Silicon nanocrystals in silica—Novel active waveguides for nanophotonics

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Abstract

Nanophotonic structures combining electronic confinement in nanocrystals with photon confinement in photonic structures are potential building blocks of future Si-based photonic devices. Here, we present a detailed optical investigation of active planar waveguides fabricated by Si+ ion implantation (400 keV, fluences from 3 to 6 × 1017 cm−2) of fused silica and thermally oxidized Si wafers. Si nanocrystals formed after annealing emit red-IR photoluminescence (PL) (under UV-blue excitation) and define a layer of high refractive index that guides part of the PL emission. Light from external sources can also be coupled into the waveguides (directly to the polished edge facet or from the surface by applying a quartz prism coupler). In both cases the optical emission from the sample facet exhibits narrow polarization-resolved transverse electric and transverse magnetic modes instead of the usual broad spectra characteristic of Si nanocrystals. This effect is explained by a theoretical model which identifies the microcavity-like peaks as leaking modes propagating below the waveguide/substrate boundary. We present also permanent changes induced by intense femtosecond laser exposure, which can be applied to write structures like gratings into the Si-nanocrystalline waveguides. Finally, we discuss the potential for application of these unconventional and relatively simple all-silicon nanostructures in future photonic devices.

Keywords: Nanocrystals; Waveguide; Silicon; Photonics

1. Introduction

Research on silicon-based photonics is motivated by the aim to combine integrated electronic and photonic structures on a single silicon chip. Silicon quantum dots or nanocrystals (Si-NCs) have attracted much attention due to their strong photoluminescence (PL) [1] and have been used to demonstrate silicon-based light-emitting diodes [2,3]. Ensembles of Si-NCs can also be employed to fabricate active optical waveguides [4–8] that exhibit spectral filtering of the Si-NC PL emission, if the refractive index profile is properly designed. The occurrence of narrow (~10 nm), polarization-dependent emission lines was reported by Khriachtchev et al. [4] for Si/SiO2 waveguides and by our group [5,9] for samples containing Si-NC prepared by Si+ implantation into silica slabs. In our previous papers we explained the unexpected wave-guiding properties using a model based on substrate leaking modes of a lossy waveguide [10,11].

In this work we compare the propagation of the intrinsic luminescence from Si-NCs with that of external light coupled into the waveguides. This knowledge is crucial for pump-and-probe measurements (e.g. optical gain) and potential application as photonic devices (modulators, amplifiers etc.). In addition we show permanent changes

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induced by femtosecond laser exposure which can be applied to write 2D structures (gratings etc.) into the Si-nanocrystalline waveguides with sub-micron resolution.

2. Experimental methods

Samples used in this study were prepared by Si-+ ion implantation into 1 mm thick Infrasil (refractive index \(n_s = 1.455\)) slabs with polished surfaces and edges, and into SiO\(_2\) layers (about 5 \(\mu\)m thick) prepared by thermal oxidation of Si wafers. An implantation energy of 400 keV and ion fluences ranging between 3.0 and 6.0 \(\times\) 10\(^{17}\) cm\(^{-2}\) were used to fabricate the slab waveguides. In order to form Si nanocrystals the samples were annealed for 1 h at 1100 °C in an N\(_2\) ambient and then passivated for 1 h at 500 °C in forming gas (5% H\(_2\) in N\(_2\)).

The implanted layer acts as an asymmetric planar waveguide. The profile of the refraction index depends not only on the implantation energy and fluence but also on the annealing conditions. Although the annealing temperatures, ambients and durations were nominally the same, various sets of samples were annealed in different laboratories and furnaces. Possible variations in the thermal history and levels of oxidation lead to apparent differences in refraction index for nominally identical samples (here, Figs. 2–4 present results from one set of samples and another set with lower refraction index is shown in Figs. 5–7). In order to numerically model the optical properties of particular samples the refraction index profiles were measured separately for each implanted sample. This was done by measuring infrared transmission spectra (see Fig. 2B) and fitting the interference fringes assuming an asymmetric double-Gaussian refraction index profile. The maximum of the profile is typically about 600 nm below surface with a half width of about 300 nm. The peak refraction index has a value as high as 2 for the highest implantation fluence [11]. The diameter of nanocrystals in the samples is estimated to be between 4 and 6 nm using Raman scattering (not shown here) [11].

PL was excited by a continuous wave He–Cd laser (325 nm, excitation intensity \(\sim\)0.3 W/cm\(^2\)). The sample was placed on a rotatable x–y–z stage. A microscope with numerical aperture (NA) of 0.075 (i.e. an angular resolution of about 8.6°) was used to collect light and send it to a detection system consisting of an imaging spectograph (Jobin Yvon Triax 190) with a CCD camera (Hamamatsu C4880) [9]. All measurements were performed at room temperature and all PL spectra were corrected for the system response.

The coupling of external light into the waveguides was achieved in two ways (Fig. 1):

(a) Prism coupling of light from the upper surface of the sample. Light from the Xe or halogen lamp was collimated into a quartz prism. For better optical contact between the prism and sample an immerse liquid (index of refraction \(n = 1.515\)) was dropped between the contact surfaces.

(b) Direct coupling into the truncated facet (Fig. 1B). The edge of the sample was polished at angle of about 70° in order to separate light refracted to the higher-index waveguide from light entering lower-index substrate. Here a warm-white LED was used as a convenient light source. The angle of incidence \(\gamma\) was between 15° and 30° with respect to the plane of implanted layer. The divergence of incident light was about 10°.

In both external-light-coupling set-ups the signal is collected by an optical fiber (detection NA \(\sim\)0.008) and guided to the entrance slit of the imaging spectrometer Jobin Yvon Triax 320 (with the low-dispersion grating of 100 grooves/mm). Spectra are detected with the PI-Max intensified CCD (Princeton Instruments).

3. Results and discussion

3.1. Transmission spectra of Si-NC layers

The color of the Si-NC waveguide layers is yellow-brown with the optical density increasing with implantation fluence. The corresponding absorbance spectra are plotted in Fig. 2A (they are measured in a direction perpendicular to the nanocrystal plane using a UV-VIS double beam spectrometer (Hitachi U-3300), the non-implanted area of a silica slab being employed as a reference). The absorption edge has approximately exponential shape. In infrared spectral region several interference fringes are observed (Fig. 2B) which are used to model refraction index profile (see above).

![Fig. 1. Two experimental arrangements for coupling of external light into a waveguide sample: (A) coupling through a quartz prism on the upper sample surface. The second prism below sample is used to inhibit the back reflection of light not coupled into the waveguide; (B) focused light directed on the truncated edge of a sample. In both cases light leaving the opposite edge of sample is collected with an optical fiber and sent to a spectrometer. Sketches not to scale.](image-url)
3.2. PL of active planar waveguides

The PL spectra of the active planar waveguides have very different shape depending on the experiment geometry. Two arrangements are used: (i) the light is collected in a direction roughly perpendicular to the sample plane (this is a conventional PL arrangement) or (ii) in the direction close to parallel to the waveguide plane (i.e. from the sample facet–waveguide arrangement) — see inset in Fig. 3. In the former geometry the PL spectra are always broad with a peak around 830 nm, typical of oxide-passivated Si NCs with mean diameter \( \leq 5 \text{ nm} \). On the other hand, the waveguide geometry reveals narrow (down to 10 nm) spectral features with a high degree of linear polarization.

Figs. 3A and B show PL spectra of implanted oxide layers (on Si substrates) measured in directions perpendicular and parallel to the layer, respectively. The conventional PL (Fig. 3A) is modulated by deep interference fringes due to high reflectivity of the Si substrate. The facet-PL (Fig. 3B) is not affected by interference; instead a relatively narrow band is observed, the position of which depends on implantation fluence (i.e. refraction index profile). This peak shows partial linear polarization.
Under identical conditions (of both fabrication and PL-experiment) the facet-PL features are much better resolved in implanted silica slabs (Fig. 4B). Here a clear splitting of the narrow PL peak into two peaks with polarization parallel (transverse electric TE or s mode) and perpendicular (transverse magnetic TM or p mode) to the Si-NC waveguide plane is observed. The following discussion is restricted to implanted fused silica slabs where the TE/TM splitted modes are nicely resolved.

PL spectra of other set of five samples prepared by implantation to fluences of 4.0, 4.5, 5.0, 5.5, and 6.0 \( \times 10^{17} \) cm\(^{-2} \) are plotted in Fig. 5. The upper spectra in Fig. 5A represent PL collected from the plane of implanted layers, while the lower PL spectra with TE/TM double-peaks are collected from the facet at angle +5° (NA\(_{\text{det}}\) = 0.075). An angle-resolved facet PL spectra from the layer implanted with dose of \( 6 \times 10^{17} \) cm\(^{-2} \) are plotted in Fig. 5B and the polar representation of their integrated intensity is shown in Fig. 5C. The TE/TM split doublets shift to longer wavelength with increasing implantation dose. The facet PL has a very narrow emission cone with the maximum slightly shifted closer to substrate (\( \alpha > 0^\circ \)) (Figs. 1B and C).

3.3. Theoretical model of the mode structure—radiative substrate modes

The surprising PL observations reported above do not correspond to simple waveguiding in ideal transparent waveguide which should transmit a continuous spectrum of guided modes up to a cut-off wavelength [12]. The cut-off for the first order modes of our waveguides can be estimated to lie above ~1500 nm. Consequently, the waveguides should transmit the entire 600–900 nm band emitted by Si-NCs, which is clearly not the case. There are two possible explanations:

(i) Delocalized guided modes: Let us assume wavelength-dependent losses in the waveguide, then those modes

![Fig. 5. PL spectra of five fused silica slabs implanted to fluences of 4–6 \( \times 10^{17} \) cm\(^{-2} \). (A) Upper curves (a single wide band) correspond to PL emitted in a direction perpendicular to the waveguide, while lower spectra with doublet peaks are facet-PL detected in a direction \( \alpha = 5^\circ \) (a sketch of the experimental arrangement is shown in the inset). (B) Angle resolved facet PL spectra of the sample \( 6 \times 10^{17} \) cm\(^{-2} \). (C) Polar representation of integrated PL intensity of angle resolved facet spectra from the panel B. Most of the PL intensity is emitted in a direction close to 0°.](image)
Radiative substrate modes

Red-shift and broaden with increasing refraction index of liquid drops on the waveguide/air surface [11,16]. If a drop is placed some millimeters away from the spot (between the photo-excited spot and the output facet), no changes in modes is observed, consistent with all the radiant power escaping into radiative substrate modes. These experiments are supported by numerical modeling of the PL spectra which show excellent agreement with experiments and provide unambiguous validation of the leaking modes model [11].

3.4. Coupling and propagation of external light in Si-NC waveguides

The transmission spectra of the five samples (implantation fluence $4\times 10^{17} \text{ cm}^{-2}$) obtained by white-light coupling through a prism (Fig. 1A) are shown in Fig. 6. In the measured spectral region two broad transmission bands (blue and red) are observed for each sample. The positions of both bands red-shifts with increasing fluence and the position of long-wavelength bands coincides with that of the PL leaking modes (Fig. 5A). Our calculation show that the red and blue bands correspond to second and third order leaking modes (the first one being in infrared). Broadening of the mode structure may be a consequence of the very low number of reflections undertaken by coupled light before escaping to the substrate [17].

Coupling of external light (the warm-white LED) through a truncated facet (Fig. 1B) gives the best result for a coupling angle $\gamma \approx 20^\circ$, as expected (Fig. 7). In this configuration we detect narrow and polarization-split peaks at an output angle $\alpha \approx 2^\circ$. The peaks are, however, not transmission but absorption peaks. This can be understood if it is assumed that the detected light is not from radiative substrate modes (which represent a small portion of transmitted light) but from filtered transmitted light propagating almost parallel to the Si-NC waveguide.

![Fig. 6. The transmission spectra of prism-coupled light detected at angle $\alpha = 7^\circ$ from samples presented in Fig. 5.](image-url)
from which a part of power escaped to the substrate modes. The blue third order modes are much stronger compared to second order because of higher absorption in blue spectral region.

3.5. Leaking modes vs. optical gain

One of the most interesting questions concerning nanocrystal waveguides is the interplay between radiative substrate modes and optical amplification by stimulated emission. Since the first report on optical gain in Si-ion implanted Si-NC layers by Pavesi et al. [18] similar samples have been investigated by other groups with both positive [4] and negative [19] results. Two aspects of this problem are addressed here.

First, experimental artefacts have been shown to play an important role when measuring optical gain close to leaking modes maxima by the commonly used variable-stripe-length (VSL) technique [20]. These artefacts are mainly due to unconventional propagation and coupling of these modes in the detection system, and their interplay with the NA of detection. In order to correct most of these artefacts it has previously been proposed that VSL measurements be combined with a shifting-excitation-spot (SES) technique [20]. Indeed, it should be stressed that the interpretation of VSL results without associated SES measurements can lead to erroneous results.

Secondly, the potential advantages of leaking modes for achieving optical gain are spectral narrowing, low losses, and directionality of propagation. On the other hand the propagation path of radiative modes through a pumped active medium (Si-NCs forming the waveguide) is limited by leakage into the substrate. Attempts to achieve optical gain on leaking modes was successful only under strong nanosecond pulsed pumping (6 ns, 355 nm from THG-Nd:YAG laser) with the gain threshold around 50 mJ/cm² and maximum gain at TM mode of about 12 cm⁻¹ for 100 mJ/cm² excitation [21].

Further theoretical investigation of the radiative modes in the loss/gain medium is in progress.

3.6. Permanent changes of Si-NC waveguides induced by laser pulses

The Si-NC waveguides in silica may be damaged by high-intensity laser excitation and apparent differences in damage are evident for nanosecond and femtosecond pulses. When irradiated with the 420-nm, 5 ns output of an optical parametric oscillator (OPO) pumped by THG-Nd:YAG (NL 303 + PG122, Ekspla) the damage threshold is very sharp at around 800 mJ/cm². The damage appears as micrometer-size granular aggregates in the Si-NC followed immediately by complete ablation of the implanted layer. The mechanism is most probably related to heating and even melting of Si-NCs [22] which leads to failure of the silica matrix. This is evidenced by the appearance of cracks and surface ruptures which can lead to complete removal of the SiNC layer.

In contrast, femtosecond laser excitation (400 fs, 400 nm from SHG-Ti:sapphire laser) starts to modify sample at much lower pulse energies $\geq 20$ mJ/cm². There are two distinct phases of layer damage. The initial stage appears as darkening (brown coloration) of the excited area. Micro-Raman measurements (not presented here) show that it corresponds to amorphization of the Si-NC layer.
(it appears similar to the implanted layer before annealing). In the second step at higher excitation the layer is ablated. Clearly, the damage mechanism for ultrashort laser pulses (400 fs) is different to that of the longer (5 ns) pulses. The advantage of fs-ablation is that the boundary between the ablated and unchanged area can be very sharp, enabling fs-laser-ablation to be used for lithography to create microstructures in the planar waveguides. In Fig. 8 we demonstrate a diffraction grating with 12 μm period written into 4 × 10^{17} cm^{-2} implanted layer by 400 fs, 400 nm fs-pulses.

4. Conclusions

Si-ion implantation into silica slabs or oxide layers on Si wafer followed by annealing is a relatively easy way to fabricate active nanocrystalline planar waveguides. In spite of their simplicity these waveguides show rich optical phenomena which are mainly connected to peculiar radiative substrate modes—so-called leaking modes. This study has investigated the influence of these complex propagation modes on PL, transmission, and gain spectra both experimentally and theoretically. Similar anomalous phenomena connected to the interplay between radiative and guided modes are expected to take place in other types of active waveguides. The possibility of spectral, polarization, and spatial filtering reported for active Si-NC waveguides offer interesting possibilities for application in silicon-based photonic devices or sensors.

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References