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Review

Doping of silicon nanocrystals

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ABSTRACT

Over the last decades silicon nanocrystals (Si NCs) were the subject of an intense research activity, due to their optical and electronic properties. Different experimental approaches were developed to synthesize Si NCs embedded in a dielectric matrix as well as freestanding Si NCs with well-controlled structural and morphological characteristics. Actually, as in the case of bulk semiconductors, the fine tuning of their optical and electronic properties is related to the effective capability to control doping, i.e. incorporation impurity atoms within these nanostructures. Even if Si NCs incorporating both p-type and n-type dopants were successfully synthetized, several fundamental issues need to be understood. First of all, from a structural point of view, it is very hard to obtain information about dopant location with respect to Si NCs surface and core. This uncertainty is related either to the intrinsic limitations of the experimental approaches for the synthesis and for the analysis of doped Si NCs, or to the difficulties in the modeling of these nanostructures. Moreover, from a fundamental point of view, it is not clear if impurity incorporation in Si NCs effectively results in the generation of free charge carriers as in the case of bulk silicon. This review presents an overview of the recent progress in the field, focusing on the latest results related to doping of Si NCs. In particular the problem of thermodynamic stability of impurities into Si NCs and the problem of modulation of electrical properties of Si NCs will be systematically addressed.

1. Introduction

Semiconducting nanostructures with reduced dimensionality have attracted considerable scientific interest due to their peculiar properties arising from the interplay between quantum confinement and surface related effects. In fact, if at least one of the dimensions of these nanostructures is smaller than twice the Bohr radius of the exciton in the bulk material, quantum confinement occurs, causing a different electronic and optical behavior of the nanostructures compared to bulk materials. Moreover, the reduced size of these nanostructures induces a remarkable increase of the surface area to volume ratio (S/V). Consequently surface related defects may significantly alter the electronic behavior of these nanostructures [1]. In particular silicon nanostructures are particularly appealing for application in several fields like microelectronics, optoelectronics, photovoltaics, plasmonics and thermoelectric [2–5]. During the last century, impurity doping of Si was used to tailor the electronic properties of bulk silicon, employing p/n junctions as common building blocks of Si-based electronic devices [6]. The exploitation of Si nanostructures as basic elements for the fabrication of complex optoelectronic and microelectronic devices requires the capability to effectively control their electronic proprieties by means of doping as in the case of bulk semiconductors.

In the last decades silicon nanocrystals (Si NCs), i.e. silicon particles having diameter (d) smaller than 100 nm and composed of atoms in either a single- or poly-crystalline arrangement, were the subject of an intense research activity, owing to their optical and electronic properties [7–9]. In Fig. 1(a) High-Resolution Transmission Electron Microscopy (HRTEM) images of a small Si-NC with spherical and non-crystalline morphology is reported [10]. Furthermore, Si NCs represent a paradigmatic system because the attainable results are in the extreme case of nanoscaling, from bulk to 0D system. Therefore they are extremely useful for the understanding of other silicon systems with reduced dimensionality like nanowires, fins or nanosheet [11–14]. Several studies are available in the literature on the synthesis of Si NCs embedded in dielectric matrix and freestanding Si NCs [15]. Si NCs embedded in dielectric matrix have been synthesized by ion implantation [16–18], chemical vapor deposition (CVD) [19–21], e-beam deposition [22,23], sputtering [24–26] and reactive ion etching [27]. As an example, in Fig. 1(b) the 3D atom map of a Si NCs layer inside a SiO_2 matrix obtained by Atom Probe Tomography (APT) is reported [28]. Most of these approaches are based on processes that are already employed by microelectronic industries in order to facilitate the integration of these nanostructures in functional microelectronic devices [29–32]. Conversely freestanding Si NCs have been synthesized

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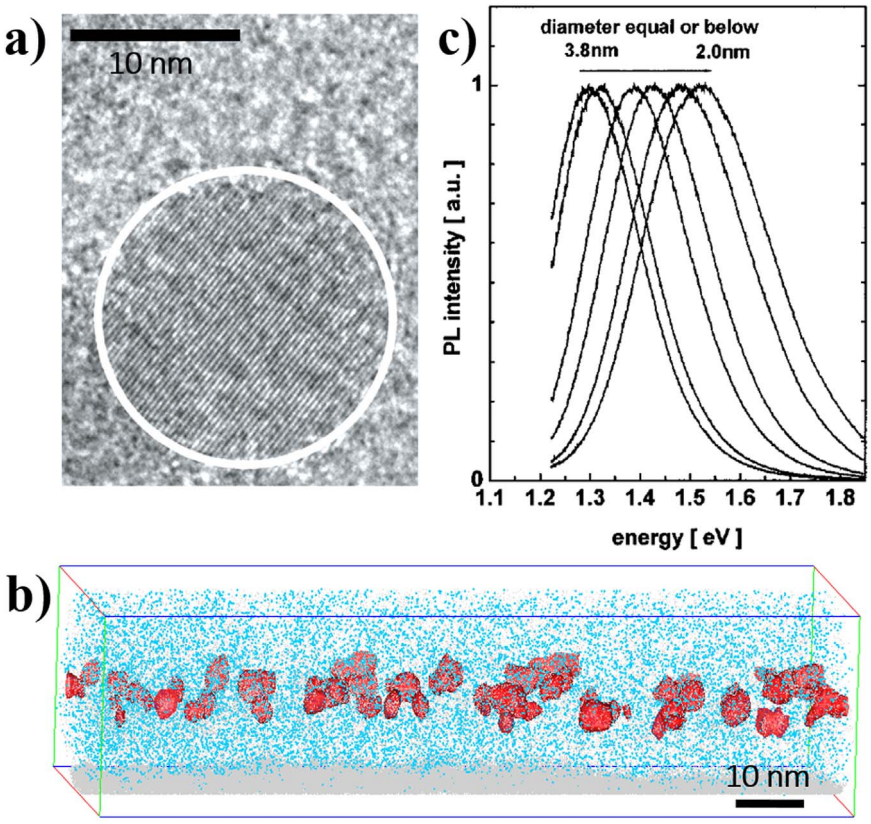

Fig. 1. (a) HRTEM of a small Si-NC with spherical and monocrystalline morphology, reprinted by Dogan et al. [10] (b) 3D atom map of Si NCs layer inside SiO2 matrix obtained by APT [28] (c) Normalized photoluminescence spectra showing a blue shift correlated with the crystal size, reprinted by Zacharias et al. [115].

by crumbling porous Si [33,34] or by gas-phase approaches, which usually concern the decomposition of a Si precursor by means of thermal heating [35], laser ablation [36] or plasma [37–39]. Freestanding Si NCs open the route to the control of surface chemistry and are extremely interesting for the development of thermoelectric devices [40,41], single electron transport device [42,43], solar cell [44], cold electron emitting device [45] and optical device [46].

In the case of very small Si NCs, quantum confinement phenomena play an important role in the definition of their electrical and optical properties. Since Bohr radius of an exciton in silicon is about 5 nm, quantum confinement phenomena have been observed for Si NCs with diameter smaller than 10 nm as widely reported in the literature [17,47–51]. The most striking effect is related to the progressive increase of the band gap [15,16,18,26,37]. An example is shown in Fig. 1(c) [18] in which the band gap increases from 1.12 eV (band gap of silicon bulk) up to 1.6 eV when decreasing the average size of the nanostructures. Actually, according to circumstances, the band gap variation induced by quantum confinement effects is in direct competition with band gap modifications determined by the presence of surface induced defects [1], the oxidation degree of the NCs [53] or the different surface passivations [54]. On one hand, surface related defects may appear as localized states within the band gap of Si NCs, further modifying the electronic behavior of Si NCs with respect to bulk silicon. In particular in a recent work Seguini et al. [1] investigated the band alignment of Si NCs embedded in a SiO_2 matrix as a function of the average diameter of the Si NCs. Three different regimes were identified by progressively shrinking Si NCs diameter; primarily quantum confinement affects the conduction band that is shifted towards high energy values, then surface effects pin the conduction states, and finally quantum confinement modifies the valence band with a shift towards low energy values [1]. On the other hand Guerra et al. [53] demonstrated that the quantum confinement dominates in the H-terminated Si NCs irrespective of their sizes. Conversely in the cases of OH-terminated Si NC and of Si NCs embedded in a SiO_2 matrix the effect of oxidation seems to override the effects of quantum confinement when the diameter decreases below 2 nm. Furthermore Konig et al. [54] demonstrated that for Si NCs core size up to 1330 Si atoms, the nature of the interface bonds can significantly influence the electronic structure of Si NCs, in direct competition with quantum confinement. Finally, it is very important to remind that this band gap evolution can be eventually associated to the transition from indirect to direct band gap as the Si NCs size decrease. Delerue et al. [55] predicted this behavior for Si crystallite sizes lower than 2.5 nm in terms of enhanced efficiency of the radiative recombination rate. Recently Hapala et al. [56] introduced a general method which allows reconstruction of electronic band structure of Si NCs from ordinary real-space electronic structure calculations. They concluded that the band-structure concept can be properly applied to silicon nanocrystals with diameter larger than 2 nm, suggesting that for smaller NCs the concept of indirect band gap has no meaning.

In addition to this very complex picture, the problems of impurities incorporation and doping in Si NCs is actually very far from being understood and some important issues still need to be clarified from the experimental and theoretical point of view. Actually, both p-type (B) and n-type (P, As) impurities have been successfully introduced in very small Si NCs by means of different experimental approaches [57–59]. Nevertheless very few data are available about the thermodynamic stability of the impurity atoms in the Si NCs [60]. This uncertainty is related to the intrinsic limitations of the experimental approaches for the synthesis and for the analysis of these Si NCs, as well as to difficulties in modeling this nanostructured system [60]. Moreover, the effect of impurities on the electronic properties of Si NCs has not been elucidated yet. In particular it is not clear if the incorporation of impurities in Si NCs corresponds to effective doping of the Si NCs, i.e. to the generation of free charge carriers [61,62].

The present review provides an overview of the most recent results