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## Introduction

### Silicon Nanocrystals; Fundamentals, Synthesis, and Applications

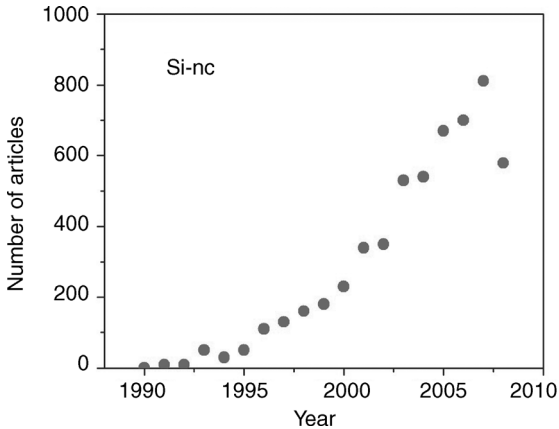
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Bulk Si crystal is the main material of today's microelectronic, photovoltaic, and MEMS technologies. Reducing the size of Si crystal to the nanoscale level brings about new properties and functionalities. Si nanocrystals (Si-nc) are expected to pave way for the new and exciting applications in microelectronic, photonic, photovoltaic, and nanobiotech industries. Being fully compatible with the existing technologies makes the use of Si nanocrystals easier and more attractive than other kind of nanoparticles. Thus, it is of great technological and scientific interest to know the physical and chemical properties of Si nanocrystals, its production methods, applications, and the way of their characterization.

This book presents fundamentals of Si nanocrystals and their applications in microelectronics, photonics, photovoltaics, and nanobiotechnology. Methods of preparation, growth kinetics, basic physical, chemical and surface properties, various applications such as flash memories, photonic and photovoltaic components, biosensing are extensively reviewed.

Figure 1.1 reports the number of results one gets when one looks for Si-nc in Google™ Scholar. A steady rise in the number of publications witnessing the rising interest in this material is observed. The initial search results refer to four papers reporting about different properties of Si-nc: the first is the paper by Pavesi *et al.* on the observation of optical gain [1], the second is the paper by Tiwari *et al.* on the use of Si-nc for memories [2], the third is the paper by Wilson *et al.* on the demonstration of quantum size effects in Si-nc [3], and the fourth is the paper by Mutti *et al.* on the observation of room temperature luminescence in Si-nc [4]. When one makes the same search on Google™ the first result concerns the use of Si-nc for photovoltaics [5]. All the key ingredients that make Si-nc appealing for photonics and microelectronics are discussed in these papers: quantum size effects make new phenomena appear in silicon, such as room temperature visible photoluminescence, optical gain, coulomb blockade and multiexciton generation.

However, Si-nc has a much wider application spectrum than bare silicon photonics or microelectronics. The goal of this book is to present the various applications of



**Figure 1.1** Number of articles versus year as reported by Google™ Scholar in a search performed on December 31, 2008. The search keys were “low-dimensional silicon” or “silicon nanocrystal(s)” or “silicon nanocluster(s).” The total number of articles integrated over the years

is 6220, while the results for “silicon photonics” is 1740 and for “porous silicon” is 28 800. The single point referred to year 2008 is low due to the time delay between the search date and the actual database construction.

Si-nc and introduce the first comprehensive collection of chapters on the technology, the synthesis and the applications of this new material.

The book is introduced with a chapter on fundamentals of Si nanocrystals, where a comprehensive theoretical overview of the electronic structure and optical properties of Si nanocrystals is given. The theoretical calculations are compared with experimental and first principles data. Chapter 3 discusses the main issues on optical properties of intrinsic, compensated and doped nanocrystals. Extensive experimental data and their analyses from a fundamental point of view can be found in this chapter. In Chapter 4, electrical transport through SiO<sub>2</sub> containing Si nanocrystals is presented. Transport mechanisms in low and high density regimes are shown to be different in nature. Hopping conduction, tunneling, and percolation mechanisms are discussed in detail. Chapter 5 deals with thermal properties of nanostructured Si. Lattice thermal conductivity in semiconductors, and specifically phonon boundary scattering, which is primarily responsible for the observed thermal conductivity reduction in different forms of Si nanostructures are discussed. A brief overview of thermal conductivity measurement is also provided in this chapter. Nanoparticles exhibit enormous surface area to volume ratios. It is expected that surface properties, including chemistry, of these versatile materials will strongly influence their material characteristics. Chapter 6 presents key studies of foundational silicon surface chemistry as it pertains to methods for controlling silicon nanocrystal surfaces for their functionalization. One of the extraordinary applications of Si nanocrystals can be found in Chapter 7 where the exciting story of chase after Si nanocrystals in cosmic dusts is presented. In Chapter 8, the control of the size of nanocrystals is discussed where it is shown that this can be achieved by using a Si/SiO<sub>2</sub> superlattice structure.

A comprehensive review of investigation of defect structure with ESR studies is also presented in Chapter 8.

Chapters 9–11 summarize the main three fabrication techniques for Si-nc: namely ion implantation (Chapter 9), PECVD (Chapter 10), and sputtering (Chapter 11). In order to form nanocrystals, the most common approach is to form a substoichiometric glass (i.e., rich in Si) and then by thermal annealing to cause a partial phase separation that yields a nucleation of small Si aggregates (Si-nc) in a dielectric matrix. The three fabrication techniques differ in their methods of producing the substoichiometric glass. Excess Si ions can be inserted into the glass by ion implantation, which is compatible with the existing Si technology. The number of ions embedded into the matrix can be determined precisely and the nanocrystal size can thus be controlled. As an alternative method, PECVD has been applied to form Si nanocrystals in matrices such as  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ , and SiC. PECVD offers a low temperature process that is fully compatible with the mass production of integrated electronic circuits. PECVD is widely used for thin film deposition in the semiconductor industry. Magnetron sputtering has also been used to fabricate single and multilayer structures successfully. As a low temperature and nontoxic method, sputtering is an attractive technique for applications such as solar cells, flash memories. In Chapter 12, an alternative technique to form the substoichiometric glass is presented: the sol-gel technique, which offers a low cost alternative to vacuum base technologies. After a brief description of the technology and an introduction on the polymer pyrolysis, the synthesis of Si-nc/ $\text{SiO}_2$  materials, either as bulk or thin films is described, followed by the synthesis of Si-nc and SiC-nc containing  $\text{SiO}_2$ . In Chapter 13, synthesis of Si nanocrystals by means of nonthermal techniques is presented. Free-standing crystalline silicon particles of about 10 nm can be prepared by nonthermal plasmas at gas temperatures as low as room temperature. Use of several plasma processes, both inductively and capacitively coupled plasmas are shown to yield silicon nanocrystals several tens of nanometers in size.

Formation of nanocrystals in porous Si has been of interest since its invention in the beginning of 1990s. In spite of the fact that commercially viable light-emitting devices have not been achieved, the interest for porous Si has kept on growing due to its wide range of applications such as photonics, sensing, biotechnology, and acoustic. These interesting features of porous Si can be found in Chapter 14.

Chapter 15–20 presents an extensive review of various applications of Si-nc with updated research results. Chapter 15 describes how Si nanocrystals are applied to flash memory cells. The high dense integration capability, low voltage operation and low power consumption allow them to be one of pioneering candidates for the next generation flash memory. Chapter 15 attends to address the key subjects of nc-Si flash memory, encompassing fabrication methodologies, operation mechanisms, tolerance, present advances, and future prospects. Photonic applications are given in Chapter 16, where the exploitation of Si nanocrystals in various photonic building blocks for an all Si nanophotonics is reviewed. Applications of Si nanocrystals for guiding, modulating and generating, and/or amplifying light are reviewed. Integration of Si nanocrystal-based light sources and/or amplifiers within CMOS photonics platform is particularly focused in this chapter. Si-based lightening is a revolutionary

development in Si technology. One of the expected gains of Si at nanometer dimension is the light generation based on quantum size effect. This promising feature of Si nanocrystals is extensively discussed in Chapter 17. A new generation of solar cell devices toward record high converging efficiencies are expected to utilize nanostructured materials. All Si quantum dot solar cell devices have attracted quite much attention in recent years. These new approaches are described in Chapter 18. Silicon nanoparticles have the potential to be useful in the biomedical applications since silicon is inert, nontoxic, abundant, and economical. Moreover, the silicon surface is apt for chemical functionalization, thus allowing for numerous stabilization and bioconjugation steps. Chapter 19 summarizes the use of Si nanoparticles in these biomedical applications. An interesting application of Si nanocrystals is found in Chapter 20 where highly explosive binary system based on porous silicon layers is described. The porous layers exhibit morphological properties that are different from most other energetic materials. Their production is completely compatible with the standard silicon technology and a large number of small explosive elements can be produced simultaneously on a single bulk silicon wafer.

Finally characterization issues are discussed in Chapter 21 where the most important characterization and diagnostic techniques such as TEM, Raman, and XRD are presented from a metrology point of view.

## References

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