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# Microstructure evolution of $Ge^+$ implanted silicon oxide thin films upon annealing treatments

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ABSTRACT

The structural evolution of silicon oxide films with $Ge^+$ implantation was traced with a positron beam equipped with positron annihilation Doppler broadening and lifetime spectrometers. Results indicate that the film structure change as a function of the annealing temperature could be divided into four stages: (I) $T < 300$ °C; (II) 300 °C $\leqslant T \leqslant$ 500 °C; (III) 600 °C $\leqslant T \leqslant$ 800 °C; (IV) $T \geqslant$ 900 °C. In comparison with stage I, the increased positron annihilation Doppler broadening $S$ values during stage II is ascribed to the annealing out of point defects and coalescence of intrinsic open volumes in silicon oxides. The obtained long positron lifetime and high $S$ values without much fluctuation in stage III suggest a rather stable film structure. Further annealing above 900 °C brings about dramatic change of the film structure with Ge precipitation. Positron annihilation spectroscopy is thereby a sensitive probe for the diagnosis of microstructure variation of silicon oxide thin films with nano-precipitation.



## 1. Introduction

Measurement of nanocrystals in a matrix is a challenging issue due to the difficulties in probing embedded structures with nanometric size. Most of the recently published reports on semiconductor nanocrystals embedded in $SiO_2$ are based on photoluminescence measurements with limited structural evidence [1,2]. It is quite desirable to improve the metrology of the nanostructures with new experimental approaches. In this paper, we report on the positron annihilation analysis of the nano-precipitates/dielectrics system in order to monitor the structural evolution of the matrix material rather than the nanocrystals themselves. Such an analysis would provide not only evaluation of the matrix for potential device applications but also an indirect method for the diagnosis of the nanocrystals.

## 2. Experimental

Silicon oxide films used for this study were thermally grown on p-type Si wafers in a tube furnace with stable dry oxygen flow. Final thickness of the thermal oxidized films was approximately 1000 nm. $Ge^+$ ion implantation was carried out with a Tandem accelerator. The ion energy and implantation dose was 800 keV and $2.5 \times 10^{16}$ cm$^{-2}$, respectively. After implantation, the samples were isochronally annealed in Ar ambient at elevated temperatures ranging from 100 to 1000 °C with 100 °C in step, and each step takes 0.5 h.

After each step of annealing treatment, positron annihilation Doppler broadening and lifetime measurements were subsequently conducted. For Doppler broadening measurements, the annihilation gamma-rays were recorded with an intrinsic Ge detector, and Doppler broadening of positron annihilation radiation is characterized by $S$ and $W$ parameters. The $S$ parameter is defined as the ratio of the gamma-ray counts in the central part of the 511 keV peak (510.24–511.76 keV) to that in the entire peak (504.2–517.8 keV). $W$ parameter was defined as the ratio of the summed gamma-ray counts in the range of 513.6–517.8 keV and 504.2–508.4 keV to the total number of counts in the entire peak. For positron lifetime measurements, the start and stop signals were, respectively, obtained from a $BaF_2$ detector and from a pulse generator. Obtained lifetime spectra were resolved into two components, the longer-lived one with a lifetime of $\tau_2$ was attributed to pick-off annihilation of ortho-positronium (*o*-Ps) atoms.

## 3. Positron annihilation results

Positron annihilation Doppler broadening data for the as-implanted as well as annealed samples are shown in Fig. 1. It can be seen that starting from 300 °C, annealing effect on positron

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annihilation results turns clear. *S* parameters corresponding to the $Ge^+$ implanted region (∼2–8 keV incident positron energy) are increasing along with the enhancement of the annealing temperature up to 500 °C. Between 600 and 800 °C there is no much difference in the obtained results. It is interesting that above 900 °C, further annealing leads to a decrement of *S*.

The positron annihilation lifetime results for silicon oxide films are shown in Fig. 2. Note that at the beginning of the measurements, increase of the annealing temperature gradually enhances the long positron lifetime (>0.8 ns) component $\tau_2$, which should be originated from pick-off annihilation of *o*-Ps in the voids of silicon oxide [3]. $\tau_2$ reaches its largest value at the annealing temperature of 500 °C, but it is still smaller than that in the un-implanted virgin $SiO_2$. Similar to the *S* parameter variation, further increment of the annealing temperature above 900 °C leads to a clear decrement of the *o*-Ps lifetime.

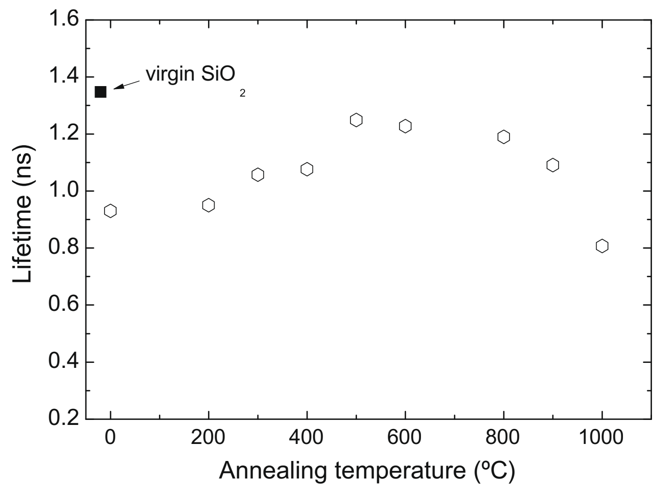


**Fig. 2.** *o*-Ps lifetime for the $Ge^+$ implanted silicon oxide film annealed at different temperatures. Result for the un-implanted virgin film is also plotted for comparison.

## 4. Discussions

We may divide the structural change of the $Ge^+$ implanted silicon oxide films as a function of the annealing temperature into four stages: (I) $T < 300$ °C; (II) $300\,°C \leqslant T \leqslant 500$ °C; (III) $600\,°C \leqslant T \leqslant 800$ °C; (IV) $T \geqslant 900$ °C. The significant reduction of *S* for the as-implanted sample compared with that of the virgin silicon oxide could be ascribed to suppression of the Ps formation probability in silicon oxide, owing to the defects generation by ion implantation. At the same time, after $Ge^+$ implantation, *o*-Ps lifetime $\tau_2$ was also found reduced from that of the un-implanted virgin film. In general, *o*-Ps atom lives longer if it resides in an open volume having a larger size, and when it annihilates into two-gamma-rays via pick-off process, a smaller Doppler broadening (corresponding to larger *S*) of annihilation radiation is expected in the light of the uncertainty principle [4]. Hence, the reduced *S* upon ion implantation shall be from the summed effect of defects generation as well as shrinkage of intrinsic open volumes consist in silicon oxides.

Increment of *S* during post-annealing stage II thereby shall be related to the annealing out of point defects and coalescence of the intrinsic open volumes. When annealing temperature is within 600–800 °C (stage III), high *S* and $\tau_2$ were obtained and without much fluctuation as post-annealing temperature varies, suggesting a rather stable film structure in this stage. Nevertheless, $\tau_2$ for annealed film at stage III is still smaller than that for the un-implanted one, indicating that ion irradiation damage could not be completely recovered by post-annealing.

Further annealing above 900 °C brings about significant reduction of *S* and $\tau_2$, indicative of the dramatic change of the silicon oxide film structure. It is known that melting point of Ge is about 940 °C, therefore such change might be related to Ge precipitation in silicon oxide matrix. Results for catholuminescence (CL) measurements of the as-implanted as well as annealed specimens support this postulation. As Fig. 3 shows, a blue–violet luminescence band with wavelength at about 400 nm appear for the as-implanted specimens as well as those annealed at 300, 600, and 900 °C. Since this band could not be observed in the un-implanted virgin silicon oxide film, it may be due to the formation Ge-related chemical bonds or defects (luminescence centers). Moreover, the intensity of this luminescence band corresponding to the film annealed at 900 °C is overwhelmingly stronger than those annealed at other temperatures. Also, a new luminescence band at about 850 nm appears at 900 °C. This infrared band has been ascribed to the formation of Ge nanocrystals which give light emission owing to the quantum confinement effect [5]. Therefore, the 900 °C luminescence data might indicate that coalescence of Ge atoms/clusters near melting state not only generates Ge nanocrystals,

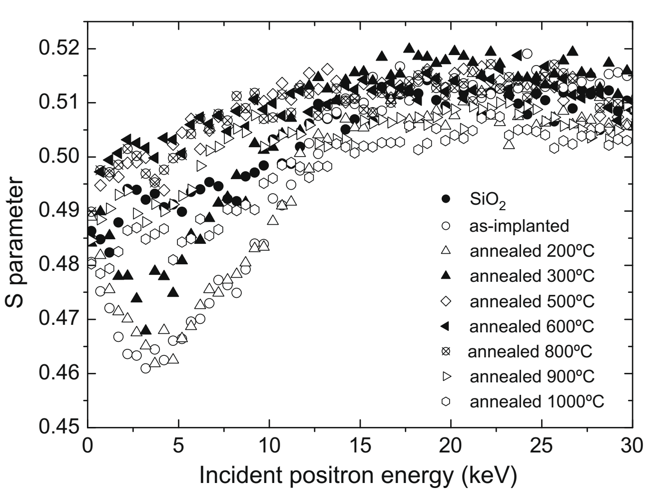


**Fig. 1.** *S* values as a function of the incident positron energies for $Ge^+$ implanted silicon oxide annealed at different temperatures. Result of the un-implanted virgin $SiO_2$ film is also plotted for comparison.

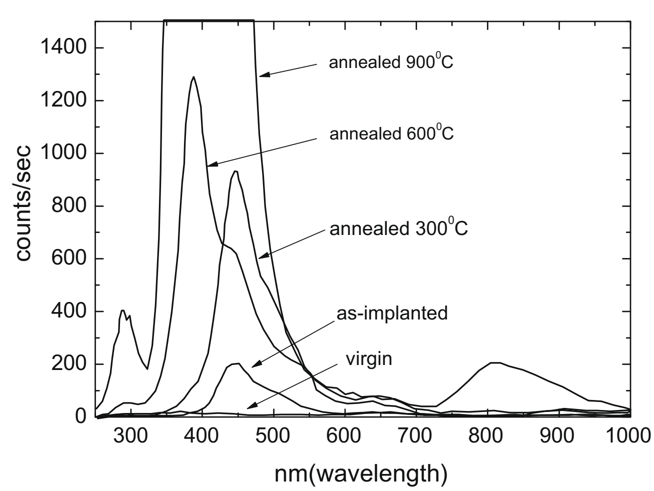


**Fig. 3.** Catholuminescence spectra of virgin as well as ion implanted silicon oxides upon annealing treatments.

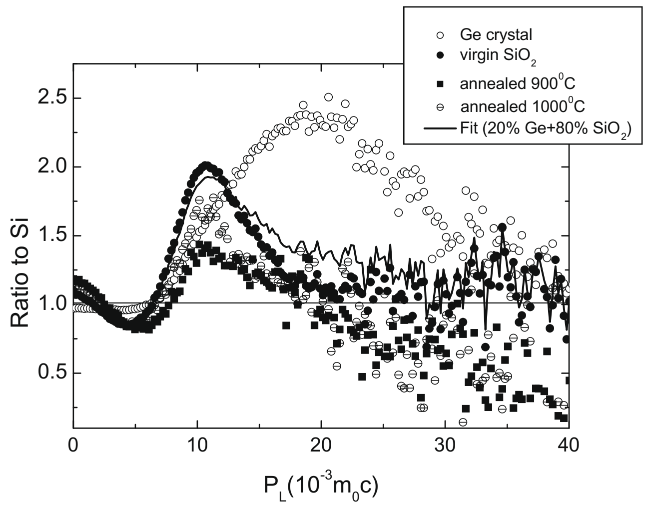


**Fig. 4.** Ratio curves of CDB spectra for annealed silicon oxide films after $Ge^+$ implantation relative to that of Si. Ge crystal and virgin silicon oxide were also plotted for comparison. The solid line is obtained by adding the contribution only from Ge crystal and thermally oxidized silicon oxide with different fractions.

but also enhances formation of Ge-related luminescent centers, which might locate at nanocrystal surfaces since surface-to-volume ratio at nanometer scale for precipitates is greatly enlarged.

So as to examine precipitation effect associated with Ge, positron annihilation coincidence Doppler broadening measurements were carried out. Fig. 4 shows the ratio curves of coincidence Doppler broadening (CDB) spectra for silicon oxide films annealed at 900 and 1000 °C (corresponding to stage IV) relative to crystalline Fz–Si. For comparison, results for Ge crystal as well as virgin silicon oxide film are also shown. The peak at about $12 \times 10^{-3}$ $m_0c$ in the ratio curve for virgin $SiO_2$ relative to Si could be attributed to positron annihilation on oxygen [6]. Further, one may find that ratio curve for the virgin silicon oxide at high momentum region is close to 1, indicative of the dominant effect of high momentum electrons belonging to Si. For Ge crystal, however, there exists a broad peak in the ratio curve at high momentum region, which should be contributed from 3d electrons of Ge. At the same time, it is seen that above $25 \times 10^{-3}$ $m_0c$, ratio curves for 900 and 1000 °C annealed silicon oxide films are parallel to that of Ge, suggesting considerable amount of positrons are trapped by Ge embedded in the silicon oxide matrix. Despite this, strong oxygen peak at about $12 \times 10^{-3}$ $m_0c$ can still be observed for the two annealed films, indicating the mixed effect of both Ge precipitates and $SiO_2$ matrix on positron annihilation. Nevertheless, simulation showed that ratio curves for annealed silicon oxide could not be reproduced by a simple overlapping of the contributions from Ge crystal and thermally oxidized $SiO_2$ (see the solid line in Fig. 4 which assumes 20% contribution from Ge crystal and 80% from the virgin $SiO_2$ film, this line is deviated away from experimental results at high momentum region). Hence, we infer that positron annihilation in annealed silicon oxide films after $Ge^+$ implantation is also affected by new trapping centers which do not exist or has a much smaller concentration in the virgin silicon oxide films, e.g. implantation induced microvoids.

## 5. Summary

It was shown that four stages can be distinguished for the $Ge^+$ implanted $SiO_2$ films as a function of annealing temperature, i.e. (I) $T < 300$ °C; (II) 300 °C $\leqslant T \leqslant$ 500 °C; (III) 600 °C $\leqslant T \leqslant$ 800 °C; (IV) $T \geqslant$ 900 °C. The increased $S$ values as a function of the annealing temperature during stage II is ascribed to the annealing out of point defects and coalescence of intrinsic open volumes in silicon oxides. Results also show that the film structure is rather stable in stage III. Further annealing above 900 °C brings about dramatic change of the film structure with Ge precipitation. CDB results suggest that in stage IV, the film is not only composed of Ge precipitates and $SiO_2$ matrix, but also implantation induced microvoids, which disturb preferential residence of positrons in Ge nano-precipitates though the positron affinity in Ge is much less than that in $SiO_2$ [7,8].

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