Ordered silicon nanostructures for silicon-based photonic devices

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Light-emitting silicon nanocrystals are prepared by the pyrolysis of silane and subsequent controlled size-reduction by chemical etching. These nanocrystals show luminescence tunable through the full visible spectral region. The luminescence rate increases by two orders of magnitude when shortening wavelength from red to blue side of the spectrum, which is interpreted as relaxation of the indirect band-gap energy structure. In addition we demonstrate a novel method to prepare regular arrays of nanospikes via deposition of suitable materials through the mask formed by a self-assembled monolayer of polystyrene beads. These structures could be used to improve light-emitting silicon devices and enable advancement on the way to true integrated silicon laser.

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At certain stage of the permanent race for ever faster CPU clocks optical data transmission technique within silicon chips should be mastered. This would require an electrically pumped embedded laser made of the same material as the chip itself. Silicon as the mainstream material of electronics is cheap, abundant, and exhibits the right electrical and mechanical properties. However, due to an indirect bandgap in bulk silicon crystals a reasonably efficient light emission is very difficult to achieve. An auxiliary phonon is needed to participate[1,2] thus making the whole process of recombination accompanied by the light emission rather unlikely. This is the main reason why all active optoelectronic devices developed so far are based on group III-V materials (such as GaAs and InP) possessing a direct bandgap.

To overcome difficulties associated with indirect band gap, stimulated Raman scattering has been recently employed for light amplification and lasing in silicon. Due to the two-photon absorption nonlinear optical loss this scheme was initially working only in pulsed operation mode[3]. This was followed by an improved design allowing for the continuous operation[4]. However, both silicon Raman lasers have two principal drawbacks: 1) a separate external optical pumping source is needed for their operation, 2) the Stokes wavelengths produced are far too long for an effective optical signal registration based on silicon detectors. Therefore, some innovative approach is required. Based on our experience it became tempting to look into a possibility of dealing with this problem by switching from the bulk silicon into its properly prepared nano-crystalline form.

Somewhere on the way from bulk crystals to individual atoms (usually for typical dimensions of the order of tens of nanometers and smaller) character of electronic states found in crystals starts to change. This is particularly true for silicon where these changes are quite pronounced due to an indirect bandgap. With decreasing size of these small structures (Si-nc) the width of the bandgap is increasing. Moreover, energetic profiles of the

regions around the maximum of the valence band as well as the minimum of the conducting band are becoming wider thus appearing more similar to the direct bandgap energetic structures. As a result of these changes emitted wavelengths are getting shorter and probability of emission increases. Both of these effects are happening in the right direction on the way to the true silicon laser development.

Four important areas of research can be identified and are being worked upon: 1) technology of Si-nc preparation[5], 2) photoluminescence (PL) of Si-nc[6], 3) electroluminescence of Si-nc[7], and 4) optical signal amplification by Si-nc[8]. An overview paper about these efforts proving the principle was published recently[9].

The last major step to be made is finding the way how to prepare the Si-nc as embedded within the chip itself. For this purpose a novel nano-lithography technique is currently under investigation. The very first results obtained in this research together with a substantial progress achieved in preparation and photoluminescence of Si-nc will be reported.

Let us start by the statement that only a minor modification of the already proven technology for Si-nc preparation has been required. It is schematically shown in Fig. 1. In the first step rather big pyrolytic Si particles (of the order of 100 nm) coated by an oxide layer are produced. In order to obtain luminescing Si-nc the size of particles is reduced by etching with hydrofluoric acid in a two-phase cyclohexane/propanol-2 solution. Depending on the etching time a desired size of Si-nc can be obtained.

Very encouraging new results were obtained in studies of PL from the Si-nc prepared by the technology described in the previous section. With increasing etching time gradually smaller and smaller Si-nc was produced. After irradiation by ultraviolet (UV) pulses ($\lambda = 308$ nm) PL characteristics of these samples were recorded (Fig. 2). With smaller Si-nc the peaks of their respective spectra kept steadily moving towards the shorter wave-

length. According to widely accepted opinion the PL should start disappearing after approaching the region of ∼650 nm. This effect was apparent from our measurements as well. However, continuation of Si-nc size decrease revealed a very interesting new feature: second maximum in the PL spectrum started to emerge at 500 nm gradually taking over the first one and eventually becoming the only maximum in the photoluminescence spectrum.

Importance of this phenomenon was further enhanced by measurements of the luminescence lifetime associated with various Si-nc samples which revealed its dramatic decrease (two orders of magnitude) between samples with their respective spectra centered at 630 nm (No. 8) and 527 nm (No. 5). This feature could be understood as a result of switching from the indirect to the direct gap mechanism between the corresponding Si-nc samples. Needless to say that such feature (if confirmed) would play a crucial role in the construction of Si-nc based lasers making the challenging idea of the embedded Si-nc laser even closer to reality.

In case of Si-nc based light emitting diodes (LEDs) there are practically no reports on attempts to organize individual nanocrystals some orderly way. Usually it was quite sufficient to see if the electroluminescence as such would work for those individual Si-nc which would happen to be in the right position and orientation with respect to the voltage applied. However, in case of a potential Si-nc based laser (and even more so for its embedded version) such simple approach would be inadequate. New ideas need to be explored in order to get reasonably well organized Si-nc structures. One such method presently under investigation will be briefly outlined in the following.

In the ideal case some very regular Si-nc pattern should be prepared. A new technology of creating such patterns is presented in Fig. 3. First of all a monolayer (hexagonal closely packed structure) of tiny polystyrene balls (diameter ∼1.5 μm) was prepared (Figs. 3(a) and (b)). Subsequently this monolayer was used as a mask
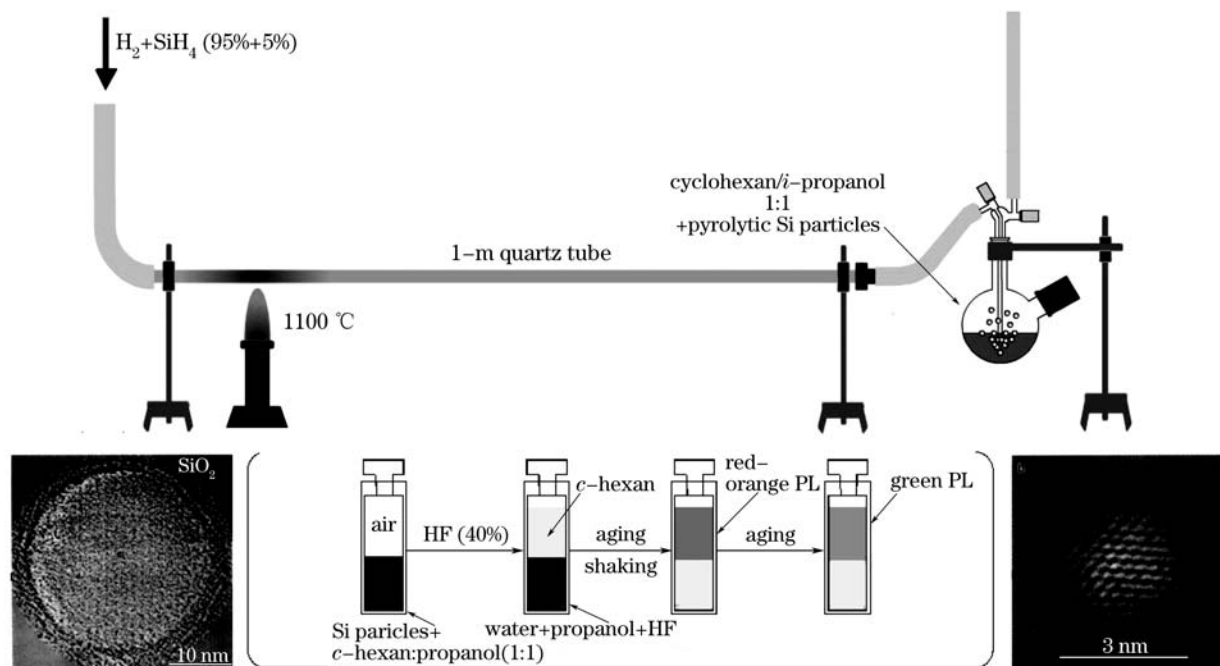

Fig. 1. Schematic diagram of two-step fabrication of Si-nc with desired size.
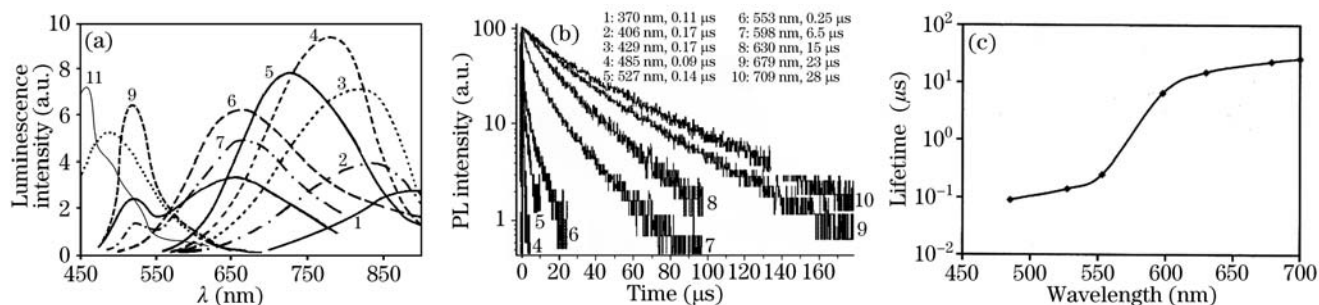

Fig. 2. Changing (a) spectral and (b, c) temporal characteristics of Si-nc PL as a result of increasing etching time applied. Samples were irradiated by UV pulses (λ = 308 nm). Note the dramatic decrease in the luminescence lifetime (two orders of magnitude) between samples with their respective spectra centered at 630 nm (No. 8) and 527 nm (No. 5) suggesting possibility of switching from the indirect to the direct gap mechanism.
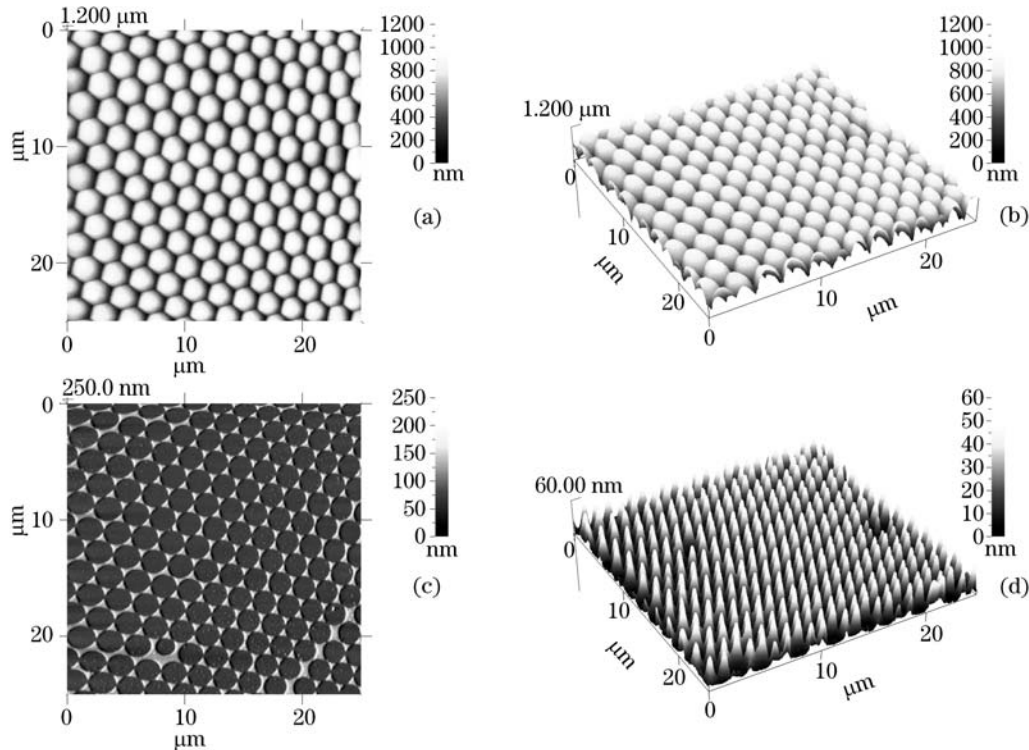
Fig. 3. AFM images of the novel arrays of nanospikes. A monolayer of polystyrene beads (a, b) is used as a mask for initial deposition of nickel and/or silicon through the narrow gaps. After polystyrene removal (c) these initial depositions can serve as bases for subsequent deposition and creation of nanospikes (d).

to allow some material of our choice (e.g. evaporated) to penetrate to the substrate through the gaps present between three adjacent individual balls (open channels to the substrate surface)[10,11]. After the deposition the polystyrene balls are being removed by some suitable solvent (e.g. tetrahydrofuren $- C_4H_8O$) leaving only a regular pattern of deposited material on the substrate surface (triangles on the Fig. 3(c)). Eventually, additional deposition of the material is taking place creating (under suitable conditions) spike looking regular structures (Fig. 3(d)). Provided the diameter of each spike (at least at its upper part) will be small enough, such spikes can play the role of nanostructures thus bringing us closer to our ultimate goal.

Several interesting observations were made during the studies performed. Perhaps the most important one was obtained when using the silicon substrate in the crystalline form and selecting also silicon for initial deposition. In that particular case the created individual bases assumed an amorphous form thus preventing any subsequent silicon deposition becoming crystalline. On the contrary, when Ni was used for initial deposition (10 nm) the subsequent Si deposition (50 nm) created a nice crystalline spike.

These original experiments opened new opportunities for further research in this field. Smaller balls from new materials for monolayer preparation allowing even narrower spikes (true nanospikes) to be created are under preparation. Alternative technologies to overcome difficulties connected with Si initial layers becoming amorphous are also being worked upon. One such possibility

under consideration is usage of Si-nc supply (prepared in advance) for direct deposition into the channels. In this way the larger diameter of individual channels would pose no problem. On the contrary, it could be even beneficial, accommodating more Si-nc and thus creating a denser system of emitting nanoparticles. On the other hand, care will have to be taken to avoid possible light scattering (optical loss) in resulting inhomogeneous system.

In conclusion, it is possible to say that some new exciting results obtained on the way to embedded Si-nc based laser were reported. They concerned improved technologies of Si-nc preparation as well as new important features observed in their PL. A novel method of regularly arranged Si-nc arrays was explored and its results described. Perhaps the best aspect of this research lies in the fact that it has many potential applications outside of the initial aim (e.g. in medicine and optoelectronics - to name the few).

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