Origin of room temperature broadband light emission and carrier dynamics in Ag ion-implanted Silicon nanocrystals

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Abstract: We studied the origin of broad band light emission in the Ultraviolet (UV) to the red from silicon nanoparticles fabricated using a single low energy (32 keV) silver ion implantation with a fluence of 5*10^{15} ions/cm^2 in crystalline Si. It is found from a systematic study of the annealing carried out at certain temperatures that the spectral characteristics in the UV and blue region remains unchanged except for the enhancement of light emission intensity due to annealing. The annealing results in nucleation of Ag nanoclusters in the vicinity of Si nanoparticles which enhances the emission intensity. Time-resolved photoluminescence (TRPL) measurement demonstrates that the emission originates from both highly localized defect bound excitons at the nanoscale Si interface, as well as surface and interface traps associated with the increased surface area of the Si nanocrystals. The emission in the UV is due to interband transitions from localized excitonic states at the interface of Si/SiO_2 or from the surface of Si nanocrystals. The radiative efficiency of the UV and the green emission from the Si nanoparticles can be modified by the localized plasmons interaction induced by the nucleation of Silver nanoparticles on controlled annealing of the samples. Broadband emission ranging from the UV to the red wavelength range can be obtained on Ag implanted onto a single silicon substrate.

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References and links

1. L. T. Canham, “Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers,” Appl. Phys. Lett. 57(10), 1046–1048 (1990).
2. V. Lehmann and U. Gosele, “Porous silicon formation: A quantum wire effect,” Appl. Phys. Lett. 58(8), 856–858 (1991).
3. S. S. Iyer and Y. H. Xie, “Light emission from silicon,” Science 260(5104), 40–46 (1993).
4. S. Tiwari, F. Rana, H. Hanafi, A. Hartstein, E. F. Crabbé, and K. Chan, “A silicon nanocrystals based memory,” Appl. Phys. Lett. 68(10), 1377–1379 (1996).
5. N.-M. Park, C.-J. Choi, T.-Y. Seong, and S. J. Park, “Quantum confinement in amorphous silicon quantum dots embedded in silicon nitride,” Phys. Rev. Lett. 86(7), 1355–1357 (2001).
6. R. M. Sankaran, D. Holunga, R. C. Fligan, and K. P. Giapis, “Synthesis of blue luminescent si nanoparticles using atmospheric-pressure microdischarges,” Nano Lett. 5(3), 537–541 (2005).
7. D. Zhang, R. M. Kolbas, P. D. Milewski, D. J. Lichtenwalner, A. I. Kingon, and J. M. Zavada, “Light emission from thermally oxidized silicon nanoparticles,” Appl. Phys. Lett. 65(21), 2684–2686 (1994).
8. A. Arbouet, M. Carrada, F. Demangeot, V. Paillard, G. Ben Assayag, C. Bonafos, A. Claverie, S. Schamm, C. Dumas, J. Grisolia, M. A. F. Van den Boogaart, J. Brugger, and L. Doeswijk, “Photoluminescence characterization of few-nanocrystals electronic devices,” J. Lumin. 121(2), 340–343 (2006).
9. L. J. Mitchell, O. W. Holland, A. Neogi, J. Li, and F. D. McDaniel, “Formation of optically active osmium silicide in silica using ion implantation and thermal annealing,” J. Non-Cryst. Solids 352(23-25), 2408–2410 (2006).
1. Introduction

The indirect bandgap of silicon reduces the radiative recombination to be used as a light emitter. However, the modification of silicon by forming silicon nanocrystals, quantum dots or porous silicon in the microscopic scale can result in light emission from Silicon, though it has not yet been possible to fabricate light emitting devices from such system. Since the discovery of room-temperature (RT) visible photoluminescence (PL) from porous Si in 1990 [1,2], light-emitting Si from nanostructures has become very interesting because of its huge potential in optoelectronic devices of integrated circuits [3–5]. There have been reports about red and near infra-red (NIR) light-emitting Si nanostructures; however, the reports on ultraviolet to green region emission requires various synthesis techniques varying from chemical synthesis, etching of porous Si, Si in SiO$_2$ matrix etc. There does not exist a single technique to generate broad band emission. UV emitting Si nanocrystals (NC) can be prepared by plasma synthesis [6], and chemical vapor deposition [7]; however, ion beam implantation in SiC or SiN [8–11] has been used for the nucleation of Si quantum dots that can have a wide range of applications.
range of light emission. Even though, the origin of light emission from Si is controversial, a consensus has been reached that highly localized defects at the Si/SiO$_2$ [12–14] and the quantum confinement (QC) of excitons both play important roles [15–17].

In this work, we investigate the origin of broadband light emission (UV-red) from Si NCs formed by silver ion beam implantation in crystalline Si substrate using TRPL spectroscopy. The ambiguity in the origin of light emission can be resolved by studying the decay rates, which are conventionally in the ms to µs range due to the indirect or quasi-direct nature of the transitions in Si light emitters. Current approaches of the synthesis of Si NCs use high-energy ion implantation in the MeV range that can result in nonradiative defect centers in the crystal lattice without any broadband emission. In this study, we utilize a low-energy ion beam (< 50 keV) and controlled annealing for the nucleation of Si NCs to reduce the surface and defect – induced non-radiative process.

2. Experimental

The Si NCs were fabricated at RT using ion beam implantation using Ag as the ion source. The substrates used in this work were p doped n-type Si(100) with a resistivity of 1-10 Ohm-cm. Ag$^{+}$ was implanted into the Si(100) substrate at an energy of 32 keV and with a fluence of $5\times10^{15}$ ions/cm$^2$ at beam currents 250 nA. The implanted samples were thermally annealed in atmospheric O$_2$ at 500°C, 600°C and 700°C for an hour. The annealing was performed below the Ag-Si eutectic temperature (835°C). The effect of oxidation during the annealing process was investigated by using an inert gas such as Argon. It is observed from a systematic study of the annealing carried out at these temperatures that the characteristics of the PL emission energy in the UV and the blue region remains unchanged. However, a significant enhancement of light is observed due to the annealing. The emission in the visible wavelength is observed only after annealing in oxygen rich environment and does not occur in as-implanted samples. Annealing without any oxygen under inert conditions such as nitrogen or Argon does not change the UV and blue emissions significantly and has a very slight influence on the intensity of the green emission. The annealing of the ion implanted wafer results in the formation of silver nanocrystals at depths of up to 40 nm from the surface of the Si substrate. However, for the UV laser with excitation wavelength at 3.81 eV (CW laser) or 3.4 eV (pulsed laser), the penetration depth of the light in the ion-implanted amorphised Si layer is shallow and the subsequent PL observed is within 10 nm –20 nm from the surface. However, the penetration depth for the 2.8 eV excitation (442 nm) is relatively larger (~500 nm) in the ion-implanted silicon substrate and has a higher efficiency for the green or red emission. Broad-band efficient RT emission ranging from the UV to the NIR/red was observed from various sections of the single wafer of silicon substrate.

Continuous wave (CW) - PL measurements were carried out using a Helium-Cadmium (HeCd) laser with excitation at 3.81 eV (325 nm) and 2.80 eV (442 nm). The UV and blue emissions is observed using the 325 nm excitation, whereas the green and red emission is observed using the 442 nm excitation. The photoluminescence lifetime was measured using a Ti: Sapphire 80 MHz, femtosecond (fs) with an excitation wavelength at 3.4 eV (360 nm), with an average power 100 mW and a Hamamatsu Streak camera for detection. The PL lifetime for the emission in the blue wavelength was measured using a picoQuant system with a 15 picosecond diode laser with an excitation energy at 3.30 (375 nm), whereas the TRPL of the green emission was measured using a doubled Ti:Sapphire laser at 400 nm. Various bandpass filters depending on the emission wavelength was used to separate the excitation source.
Fig. 1. (a) HRTEM image showing formation of Si nanocrystals. (b-e) shows the micro PL emission from various sections of the same wafer due to optical excitation with the HeCd laser source. (b) corresponds to the UV emission centered at 3.27 eV nm shown in Fig. 2, (c) corresponds to the blue spectral emission as shown in Fig. 3, (d) corresponds to the green spectral emission as shown in Fig. 4, (e) corresponds to red spectral emission as shown in Fig. 5. (f-right side) shows size distribution of Si NCs formation.

3. Results and discussions

High Resolution Transmission Electron Microscopy (HRTEM) image in Fig. 1(a) shows formation of Si NC in crystalline silicon formed by the implantation and annealing process. NCs of different sizes (1.5 - 10 nm) can be clearly seen from HRTEM image in Fig. 1(a), which directly or indirectly play a role for different color of efficient broadband RT light emission from the single wafer. All the emission ranging from the UV to the red has been observed from the Ag ions implanted into the identical Si wafer. The annealing process also nucleates the formation of Ag nanoclusters in the sample and brings it close to Si NCs as well as towards the surface. Ag NCs were not observed before the annealing process. The micro-PL emission at various wavelengths (energy) is shown in the Figs. 1(b)–1(e). Room temperature (RT) emission can be observed over the entire UV-Visible range. The optical properties have been analyzed using TRPL measurement.

In the present ion-beam implanted Si NCs, the mean diameter of Si nanoparticle is nearly 2.4 nm as shown in Fig. 1(f). The detail explanation is elsewhere [18–20]. The distributions of size of nanoparticles don’t agree with effective mass theory. Thus, emission ranging from the UV to the red as shown in Figs. 2–5 indicates that these emissions are not due to quantum confinement effect which will be further strengthened by TRPL analysis. The internal quantum efficiency is measured using the temperature dependent PL spectroscopy by considering that at 15 K the photoluminescence process is dominated by the radiative recombination process with no loss due to non-radiative recombination process. (IQE) from the crystalline nanostructures is estimated to be 5% at RT.
Figure 2(a) shows the PL emission from Si NCs which emits at 3.27 eV at RT with a linewidth of ~80 meV. HRTEM micrographs show that the average diameters of the Ag nanoclusters ~6.5 nm. Any UV emission ranging from 364 to 384 nm can be resonantly coupled to Ag NCs formed by ion implantation [20]. This wavelength range is suitable for emission from interface states between the Si and its oxide namely the –SiO$_2$ group, which bonds to Si structural surface and results in a strong 370 nm PL [21]. Similar broadband UV emission has been reported in silica nano-rings coated with ultra-thin Ag films [22]. However, the emission from these annealed Silica nano-rings in the presence of Ag were limited to the emission at higher energy > 2.9 eV. In our Ag-implanted Si nanocrystal system the origin of emission in UV region is from highly localized defects at the interface of Si/SiO$_2$. The emission from highly localized defects at the interface of Si/SiO$_2$ plays equally important roles as QC emission [12–14,23].

Confined bound-exciton emission in the UV region can be enhanced at RT due to exciton plasmon coupling induced by the Ag induced localized surface plasmon polaritons (LSP) [20]. For an appropriate size of the Ag nanoparticles, the localized surface plasmons can be coupled to the emission from the Si nanoclusters in the UV region. We have observed that the average size of silver nanoparticles is ~6.5 nm, which yields a surface plasmon energy of ~3.27 eV as estimated from the theoretical estimation of Mie scattering. The average distance between Si nanoparticles and silver nanoparticles was observed to be about 20 nm from the TEM measurements. The silver nanoparticles have a relatively sharp resonance and is most favorable for the surface plasmon induced enhancement of the PL emission. The recombination lifetime of the electron-hole pair as estimated from the TRPL measurement changes from ~2 ns to 400 ps in the presence of silver ion induced surface plasmon polaritons as shown in Fig. 2(b). If the carriers recombination at 15 K is considered to be dominated solely by radiative recombination process, the internal quantum efficiency (IQE) from the crystalline nanostructures is estimated to be 5% at RT.
Figure 3(a) shows the PL emission from Si NCs which emits in the blue region. The emissions observed at ~2.98, 2.84, and 2.63 eV emanates from Si-related defect center. The mechanism of emission for peaks centered nearly at 2.98 and 2.84 eV is possibly from excess Si defect centers in Si nanostructures [24,25]. Fourier transform infra-red (FTIR) spectroscopy measurement of sample shows Si-O-Si vibration band ~1100 cm$^{-1}$, indicating the excess Si defects states [19]. It is likely to involve states produced by the Si-O–Si bonds at the surface of NCs or the interface between the Si NCs and the SiO$_2$ [25]. Figure 3(b) shows carrier decay lifetime which is similar to the relaxation from oxygen-related states. These states are evidently shallow as the decay life time and the carrier life time in these states is short in the range of 1-2 ns. The shorter life time is due to trapped bound exciton at the defect centers. The IQE in this case at RT is found to be 7% which is also significant for RT emission.
Figure 4(a) shows the PL emission from Si NCs at 2.4 eV which is in the green region at RT. The green emission is only observed after annealing in oxygen rich environment and wasn’t observed in the case of as-implanted samples. The green emission doesn’t change significantly when annealed under inert gas such as Nitrogen or Argon. It is observed that the emission efficiency at the green wavelength regime is significantly higher compared to the UV or blue emission and is estimated to be ~11% IQE at 300 K. The ns PL lifetime indicates that the green PL peak emission arises from surface trapped excitons (STEs). The STEs are caused by the hole and electron localization at the surface of the NCs as reported by Pan et al. [26]. The ns PL decay time compared to ms or µs lifetime eliminates the possibility of emission from quasi direct emission from the quantum confined states [27]. Thus, we can clearly conclude the origin of green emission on the basis of lifetime that emission is from STEs. There is no significant change in the PL lifetime due to the presence of the Ag nanoparticles which rules out the probability of surface plasmon mediated radiative recombination as observed in semiconductor light emitters [28].
Figure 5 shows the PL emission from Si NCs emitting in the NIR/red region. At RT, the PL peak is observed at 1.60 eV which is likely due to the quasi-direct transitions in Si NPs, and is caused by the partial confinement of hole and electron. The effective mass theory can be applied to demonstrate that the origin of this emission is not from QC. The origin of emission is attributed to defect in the SiO$_2$ matrix [29]. The PL lifetime could not be measured as the emission is rather long lived compared to the repetition rate of the pulsed laser. In addition the emission intensity is rather weak under the influence of the fs pump compared to a CW excitation source. The IQE of the red emission is observed to less than 3% at RT.

Figure 6 shows the photoluminescence excitation (PLE) spectra in the UV and blue wavelength region, which depicts the absorption states associated with the light emission in the UV and blue regimes [19]. The PLE spectra in the UV region was measured with detector at 3.3 eV, whereas for the visible wavelength region it was measured with the detector at energies 2.98, 2.84 and 2.63 eV. It has been observed that the presence of the high energy states at 4.14 eV is likely to influence the emission at 3.27 eV. In case of PLE in the blue wavelength regime, another high energy state at 3.28 eV also exists along with 4.14 eV as shown in Fig. 3 and confirmed in Fig. 6. The emission peak at 3.28 eV is independent of the detection energy. It is also observed that the PLE properties in the blue wavelength remain unchanged for the various emission energy states. It can be clearly seen from Fig. 6 that the UV emission at ~3.27 eV has its origin from the absorption energy states exceeding 4.45 eV. Thus, as observed in [29], we can conclude from the PLE spectra of the UV and the blue region that the PL energy is not a characteristic of the emission from the quantum confined structure and supports the fact that the origin of emission is from localized defect bound-excitons.

4. Conclusion

We studied the origin of broad band tunable light emission from the UV to the red in metal implanted into silicon on the basis CW-PL measurement which is further strengthened and confirmed by life time measurement. The emissions at various wavelength ranging from the UV, blue, green and red wavelength were observed on the same silicon substrate which was implanted with 32 keV Ag ions at a relatively shallow depth with a fluence of $5 \times 10^{15}$ ions/cm$^2$. The formation of the nanocrystals increases the surface area at the interface of the crystalline Si and SiO$_2$ or amorphous Si layer. This results not only in an increased probability
of forming surface trapped excitons resulting in the green emission but also results in an exchange between the localized defects and Si nanocrystals formed due to annealing after the implantation process. It is observed that spectra in the UV and the blue region remains unchanged except enhancement of light in the case of post annealing compare to pre annealing. The IQE of the UV emission is enhanced due to the presence of the resonant localized plasmon modes generated at the surface of the Ag nanoparticles which are nucleated due to annealing. The blue PL is also observed whose origin is possibly from defects at Si/SiO₂ interface. CW-PL combined along with TRPL in the green emission region suggests that origin of emission is from STEs. The TRPL measurements also show that the localized plasmon modes do not affect the recombination of the STEs. A further detailed quantitative study will be helpful for controlling the STEs or QC emission which can fulfill the requirement for optoelectronic devices of integrated circuits and a new generation of flash memory.

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