Formation of light-emitting silicon nanoclusters in SiO₂

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Abstract. Silicon nanoclusters/nanocrystals (Si-nc) in an SiO₂ matrix exhibit strong visible luminescence, and so are of interest in the pursuit of a silicon-based light emitter for optoelectronics. We have investigated the formation of Si-nc by implanting excess Si at 90 keV into SiO₂ films and then annealing to form nanoclusters by precipitation and ripening. The use of ion implantation provides control over composition and so allows us to optimize the light output. Positron annihilation provides information on vacancy-type defects produced during implantation. Our results suggest that defects may play a key role in Si-nc formation. The depth and size distributions of Si-nc are obtained by transmission electron microscopy, and are correlated with light emission measured by photoluminescence.

1. Introduction

There is considerable interest in making all-silicon integrated circuits with optoelectronic functions. The key element missing from this strategy is an efficient silicon-based light emitter. Silicon nanoclusters/nanocrystals (Si-nc) embedded in SiO₂ exhibit strong luminescence at room temperature and so have attracted considerable research interest. Si-nc can be fabricated by a variety of methods including cosputtering [1], plasma enhanced chemical vapour deposition [2], laser ablation [3], ion implantation [4], and molecular beam epitaxy [5]. We have used ion implantation of Si into SiO₂ because (i) implantation is widely used in silicon processing, (ii) it provides the ability to precisely control the distribution and concentration of silicon, and (iii) it does not introduce any undesirable impurities.

There are multiple mechanisms for luminescence from Si-nc, including quantum confinement [6], interface states [7], and oxide defects [8]. The dominant luminescent mechanism varies with the Si-nc size [9]. In implanted samples, the stoichiometry of the oxide layer varies as a function of depth, which leads to a varying Si-nc size distribution versus depth. In this study, transmission electron microscopy was used to determine the Si-nc size distribution as a function of depth from the surface to the bulk silicon interface. The size distribution of Si-nc from the surface to the oxide/substrate interface has been previously reported by Brongersma et al. with the sizes ranging from 2-5 nm [10]. We found that the Si-nc size distribution does not correlate strongly with the implanted ion distribution as we would expect, but is correlated more closely with the distribution of vacancies generated during implantation. This may be indicative of the role played by vacancies in the Ostwald ripening process by which the Si-nc evolve during annealing.
Positron Doppler broadening measurements were used to probe defects, particularly vacancies introduced by ion implantation and their reduction after high temperature anneals. PAS data correlate with the location of Si-nc formed in the SiO$_2$ film after a long anneal, presumably due to positron trapping into silicon/SiO$_2$ interfaces, which are efficient traps [11]. In this report we focus primarily on the positron annihilation results; electron microscopy and photoluminescence data are reported in more detail elsewhere [12].

2. Experiment
Oxide films of thickness 430nm were thermally grown in wet O$_2$ at 1000°C on a boron-doped (100) silicon substrate. The films were implanted with Si$^-$ ions at 90 keV. The projected range predicted by stopping and range of ions in matter (SRIM) simulations [13] is 130 nm. Ion fluences ranged from $6 \times 10^{16} – 1.4 \times 10^{17}$ ions/cm$^2$, resulting in excess silicon (i.e. compared with stoichiometric SiO$_2$) of 9 – 20 at. %. Growth and ripening of Si-nc was achieved by high temperature anneals in a Jipelec Jetfirst rapid thermal annealer (RTA) or in a furnace, at 1070°C or 1170°C, both in high-purity nitrogen. Finally, to reduce the effects of non-radiative electron-hole recombination and dangling bonds, a 1 hour furnace anneal in forming gas (5% H$_2$ 95% N$_2$) at 450°C was performed. The diffusion coefficient for Si in SiO$_2$ is small [14]. Rutherford Backscattering measurements of the silicon distribution in some of our samples before and after annealing confirmed that there is very little redistribution of the implanted silicon.

Positron annihilation Doppler-broadening spectra were obtained using the University of Western Ontario positron accelerator, using a range of positron energies from 0.5 to 30 keV. Samples were measured using PAS to examine the evolution of defects in the oxide films due to annealing, to enable comparison with PL data. Data shown in figures 1 and 3 typically represent an average of 6 measurements each containing 100 000 counts. For the investigation of difference spectra shown in figure 2, approximately 100 measurements, each of 100 000 counts, were acquired at selected positron energies. Spectra were collected using a high-purity Ge detector of volume ~210 cm$^3$, with a resolution at 511 keV of 1.3 keV.

3. Results
A variety of defect species can be formed in SiO$_2$ by ion implantation [15]: peroxy radicals, $E^-$ centres, non-bringing-oxygen hole centres (NBOHC), and vacancy-type defects. Peroxy radicals are found more commonly in oxygen-rich SiO$_2$, making them less likely in our silicon-rich films [16]. $E^-$ centres are found more frequently in silicon-rich SiO$_2$ [17], but they are positively charged making them inefficient positron traps. NBOHC are a result of the electronic stopping of the implanted ions (i.e. energy loss to electrons of the medium) [18], and have been reported to result in a reduction in the positron annihilation $S$ parameter [19]. Vacancy-type defects are caused by the nuclear stopping of the implanted ions (i.e. direct nuclear collisions) and result in an increase in the $S$ parameter. If the vacancy-type defect is large enough positronium can form and be observed [20].

Our implants were performed at 90 keV, at which energy the two stopping powers are nearly equal ($dE/dx = 1.26$ (nuclear) vs. 1.39 (electronic) MeV cm$^2$/mg [13]), meaning that both types of defects should be present, and should exert opposing influences on the $S$ parameter. In figure 1, PAS measurements for three different implant doses show an $S$ parameter value higher than the starting material, and increasing with increasing ion fluence. This suggests that the PAS results are influenced most strongly by the creation of vacancy-type defects.

Previous reports suggest this may only be the case for high implant doses: Ghislotti et al. [16] performed a similar experiment with similar results at high doses, but for lower implant doses the $S$ parameter was reduced by the implant, indicating the presence of NBOHC defects. Knights et al. [19] and Simpson et al. [20] have previously reported a reduced $S$ parameter due to Si implantation into SiO$_2$, but for much lower doses than those described here.

Ghislotti et al. [16] suggested that the increased $S$ parameter that they observed for high dose implants was due to the increase in silicon concentration. However we note that (i) the $S$ parameter is
higher than that for bulk silicon, and therefore more consistent with open-volume defects, (ii) the peak $S$ parameter (in their data and in ours) is located at a depth which is better correlated with the vacancy-type defect profile predicted by SRIM [13] than with the peak of the implanted silicon, and (iii) the observation of positronium (see below) suggests the presence of open volume defects of significant size.

Figure 1. $S$ parameter data obtained from 430 nm thick SiO$_2$ films implanted with Si at 90 keV to various fluences. Solid lines are a guide to the eye.

Figure 2. Annihilation spectra obtained at a positron energy of 3 keV, comparing the reference SiO$_2$ with the as-implanted, 10s anneal and 30min anneal at 1170°C, for a sample implanted to a fluence of $1.35 \times 10^{17}$ ions/cm$^2$. Data have been smoothed for clarity.

Examining the Doppler-broadened annihilation spectra in detail is revealing. Figure 2 shows difference spectra obtained by subtracting the spectrum of ‘bulk’ defect-free silicon from various spectra of interest. Considering first the reference SiO$_2$ spectrum we propose that the narrow peak in the central region is due to 2-gamma annihilation of positronium. This suggests that the as-grown SiO$_2$ film contains open volumes of sufficient size for Ps to form within them. We do not see in our spectra any evidence for 3-gamma annihilation of orthopositronium, which suggests that any orthopositronium that is formed annihilates by pick-off. Considering next the spectrum of the as-implanted sample, we
note an increase in the narrow Ps peak, which suggests an increase in the size and/or number of open volumes large enough to accommodate the formation of Ps. This is consistent with the fact that the very high implantation dose ($1.35 \times 10^{17}$ ions/cm$^2$) produces a very large number of atomic displacements. Annealing for 10 seconds at 1170°C restores the annihilation spectrum to very nearly that of the as-grown film prior to implantation. Further annealing for 30 minutes, yields a spectrum that shows no evidence at all of 2-gamma positronium annihilation.

It is of interest to examine how these results correlate with the evolution of photoluminescence during a similar annealing sequence [12]: the peak wavelength of photoluminescence evolves to its final value within ~2 minutes of annealing or less, and thus correlates strongly with the fact that a 10 second anneal is sufficient to restore the positron annihilation spectrum almost to its pre-implant appearance. If we assume that the mechanism responsible for the photoluminescence is quantum confinement, then the peak wavelength is an indication of the size of the nanocrystals formed, and this then suggests that the nanocrystals evolve to their final size very rapidly during annealing. The intensity of the photoluminescence evolves more slowly, requiring ~10 minutes of annealing to reach its final value, suggesting that the longer annealing removes defects which compete with the luminescence mechanism by providing sites for non-radiant recombination of electron-hole pairs.

The positron annihilation spectrum for a sample annealed for 30 minutes shows no 2-gamma Ps annihilation, suggesting the elimination of sites with sufficient open volume for Ps formation. Transmission electron microscopy shows that the mean distance between Si-nanocrystals (Si-nc) is approximately 7 nm, which is comparable with reported values [20] for the positron diffusion length in SiO$_2$. So it may be the case that in annealed films the positrons trap primarily in the interfaces between the Si-nc and the surrounding SiO$_2$ matrix, and that longer annealing creates greater ordering of these regions, with reduced open volume.

The positron data shown in figure 3 have been modelled using POSTRAP5 [22]. The data for the as-implanted sample cannot be fitted well without including both a layer of vacancy-type defects in the near surface region (0 to 285 nm) and a deeper layer (285 nm to 430 nm) with an $S$ parameter lower than that of the unimplanted film. The depth of the vacancy-type layer is in good agreement with the profile of vacancy-type defects predicted by SRIM [13] simulations, shown in figure 4. Results of fitting are summarized in table 1.

We have obtained transmission electron microscopy images as a function of depth into the sample [12], and from these we extract the nanocrystal size and concentration vs. depth summarized in table 2. Of particular interest is the fact that the nanocrystal size distribution is not well correlated with the
profile of implanted silicon (predicted by SRIM). This is the case despite the low diffusivity of Si in SiO$_2$ (which is supported by our Rutherford Backscattering measurements of the silicon distribution before and after annealing). There is however, strong correlation between the profile of vacancies, predicted by SRIM and supported by positron annihilation, and the depth distribution of nanocrystal size. This may suggest that vacancies play a key role in the diffusion required to form the nanocrystals. Further experiments are underway to better understand this phenomenon.

**Figure 4.** Prediction from SRIM simulation [13] of the depth distribution of implanted ions (90 keV Si into SiO$_2$) and of vacancy-type defects. The vacancy-type defect concentration has been divided by 1000 for clarity.

**Table 1.** Normalized $S$-parameters obtained from POSTRAP5 by fitting PAS data collected from the 430 nm thick SiO$_2$ film implanted at 90 keV to a fluence of $1.35 \times 10^{17}$ Si ions/cm$^2$. Data were normalized so that the $S$-parameter for the Si substrate was equal to 1.00 in all cases. Parameters are reported to 3 digits of precision, although the coupling between related parameters in the modeling limits the real accuracy to roughly 0.01; values reported provide the best fit but slightly different parameters yield acceptable fitting also.

| Sample                        | Surface | Implanted Region | SiO$_2$ film | Si/SiO$_2$ Interface |
|-------------------------------|---------|------------------|--------------|---------------------|
| Reference SiO$_2$ film        | 0.917   | -                | 0.983        | 0.972               |
| As-implanted film             | 0.950   | 1.02             | 0.834        | 0.979               |
| 10s anneal at 1170°C          | 0.947   | 0.995            | 0.979        | 0.958               |
| 30min anneal at 1170°C        | 0.907   | 0.958            | 0.984        | 0.954               |

**Table 2.** The median and average diameter of Si-nc as a function of depth compared with the normalized vacancy-type defect and implant concentrations simulated by SRIM for an implant at 90 keV and a fluence of $1.35 \times 10^{17}$ ions/cm$^2$. TEM images analyzed are those from ref [12]. The median and average diameters obtained may be skewed by the inability to observe nanoclusters below ~1 nanometre diameter.

| TEM Image Depth Range (nm) | Median Diameter (nm) | Average Diameter (nm) | Normalized Vacancy-type Defect Concentration | Normalized Implant Concentration |
|----------------------------|----------------------|-----------------------|---------------------------------------------|----------------------------------|
| 0 – 45                     | 1.71                 | 1.77 ± 0.05           | 0.66                                        | 0.08                             |
| 45 – 90                    | 1.79                 | 1.82 ± 0.05           | 0.99                                        | 0.44                             |
| 90 – 135                   | 1.82                 | 1.86 ± 0.05           | 1.00                                        | 1.00                             |
| 135 – 180                  | 1.61                 | 1.67 ± 0.04           | 0.54                                        | 0.98                             |
| 180 – 225                  | Too small to distinguish |                     | 0.11                                        | 0.33                             |
4. Conclusions
We have previously found that silicon nanocrystals grown by silicon implantation at 90 keV and annealing exhibit a broad photoluminescence peak centred at ~800 nm [12]. Positron annihilation was used to probe the defects created by implantation, and their recovery during annealing. We found that for the very high implantation doses used here, vacancy-type defects dominate the positron annihilation behaviour, resulting in an increased $S$ parameter, contrary to results for low-dose implantation into SiO$_2$. The depth profile of the vacancy-type defect layer needed to model the data is in good agreement with that predicted by SRIM simulations. Examination of annihilation spectra shows that the increased $S$ parameter caused by implantation is due to the formation of positronium, and its 2-gamma annihilation. We find that the nanocrystal size distribution obtained from electron microscopy [12] correlates with the profile of implant-induced vacancies, and not with the profile of implanted ions, suggesting that vacancies may play a role in the silicon diffusion required to form nanocrystals.

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