Extended Abstracts of the 1994 International Conference on Solid State Devices and Materials, Yokohama, 1994, pp. 739-741

Direct Observation of Vacancy Supersaturation in Retarded Diffusion of Boron in Silicon Probed by Monoenergetic Positron Beam

K.Osada[a], Y.Zaitsu[a],S.Matsumoto[a],
S.Tanigawa[b], A.Uedono[b], M.Yoshida[c],
E.Arai[d], and T.Abe[e]

Faculty of Science and Technology, Keio University[a], Hiyoshi, Yokohama 223, Japan
Institute of Materials Science, University of Tsukuba[b], Tsukuba, Ibaraki 305, Japan
Kyusyu Insti. of De.[c], Shiobaru, Minami-ku, Fukuoka 815, Japan
NTT LSI Labs.[d], Morinosato Wakamiya, Atsugi-si, Kanagawa 243-01, Japan
SEH R&D Center Shin-Etsu Handotai Co.,Ltd.[e], Isobe, Annaka, Gunma 379-01, Japan

The effect of deposited Si_3N_4 films on point defects during annealing has been studied by monoenergetic positron-beam technique. Its effect on diffusion of boron has also been studied. During annealing, vacancy supersaturation is observed and diffusion of boron is retarded in FZ-Si under Si_3N_4 films compared to under double-layered SiO_2-Si_3N_4 films. These results indicate that boron diffuses predominantly by interactions with not vacancies, but self-interstitials.

1 Introduction

It has been recognized that dopant diffusion in silicon is assisted by both self-interstitials and vacancies, and that boron diffuses predominantly by interactions with self-interstitials[1]. However, it was recently proposed by Van Vechten et al.[2] that self-interstitials played no role in thermal process in Si and all dopants diffused by interactions with only vacancies. It is necessary to clarify directly the role of point defects on impurity diffusion in Si.

The positron annihilation technique has become an established tool in the study of vacancy-type defects in metals and semiconductors. The measurements of S parameter as a function of incident positron energy can provide the depth distributions of vacancy-type defects.

In the present paper, we have investigated the effect of stress in deposited Si_3N_4 films on boron diffusion and point defects in FZ-Si by SIMS and monoenergetic positron-beam technique.

2 Experimental Procedure

The used substrates were p-type (100) FZ-Si wafers with resistivities of 3-5Ωcm. Samples were oxidized at 1000°C in dry O_2 for 60min. This permitted growth of 50nm thickness of SiO_2 films. Boron ions implanted into the wafers through SiO_2 with a dose of $7.5 \times 10^{13}/cm^2$ at 70keV. Samples were annealed at 900 or 950°C in N_2 for 30min to remove the implantation damage. After removing SiO_2 films selectively, Si_3N_4 films were deposited on the samples by ECR plasma CVD at 100°C using SiH_4 and N_2 as sources. Thickness of Si_3N_4 films was 50nm. The area masked with double-layered SiO_2-Si_3N_4 films (ON-area) and the area directly masked with Si_3N_4 films (N-area) were formed. The bottom side of samples was masked with SiO_2-Si_3N_4 films.

Annealing was performed in N_2 at temperatures ranging from 900 to 1141°C for times varying from 60 to 600min. After etching SiO_2 and Si_3N_4 films, boron profiles were measured by using SIMS(ATOMIKA 6500). The diffusion coefficients of boron in Si were determined by fitting measured profiles with simulated profiles ob-

tained by solving Fick's diffusion equation.

The depth distributions of vacancy-type defects were measured using the monoenergetic positron beam line installed at the University of Tsukuba. Doppler-boardening profiles of annihilation radiation were measured by a Ge detector as a function of incident positron energy The spectrum with a total count of 10^6 was measured for each incident positron energy. The annihilation spectrum was characterized by S parameter, where the central region of the spectrum was defined from 510.5 to 511.5keV.

3 Results and Discussion

Figure 1 shows the boron cencentration profiles by SIMS for samples diffused for 300min at 1014°C in N_2. Boron diffusion under N-area is retarded compared to that under ON-area. Figure 2 shows boron diffusion coefficients of samples as a function of diffusion time at 1014°C. Almost independent of annealing time, diffusion of boron in Si under N-area is retarded compared to that under ON-area.

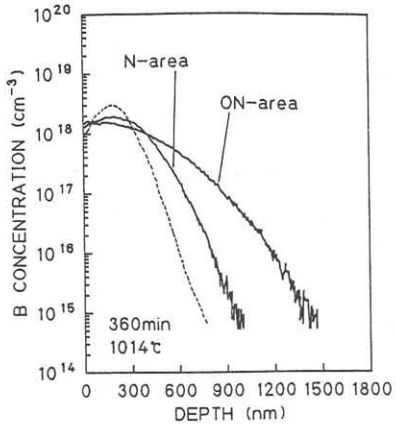

Fig. 1: Comparison of B profiles under N-area and ON-area experimentally obtained from SIMS analysis are presented. The corresponding 360min annealing temperature is 1014°C. Dashed line is initial profile.

S parameters of samples for both N-area and ON-area diffused for 360min at 1036°C in N_2 are

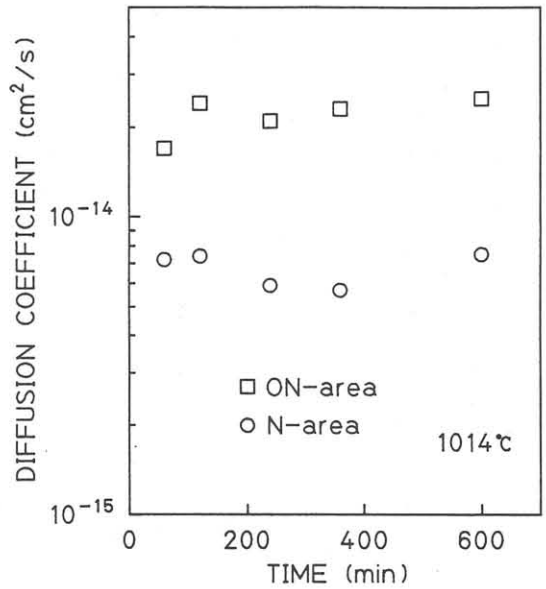

Fig. 2: Diffusion coefficients under N-area and ON-area as a function of diffusion time at 1014°C.

shown in Fig.3 as a function of incident positron energy. Positron energy can be converted to the mean implantation depth of positrons as shown in the figure[3],[4]. At high E (E> 5keV), the values of S are found to be a constant value. The values of S at low E (E<5keV) are found to be smaller than the constant value of S. The small value of S at low E can be attributed to the positron state at the surface[5]–[7]. The average values of S were calculated using values of S at high E (E>5keV) in order to exclude the influence of the region near the surface of the substrates. Thus obtained values correspond to the positron annihilation in the region where boron atoms diffuse. Figure 4 shows the ratio of the average values of S under N-area, $S_{ave.}$, to the average values of S under ON-area, $S_{ave.}^{ref}$, as a function of diffusion time at 1036°C. Most $S_{ave.}/S_{ave.}^{ref}$ values are greater than 1 and become bigger as diffusion time becomes longer.

These results indicate that the vacancy concentration under N-area is greater than that under ON-area and that it increases with the increase of diffusion time.

Since boron diffusion is performed via equilibrium concentration of point defects in ON-area, it is destinct that there is supersaturation of vacancy concentration under N-area where boron diffusion is retarded. Therefore, boron diffuses by interactions with not vacancies but self-interstitials.

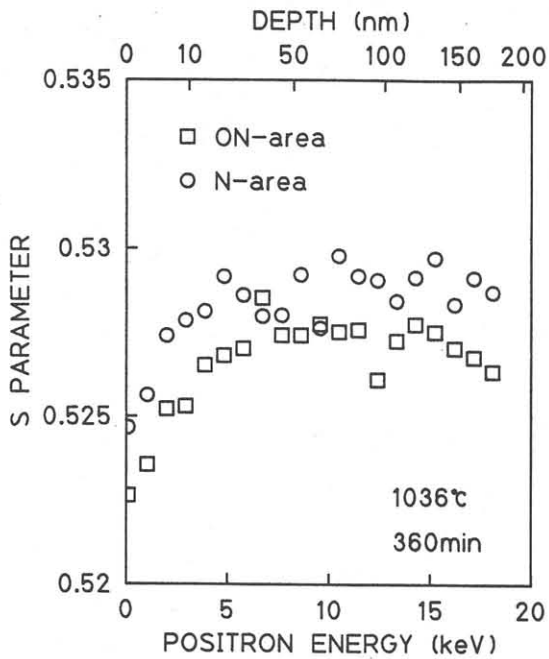

Fig. 3: The Doppler broadened parameter S under N-area and ON-area for the samples diffused for 360min at 1014°C as a function of incident positron energy.

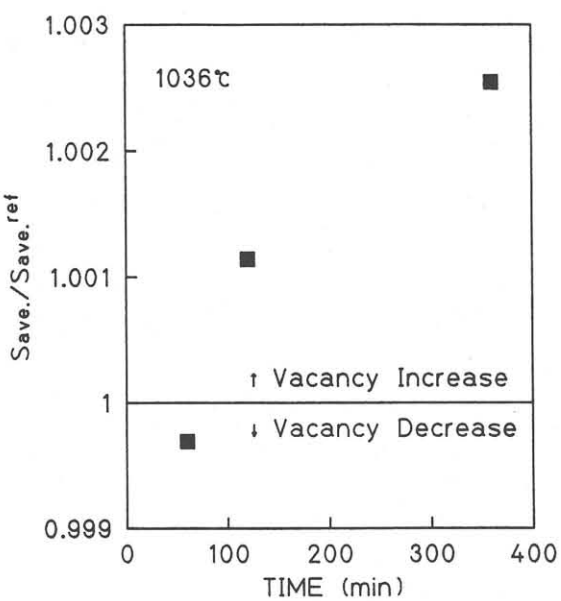

Fig. 4: $S_{ave.}/S_{ave.}^{ref}$ as a function of diffusion time at 1036°C.

4 Conclusion

The effect of stress in deposited Si_3N_4 films on point defects has been studied by monoenergetic positron-beam technique during annealing. Its effect on diffusion of boron has also been studied. During annealing, there is supersaturation of vacancies and diffusion of boron is retarded in FZ-Si under Si_3N_4 films. These results indicate that boron diffuses by interactions with not vacancies, but self-interstitials.

5 Acknowledgements

The authors would like to thank Dr. S.Matsuo and Dr. M.Tabe for the preparation of samples, M.Sakurazawa for SIMS measurements.

References

[1] P.A.Packan and J.D.Plummer, J.Appl.Phys. 68(1990) 4327.

[2] J.A.Van Vachten, U.Schmid, and Q.S.Zhang, J.Electron.Mater. 20(1991) 431.

[3] A.Vehanen, K.Saarinen, P.Hautojarvi, and H.Huomo, Phys.Rev.B 35(1987) 4606.

[4] S.Valkealahti and R.M.Nieminen, Appl.Phys. A35,51(1984).

[5] A.Uedono, S.Tanigawa, J.Sugiura, and M.Ogasawara, Jpn.J.Appl.Phys. 28(1989) 1293.

[6] A.Uedono and S.Tanigawa, Jpn.J.Appl.Phys. 29(1990) 909.

[7] A.Uedono, L.Wei, S.Tanigawa, R.Suzuki, H.Ohgaki, T.Mikado, and K.Fujino, J.Appl.Phys. 75(1994) 216.