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Oxygen-related vacancy-type defects in ion-implanted silicon

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Abstract

Czochralski silicon samples implanted to a dose of 5×10^{15} cm^{-2} with 0.5 MeV O and to a dose of 10^{16} cm^{-2} with 1 MeV Si, respectively, have been studied by positron annihilation spectroscopy. The evolution of divacancies to vacancy (V)–O complexes is out-competed by V–interstitial (I) recombination at 400 and 500 °C in the Si- and O-implanted samples; the higher oxygen concentration makes the latter temperature higher. The defective region shrinks as the annealing temperature increases as interstitials are injected from the end of the implantation range (R_p). V_mO_n ($m > n$) are formed in the shallow region most effectively at 700 °C for both Si and O implantation. V_xO_y ($x < y$) are produced near R_p by the annealing. At 800 °C, implanted Si ions diffuse and reduce m and implanted O ions diffuse and increase n in V_mO_n. All oxygen-related vacancy-type defects appear to begin to dissociate at 950 °C, with the probable formation of oxygen clusters. At 1100 °C, oxygen precipitates appear to form just before R_p in O-implanted silicon.

1. Introduction

Ion implantation has been one of the most important tools in the Czochralski (Cz) Si-based microelectronics industry. An inevitable outcome of ion implantation is the damage—mainly vacancy (V)- and interstitial (I)-type defects—induced by the incident energetic ions. It is well known that oxygen is one of the most important impurities in Cz Si, with a concentration of usually around 10^{18} cm^{-3}. Oxygen is also often used as the implanted ion to produce Si-on-insulator devices, which are very suitable for radiation-hardness, low-power and low-voltage application [1, 2]. Previous studies have demonstrated that oxygen readily reacts with vacancies to form complexes in ion-implanted Si. These complexes can be effectively investigated by positron annihilation spectroscopy (PAS), which is a useful technique to detect V-type defects [3]. Fujinami [4] used PAS to study O-related defects in Si implanted with

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180 keV O to a dose of 2×10^{15} cm^{-2} by annealing it from 300 to 800 °C. He found that O–V complexes evolved to multioxygen–multivacancy complexes and then finally to oxygen clusters around the ion-projected range (R_p). In addition, he showed that O-related multivacancy-based defects were also formed in the proximity of the surface, but their behaviour was not described as completely as those near R_p. In high-energy ion implantation this V-excess region exists at depths further away from the surface and is therefore relatively unaffected by the surface or by the interstitials from the end of range (EOR). Hence, following high-energy ion implantation, O-related V-type defects in this shallow region can be studied more clearly.

In the present work, 0.5 MeV O-implanted Cz Si has been studied. Also investigated was 1 MeV Si-implanted Cz Si, in order to find the dependence of O-related V-type defects on oxygen concentration and distribution. It was found that V-dominated defects V_mO_n $(m > n)$ formed in the shallow region and O-dominated defects V_xO_y $(x < y)$ formed near R_p in both Si- and O-implanted Cz Si. The formation and evolution of these O-related V-type defects as a function of temperature are discussed in this paper.

2. Experimental details

P-doped 2–4 Ω cm ⟨100⟩ Cz Si samples, implanted with 0.5 MeV O to a dose of 5×10^{15} cm^{-2} and with 1 MeV Si to a dose of 10^{16} cm^{-2}, were used. The implantation was performed at room temperature with a tilt of 7°. The samples were then annealed at different temperatures with electron-beam bombardment in vacuum. The annealing time is about 10 s at every temperature.

Beam-based PAS was employed to measure all the as-implanted and annealed samples at room temperature. The variable measured by PAS is the Doppler-broadened line-shape parameter S [3]. The value of S is larger when positrons annihilate at vacancies than in defect-free Si. However, when vacancies are decorated by oxygen, the value of S can be reduced to below that measured in defect-free Si [5]. The VEPFIT program [6] was used to analyse the measured S versus incident positron energy E. In this work, VEPFIT adopted a layer structure in which there was a general S parameter for each layer in a sample. A good and reasonable fit of the experimental data gave the boundaries and general S for each layer.

Another program, FAST (Fractions in Annihilation STates) was also used in this work. FAST employs a technique also used by van Veen *et al* [6] in which three annihilation gamma spectra (i.e. the 511 keV photo-peaks measured by a Ge detector), associated with positron annihilation at the Si/SiO_2 surface, in divacancies (V_2) and in the Si bulk, are combined in appropriate proportions to fit the measured spectra from the samples. The proportion of each spectrum used for the fit then gives directly the fractions of positrons annihilated at the surface, in V_2-type defects or in bulk Si. The standard spectrum for the surface was obtained by calibrating the spectrum from the annihilation of 2 keV implanted positrons in a virgin silicon sample with natural oxide on the surface (the effect of epithermal positrons is negligible). The other two were recorded by implanting 30 keV positrons into the virgin sample and 14 keV positrons into a silicon sample implanted with 1.5 MeV to a dose of 10^{15} cm^{-2}, for which there was saturation trapping of positrons in V_2 defects [7], respectively.

3. Results and discussion

The positron measurements for Si- and O-implanted Cz Si samples are shown in figures 1 and 2, respectively. The S parameters presented here have been normalized with respect to that for the bulk (defect-free layer) of these samples, for which S is thus 1. It can be seen that in the as-implanted samples the values of S are exclusively larger than 1 except for those near

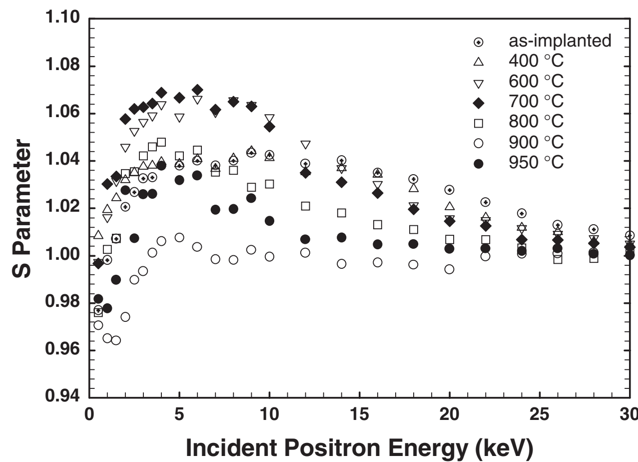

Figure 1. *S* parameter versus incident positron energy measured in Si-implanted Cz Si (1 MeV, 10^{16} cm^{-2}) after implantation and annealing at different temperatures.

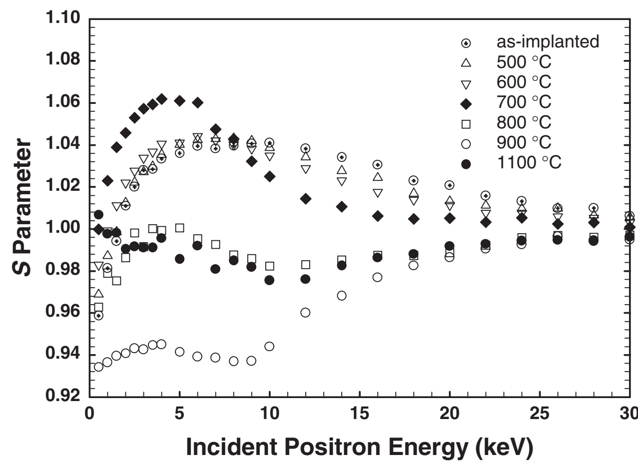

Figure 2. *S* parameter versus incident positron energy measured in O-implanted Cz Si (0.5 MeV, 5×10^{15} cm^{-2}) after implantation and annealing at different temperatures.

the surface (low E), which are lowered by the presence of oxide at the surface. This means that there are V-type defects in the as-implanted samples, and that their distribution extends to depths such that the values of S at $E = 30$ keV (corresponding to a mean probed depth $\overline{z} \sim 4$ μm, according to the expression $\overline{z}$ (nm) $= 17E$ (keV)$^{1.6}$) are still larger than 1. Such a deep distribution of defects is a natural result of high-energy ion implantation and has been observed in previous work [4, 8, 9].

Figures 3 and 4 show the fitted S values characteristic of each layer in Si- and O-implanted samples, respectively. The distributions of ions in the as-implanted samples predicted by the simulation code TRIM [10] are also included. In both as-implanted samples the S values for the defective layers are ~1.041, characteristic of V_2 with our slow positron beam [7]. Therefore it is considered that V_2 are the dominant V-type defects in O and Si as-implanted samples and that the saturation of positron trapping in V_2 is reached due to the high implantation doses.

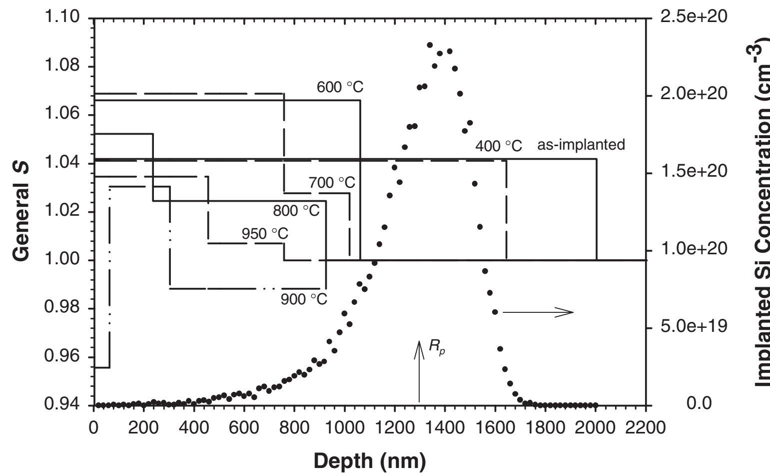

Figure 3. The change of general S with depth in Si-implanted Cz Si (1 MeV, 10^{16} cm^{-2}) for the as-implanted sample and after annealing to different temperatures, obtained from the fitting program VEPFIT. The implanted Si ion distribution, as calculated by the code TRIM, is also shown.

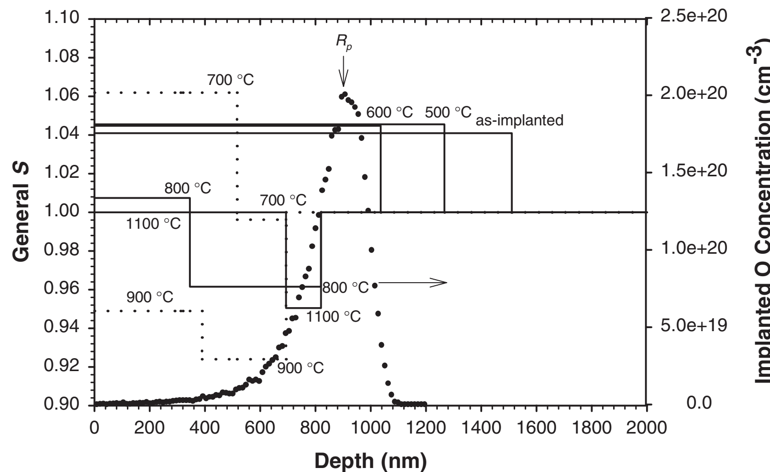

Figure 4. The change of general S with depth in O-implanted Cz Si (0.5 MeV, 5×10^{15} cm^{-2}) for the as-implanted sample and after annealing to different temperatures, obtained from the fitting program VEPFIT. The implanted O ion distribution, as calculated by the code TRIM, is also shown.

In the Si-implanted sample, $S(E)$ (figure 1) does not change until the temperature reaches 400 °C. The first change is seen only in the region beyond R_p (1300 nm). It is well known that, in Cz Si, V_2 are annealed out at ∼250 °C to form divacancy–oxygen (V_2O) complexes. At ∼400 °C these form V_3O or V_2O_2, which at 440 °C form V_3O_2 and which finally at 475 °C change to more advanced complexes [11]. It is believed that, in our Si-implanted sample, V_2 mainly evolve to V_3O in the region $<\sim$1600 nm at 400 °C. The positron lifetime in V_3O (325 ps) is close to that in V_2 (320 ps) [11], and it is supposed that their corresponding characteristic S values may also be very similar. Therefore, the S curve is not changed by this evolution in the region $<\sim$1600 nm. It is clear in the raw data of figure 1 that S decreases in the tail of the S curve at 400 °C; this is confirmed in figure 3, which shows that the value of S drops

to unity between 1600 and 2000 nm. It is known that the region beyond R_p is interstitial-rich. The annealing of vacancies depends strongly on the injection of interstitials from EOR [12]. Therefore we propose that, between 1600 and 2000 nm, I–V_2 combination, rather than the evolution of V_2 into V_3O, is dominant at 400 °C. The consequent disappearance of vacancies results in the decrease in S.

The situation is different in the O-implanted sample; the much higher oxygen concentration (predicted by TRIM to reach around 2×10^{20} cm^{-3}—see figure 4) means that, beyond R_p, evolution of V_2 to more complex defects outweighs the recombination with interstitials. Oxygen is ready to react with vacancies to form oxygen–vacancy complexes, to which more vacancies or oxygen tend to adhere. It is seen in figures 2 and 4 that I–V_2 recombination is not dominant in the region beyond 1250 nm until the temperature reaches 500 °C, which is consistent with Fujinami's work [4]. At shallower depths, V_2 can evolve to complexes more advanced than V_3O_2 (figure 4), apparently with a characteristic S slightly larger than that for V_2. After annealing at 600 °C, the tail of the S curve (figure 2) continues to decrease and the boundary between the bulk and the defective layer shrinks to just over 1000 nm (figure 4). However, the value of S for the defective layer remains nearly the same as that at 500 °C, suggesting that V_2 evolve to similar advanced oxygen–vacancy complexes at 600 °C as at 500 °C.

More insights into the formation of V_xO_y $(x < y)$ in the O-implanted sample can be gained from the results of FAST fitting (figure 5). Here, the fraction of positrons, f_s, annihilated in a surface-like state is plotted against incident positron energy. Although the V-type defects are not V_2 exclusively, as assumed by FAST, the trend of the change in f_s is reliable. It is interesting that, for annealing temperatures between 500 and 700 °C, f_s is not zero at $E \sim 14$ keV (mean probed depth ~1000 nm). This does not indicate annihilation at the real surface, rather that there are surface-like sites at a depth of ~1000 nm (~R_p) where the oxygen concentration is so large that oxygen atoms react with V_2 to form O-dominated clusters which are more advanced than the O–V complexes produced in the shallower region. These defects behave as positron traps in a way similar to the O-related surface state. However, the effect on S of this cluster formation is too small to be seen in the VEPFIT results (figure 4) for the O-implanted sample annealed at 500 and 600 °C.

When the Si-implanted sample is annealed to 800 °C, the defective layer continues to shrink (figure 3). With the increase in temperature, besides the diffusion of interstitials from EOR, the diffusion of implanted Si ions—most of which are in interstitial sites and located around R_p—also occurs [13]. Both of them can make the value of S decrease to about 1 via the annihilation of vacancies. Therefore, it is seen that the boundary of the defective layer decreases to ~900 nm at 800 °C. In addition, the value of S in the shallow region is observed to increase significantly at 600 and 700 °C (figures 1 and 3). This implies that V_2 evolve to advanced V–O complexes and finally agglomerate to form V_mO_n $(m > n)$, escaping the recombination with interstitials from R_p. It is also shown that the value of S in the region between 750 and 950 nm is much smaller than that in the shallower region at 700 °C (figure 3). Figure 6 shows f_s for the Si-implanted sample. It is seen that a broad peak appears at high incident positron energies (mean probed depth ~ 1000 nm) at 700 °C. As in the O-implanted sample, it is believed that V_xO_y are formed between 750 and 950 nm. In this region V_mO_n are produced, which then react with silicon diffusing from the R_p region to be transferred to V_xO_y. Apparently, not all V_mO_n are changed here, so the value of S is not reduced to less than 1. Despite the similarity between the reactions in the shallow region at 600 and 700 °C, the reaction near R_p is dominated by V–I recombination, which accounts for the absence of f_s signature at high E in figure 6 for temperatures below 600 °C. At 800 °C the second defective layer (figure 3) becomes shallower and wider and its S continues to decrease. This implies

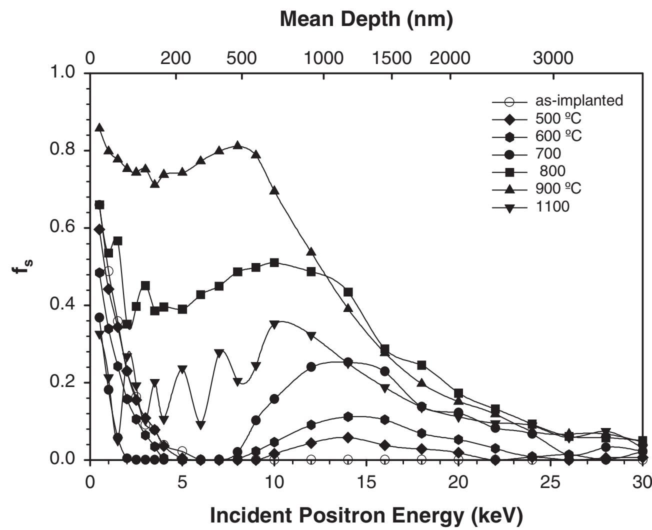

Figure 5. The fraction of positrons annihilated in the surface-like state for O-implanted Cz Si (0.5 MeV, 5×10^{15} cm^{-2}) obtained from the program FAST. The solid curves are used to guide the eye.

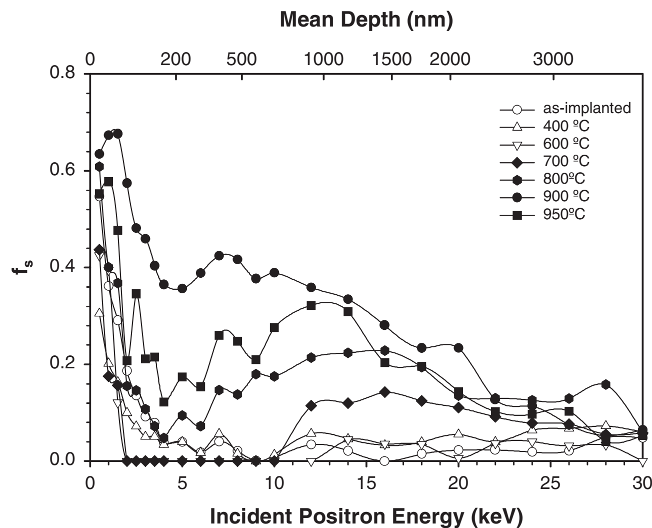

Figure 6. The fraction of positrons annihilated in the surface-like state for Si-implanted Cz Si (1 MeV, 10^{16} cm^{-2}) obtained from the program FAST. The solid curves are used to guide the eye.

that silicon ions can travel further toward the surface to transfer a part of V_mO_n to V_xO_y. This agrees with the increase in f_s in the shallower region (figure 6). It can be observed that V_mO_n formed in the first ~250 nm may also be affected by the silicon ions diffusing from the R_p region at 800 °C (figure 3). The point is that the arriving silicon ions are limited so that few V_xO_y are produced.

At 700 °C in the shallow region in O-implanted Si, V_2 evolve to advanced vacancy–oxygen complexes and agglomerate to form V_mO_n, resulting in a significant increase in S (figures 2 and 4). It is interesting that the biggest values of S for V_mO_n appear at 700 °C for both Si-

and O-implanted samples, signifying that V_mO_n are formed most effectively at 700 °C, while being less significant for the latter because of the much higher oxygen concentration (figures 3 and 4). This also proves that these vacancy-type defects are oxygen related in the shallow region. In addition, a higher oxygen concentration appears to results in the formation of more advanced V_mO_n, which has higher activation energy. Therefore, the temperature is higher for the commencement of V_mO_n formation in the O-implanted sample (700 °C) than in the Si-implanted sample (600 °C).

It is evident that f_s, measured at around 14 keV, increases significantly at 700 °C in the O-implanted sample in figure 5; here the two-defective-layers model works well. This implies that the formation of V_xO_y at 700 °C is more efficient than at 500 and 600 °C, so that the reduction in S is large enough to be seen by VEPFIT. At 700 °C a change similar to that in the shallow region occurs near R_p, except that many more oxygen atoms are involved. Hence V_xO_y are formed, rather than V_mO_n, reducing the value of S to below 1 (figure 4). The boundary between the V_xO_y and the bulk is determined from VEPFIT to be at 700 nm, which is shallower than that at 800 °C (820 nm). This result may be not reliable, because S for the V_xO_y layer is very close to 1.

The value of S for the V_xO_y layer decreases to far below 1 when the O-implanted sample is annealed at 800 °C (figure 4). Moreover, this layer extends towards the surface. These observations are consistent with the significant increase in f_s that is measured at around 10 keV (figure 5). At 800 °C the concentration of oxygen in the region between 350 and 820 nm increases due to the diffusion of oxygen from the region around R_p [14]. This results in an increase in the ratio y:x in V_xO_y, resulting in a value of S much smaller than 1. The change of the boundary between the defective and defect-free layers from 500 to 800 °C also benefits from the diffusion of interstitials from EOR, similarly to the situation at 500 °C.

After annealing at 800 °C, the value of S in the first 340 nm decreases in O-implanted Si compared to that at 700 °C, which is the same as that in Si-implanted silicon. It is proposed that the y:x ratio in the V_xO_y defects increases near R_p, as a result of the diffusion of oxygen from around R_p. The increase in the y:x ratio is also made apparent by the increase in f_s at E below 8 keV from zero to ∼0.4 (figure 5). The effective positron diffusion length in the first 340 nm is ∼56 nm, and the fraction of positrons implanted at 8 keV which diffuse back to the real surface is expected to be negligibly small. Hence, the above-mentioned increase in f_s must be linked to the effect of oxygen in the defects.

In addition, it should be noted that the decrease in S is more significant in the O-implanted sample than in the Si-implanted sample, due to the different formation mechanism of oxygen-related V-type defects at 800 °C. In the Si-implanted sample interstitials reduce the number of vacancies in these defects, but the consequent decrease in S is tempered by the parallel decrease in the specific trapping rate associated with the defects. In the O-implanted sample the number of oxygen atoms in the defects is increased without significantly decreasing the specific trapping rate and, because positrons see more oxygen atoms, a substantial decrease in S is observed. This also explains the large increase in f_s in the shallow region at 800 °C in O-implanted Si (figures 5 and 6).

When the O-implanted sample is annealed at 900 °C the values of S in both defective layers are reduced to well below 1 (figures 2 and 4). It is believed that the profile of oxygen becomes less sharp because of the diffusion of implanted oxygen. The oxygen concentration in the near-surface region ($<$390 nm) is increased sufficiently to produce V_xO_y. However, the oxygen concentration between ∼ 390 and 700 nm is bigger after all, because of the proximity of R_p. This introduces a larger y:x ratio in the resultant defects, and hence smaller S than at $<$390 nm (figure 4). The formation of V_xO_y in the entire first 700 nm significantly increases the value of f_s measured at $<$9 keV (figure 5).

The boundary between the defective and defect-free layers is closer to the surface than at 800 °C. This is due to the recombination between vacancies and interstitials from the EOR. It is supposed that more interstitials can be injected and they can travel a longer distance at 900 °C.

It is shown that the layer between ∼300 and ∼900 nm is also characterized by a value of S that is smaller than 1 when the Si-implanted Si is annealed at 900 °C (figure 3). It is believed that interstitials, whose concentration is increased significantly by the diffusion of implanted Si, can transfer V_mO_n, which are formed at ∼700 °C, to V_xO_y in this layer at 900 °C. A smaller decrease is seen in S for the layer between ∼60 and 300 nm, to a value still larger than 1, because a smaller number of interstitials diffuse to this shallower region. The significant effect of oxygen in the defects on positron annihilation is illustrated by the large increase in f_s in the shallow region between 800 and 900 °C (figure 6). It can be also seen in figure 3 that the value of S for the first ∼60 nm is much smaller than 1; it is likely that defects in this layer are associated with oxygen from the surface.

After annealing at 950 °C, the values of S for the regions shallower than ∼900 nm exclusively increase in the Si-implanted sample (figure 3), implying that all the oxygen-related vacancy-type defects begin to dissociate at this temperature. The first defective layer, whose width is smaller than ∼30 nm, is not shown in figure 3. Oxygen atoms that are released following dissociation do not trap positrons effectively. Vacancies from the dissociation recombine with interstitials, whose concentration is mainly determined by the redistribution of implanted Si ions. Most vacancies in the first 450 nm can escape the recombination with interstitials because of the low concentration of the latter, and hence S increases in this region. However, between 450 and 750 nm a fraction of the vacancies from the dissociation recombine with interstitials, so a somewhat smaller increase in S is observed. In figure 5 it is clear that the values of f_s at 12 and 14 keV at 950 °C are very close to those at 900 °C. Given the Makhov distribution of positrons and the much smaller f_s in the shallow region compared with those at 900 °C, it is believed that the values of f_s measured at around 12 and 14 keV are actually larger than those measured at 900 °C. The region associated with these larger values of f_s is estimated to be around 900 nm. It is considered that oxygen clusters are formed in this region, because high-concentration interstitials annihilate nearly all the vacancies so that the released oxygen atoms can migrate easily to agglomerate. However, the region is so narrow that it cannot be demonstrated by VEPFIT.

It is presumed that V_xO_y also begin to dissociate at 950 °C in the O-implanted sample. Figure 4 shows that only one defective layer, with a value of S smaller than 1, exists between ∼700 and 800 nm after annealing at 1100 °C. This layer is beyond the two defective layers at 900 °C; this suggests that most of V_xO_y in the first ∼700 nm have dissociated. The residual defects are responsible for the non-zero values of f_s measured at between ∼4 and 8 keV (figure 5). It is well known that oxygen precipitates grow effectively at high temperatures such as 1050 °C [15], and we suppose that some defects in the region between ∼700 and 800 nm—probably surviving vacancies—can facilitate the nucleation of oxygen precipitates at 1100 °C. The precipitates give rise to a value of S smaller than 1 (figure 4) and the high f_s measured at 10 keV (figure 5). It is evident that oxygen precipitates do not appear beyond ∼800 nm, although there is high oxygen concentration around R_p, because of the shortage of nuclei (the vacancy concentration is too low close to EOR). During the formation of oxygen precipitates, interstitials may be emitted because of the relaxation of stress [16]. The vacancies resulting from the dissociation of V_xO_y in the first 700 nm can annihilate with the interstitials from both oxygen precipitates and the EOR or just diffuse out at 1100 °C. However, the oxygen concentration is not enough to make precipitates grow effectively in the first 700 nm, as happened in the region closer to R_p, and hence the value of S becomes almost 1.

4. Conclusions

High-energy O- and Si-implanted Cz silicon samples have been studied by PAS. The evolution of V_2 to V–O complexes is out-competed by V–I recombination at 400 and 500 °C in the Si- and O-implanted samples; the higher oxygen concentration makes the latter temperature higher. The defective region shrinks as the annealing temperature increases as interstitials are injected from the EOR. V_mO_n ($m > n$) are formed in the shallow region most effectively at 700 °C for both Si and O implantation. V_xO_y ($x < y$) are produced near R_p by the annealing. At 800 °C, implanted Si ions diffuse and reduce m and implanted O ions diffuse and increase n in V_mO_n. All oxygen-related vacancy-type defects appear to begin to dissociate at 950 °C, with the probable formation of oxygen clusters. At 1100 °C, oxygen precipitates appear to form just before R_p in O-implanted silicon.

Acknowledgments

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