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Review article

Doped and codoped silicon nanocrystals: The role of surfaces and interfaces

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A B S T R A C T

Si nanocrystals have been extensively studied because of their novel properties and their potential applications in electronic, optoelectronic, photovoltaic, thermoelectric and biological devices. These new properties are achieved through the combination of the quantum confinement of carriers and the strong influence of surface chemistry. As in the case of bulk Si the tuning of the electronic, optical and transport properties is related to the possibility of doping, in a controlled way, the nanocrystals. This is a big challenge since several studies have revealed that doping in Si nanocrystals differs from the one of the bulk. Theory and experiments have underlined that doping and codoping are influenced by a large number of parameters such as size, shape, passivation and chemical environment of the silicon nanocrystals. However, the connection between these parameters and dopant localization as well as the occurrence of self-purification effects are still not clear. In this review we summarize the latest progress in this fascinating research field considering free-standing and matrix-embedded Si nanocrystals both from the theoretical and experimental point of view, with special attention given to the results obtained by ab-initio calculations and to size-, surface- and interface-induced effects.

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1. Introduction

Silicon has become the most studied material in the past decades owing to its unique characteristics: Si is the second most abundant element (after oxygen) in the Earth's crust, making up 25.7% of its mass; it can be produced with impurity levels of less than 10^{-9}; it remains a semiconductor at higher temperatures than germanium; its native oxide is easily grown in a furnace and forms a better semiconductor/insulator interface than any other material. Silicon is not only easy to handle and fairly simple to manufacture but it is also cheap. Moreover it shows excellent electrical properties, high stability, optimal thermal characteristics and high mechanical strength. For these motives, this environmental friendly material is the most used element in semiconductor industry and, today, it represents the electronic material per excellence. It is also commonly used for solar or photovoltaic applications and its role in the optoelectronic industry is becoming more and more important.

However, the rapid evolution in the electronic, optoelectronic and photovoltaic sectors is facing severe constrictions due to the actual physical limits of Si-based technologies [1–3]. Some examples are: (i) the limitations in the operating speed of microelectronic devices due to interconnects, (ii) bulk Si is an indirect band-gap material which emits in the infrared region with very low efficiency, (iii) radiative recombination times in Si are very large, so the de-excitation dynamics are strongly affected by the occurrence of fast non-radiative recombinations mechanisms, (iv) bulk Si shows a significant free carrier absorption and Auger recombination rates which impede population inversion and, hence, optical gain, (v) its band gap impedes fully exploitation of solar radiation in photovoltaic applications, (vi) the absence of a bulk second-order dipolar non-linear optical susceptibility due to the bulk crystal centrosymmetry, that do not permit to use bulk Si in order to produce a wide variety of wavelengths from an optical pump.

The increasing demand for new, innovative and more efficient devices has driven scientists to explore new functionalities in Si-based materials. In photonics the main interest lies in the possibility to merge electronics and photonics on the same chip and therefore to render Si a good light emitter. Moreover the introduction of second-order nonlinearity by proper material engineering would be highly desirable, because the all-optical data management requires nonlinear silicon photonics [4]. Finally, for photovoltaic applications we have to add to Si new features in order to maximize solar radiation harvesting and to minimize loss by thermalization processes.

The advent of nanoscience and nanotechnologies and the consequent scaling down of Si structures to nanometer sizes have opened new possibilities to overcome the inability of bulk-Si as efficient light emitter. Moreover, the capacity of altering energy gap and optoelectronic properties by size reduction, and therefore to enhance solar light harvesting, has opened new possibilities in the development of new efficient, nanostructured, Si-based solar cell devices.

It has been suggested that the problems related to the indirect band-gap of bulk-Si might be overcome in highly confined systems. For example, in low-dimensional Si-based nanostructures such as porous-Si, a quantum sponge made up of Si nanostructures, nanowires (Si-NWs) and nanocrystals (Si-NCs), the possibility to achieve efficient visible photoluminescence (PL) has been demonstrated [5–8]. In these nanostructures the low-dimensionality causes the zone folding of the conduction band minimum of bulk Si, that is located near the *X*-point, thus introducing a quasi-direct band gap. Moreover the quantum confinement (QC) effect associated with the reduced size of the nanosystems enlarges the energy band gap enabling light emission in the visible range [9]. This effect can also enhance the spatial localization of electron (e) and hole (h) wave functions and their overlap, and therefore the probability of e-h recombination (see Fig. 1).

Among the different Si-based nanostructures, Si-NCs have attracted, from the beginning, much interest because they exhibit very bright visible PL (see Fig. 1), which is tunable with respect to the dimension of the Si-NCs [10], and sample dependent high quantum yields, ranging from 1% up to 60%. The quantum yields can be enhanced by careful surface passivation and by avoiding oxygen contamination during all stages of the Si-NC preparation [11]. Moreover optical gain in Si-NCs has been successfully observed and discussed [12–19] as well as giant Raman gain [20,21]. Finally carrier multiplication effects in excited carrier dynamics after the absorption of a single high-energy photon have been observed in ensemble of Si-NCs, proving thus the possibility of better exploiting processes of photo-generated carriers to increase solar cell performances [22–29].

The possibility to exploit the size, shape and surface termination [30] of the Si-NCs together with their low toxicity and good biocompatibility has prompted their application in several broad fields such as microeletronics [2,31,32], photonics [33,34], non-linear optics [35–37], secure communications [36], photovoltaics, in the so-called third-generation solar cells, solar fuels [3,38–43], thermoelectrics [44,45] and biomedicine [46–50].

Visible PL in Si nanostructures has been attributed to transition between states localized inside the Si-NC [51–54], or between defects and/or interface states [55–60]. Despite the discussion on which of the above mechanisms primarily determines the emission energy is still open, recent results seem to indicate the coexistence of both the effects, whose relevance depends on the structural properties of the sample [55,56,61–71]. In particular, it was suggested that for diameters above a certain threshold (from about 3 nm up to diameters of the order of two times the bulk Si exciton Bohr radius, about 9 nm) the emission peak of the Si-NCs simply follows the QC model, while interface states assume a crucial role only for small-sized Si-NCs (less than 3 nm) [69,72–74].