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 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 place during a subsequent high temperature (>1000 C) annealing step. In this current work, we show

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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 SiO₂. We demonstrate that VEPAS shows a strong relationship between the damage contained in the SiO₂ (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 light emission. 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 silicon (>1x10¹⁶cm⁻²) Si⁺ ion implantation into thermally grown SiO₂ thin films on a low-doped p-type silicon substrate; followed by a high temperature (>1000°C) anneal in N₂. A fraction of the films were subsequently annealed at 500°C for 10 minutes in forming gas (N₂:H₂ 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 8x10¹⁶cm⁻² and energy of 80keV. Following ion implantation the sample was annealed at a temperature of 1150°C for 50s.

Phase separation leading to the formation of 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. Annealing at temperatures in the range 1000-1200°C and times from 1-100secs produced similar arrays of Si-ncs (as observed by TEM), albeit their concentration and mean diameter varied with each thermal treatment. The description of this variation will be the subject of a future publication.
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 tarping at the SiO₂/Si interface. Following the relatively high dose Si⁺ 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, or at least a significant change in the film composition/structure. Somewhat remarkably, even for an annealing time of only 1sec, there is a significant drop in S-parameter at an energy (1-5keV) which would be consistent with the expected depth at which phase separation of excess Si would occur. This reduction in S-parameter continues to an annealing time of 100 secs, after which negligible evolution in the shape of the S-E data is observed (data not shown for clarity). Consistent with previous reports [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 (the Si-nc/SiO₂ interface closely resembles that of a thin slick SiO₂/Si interface).

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 100sec results in a small red-shift of emission wavelength (consistent with an increase in size of the average diameter of the Si-ncs) and an increase

![Figure 2. Normalized S-parameter versus positron energy (and mean positron implantation depth) 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 film shown as closed squares, and for the as-implanted (unannealed) shown as open squares.](image)

![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).](image)
in luminescence intensity. This increase occurs with concomitant reduction in structural damage of the SiO₂ shown by figure 2. This increase is likely 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. In figure 4 we show data similar to that in figure 2. In this case the excess silicon has been introduced via a 40keV Si⁺ ion implantation to a dose of 4x10¹⁶cm⁻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 [6].

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.

5. References
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