Applied Surface Science 255 (2008) 624–627

Contents lists available at ScienceDirect

Applied Surface Science

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

Low dimensional silicon structures for photonic and sensor applications

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ARTICLE INFO

Article history:
Available online 12 July 2008

PACS:
42.70.−a ;1.46.Hk
78.67.Bf
81.07.Pr

Keywords:
Low dimensional silicon
Photonics
Luminescence
Electroluminescence
Sensor

ABSTRACT

We review here our work on the photonic and sensor applications of nanostructured silicon. As we change the dimensionality of silicon very fascinating and new optical properties of the material appear. Light sources, modulators, waveguides, logical gates are a few examples of the various photonic devices which have been developed based on silicon nanocrystals. Needless to say, all these devices rely on quantum confinement and on the interplay between bulk and surface properties. Size effects and surface reconstructions are two critical issues which one has to master to employ silicon nanocrystals. Finally the use of silicon nanocrystals to develop innovative sensing mechanisms to reveal biomolecules or poisoning gasses will be discussed.

1. Introduction

Low dimensional silicon is a fascinating material which still has many unfold properties. The main motivation to study silicon comes from its success and dominance in modern technology, especially in microelectronics. Indeed nm-sized transistors are now switching in computers at working frequency exceeding few GHz. Convergence between microelectronics and telecommunications is looked for, in order to couple the computing power of microprocessor with the transmission power of optical fibers. In this effort, merging of various semiconductor technologies is attempted in order to improve the optical properties of microelectronic materials and to reduce the cost of photonic devices. With this respect silicon photonics is playing a key role. We have already reviewed in the past several aspects of this emerging technology [1,2]. In this paper, we aim to give an overview of our recent work towards the exploitation of low dimensional silicon to enable new photonic devices.

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doi:10.1016/j.apsusc.2008.07.065

2. Silicon nanostructures

The first motivation to the study of Si-nc (silicon nanoclusters) was the hope to get luminescent silicon [2]. In fact silicon has an indirect band-gap which causes a very long radiative lifetime (ms) for excited electron–hole pairs. Competing non-radiative recombinations prevail and cause most of the excited electron–hole pairs to recombine non-radiatively. In Si-nc, the radiative recombination rate is increased by quantum confinement. Another effect improves the emission efficiency of Si-nc: the spatial localization of excited electron–hole in a small region of the sample.

Si-nc are formed by deposition of a Si-rich silicon oxide followed by a thermal treatment which causes a phase separation between Si-nc and silica. Room temperature emission in Si-nc is routinely observed independently on the preparation method. The emission is usually characterized by a band centered at about 500 nm whose position is independent on the processing parameters and a second band in the wavelength range 600–900 nm whose exact spectral position depends strongly on the process (Fig. 1). The first band is defect-related and can be quenched by post-growth passivation with hydrogen. The second band is related to the presence of Si-nc: when the Si-nc size decreases, due to a low Si-content in the deposited film or to a low annealing temperature treatments, the emission band shifts to the

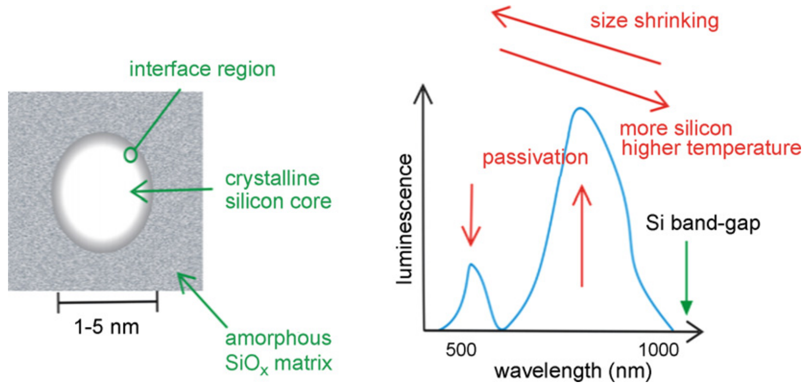

Fig. 1. Schematic diagram of a Si-nc (left) and of the corresponding emission spectrum (right). The influence of the various processing parameters on the emission spectrum is shown by the arrows.

blue. On the contrary for high Si-content in the film or high annealing temperature the emission band shows a red-shift.

From a device point of view, photoluminescence (PL) is interesting but much more appealing is electroluminescence where light is generated by current injection into the Si-nc [3]. Here the problem is tough since carriers have to pass through a dielectric to excite the Si-nc. Indeed in most of the reported devices the electroluminescence is produced either by black-body-like radiation or by impact excitation of electron–hole pairs in the Si-nc by energetic electrons which tunnel through the dielectric by a Fowler–Nordheim process. Electron–hole pairs excited in this way recombine radiatively with an emission spectrum which is very similar to that obtained by PL. The problem with impact excitation is its inefficiency (maximum quantum efficiency of 0.1%) and the damage it induces in the oxide. To get high electroluminescence efficiency one should try to get bipolar injection. What most impedes this, is the fact that the effective barrier for tunneling of electrons is much smaller than the one for holes. That, such separate tunneling of electrons and holes is possible, is well known in the literature [4,5]. We are now working on a new injection scheme which aims to control the injection rate of electrons and holes by using band-gap engineering.

Active devices, such as lasers or amplifiers, need optical gain in the active material. We have found that Si-nc have net optical gain. To measure optical gain, we used the variable stripe length (VSL) method, where the luminescence of Si-nc is used as a probe beam and one looks for enhancement as it propagates in an optically pumped waveguide. Fig. 2 shows on the top-left the idea of the VSL method. Losses or gain can be measured depending on

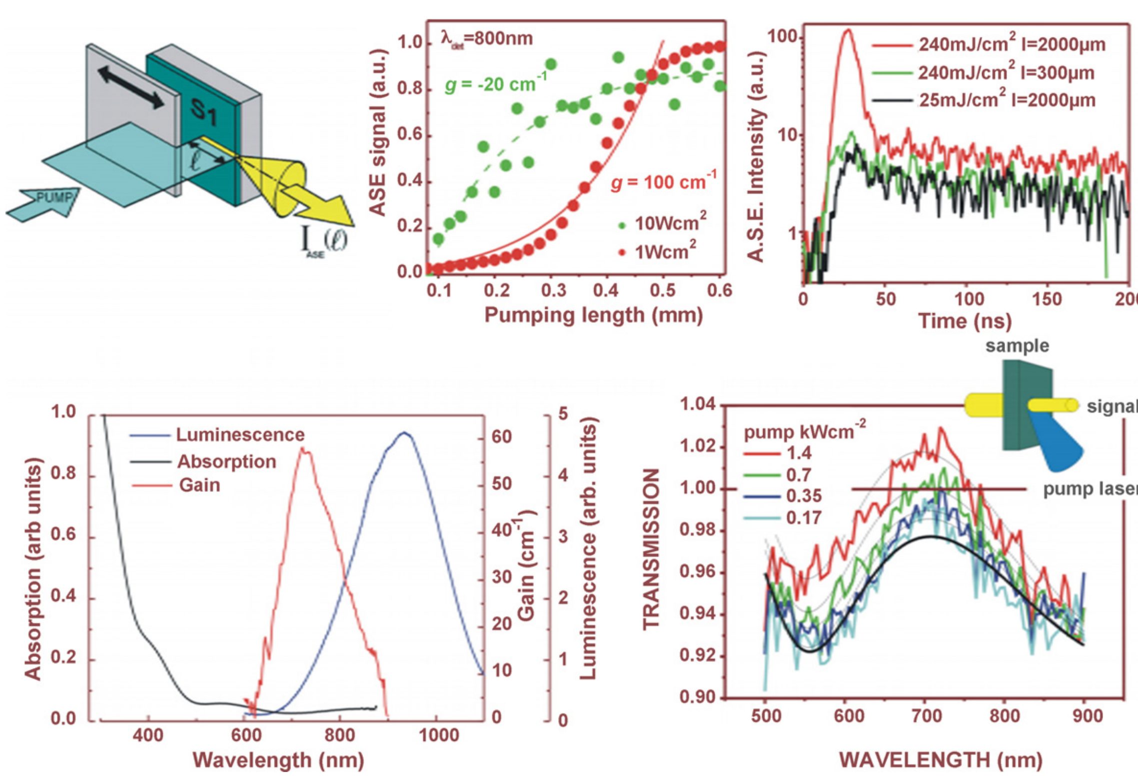

Fig. 2. Top-left: scheme of the VSL method. Top-center, amplified spontaneous emission ASE vs. the pumping length for two pumping powers at 800 nm and for a PECVD slab waveguide. Data are from Ref. [6]. Top-right: time resolved ASE for various pump power and excited volume. Bottom-left: summary of the optical properties of Si-nc. Black curve is the absorption spectrum, dashed curve is the gain spectrum, dotted curve is the luminescence spectrum. Data from Ref. [6]. Bottom-right: transmitted intensity vs. the pump power density. Dark line refers to the transmission of the sample without pump. The inset shows the idea of the experiment. From Ref. [7].

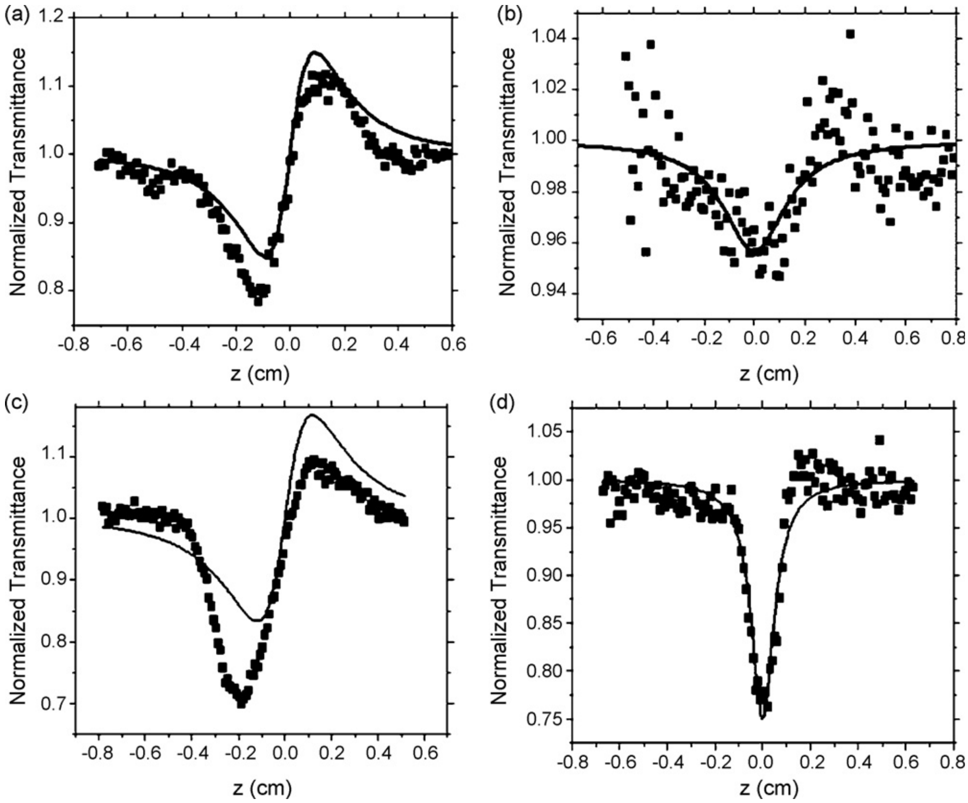

Fig. 3. Representative z-scan traces for 1-nm Si-nc sample: closed (left-top) and open (right-top) aperture; and for a sample with 4 nm large Si-nc: closed (left-bottom) and open (right-bottom) aperture. The theoretical fitting is the solid curve. The laser is at λ = 1550 nm, 1 kHz repetition rate with 100 fs pulse duration and a peak intensity 6×10^{11} W cm^{-2}.

the pump power, see Fig. 3 top-center, and by modeling the system within a one-dimensional amplifier scheme the gain spectrum can be measured (Fig. 2 bottom-left) [6]. Gain is also observed in signal amplification experiments (Fig. 2 bottom-right) [7].

We used a thin layer of Si-nc formed on a transparent quartz substrate. As the pumping rate is increased the transmission intensity increases too. For 1.4 kW cm^{-2}, the transmitted intensity is larger than 1. This means that overall amplification of the signal beam is achieved: the transmitted intensity is larger than the incident intensity even accounting for the losses through the substrate. A summary of the optical properties of the Si-nc system is shown in Fig. 2 bottom-left, where absorption, gain and luminescence spectra are compared. It is worth noticing the large energy difference between absorption and emission spectra where absorption is negligible, emission (either stimulated or spontaneous) is strong. Furthermore, the gain spectrum peaks at the high-energy side of the luminescence spectrum. These data can be explained with a four-level model of gain where lattice relaxation of Si=O double bonds at the interface of the Si-nc provides the energetic for the four-level model. The exact theoretical model is still under discussion in the literature.

Nonlinear photonic materials are widely used in many key-devices for the telecom industry such as switches, routers, wavelength converters. As an example, optical logic gates realized with nonlinear Mach–Zehnder interferometer (MZI) offer a very attractive feature for mass-manufacturing such as scalability and flexibility. Si-nc are very promising material for nonlinear applications. By using z-scan techniques we performed a detailed analysis of the nonlinearities of Si-nc at 1550 nm. Representative experimental data are shown in Fig. 3. It was found a positive z-scan trace (positive nonlinear refraction index, n_2). This kind of nonlinearity is due to the bound electronic response. n_2 is estimated of the order of 10^{-13} cm^2 W^{-1}. In addition a nonlinear absorption is also observed, whose nonlinear absorption coefficient β is in the range of 10^{-9}–10^{-8} cm W^{-1}.

3. Nano-biotechnology of Si-nc

Inorganic nanocrystals (quantum dots, QDs) such as CdSe [8], InP [9] and InAs [10] can be used as fluorescent probes in biological sensing and diagnostic. Compared to organic fluorophores, inorganic QDs exhibit symmetric and tunable emission spectra, stability to photo-bleaching and broader excitation spectra, so that emission from QDs of different sizes and colors can be excited by a single source [8]. Silicon (Si) QDs as fluorescent probes for biological applications have been investigated to a lesser extent. Derivatized porous Si (p-Si) displays a good biocompatibility [11] and porous Si has also been used as the starting material for preparation of colloidal Si solutions by sonication [13]. Si-nc solutions have been obtained by sonication of p-Si in acetonitrile and toluene and in acetone and other solvents [12]. For *in vivo* applications, however, it would be much more interesting to prepare and to characterize luminescent Si QDs in water since most of their biological applications occur in aqueous environment. Notwithstanding the oxide layer has been shown to strongly affect the chemistry and emission of porous Si, only few theoretical studies on the behavior of Si nanoparticles in water, in relation to surface oxidation, have been carried out [13]. In our work the processes of formation of luminescent Si-nc by sonication in water and on the influence of starting porous Si aging has been investigated [14]. It is shown that the peak emission wavelength and the PL intensity of Si-nc depend on the native oxide layer present on porous Si. We then obtained luminescent Si-nc (see

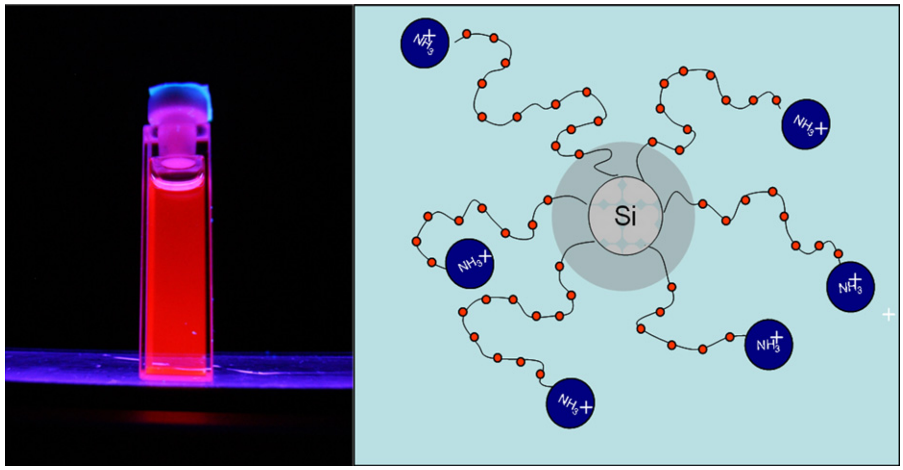

Fig. 4. Example of fluorescence from silicon nanocrystals in colloidal solution (left) and schematic diagram of a Si-nc (right) sensitized with chemical species for sensors applications.

Fig. 4) whose optical characteristics are strongly dependent on the chemical environment surrounding them. Thus interesting application in the field of sensing of chemical and poisonous species are opening based on this first results.

4. Conclusion

In this paper, we have shown some of the various applications of Si-nc in photonics. Quantum size effects and the new chemistry which occurs at the Si-nc surface allow to generate new phenomena which can be used to add new functionalities to silicon and enables silicon photonics.

Acknowledgements

We acknowledge the help of many co-workers both from national and from international collaborations. They can be recognized in the cited literature. The research here discussed has been made possible by the financial support of many projects: FP6-IST LANCER, FP6-NMP SEMINANO, FP6-IST PHOLOGIC, FP6-TMR POLYCERNET, FP6-IST LANCER, FIRB RBNE01P4JF, FIRB BNE012N3X and COFIN (2004023725). Support by Intel is also appreciated.

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