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Probing the formation of Silicon nano-crystals (Si-ncs) using Variable Energy Positron Annihilation Spectroscopy

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Abstract

We describe preliminary results from studies of the formation of silicon nano-crystals (Si-ncs) embedded in stoichiometric, thermally grown SiO₂ using Variable Energy Positron Annihilation Spectroscopy (VEPAS). We show that the VEPAS technique is able to monitor the introduction of structural damage in SiO₂ created through the high dose Si⁺ ion implantation required to introduce excess silicon as a precursor to Si-nc formation. VEPAS is also able to characterize the rate of the removal of this damage with high temperature annealing, showing strong correlation with photoluminescence. Finally, VEPAS is shown to be able to selectively probe the interface between Si-ncs and the host oxide. Introduction of hydrogen at these interfaces suppresses the trapping of positrons at the interfaces.

1. Introduction

Low dimensional silicon continues to be of considerable interest for applications such as silicon based solid state lighting, non-volatile memories and dielectric engineering [1]. Specifically, silicon nano-crystals (Si-ncs) formed in the dielectric material SiO₂ or Si₃N₄ have been shown to possess a range of properties not usually associated with the silicon bulk. Such nano-crystals are formed via phase separation in silicon-rich dielectric. This precursor material may be fabricated using a number of standard processes such as plasma enhanced chemical vapour deposition [2] or sputtering, both suitable for high-volume, large area applications. The most controllable fabrication technique (and thus the preferred method for the methodical study of Si-ncs) is ion implantation [3]. In this case, excess silicon is introduced into stoichiometric, thermally grown SiO₂, with phase separation taking

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place during a subsequent high temperature (>1000 C) annealing step. In this current work, we show the significant potential of Variable Energy Positron Annihilation Spectroscopy (VEPAS) for obtaining novel information on the formation and light emitting potential of Si-ncs formed via high dose Si^+ ion implantation of SiO_2 . We demonstrate that VEPAS shows a strong relationship between the damage contained in the SiO_2 (resulting from the implantation process) and the formation mechanics of the Si-ncs. We confirm previous hypotheses that the interface plays a significant role in the light emission from Si-ncs. This is achieved through the observation of the VEPAS signal for Si-ncs with and without interface passivation.

2. Experimental

2.1. Sample preparation

All of the samples reported here were prepared via high dose ($>1 \times 10^{16} \text{cm}^{-2}$) Si^+ ion implantation into thermally grown SiO_2 thin films on a low-doped *p*-type silicon substrate; followed by a high temperature ($>1000^\circ\text{C}$) anneal in N_2 . A fraction of the films were subsequently annealed at 500°C for 10 minutes in forming gas ($\text{N}_2:\text{H}_2$ 95:5). Details of specific sample preparation are provided in the text.

2.2. Sample Characterization

Confirmation of the presence of Si-ncs was obtained via Transmission Electron Microscopy (TEM) using a conventional CM-12 microscope operated at 120 kV. Cross-sectional specimens oriented along the $\{110\}$ zone axis were prepared by mechanical polishing, followed by ion milling. Dark-field examinations were carried out with two beam diffraction condition ($g = 220$) relative to the Si substrate.

Photoluminescence (PL) measurements were performed using the 405nm line of an InGaN/GaN laser diode operating at 50mW. The spectra were collected using a CCD array. Variable Energy Positron Annihilation Spectroscopy (VEPAS) was performed using the University of Bath slow positron beam, details of which are described elsewhere [4]. The annihilation spectra were analysed in terms of the classic *S*-parameter for incident positron energies ranging from 0.1-30keV.

3. Results and Discussion

Figure 1 shows an example of a TEM image of a collection of Si-ncs, in this case for a sample prepared using an implantation dose of $8 \times 10^{16} \text{cm}^{-2}$ and energy of 80keV.

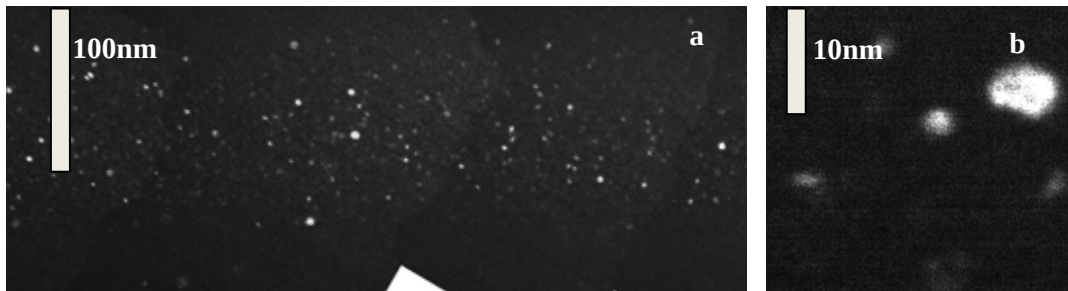


Figure 1. Dark field TEM image of Si-ncs in SiO_2 ; (a) wide view of distribution; (b) enlarged view of Si-nc.

Following ion implantation the sample was annealed at a temperature of 1150°C for 50s. The phase separation leading to the formation of the Si-ncs is confirmed, with the Si-ncs showing as light regions (in the dark field image). In this case the mean diameter of the Si-ncs was approximately 3nm.

The structure of Si⁺ ion implanted SiO₂/Si (SiO₂ film thickness = 500nm) as a function of annealing time was characterized using VEPAS for a sample set again prepared using an implantation energy and dose of 80keV and 8x10¹⁶cm⁻² respectively. The annealing was performed at 1100°C for times ranging from 1-100secs. The S-parameter (normalized to bulk silicon) versus incident positron energy is shown in figure 2. Data for annealing times between 1 and 100 seconds (exclusive) showed a slowly varying trend of reduction in S-parameter for the region between 1-7keV, and is not shown in order to maintain clarity.

The data for the unimplanted SiO₂/Si film is consistent with a film thickness of 500nm with strong positron trapping at the SiO₂/Si interface. Following the relatively high dose ion implantation the S-parameter corresponding to the end of range of the implanted ions increases (positron energy ~3.5keV), signifying the likely introduction of large open volumes. Somewhat remarkably, even for an annealing time of 1sec, there is a significant drop in S-parameter at an energy (1-5keV) which would be consistent with the expected phase separation of the excess implanted Si. This reduction in S-parameter continues to an annealing time of 100 secs, afterwhich negligible evolution in the shape of the S-E data is observed (data not shown for clarity). Consistent with a previous report [5] we ascribe the 'dip' in the VEPAS data at ~2.5keV with annihilations which take place at the interface of the Si-ncs and the host SiO₂.

Photoluminescence data shown in figure 3 was obtained from the same samples as those used to obtain the VEPAS data. For the as-implanted sample there is a measurable but small luminescence signal centred at 670nm which likely results from luminescent defects. After annealing for 1 sec the formation of Si-ncs is confirmed by the large increase in signal strength and the shift in emission wavelength to ~770nm. Further annealing for 100secs results in a small red-shift of emission wavelength (consistent with an increase in size of the average diameter of the Si-ncs) and a significant

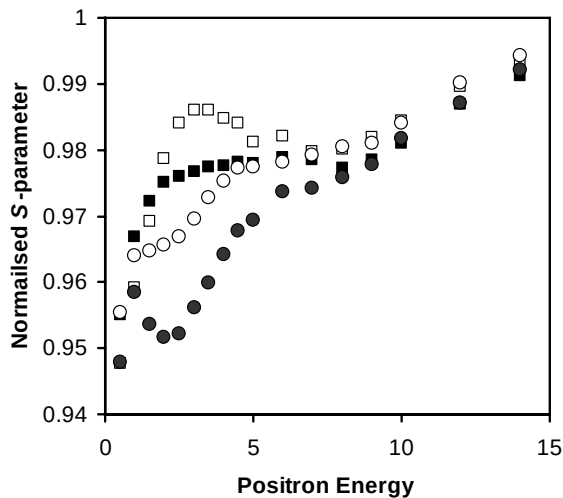


Figure 2. Normalized S-parameter versus positron energy for samples implanted with 8x10¹⁶cm⁻² at an ion energy of 80keV and annealed at 1100°C for 1 sec (open circles) and 100sec (closed circles). Data for the unimplanted SiO₂/Si film is shown as closed squares, and that for the as-implanted (unannealed) is shown as open squares.

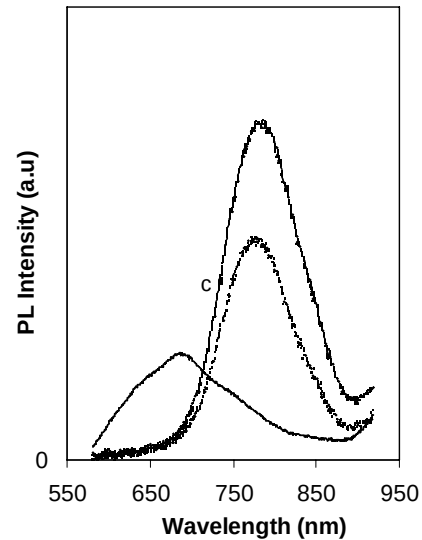


Figure 3. Photoluminescence data for samples implanted with 8x10¹⁶cm⁻² and annealed at 1100°C for 1 sec (dotted line) and 100sec (dashed line). Data for the as-implanted sample is shown as a solid line (data has been multiplied by 10 times to allow comparison).

increase in luminescence intensity. This intensity increase occurs with concomitant reduction in structural damage of the SiO₂ shown by figure 2. This is likely then due to the removal of non-radiative recombination centres. The VEPAS technique thus provides an important method through which the removal of luminescence suppression may be monitored.

Finally, we discuss the important role which VEPAS provides in relation to the characterization of the Si-nc/SiO₂ interface. Despite the importance of the interface to luminescence [1] there remain few techniques which may be used to probe the bonds between the oxide and silicon directly. In figure 4 we show data similar to that in figure 2. In this case though, the excess silicon has been introduced via a 40keV Si⁺ ion implantation to a dose of $4 \times 10^{16} \text{cm}^{-2}$. The thickness of the SiO₂ film was nominally 100nm. The implantation again induces structural damage to the oxide film indicated by an increased S-parameter in the energy range 1.5-3keV. Following annealing at 1100°C for 100secs in N₂ the formation of Si-ncs results in a ‘dip’ in the data, centred at ~2keV, associated with trapping of positrons at the Si-nc/oxide interface. Following a second anneal at 500°C for 600secs in forming gas (containing 5%H₂), the trapping of positrons at the interface is significantly suppressed, and hence the ‘dip’ is removed. This is consistent with the passivation of defects at the Si-nc surface, an effect which has been documented as inducing a large increase in the luminescence yield [5].

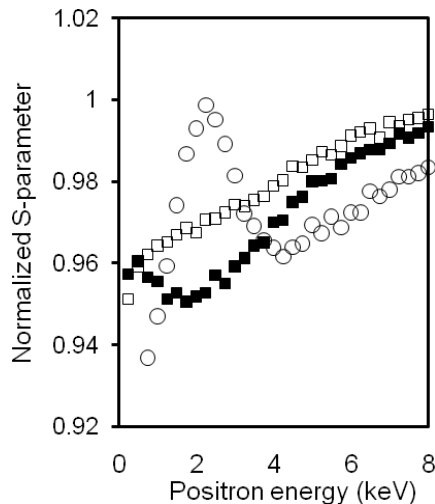


Figure 4. Normalized S-parameter versus positron energy for samples implanted with $4 \times 10^{16} \text{cm}^{-2}$ at an ion energy of 40keV and annealed at 1100°C for 100 sec in N₂ (closed squares); 1100°C for 100sec N₂, followed by forming gas anneal at 500°C for 600secs (open circles). Data for as-implanted (unannealed) is shown as open circles.

4. Conclusion

We have presented preliminary data on the use of VEPAS to probe the formation of Si-ncs in SiO₂. There are few techniques (if any) which can provide similar depth-resolved information on this technologically important system. VEPAS monitors the removal of luminescence suppressing defects following high dose ion implantation. Further, it is able to sensitively probe the interface of Si-ncs and the host SiO₂. Significant work is planned in the near future combining VEPAS, electron microscopy and photoluminescence on similar material systems and those doped with rare-earths such as erbium and cerium.

5. References

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