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A positron beam study of defects in SiO₂

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Abstract

Defects in crystalline and amorphous SiO₂ were studied by variable-energy positron annihilation spectroscopy in an attempt to clarify what defects in SiO₂ are observable in positron annihilation studies. The level of the S parameter in amorphous SiO₂ films grown by plasma chemical vapor deposition (CVD) in a tetraethylorthosilicate (TEOS) and O₂ atmosphere was found to be correlated to the concentration of Si-OH in the silicon dioxide layer. The difference in S parameter between crystalline and amorphous SiO₂ is assumed to be due to the effects of para-Ps self-annihilation in free volumes in the amorphous sample. The S parameters in crystalline and thermally grown silicon dioxide were both found to decrease after C ion implantation ($1 \times 10^{14} \text{ cm}^{-2}$, 140 keV) or alternatively, ArF excimer laser (6.4eV) irradiation. Both methods are expected to produce numerous types of Frenkel defects of which, it is most likely that negatively charged species such as $\equiv\text{Si-O}^-$ are the trapping sites. In the case of ion implantation into amorphous SiO₂ a greatly lowered S parameter is observed, this is explained as a combination of defect trapping and reduction in para Ps production after ion implantation.

Introduction

The analysis of near-surface defects by use of variable-energy positron beams has, in the last decade, become practical(1). As research efforts are afforded to understanding the behavior of the positron when it interacts with various defects, this technique is able increasingly to provide unique information about the defects themselves and the processes by which defects are created or recovered. In particular, the behavior of defects (vacancies) in ion implanted silicon is gradually becoming understood(2-4). However, in order to interpret precisely the positron data from *real* silicon-based semiconductors, it is very important to understand the behavior of positrons in SiO₂ and at the SiO₂/Si interface because such device quality wafers usually incorporate an oxide film of some thickness which can strongly influence the positron data(5,6). For example, annihilation in the thin native oxide layer of a Si wafer gives rise to a lower S parameter than for annihilation in bulk amorphous SiO₂. We always observe the S parameter for annihilation at the SiO₂/Si interface to be slightly lower than that of bulk Si or SiO₂(7). Further, it has been found that ion implantation into amorphous SiO₂ results in a very low S parameter(8,9). The origins of these phenomena are still unresolved.

We have studied crystalline and vitreous bulk SiO₂, and thermally oxidized and plasma CVD grown SiO₂ films on Si. The former three samples have been irradiated with an ArF excimer laser (6.4eV) or C ion implanted ($1 \times 10^{14} \text{ cm}^{-2}$, 140 keV) in order to induce positron trapping centers in the samples. The many types of defects generally present in irradiated/implanted SiO₂ samples are summarized in Table 1. The aim of this article is to recognize which of these defects in SiO₂ are observable in positron annihilation studies.

Table 1 Defects in silicon dioxide. The • mark indicates an unpaired electron (radical) and the ≡ mark indicates silicon bonding with 3 oxygen atoms.

name of defect	schematic	charge transfer state
E' center	≡Si•	≡Si ⁺
nonbridging-oxygen hole center (NBOHC)	≡Si-O•	≡Si-O ⁻
peroxy radical (PR)	≡Si-O-O•	≡Si-O-O ⁻
oxygen vacancy	≡Si-Si≡	
peroxy linkage (PL)	≡Si-O-O-Si≡	
dissolved oxygen	O ₂	O ₂ ⁻
impurity	≡Si-OH	
impurity	≡Si-H	

Experimental

The crystalline and vitreous SiO₂ bulk samples were of commercially available type. The wet oxidation SiO₂ film (abbreviated in the following as wet SiO₂/Si) had 500nm thickness and was grown on a Czochralski (Cz) Si(100) wafer (10 Ωcm, p-type) in O₂ and H₂ at 1100°C for 55 minutes. The plasma CVD oxide films (abbreviated in the following as plasma CVD SiO₂/Si) were deposited on a Cz-Si(100) wafer (1-3Ωcm, p-type) using tetraethylorthosilicate (10) (TEOS, Si(OC₂H₅)₄). During plasma CVD growth, oxygen and TEOS gases flowed into the deposition chamber at a rate of 10 sccm and 1 sccm, respectively. During deposition, RF power of 20W was applied and the pressure was 0.2 Torr. Six samples with Si substrate temperatures ranging from 100°C to 600°C were grown by the plasma CVD technique. The thickness of these SiO₂ films was measured to be 300nm for the films deposited at 100°C and 600°C, and 500nm for the others. For each of these SiO₂ films, an etching rate determination was made using a solution of 0.25 vol% HF. The films mentioned above are, of course, amorphous.

Crystalline and wet SiO₂ samples were either irradiated by an ArF excimer laser (6.4eV) or implanted with C ions. For the laser irradiation, an area of 150 mm² was exposed to the unfocused beam from an excimer laser (Lambda Physik 210i"F") at 50Hz for 15 minutes, the exposed area is much larger than that of the positron beam used for analysis. The average power density was estimated to be 30 mJ/cm² per pulse. For C ion implantation, the energy and dose were 140 keV and 1×10¹⁴ cm⁻², respectively. The mean projected range and standard deviation of the C ions in the samples were 297 nm and 58 nm, respectively.

The Nippon Steel Corporation variable-energy positron beam was used to measure the S parameter data with respect to incident positron energies in the range 0 to 30 keV at room temperature(11). The experimental pressure was maintained at 10⁻⁹ Torr. Infrared absorption spectra were measured for plasma CVD SiO₂ using a JIR-100 FT-IR spectrometer (JEOL) at room temperature. Quantitative analysis of the Si-OH and H-OH content in these SiO₂ films was made by Pliskin's method using the absorption lines: Si-OH (3650cm⁻¹) and H-OH (3330cm⁻¹)(12). We define and use H-OH here as meaning hydrogen bonded OH.

Results and discussion

Fig. 1 shows the S parameters vs. positron energy curves (hereafter referred to as S-E curves) for the crystalline and vitreous SiO₂ bulk samples, and the wet SiO₂/Si sample. The S parameter of the vitreous and the thermally oxidized SiO₂ was almost identical to that of bulk Si. The fortuitous identical S parameters for Si and amorphous SiO₂ makes it very easy to see a lowering of the S parameter at around 8 keV due to the SiO₂/Si interface. Further, the S-E curves of crystalline SiO₂ have a gentle change in the low positron energy region, indicating that the diffusion length of the positron in crystalline SiO₂ is much longer than that in amorphous SiO₂.

Fig. 1 The S parameter-positron energy curves for crystalline(●) and vitreous(◇) SiO₂, and the wet thermally grown SiO₂ film(+) of 500nm thickness on Si(100).

The S parameter for bulk crystalline SiO₂ is greatly different to that of amorphous SiO₂. Due to the greater free volume in amorphous SiO₂, the formation probability of positronium (Ps), is much higher than that in the crystal and usually goes up to several tens of % (13,14). Such Ps formation results in an increase in the S parameter due to its subsequent self-annihilation with consequently low Doppler broadening. The density of amorphous SiO₂ is lower than that of the crystal and this is also indicative of the greater free volume in the amorphous material. It can be concluded that a difference in Ps formation is primarily responsible for the difference in S parameters between amorphous and crystalline SiO₂.

Fig. 2 shows the S-E curves of the plasma CVD SiO₂ films. It was found that the S parameter level in the SiO₂ was strongly dependent on the deposition substrate temperature. The curvature in the data in the near surface region is either due to positron diffusion in the oxide layer (unlikely as it is amorphous), or that there is a gradient concentration of out-diffusing impurities in the near surface region. Whatever the reason, it does not affect the conclusion that the level of the S parameter at an energy where the positrons all annihilate in the oxide layer (≈ 3 keV) varies in correspondence with the substrate temperature. At 600°C the curve is almost identical to that of the thermally grown SiO₂ specimens.

The etching rates (which are an index to the density of the SiO₂ films) for the plasma CVD SiO₂ samples are shown in Table 2. As the substrate temperature increased, the etching rate decreased thus indicating that the SiO₂ deposited at higher temperature was denser, or has smaller free volume. Therefore, the difference in S parameters for the plasma CVD SiO₂ films was not caused by a differing para-Ps self annihilation rate as this would cause an opposite trend to that observed. We thus have to consider other types of defects which may suppress Ps formation or otherwise affect the Ps annihilation, pick-off or spin conversion processes.

Fig. 2 The S parameter-positron energy curves for the plasma CVD SiO₂ films deposited on Si(100) in a tetraethylorthosilicate and oxygen atmosphere at the indicated substrate temperatures.

Table 2 lists the concentrations of Si-OH and H-OH derived from our IR data. It should be noted that the Si-H absorption band (around 2100 cm⁻¹) was absent and that a very sharp absorption peak at 1070 cm⁻¹ due to Si-O-Si appeared in all of the IR spectra. It was found that there was a rather high concentration of Si-OH and H-OH involved in the plasma CVD SiO₂ films, whereas this means of analysis indicated that none of the thermally oxidized SiO₂ films contained detectable Si-OH or H-OH. The crystalline SiO₂ sample is stated to have an OH concentration of less than 2ppm. The content of H₂O monotonically decreased as the substrate temperature increased, whereas that of Si-OH was almost constant in the range 100°C to 400°C and greatly decreased at 500°C and 600°C. Thus, the level of the S parameter in the oxide film, shows a correlation to the Si-OH concentration at those temperatures. It is, therefore, proposed that the S parameter in amorphous SiO₂ is strongly influenced by the Si-OH concentration present and that positrons or Ps tend to be trapped in the region of the Si-OH species. The porosity of the SiO₂ films increased as the Si-OH concentration increased thus indicating that the surroundings of the Si-OH species has more open space than that of normally bonded ≡Si-O-Si≡. As the presence of Si-OH (silanol) resulted in a lowering of the S parameter, we propose that the silanols are related to a Ps reaction, which suppresses the formation of para-Ps or its self annihilation.

Table 2. Influence of substrate temperatures for the plasma CVD SiO₂ films on etch rate, and the H-OH and Si-OH concentrations deduced from IR measurement. The data of wet SiO₂ films are shown for comparison.

Substrate temperature (°C)	Etch rate (nm/min.)	H-OH concentration (wt%)	Si-OH concentration (wt%)
100	25	4.1	2.2
200	21	3.4	3.4
300	16	2.4	4.5
400	13	1.5	4.0
500	9.6	not detectable	2.0
600	5.3	not detectable	0.3
wet SiO ₂	1.5	not detectable	not detectable

Figure 3 shows the data for the crystalline and wet SiO_2/Si samples before and after irradiation with the ArF excimer laser (6.4eV). Laser radiation is known to cause the formation of some of the Frenkel-type defects, shown in Table 1(15,16). The primary defects created are the E' center, NBOHC and their charge transfer states. As the laser is unable to structurally alter SiO_2 , these samples are unaffected by free volume change, so that we can assume that Ps formation probability is unchanged by the laser irradiation. The high transmittance of the laser radiation in the SiO_2 can be seen in the effect it has on the crystalline sample. The irradiation causes uniform defect formation to a depth far below the maximum depth probed by the positrons, hence the S-E curves are parallel up to 30keV and the S parameters decreased slightly and uniformly. Radicals species such as the E' center and NBOHC are likely to promote pick-off annihilation which would result in an increase of S parameter. Therefore, we conclude that it is the charge transfer species that react with positrons or Ps, and thus lead to a lowering of S parameter.

For the wet SiO_2/Si sample the effect of the laser is again to uniformly lower the S-E curve in the energy region corresponding to positron annihilation in the SiO_2 layer (0-8 keV). Further, the laser irradiation lowers the S-E curve in the Si substrate region more strongly. The origin of the lower S parameter in the SiO_2 region is the same as that for the crystalline sample. On the other hand, the low S parameters in the Si region cannot be explained by the same reasoning. It was found that the level of lowering was largest at the SiO_2/Si interface. We can explain this behavior if a charge transfer species accumulates at the SiO_2/Si interface and thus leads to an electric field which strongly influences the positron diffusion behavior.

Fig. 3 The S parameter-positron energy curves for crystalline SiO_2 (●:as-received, ○:after laser irradiation) and the 500nm wet thermally grown SiO_2 on Si films (+:as-grown, △:after laser irradiation). Laser radiation 6.4eV.

Figure 4 shows the effect of carbon ion implantation on the S-E curves for the crystalline and wet SiO_2/Si samples. For both samples, the effect of ion implantation is to lower the S parameter in the region in which C ions are implanted. The positron trapping is saturated for the amorphous sample shown here as higher dose implantation was not found to further change the S-E curve. It is important to note that the S parameter is lowered by ion implantation in crystalline SiO_2 whereas it is raised by similar ion implantation into crystalline Si. The formation of vacancy type defects in Si is accepted to be responsible for a raised S parameter but in SiO_2 the positron trapping is dominated by the types of defects listed above for the laser irradiated case. Ion implantation into the crystalline sample may cause some free volume increase by vacancy formation, yet the S parameter is lowered, hence it may be that there are two competing effects here. The two competing effects are positron trapping at Frenkel type defects, which gives rise to a low S parameter, and, positron trapping at open volume defects, which give rise to a high S parameter. It is concluded that the former is predominant in this

system. For implantation doses high enough to amorphize the crystalline sample it is expected that the S parameter would increase.

For the case of the wet SiO₂/Si sample the S parameter after implantation is seen to drop to an extremely low level and the positron or positronium is strongly trapped. This drop is attributable to the Frenkel defects and their charge transfer states listed above. In particular our previous study utilizing electron spin resonance (ESR) and annealing behavior analysis revealed that the positron is most likely to be trapped at the negatively charged states such as NBOHC⁻ or O₂⁻(8). The drop seen in S parameter is larger than that observed for the crystalline case, this may be because of competing S parameter effects in the crystalline case or, it may be due to a decrease in free volume caused by ion implantation. The latter assertion is not based on experimental results or observations.

Fig. 4 The S parameter-positron energy curves for crystalline SiO₂ (•:as-received, o:after ion implantation) and the wet thermally grown SiO₂ films of 500nm thickness on Si(100) (+:as-grown, Δ:after ion implantation). C ion implantation (140keV, $1 \times 10^{14} \text{ cm}^{-2}$).

Conclusion

The origins of change in the S parameter in SiO₂ were discussed. The S parameter difference between amorphous and crystalline SiO₂ is almost certainly caused by differences in Ps formation probability due to differing internal free volumes. It is, further, postulated that the Si-OH content in plasma CVD SiO₂/Si is responsible for the different S parameter levels observed in those samples. We conclude that the silanol species are participating in a reaction that causes the suppression of para Ps formation or its self-annihilation. Laser irradiation is seen to produce defects of a similar type to those caused by C ion implantation but causes none of the structural modification that clouds the interpretation of the ion implanted data. The structural changes in the ion implanted samples give rise to two effects: the lowering of S parameter for annihilation in the Frenkel defects, and the increasing (lowering) of S parameter as internal free volume increases (decreases). These effects may combine to produce the very low value of S parameter seen in the ion implanted amorphous sample but compete in the ion implanted crystalline case.

There are thus many factors which affect the positron data for SiO₂ and until these factors are fully understood we cannot analyze unambiguously positron data for true industrial semiconductor samples. Further systematic research, particularly in the field of positron lifetime studies and reliable preparation of SiO₂ samples is necessary in order to be able to classify the defects present and understand which are observable in positron annihilation spectroscopy.

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