Positron annihilation studies of silicon-rich SiO$_2$ produced by high dose ion implantation

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Positron annihilation spectroscopy (PAS) is used to study Si-rich SiO$_2$ samples prepared by implantation of Si (160 keV) ions at doses in the range $3 \times 10^{16}$--$3 \times 10^{17}$ cm$^{-2}$ and subsequent thermal annealing at high temperature (up to 1100 °C). Samples implanted at doses higher than $5 \times 10^{16}$ cm$^{-2}$ and annealed above 1000 °C showed a PAS spectrum with an annihilation peak broader than the unimplanted sample. We discuss how these results are related to the process of silicon precipitation inside SiO$_2$.© 1997 American Institute of Physics.

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The study of silicon-rich SiO$_2$ (Si$_2$O$_3$) has been the matter of several papers. Different models have been proposed to describe this structure: a random-bonding model in which Si-Si and Si-O bonding are randomly distributed; a random-mixture model for which tetrahedral units are grouped together; finally, a shell model in which silicon clusters are embedded in stoichiometric SiO$_2$. Each of these models gives a correct picture for a different degree of silicon excess. Apart from these fundamental questions, Si precipitation in Si-rich SiO$_2$ has been used to produce Si nanocrystals inside a dielectric matrix which can give visible luminescence at room temperature.

In this study we examined annealing behavior of Si-rich SiO$_2$ using positron annihilation spectroscopy (PAS). This technique is based on the fact that positrons, when implanted at a given energy, thermalize and diffuse inside the medium, and finally annihilate with electrons. Gamma-rays emitted after the annihilation carry information about the annihilation site. In a Doppler broadening measurement this information is extracted by analyzing the broadening of the 511 keV annihilation peak, due to the non-zero momentum of electrons. The availability of variable energy positron beams allow non-destructive depth-profiling of materials.

The technique has been extensively used to study the Si-SiO$_2$ system (for a review see Ref. 9).

Samples were prepared by implanting 160 keV $^{28}$Si$^+$ ions into 430 nm thick SiO$_2$ layers thermally grown on a (100) oriented $p$-type Si substrate kept at room temperature during implantation. Fluences ranged from $3 \times 10^{16}$ cm$^{-2}$ to $3 \times 10^{17}$ cm$^{-2}$, the ion current density was 0.3 \( \text{A/cm}^2 \). For a set of samples, obtained by implanting in fused quartz Suprasil substrate was considered. Suprasil samples were implanted at doses from $5 \times 10^{16}$ cm$^{-2}$ to $1.5 \times 10^{17}$ cm$^{-2}$.

Positron annihilation spectroscopy measurements were performed in an ultrahigh vacuum chamber ($<10^{-7}$ Torr) using a variable energy positron beam. In each measurement $10^6$ counts were accumulated. The Doppler broadening of the 511 keV annihilation line was measured with an HPGe-detector based gamma spectroscopy system. The broadening was characterized using the line shape parameter ($S$-parameter), defined as the area of a fixed region ($\approx 1.59$ keV wide) in the center of the annihilation peak divided by the total area of the peak. The sharpness of the annihilation peak is related to the $S$-parameter, namely sharper peak produces a higher $S$-value. In order to compare different $S$-E spectra, it is customary to divide measured $S$-parameter by that of a reference sample measured under the same experimental conditions. A $p$-type high resistivity Si sample was taken as a reference.

Suprasil samples were annealed in a vacuum furnace ($\approx 10^{-6}$ Torr). Thermal SiO$_2$ layers on Si samples were annealed in situ up to 700 °C with a resistively heated tantalum foil, at $10^{-7}$ Torr. Above 700 °C, annealing was performed in N$_2$ atmosphere. Annealing time was 30 min.

Figure 1 shows the $S$-parameter values as a function of the positron implantation energy $E$ ($S$ vs $E$) for Suprasil samples implanted at different fluences. The upper abscissa represents the mean positron implantation depth $z$ calculated according to the relation: $z = AE^p/n$, where, in case of SiO$_2$, $\rho = 2.33$ g/cm$^3$, $n = 1.6$, and $A = 4.0$ $\mu$g cm$^{-2}$ keV$^{-1}$.$^9$ The $S$-parameter versus implantation energy curve for unimplanted sample is also reported. The low $S$-value observed at the surface for this sample is related to positrons implanted at zero energy, diffusing back to the surface and annihilating there. When the implantation energy increases,

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of annealing temperature are reported for samples implanted at $5 \times 10^{16}$ cm$^{-2}$ and $1 \times 10^{17}$ cm$^{-2}$, respectively. In the temperature interval from 100 °C to 300 °C the $S$-parameter increases to values close to 1 (the reference silicon $S$ value) and it remains constant up to 800 °C. A decrease is observed only after annealing at 900 °C. Further annealing at 1100 °C shows a larger reduction: while for sample implanted at $5 \times 10^{16}$ cm$^{-2}$ the unimplanted $S$ value is restored, for sample implanted at $1 \times 10^{17}$ cm$^{-2}$ fluence the $S$-parameter goes below this limit.

This behavior could be related to defects produced during implantation with Si atoms. Different kind of defects can be produced in SiO$_2$ by implantation: E$'$, non-bridging-oxygen hole centers (NBOHC), and peroxy radicals. In a PAS Doppler broadening spectrum NBOHC give rise to a low $S$-value and they are not stable above 300 °C. Peroxy radicals are typical of oxygen-rich samples. In a Si-rich region E$'$ defects are more probably produced. However, they are positively charged and therefore they cannot trap positrons efficiently. A high $S$-value can be related to positronium ($Ps$) formation inside voids. In this case ion implantation should decrease $Ps$ formation by producing smaller defects and reducing free spaces. Therefore $S$ value in as-implanted samples should decrease as a function of the dose.

Assuming that the high $S$-parameter and its observed annealing behavior are related to defects, we would expect that $S$ decreases to the unimplanted value after annealing at 1100 °C (the level reported in Fig. 2 refers to unimplanted sample annealed at 1100 °C). This is observed in the sample implanted at $5 \times 10^{16}$ cm$^{-2}$ but not at $1 \times 10^{17}$ cm$^{-2}$, where $S$ decreases below the unimplanted value. The previous arguments exclude that the decrease in $S$ after annealing at 1100 °C is related to defect recovery. The region of interest corresponds to a Si-rich zone. We propose that the high $S$-parameter is related to the presence of Si-atoms in a concentration higher than that of stoichiometric SiO$_2$. The first annealing stage observed around 300 °C could be due to recovery of defects, like E$'$, typical of a Si-rich SiO$_2$. It is known that these defects anneal out in this temperature range.

When heated at high temperature, ordering processes can take place in amorphous SiO$_2$, as already observed using PAS. However such a phenomena are effective above 1200 °C or, around 900–1000 °C, for very long annealing time (48 h in Ref. 21). The experimental conditions to observe ordering in SiO$_2$ are therefore different from those adopted in the present case. Moreover $S$-value for unimplanted sample reported in Fig. 2 refers to a sample annealed under the same conditions than implanted ones. $S$-value in this case is higher than for non-annealed sample, whereas $S$-parameter is expected to decrease when ordering processes or crystalline phases are present. Our results agree with data presented by Shimura et al., who observed crystalline phases in as-grown thermal SiO$_2$ layers, but no changes after annealing for 1 h at 950 °C. Therefore another kind of structural changes are responsible for $S$-value decrease in implanted samples after annealing at high temperature.

Above 1000 °C SiO$_2$ dissociates according to the reaction: $24,25$ SiO$_2$ → Si + SiO$_2$, therefore the Si excess pre-
reduction has a monotonic dependence on dose and Fig. 3 -value is lower than the unimplanted oxide, and SiO$_2$ system is observed for positrons trapped at the interface of Si nc inside SiO$_2$ is also the observation of a photoluminescence centered at around 780 nm. PL spectrum for unimplanted samples. Samples implanted at a dose higher than $5 \times 10^{16}$ cm$^{-2}$ present $S$-parameter lower than unimplanted value. This difference is related to silicon precipitation in SiO$_2$.

In conclusion silicon-implanted fused quartz and thermal SiO$_2$ layers have been studied using positron annihilation spectroscopy. After annealing at 1100 °C, samples implanted at $5 \times 10^{16}$ cm$^{-2}$ showed no difference in $S$-parameter respect to unimplanted samples. Samples implanted at a dose higher than $5 \times 10^{16}$ cm$^{-2}$ present $S$-parameter lower than unimplanted value.

FIG. 3. Normalized $S$ vs energy curves for SiO$_2$ layers on Si implanted at different doses ($3 \times 10^{16}$ cm$^{-2}$-$3 \times 10^{17}$ cm$^{-2}$) and subsequently annealed at 1000 °C.