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Citation: Applied Physics Letters **70**, 1207 (1997); doi: 10.1063/1.118275
View online: http://dx.doi.org/10.1063/1.118275
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/70/10?ver=pdfcov
Published by the AIP Publishing

Visible light emission from Si nanocrystals grown by ion implantation and subsequent annealing

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(Received 29 October 1996; accepted for publication 3 January 1997)

Photoluminescence (PL), electron spin resonance (ESR), and high resolution transmission electron microscopy (HRTEM) were used to investigate the luminescence mechanism in Si nanocrystals. Si ions were implanted in SiO_2 films at 190 keV to a dose of $3\times10^{17}/cm^2$. An intense photoluminescence (PL) band at 755 nm (1.65 eV) was observed when the implanted films were annealed above 800 °C in air or in nitrogen. HRTEM images showed Si nanocrystals of sizes between 1 and 6 nm from these annealed samples. ESR indicated Si dangling bonds. Upon annealing at 900 °C in air a few times, the particle sizes were reduced to less than 2 nm due to oxidation. The red PL band is attributed to emission from Si nanocrystals. © *1997 American Institute of Physics.* [S0003-6951(97)02210-9]

Photoluminescence (PL) from nanocrystalline Si (nc-Si) has been a subject of considerable interest due to its potential application in Si-based optoelectronic devices. Si nanocrystals have been grown by various techniques.[1–7] Recently ion implantation[4–7] of Si into SiO_2 has drawn considerable attention in growing nc-Si because of its simplicity and compatibility with integrated circuits, and of the ease of controlling particle size and number density. Si implanted SiO_2 films, when annealed in nitrogen or vacuum above 900 °C, show[4–7] an intense red band at 790 nm (1.57 eV). Although the presence of nc-Si in these films has been established by high resolution transmission electron microscopy (HRTEM), the PL mechanism is still controversial. There still remain major problems whether the observed emission is due to exciton recombination in the quantum confined states of nc-Si or due to shallow donor states created by paramagnetic defects. In a recent paper, Min *et al.*[7] have claimed that visible light emission originates from Si nanocrystals in annealed films.

In this letter, we report results on annealed Si^+ implanted SiO_2 films that demonstrate the PL emits from nc-Si. Our work differs from Min *et al.* in the following ways. (1) We use a higher Si ion dose (3×10^{17} ions/cm^2) and energy (190 keV), and thicker (500 nm) SiO_2 films. These conditions are expected to produce a broadened Gaussian profile, with a peak Si concentration of 20 at. % at a depth of 300 nm [full width at half-maximum (FWHM) 230 nm]; (2) we anneal the samples in nitrogen or air; (3) we identify paramagnetic defects as a function of annealing time by electron spin resonance (ESR); (4) we image Si nanoparticles using HRTEM with sufficient contrast to measure the particle size; (5) we implant Ar^+ ions into SiO_2 films to investigate the role of defects on the PL spectra.

SiO_2 films, 500 nm thick, were grown on a 4 in. (100) Si wafer by thermal oxidation. The thermally oxidized Si wafer was then cut into several 1 cm^2 pieces in which Si^+ ions were implanted at an energy of 190 keV and to a dose of 3×10^{17} ions/cm^2. Ar^{++} ions were also implanted into SiO_2 films at 130 keV (equivalent to Ar^+ at 260 keV) to a dose of 2.1×10^{17} ions/cm^2; these parameters were chosen using the TRIM code[8] to simulate the range, straggling distribution, and atomic displacements obtained with 190 keV Si at 3×10^{17} ion/cm^2. Si^+ implanted films were annealed at 900 °C in air or in nitrogen. One of the Si-implanted films was reannealed in air at 900 °C four more times to reduce the particle size.[9] The duration of the annealing time was varied between 5 min (in air) to 1 h (in nitrogen).

Photoluminescence spectra were measured with a single monochromator (HR460) and a cooled charged coupled device (CCD) array. Si particle size was determined by HRTEM using a 300 keV transmission electron microscope (Hitachi H9000). Cross-sectional samples were prepared by mechanical thinning and ion milling. Prints of TEM images were scanned by an image scanner (HP Scanjet 4C), and the brightness and contrast were adjusted using Adobe Photoshop (4.0). ESR measurements were conducted using a Bruker-200DX band spectrometer, operating at a microwave power of 20 mW.[10] A modulation amplitude of 2 G at 100 kHz was used to enhance the weak ESR signals. The g factor is estimated by reference to a Mn^{2+} standard with an accuracy of ±0.001.

Figure 1(a) shows the PL spectra from a substrate (SiO_2 film), and Ar^+-, and Si^+-implanted samples. Both the substrate and Ar^+-implanted films showed a very weak PL that are probably related to some unknown intrinsic defects in the substrate. Si^+ as-implanted samples exhibited a broad photoluminescence band peaking at 660 nm (1.88 eV). We believe that this PL band is associated with defects in Si suboxides (SiO_x) created by implanted Si ions. Upon annealing at 600 °C for 1 h, the PL band was slightly redshifted. Samples annealed at 900 °C in air showed a further redshifted band [Fig. 1(b)] at 755 nm (1.65 eV) with a PL intensity increased by a factor of 10 as compared to as-implanted samples. Samples annealed in nitrogen exhibited a PL peak at 790 nm (1.57 eV), similar to that observed by Min *et al.* The PL peak position of the samples annealed in air shifted from samples to samples at the same annealing condition because of the varying degree of oxidation of Si nanocrystals in the Si:SiO_2 matrix.

Figure 1(b) shows PL spectra from an annealed substrate

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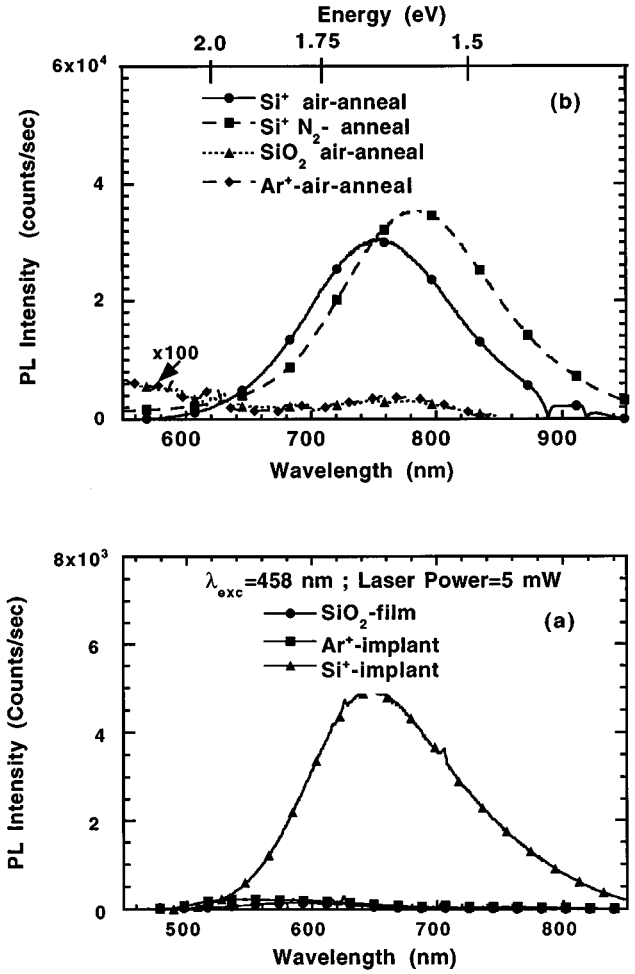

FIG. 1. (a) PL spectra of a substrate (SiO_x), and Ar^+ and Si^+ as-implanted films; (b) PL spectra of 900 °C annealed samples.

and an Ar^+ implanted film. Note that the PL intensity from the annealed Ar^+ implanted film is orders of magnitude smaller compared to the annealed Si^+-implanted SiO_2. This implies that the observed PL in annealed Si^+-implanted films is not due to defects created by high-energy ion implantation.

Figure 2(a) shows a typical nc-Si particle from a sample annealed at 900 °C in nitrogen for 1 h. Selected area electron diffraction (SAED) patterns of the annealed films were used to identify the crystalline phase as Si. The most prominent intensity in these patterns was due to Si(111) planes which appear as 0.3 nm lattice fringes in Fig. 2(a). This and numerous other particles, ranging in size from 1.0 to 6.0 nm and containing topological defects, were observed in HRTEM

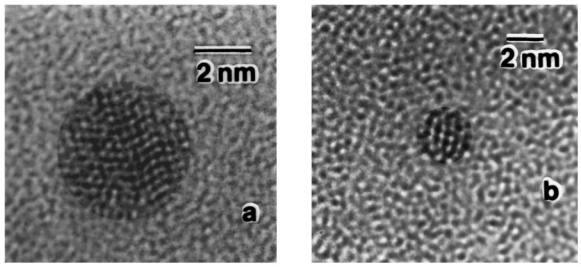

FIG. 2. HRTEM images of (a) a 900 °C annealed sample and (b) a four time annealed sample.

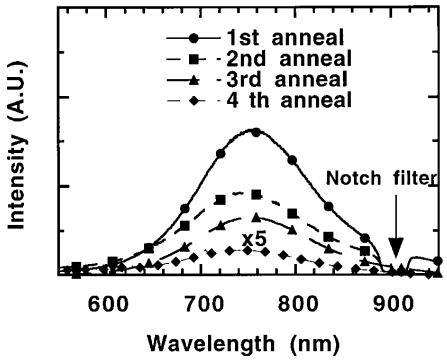

FIG. 3. PL spectra of a Si^+-implanted sample annealed in air at 900 °C for a few minutes each time.

images of all annealed films. Additional anneals in air at 900 °C showed a decrease in particle size, but did not exhibit a crystalline diffraction pattern due to a reduction in particle size and long range order. Figure 2(b) shows a typical particle, with a short range order, after four additional anneals in air at 900 °C.

Figure 3 shows PL spectra as a function of annealing time at 900 °C. A slight (10 nm) blueshift in the PL spectra was observed as a function of annealing time. The reduced intensity and a blueshift of the PL spectra are related to the decrease in number of particles and particle size which are confirmed from the HRTEM image of the four times annealed sample [Fig. 2(b)].

Figure 4 shows the ESR absorption spectra from as-implanted and annealed samples. As-implanted Ar^+ and Si^+ samples exhibited a broad range of g values between 1.996 and 2.002 that are characteristics of E' centers and their variants.[11,12] These defects are O vacancies in SiO_4 tetrahedra with a central g value of 2.000. In Ar^+-implanted films, E' centers are created by high-energy implantation where oxygen atoms are displaced from the SiO_4 tetrahedra. A higher concentration of E' centers in the Si-implanted films was observed because additional E' centers were created by the oxygen deficient SiO_x complexes formed by implanted Si atoms and their surrounding oxygen atoms.

Holzenkampfer *et al.*[13] showed that mean g values

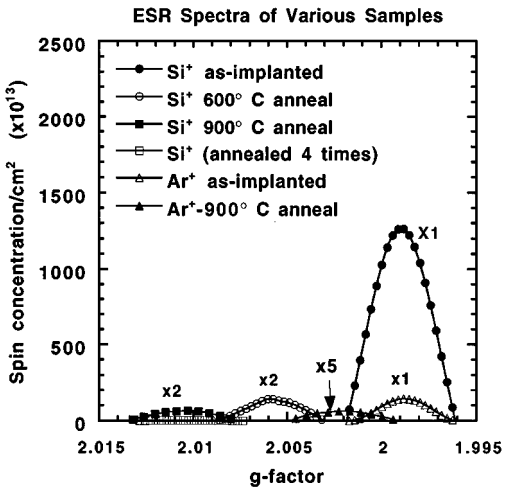

FIG. 4. ESR absorption spectra of different samples. Only $g_\perp$ is shown.

changed from 2.000 (FWHM 0.003–0.004) for an oxygen vacancy in SiO_4 tetrahedra (E'-type defects) to 2.006 (FWHM 0.004–0.006) for a Si vacancy in Si tetrahedra. We have measured both components of the g factor ($g_{\parallel}$ and $g_{\perp}$), where the parallel and perpendicular components refer to the magnetic field oriented along the (001) and (100) directions of the substrate (Si wafer). We show only $g_{\perp}$ in Fig. 4. We observed an increase in the g factor beyond 2.000 in annealed samples. This indicates that E'-type defects of as-implanted samples (both Si^+ and Ar^+) are annealed out. For annealed Si^+-implanted samples, the slightly anisotropic g values of 2.004 ($g_{\parallel}$) and 2.009 ($g_{\perp}$) are close to the measured g values for dangling bonds (P_b centers).[14] Note that, for annealed Ar^+-implanted samples, the mean g factor did not shift beyond 2.002, which implies that these defects are oxygen vacancies in SiO_4 tetrahedra.

Si dangling bonds that were observed in the annealed films are reported to quench PL from Si nanocrystals.[14] The most interesting observation in this study is the increase of PL intensity [Fig. 1(b)] with a decrease of oxygen dangling bonds (Fig. 4) and evidence of Si dangling bonds in the annealed films. The reason for such a low concentration ($\sim 10^{13}/cm^2$) of Si dangling bonds is due to oxygen passivation in the SiO_2 matrix. As the samples are reannealed for a few times in air, Si dangling bond defects should further reduce in number due to oxygen passivation, and the PL intensity should increase. But the number and size of the particles also decreased upon repeated annealing; consequently we observed a decrease in PL intensity and a slight blueshift. The theoretical calculation by Hybertsen,[15] in which the red emission band in porous Si is attributed to phonon-assisted exciton recombination in Si nanocrystals, shows a band edge at 750 nm (1.6 eV) for a mean particle size of 2.2 nm. HRTEM images from the nitrogen annealed sample showed a range in particle size between 1 and 6 nm. It is possible that the PL from these films originates from a distribution of particle sizes with a mean value of 2 nm. In air annealed samples, the 72 meV blue shift in the PL spectra indicates a slight reduction in the mean particle size. A significant reduction of particle size (<2 nm) was only observed [Fig. 2(b)] by annealing the samples in air a couple of times. According to theoretical predictions, one should observe a further blueshift of the PL spectra. However, we observe neither a narrowing nor a blueshift of the PL band. We, therefore, speculate that the excitons in smaller particles (<2 nm) have weaker oscillator strengths, luminesce very weakly, and PL from these particles cannot be detected at room temperature.

In summary, we have demonstrated that (1) Si nanocrystals can be grown by annealing Si^+-implanted SiO_2 films in air at 900 °C; (2) paramagnetic defects do not contribute to the luminescence observed in annealed Si^+-implanted films; (3) the observed photoluminescence from Si^+-implanted annealed samples is emitted from Si nanocrystals.

The authors acknowledge Randy Walker for the ion-implanting samples studied in this work. In addition, they also would like to acknowledge Dr. Mark Twigg for allowing them access to the HRTEM instrument.

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