Effect of radiation damage on luminescence of erbium-implanted SiO₂/Si studied by slow positron beam


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Abstract

The effect of damage on 1.54 μm luminescence for 30 keV-Er-implanted SiO₂ films has been studied by positron annihilation and cathodoluminescence. It was found that S-parameter in the films decreased after implantation, indicating the suppression of positronium formation. The luminescence appeared with the recovery of the S-parameter after 600 °C annealing. The intensity reached a maximum at 900 °C annealing whereas the S-parameter did not change significantly. It seems that most damages recover at 600 °C and thereafter Er ions transform to an optically active state at 900 °C.

Keywords: Er; Positron annihilation; Ion implantation; Cathodoluminescence; Defects

1. Introduction

Trivalent erbium (Er³⁺) shows a characteristic sharp luminescence line at 1.54 μm, which coincides with maximum transparence of silica-based optical fibers. Optoelectronic devices have been extensively developed using various semiconductors implanted with Er ions (see, e.g., Polman, 1997). Silicon dioxide (SiO₂) doped with Er ions is a promising light emitting material since it shows a high luminescence efficiency and a low temperature quenching as compared to Er-doped Si. It is thought that Er ions occupy interstitial sites (Kozanecki et al., 1995) and an optically active Er ion forms a compound with five to six oxygen atoms in SiO₂ (Marcus and Polman, 1991). To maximize luminescence efficiency of Er-implanted SiO₂/Si, it is necessary to eliminate radiation damage by heat treatment. It is interesting to note a report (Polman et al., 1991) that some Er ions are in an optically active state without any heat treatment after high-energy implantation. The relationship between damage recovery and optical activation processes of Er-implanted SiO₂/Si should be clarified in detail. In this research, we studied the effect of radiation damage on the 1.54 μm luminescence of Er-implanted SiO₂/Si by positron annihilation and cathodoluminescence (CL) measurements through the annealing experiment.

2. Experiment

Silicon dioxide (SiO₂) films (~500 Å thick) were deposited on Si substrates by conventional dry oxidation at 1100 °C. These were implanted with 30 keV
Er\(^{+}\) ions at doses of \(3.0 \times 10^{14}\) and \(1.5 \times 10^{15}\) Er/cm\(^2\) at room temperature. The above condition was determined on the assumption of metal-oxide-semiconductor (MOS) structure production. The mean implantation depth was estimated to be 220 Å from the TRIM-95 code. For comparison, 5000 Å thick SiO\(_2\) films were implanted with 300 keV Er\(^{+}\) ions at a dose of \(1.5 \times 10^{15}\) Er/cm\(^2\). After implantation, specimens were subjected to isochronal annealing at 300–1200°C for 30 min in a high purity argon atmosphere. Cathodoluminescence measurements were performed using a 10 keV electron beam (~10 nA) at room temperature. The Doppler broadening measurements of annihilation gamma rays were carried out using a monoenergetic positron beam (0.08–30 keV) at room temperature. Electron spin resonance (ESR) measurements were also done at room temperature with an \(X\)-band (9 GHz) microwave incident on a TE\(_{110}\) cylindrical cavity.

3. Results and discussion

Fig. 1(a) shows the CL spectra for SiO\(_2\)(500 Å)/Si implanted with 30 keV Er ions (\(1.5 \times 10^{15}\) Er/cm\(^2\)). Although no luminescence is found after implantation, the 1.54 μm peak appears after 600°C annealing. The peak intensity drastically increases after 900°C annealing and decreases at 1200°C. Similar features were also found for the lightly implanted specimen (\(3.0 \times 10^{14}\) Er/cm\(^2\)). The decrease in the intensity at 1200°C is explained as out-diffusion and/or precipitation of Er atoms (Polman, 1997). The appearance of the peak at 600°C and the increase at 900°C seem to correspond to the recovery of radiation damage and optical activation of Er ions. On the other hand, the 1.54 μm peak is observed even in the implanted state of SiO\(_2\)(5000 Å)/Si, implanted with 300 keV Er ions as seen from Fig. 1(b). No remarkable increase in the peak intensity are observed after annealing at 600 and 900°C in this case. The above results show that Er ions

![Fig. 1. Cathodoluminescence spectra at room temperature from (a) SiO\(_2\)(500 Å)/Si implanted with 30 keV Er ions and (b) SiO\(_2\)(5000 Å)/Si implanted 300 keV Er ions at a dose of \(1.5 \times 10^{15}\) Er/cm\(^2\) recorded after each annealing.](image-url)
are already optically active after the 300 keV implantation without heat treatment. Similar results are reported previously for 3.5 MeV Er-implantation (Polman, 1997). From the above difference of the annealing characteristics of the luminescence depending on the implantation energy, the following questions arose: (i) how implanted Er ions become optically active; (ii) what is the optically active state; and (iii) how created damage affects the optical transition of Er ions, etc. After the 30 keV implantation, most Er ions might not be active and also high-density defects prevent the radiative transition of Er ions. The low energy implantation is important from technological viewpoints since a typical SiO$_2$ thickness used as MOS structures is less than 500 Å.

Fig. 2 shows the $S$–$E$ ($S$-parameter versus positron implantation energy $E$) plots of the unimplanted SiO$_2$/Si specimen. It is found that $S$-parameter decreases from the value for bulk Si with decreasing $E$ and shows a dip around $E = 2$ keV, then increases and again decreases as $E$ approaches 0 keV. The above behavior of the $S$-parameter is a typical feature of the SiO$_2$/Si system (Uedono et al., 1994). The dip at $E = 2$ keV may correspond to the SiO$_2$–Si interface considering the mean positron implantation depth. The maximum around $E = 1$ keV is related to positronium formation in the SiO$_2$ film. It seems that the $S$–$E$ curves for the unimplanted SiO$_2$/Si do not change with annealing.

As shown in Fig. 3, after the 30 keV implantation, the maximum around $E = 1$ keV disappears and $S$-parameters in this region significantly decrease. This may be explained as the suppression of positronium formation due to the radiation damage induced by implantation (Hasegawa et al., 1996). Fig. 3(a) shows that for the lightly implanted specimen ($3.0 \times 10^{14}$ Er/cm$^2$) $S$-parameters in the film recover after annealing at 300–600°C and also at 1200°C. Fig. 4 shows the change in $S$-parameter (at $E = 1$ keV) from the value of the unimplanted specimen and the 1.54 μm peak intensity as a function of annealing temperature. ($\Delta S = 0$ corresponds to the completely annealed state.) It is found that the 1.54 μm luminescence appears with the disappearance of implantation damage. It is however noted that $S$-parameter in the film does not change at 900°C where as the 1.54 μm peak intensity increases further. An electron spin resonance signal related to $E'$ centers in SiO$_2$ was detected after implantation. This signal vanished after 600°C annealing. These results indicate that the growth of the 1.54 μm peak at 900°C is hardly correlated with the annealing of damage detected by positron annihilation and ESR.

As described above, in the case of 300 keV implantation, most Er ions are already in the optically active state without annealing. On the contrary, no luminescences are observed after the 30 keV implantation. The SiO$_2$ amorphous network of the specimens implanted with 30 keV Er ions may be more destructively damaged than the case of 300 keV implantation, since local Er density is one order of magnitude higher than the latter case. Optically active Er ions are thought to be located among the SiO$_2$ network to form complexes with oxygen atoms. It is thus inferred that the severe damage after the 30 keV implantation inhibits the local formation of optically active Er–O compounds in the regular site of the SiO$_2$ amorphous network. As mentioned above, for the specimen implanted with 30 keV Er ions at a dose of $3.0 \times 10^{14}$ Er/cm$^2$, although radiation damages in the film detected by positron annihilation and ESR drastically recover at 600°C, the luminescence intensity does not increase so much. Probably, the luminescence was not enhanced significantly even if discrete defects disappear since most Er ions are not in the optically active state after the implantation. Furthermore, the drastic increase in the luminescence intensity at 900°C may suggest the transformation of Er ions to the optically active state through the local rearrangements of Er and O atoms.

It is noted that the $S$-parameter for the lightly implanted specimen does not fully recover even above 900°C annealing either, as shown in Fig. 4. No major recovery of $S$-parameters in the film of the highly implanted specimen ($1.5 \times 10^{15}$ Er/cm$^2$) is observed up to 900°C as shown in Fig. 3(b). Thus, the fraction of unrecovered $S$-parameter increases with Er dose. One reason for this may be that the amount of damages increase with Er dose and they are hardly annealed out in the highly implanted specimen. Considering that Er...
ions occupy spaces in the SiO₂ network in their optically active state, the suppression of recovery in S-parameters may also be explained as the elimination of the spaces for positronium formation sites by Er ions. This is likely to occur since the maximum Er concentration for the highly implanted specimen is nearly 1 at.%. The $S$–$E$ curves (Fig. 3) also revealed that the deeper region ($E=2.5\times10^4$ keV) from the SiO₂–Si interface is also damaged so as to decrease the $S$-parameters. The amount first decreases at $300^\circ\text{C}$ and increases after annealing at $600^\circ\text{C}$. From the detailed analysis of the Doppler broadening spectra, oxygen-related peaks around $514$ keV (Myler et al., 1996) were found. Such defects are not seen in the unimplanted SiO₂/Si. It is suggested that the defects are related to the complexes between point defects and oxygen atoms. The results of ESR measurements also showed that the Si substrate is made amorphous. The above results show that the defects are created in the deeper region even if most Er ions are stopped in SiO₂ layers. Since the defects near the interface degrade the performance of

![Fig. 3. S–E plots for unimplanted SiO₂(500 Å)/Si implanted with 30 keV Er ions at doses of (a) $3.0\times10^{14}$ Er/cm² and (b) $1.5\times10^{15}$ Er/cm² obtained after annealing. Chained lines show the S–E curves for the unimplanted specimen. Dashed lines show the position of the SiO₂–Si interface.](image)

![Fig. 4. Change in the S-parameter ($\Delta S$) for the SiO₂(500 Å)/Si implanted with 30 keV Er ions at a dose of $3.0\times10^{14}$ Er/cm² from that for unimplanted SiO₂(500 Å)/Si at $E=1$ keV and the 1.54 μm peak intensity as a function of annealing temperature. The $\Delta S$ is normalized to the value before annealing.](image)
devices it is important to study them in detail. Further study is in progress.

4. Summary

In summary, we performed positron annihilation and CL measurements for SiO$_2$/Si implanted with 30 keV Er ions. Unlike the case of high energy implantation, no luminescence appeared after the 30 keV Er-implantation. From the comparison of annealing characteristics of CL intensity with the $S$-parameter, it was proposed that Er ions are optically activated during 900°C annealing after the disappearance of defects induced by implantation at 600°C. The authors sincerely thank the technical staff of the ion-implantation facility of the Japan Atomic Energy Research Institute for their help in ion-implantation.

References


