outperform their conventional planar counterparts [23].

In this article we review the surface physics and chemistry of group-IV semiconducting 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 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 orientations of nanowires and, consequently, the facet arrangement; the chemical passivation of the nanowire surface and its effect on the nanowire properties are 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 conclusions in Section 5.

2. Surface reconstruction and facet arrangement

The most fascinating aspect of Si NWs is the possibility to vary their properties by tailoring the size. As it has been demonstrated in many works (see Ref. [2] and references therein), the reduction of diameter in Si NWs can induce novel effects that have often a remarkable impact on both basic and applied 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