Depth Profiling of Defects in He Implanted SiO\textsubscript{2}

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Thin layer of SiO\textsubscript{2} thermally grown on p-type Si was implanted with He\textsuperscript{+} ions at 30 keV with a dose of $5 \times 10^{15}$ ions/cm\textsuperscript{2}. SiO\textsubscript{2}/Si samples were depth profiled by Doppler broadening positron annihilation spectroscopy to identify induced defects in the silicon oxide, at the interface and in the Si substrate. In one sample the silicon dioxide layer was removed by etching after implantation. It is shown that removing the silicon dioxide layer some more information about defects into the substrate can be found.

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1. Introduction

Silicon dioxide films are of high technological importance due to their use in the semiconductor devices based on the Si technology. Defects in SiO\textsubscript{2} and SiO\textsubscript{2}/Si interface studied by positron annihilation spectroscopy (PAS) have been reviewed by Asoka-Kumar et al. up to 1994 [1] and by Krause-Rehberg and Leipner up to 1999 [2]. From '99, works have been carried out to deepen the knowledge on SiO\textsubscript{2}/Si interface [3-8] and to study positronium (Ps) formation in SiO\textsubscript{2} thin film on crystalline Si substrate [8, 9]. The interface between Si nanocrystals embedded into thermally grown SiO\textsubscript{2} matrix has been also investigated [10, 11]. Recently, a new approach based on the interaction of many positrons with the target has been used to study the dynamics of laser-induced paramagnetic centers in a-SiO\textsubscript{2} [12].

During manufacturing processes like lithography with electrons or X-rays, ion sputtering or ion implantation, SiO\textsubscript{2} can be damaged degrading the performance of devices. Therefore, the radiation damage of SiO\textsubscript{2} is an important subject of studying. An energetic particle passing through SiO\textsubscript{2} creates in average
an electron–hole pair every 18 eV of deposited energy as a result of the breaking of Si–O bonds [1]. Defects produced by carbon [13], boron [14], silicon [15, 16], and xenon [17, 18] implantation have been studied in SiO₂. Defects evolution with thermal treatments was followed in silicon-rich silicon oxide implanted by argon [19]. Ion implantation induces several type of defects in silicon dioxide [14]. Moreover, the analysis of the positron measurements becomes more complicated due to the formation of Ps in SiO₂ [8, 20]. Positronium formation depends on the grown condition of the silicon oxide (for example, thermal or wet) and its pick-off is influenced by the radiation induced defects and by the change in the silicon dioxide morphology.

The depth resolution of PAS applied with slow positron beam worsens when the positron implantation energy increases due to the broadening of positron implantation profile. However, this effect is taken into account in the data analysis and the characteristic annihilation parameters identifying the defects can be extracted. A possible way proposed to overcome the worsening of resolution is that to improve the positron depth profiling by selective chemical etching of the sample surface [15, 21].

In this work we studied the damage produced in silicon dioxide films by helium implantation and then we removed, by etching, the silicon dioxide with the aim to improve the positron sensitivity to the vacancy-like defects produced in the silicon substrate.

The S and the W parameters vs. positron implantation energy curves of the as grown SiO₂ sample and of the damaged samples will be discussed at the light of the present knowledge on PAS measurements on the silicon dioxide system. There will be also shown the improved resolution after etching in detecting defects in Si substrate.

2. Experimental

A thin layer of SiO₂ (thickness of 81.6 nm) was thermally grown on high purity p-type (100) silicon wafers (1.7–2.5 Ω cm), Czochralski-grown. Samples were implanted keeping the sample holder at 77 K with He⁺ ions at 30 keV with a dose of 5 × 10¹⁵ ions/cm². At this energy, the He depth distribution is peaked around 270 nm [22]. The density of the beam current was about 8 µA cm⁻² and the sample holder was tilted by 7° to reduce channeling effects. In one of the samples the silicon dioxide layer was removed by etching after the implantation.

Doppler broadening PAS (DB-PAS) measurements were carried out with an electrostatic slow positron beam tunable in the 0.05–25 keV energy range [23], which corresponds to a depth scale of 1 to about 3000 nm. The mean positron implantation depth \( \tau \) is related to the positron implantation energy \( E \) through the equation \( \tau = (40/\rho)E^{1.6} \) with \( \tau \) in nanometers when density \( \rho \) and energy \( E \) are expressed in grams per cubic centimeter and keV, respectively [1]. The SiO₂ density was kept 2.2 g/cm³. For the measurements, a high-purity Ge detector
Depth Profiling of Defects in He Implanted SiO$_2$

(resolution of 1.2 keV at 511 keV with 6 µs shaping time) was used. The spectra were characterized by the shape parameter $S$, defined as the ratio of the counts in a central area ($|511 - E_\gamma| \leq 0.85$ keV) of the annihilation line and the total area ($|511 - E_\gamma| \leq 4.25$ keV) and the wing parameter $W$ defined as the fraction of the counts in the wing region ($1.6 \leq |E_\gamma - 511| \leq 4$ keV) of the peak. $S$ parameter represents the fractions of positrons annihilating with low momentum electrons, while the $W$ parameter represents the fraction of positrons annihilating with high momentum electrons (outermost core electrons); more than $2.5 \times 10^5$ counts in each annihilation spectrum were recorded. The $S$ and $W$ values have been normalized to the Si bulk value $S_b$ ($S_n = S/S_b$) and $W_b$ ($W_n = W/W_b$).

3. Results and discussion

The $S_n - E$ and the $W_n - E$ curves for the SiO$_2$/Si, He$^+$ implanted SiO$_2$/Si, and SiO$_2$ removed layer after implantation are reported in Figs. 1, 2, and 3, respectively. The curves were fitted by VEPFIT program [24]. The effective diffusion length in the Si substrate was found to be 98 nm in all samples. Also the different layers were identified in the studied samples. The characteristic values of the $S_n, W_n$ parameters, the positron diffusion length $L_+$ (in nm) and the thickness of the layers (in nm) are reported in Table.

![Fig. 1](image)

Fig. 1. Normalized $S_n$ and $W_n$ parameter vs. positron implantation energy for the SiO$_2$ (81.6 nm) on Si. The vertical dashed lines mark the interface region.

The as grown SiO$_2$/Si sample (Fig. 1) is well fitted with three layers: SiO$_2$, SiO$_2$/Si interface (3 nm thickness) and the Si substrate. In SiO$_2$ positrons are known from lifetime measurements to form Ps [8, 9, 20], the 3/4 of positronium forms o-Ps (ortho-Ps) and annihilate via pick-off with an electron of the environment into two gamma rays and a lifetime in the 1–2 ns range. The fraction of p-Ps (para-Ps) self annihilate directly into two gammas. Both Ps and the remaining fraction of free positrons are trapped into empty space of SiO$_2$. In those sites positrons have a lifetime of about half nanosecond [8, 9]. Positrons and o-Ps in
Fig. 2. Normalized $S_n$ and $W_n$ parameter vs. positron implantation energy for the SiO$_2$ (81.6 nm) on Si after implantation with He$^+$ at 30 keV. The dashed vertical lines mark the three different defected region as found by fitting the data with VEPFIT program.

Fig. 3. Normalized $S_n$ and $W_n$ parameter vs. positron implantation energy for the sample with the SiO$_2$ layer removed by etching after implantation with He$^+$ at 30 keV. The dashed vertical line marks the damage region in the Si substrate.

the empty space see mainly oxygen electrons and annihilate with them giving the same contribution to the broadening of the 511 keV annihilation line. The $S_{SiO_2}$ value in the SiO$_2$ films is mainly determined by $p$-Ps annihilation: the more Ps formation the higher the $S_{SiO_2}$ parameter value. $W_{SiO_2}$ parameter value reflects the annihilation of positrons and $\alpha$-Ps pick-off with oxygen electrons that broaden the 511 keV peak. Presence of defects in the SiO$_2$ structure, as will be discussed after, quenches the Ps formation. The quite high values of the present $S_{SiO_2}$–$W_{SiO_2}$ (see Table) are an indication of a silicon dioxide film of good quality [1].

At the thin interface the $S$ parameter value strongly decreases while the $W$ parameter remains unchanged. This behavior is recognized to be due to the quenching of Ps formation [1, 3, 5–9]: the lack of $p$-Ps decreases the $S$ value and
Values of the $S_n$ and the $W_n$ parameters, the positron diffusion length [nm] and the thickness of the layers [nm], as extracted by VEPFIT code. The estimated errors are $1 \times 10^{-3}$ on $S$ parameter, $1.5 \times 10^{-3}$ on $W$ parameter, 10% on the thickness of the layers and about 5% on the values of $L_+$ higher than 1. Values of $L_+$ equal to or lower than 1 are only indicative of a positron strong trapping.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Layer 1</th>
<th>Layer 2</th>
<th>Layer 3</th>
<th>Layer 4</th>
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<tr>
<td></td>
<td>$S_n$,</td>
<td>$L_+$,</td>
<td>$S_n$,</td>
<td>$L_+$,</td>
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<tr>
<td></td>
<td>$W_n$,</td>
<td>thickness</td>
<td>$W_n$,</td>
<td>thickness</td>
</tr>
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<td>0.943</td>
<td>1</td>
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<td></td>
<td>1.262</td>
<td>79</td>
<td>1.259</td>
<td>3</td>
</tr>
<tr>
<td>SiO$_2$/Si</td>
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<td>&lt; 1</td>
<td>0.878</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>implanted He</td>
<td>1.431</td>
<td>37</td>
<td>1.51</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.04</td>
</tr>
<tr>
<td>implanted</td>
<td>1.009</td>
<td>&lt; 1</td>
<td>1</td>
<td>98</td>
</tr>
<tr>
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<td>173</td>
<td>1</td>
<td>–</td>
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<tr>
<td>removed</td>
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</table>

positron annihilation occurs mainly with oxygen electrons. However, there is some open discussion about the origin of this quenching. Lifetime measurements [8] have pointed out that positron lifetime has two components at the interface: $215 \pm 10$ ps (62%) and $478 \pm 20$ ps (38%) suggesting the presence of large vacancy clusters or nanovoids. Brauer et al. [5–7] give evidences of densification of SiO$_2$ at the interface with the formation of a quasiepitaxial oxide growth with a structure resembling that of Brazilian quartz (low quartz structure). They show also [6, 7] a strong similarity between coincidence DB-PAS spectra of Brazilian quartz and of native silicon dioxide on Si. Most probably the interface has both a different structure and the presence of nanovoids.

Here we want to draw the attention to: (a) the $S$ interface value (0.943) is very near to the SiO$_2$ surface $S$ value (0.94), see Table and Fig. 1, and (b) the $S$ parameter of native oxide grown on Si is about 0.94 and its coincidence DB-PAS spectra resemble that of quartz [22, 25]. Besides observations (a) and (b) there is the fact that at the SiO$_2$/Si interface and at the SiO$_2$ surface the contribution from annihilation with O electrons (broadening of the 511 keV annihilation line) is higher. Thus it seems necessary to investigate in more details both the SiO$_2$/Si and SiO$_2$/vacuum termination.

The low effective diffusion length in Si substrate (98 nm) with respect to the accepted value around 200 nm is an indication of positive charge accumulation in the native oxide layer at the surface of the Si sample. Usually this charge is
attributed to fixed oxide charge [5]. This diffusion length is found to be the same even after He implantation.

The He implantation at 30 keV in the present samples (Fig. 2) produces defects in the silicon oxide layer as well as in the Si substrate. In SiO$_2$ two different defected regions are detected: a first one about 37 nm thick with $S = 0.903$ and $W = 1.431$ and a second one extending up to 90 nm with $S = 0.878$ and $W = 1.51$. The observed strong decrease in $S$ parameter (and the corresponding strong increase in $W$ parameter) is related to positron trapping in several charged oxygen-related defects ($O_2^-$, nonbridging-oxygen hole centers $\equiv$Si–O$^-$, peroxy radicals $\equiv$Si–O–O$^-$) [14]. The second layer toward the centers of the He distribution appears more defected than the first one but the reason is not yet clear. In the silicon substrate we found a layer of defects ($S$ value slightly higher than 1) extending up to 243 nm. These defects must be mostly divacancies stabilized by He or/and platelets partially filled by He [22]. In the region where He density is higher (around the peak of the He distribution, 270 nm) the vacancy-like and the extended defects (platelets) are expected to be decorated by the presence of He [22, 26]. The positron probes He decorated defects with an effective open volume smaller than a single monovacancy in Si. The $S$ value for a pure monovacancy in Si is about 1.02 [27].

To improve the depth profiling resolution we have removed the SiO$_2$ layer by etching. The $S_n$–$E$ and the $W_n$–$E$ measured curves are shown in Fig. 3. We found a defected layer of 173 nm meaning that the positron traps extended up to 263 nm instead of 243 as found without oxide removing. Due to the error bar ($\pm 10\%$) the two values are comparable. Instead, the characteristic $S$ value for these defects is found to be 1.009 $\pm$ 0.001. The VEPFIT analysis of the sample with oxide layer gave a reduced value of 1.006 $\pm$ 0.001. This difference, although very small, can be attributed to the reduced resolution increasing the positron implantation depth [15, 21].

4. Conclusion

We have investigated the radiation damage produced in SiO$_2$ film on Si. A strong reduction of the $S$ and a strong increase in $W$ parameters were observed in the silicon dioxide layer. This behavior was understood as an efficient production of oxygen related defects. The selective chemical etching used to remove the silicon dioxide layer allowed to achieve some details about the deep extension of He decorated defects in the Si substrate.

References