Extended Abstracts of the 1997 International Conference on Solid State Devices and Materials, Hamamatsu, 1997, pp. 116-117

Deactivation of Boron in Highly Boron-Doped Silicon

I. Mizushima, Y. Mitani,[1] M. Koike,[1] M. Yoshiki,[1] M. Tomita[1] and S. Kambayashi[1]

Microelectronics Engineering Laboratory, [1]R&D Center
Toshiba Corporation
Isogo-ku, Yokohama 235, Japan
Phone: +81-45-770-3662, Fax: +81-45-770-3577, E-mail: mizushima@amc.toshiba.co.jp

1. Introduction

Atomic configurations and electrical characteristics of dopant atoms in highly doped silicon have attracted interest, because super saturation of dopants is useful for realizing low resistivity contact between the doped silicon and the metal. An understanding of the deactivation mechanism is especially required in order to control the electronic properties of such a high concentration dopant. For boron, the formation of silicon-boride is proposed as a candidate of inactive configuration from the TEM observation of boron-doped samples annealed at extremely high temperature about 1100°C[1]. However, deactivation of boron occurs at lower temperatures. What happens during the deactivation process has not been understood yet.

In this paper, the clustering of boron in highly boron doped silicon and its influence on the electrical deactivation is reported. In order to obtain a highly boron-doped silicon without defects as a starting material, solid phase epitaxy (SPE) of boron doped amorphous silicon was used. Boron can be supersaturated in the crystallized samples annealed at a low temperature, whereas a lot of precipitates including boron were observed in the samples annealed at high temperatures. The chemical states and the atomic configuration of boron in samples annealed at various temperatures corresponded to the electrical deactivation of boron.

2. Experiment

Boron doped amorphous Si films were deposited on HF cleaned (001) Si substrates with Si_2H_6 and B_2H_6 by LPCVD at 350°C. The boron concentration of the deposited layer was $1 \times 10^{21} cm^{-3}$. The samples were annealed at various temperatures in a nitrogen ambient. Crystallographic structure was investigated by TEM. EELS was used for the investigation of the dopant distribution in micro areas. Electrical active boron concentration was measured by the Hall effect. Chemical states of boron were investigated by XPS. SIMS was used for detecting the clustered boron as well as for measuring the boron concentration.

3. Precipitation and Deactivation of Boron

Figure 1 (a) shows the cross-sectional TEM for the sample annealed at 600°C for 1 hour. The deposited boron doped Si was epitaxially crystallized. No defects were recognized in the deposited layer. Boron atoms were super saturated in the Si lattice because of the low temperature SPE[2]. In the sample annealed at 1000°C, a lot of precipitates were observed, as shown in Fig. 1 (b). The radius of the precipitates was about 5 nm. The formation of the precipitates was due to the high doping of boron, because they were observed only in the deposited layer.

The distribution of boron was investigated by FE-TEM equipped with EELS. Figure 2 shows the EELS spectra for the precipitate and the surrounding area. The peak indicating boron was detected only in the spectrum for the precipitate. This means that this region is formed by the precipitation of boron-rich phase.

It was confirmed by Hall measurements that the electrical deactivation of boron corresponded to the precipitation of boron. Annealing temperature dependence of the electrically active hole concentration, measured by Hall effect, and of the chemical boron concentration, measured by SIMS, are shown in Fig. 3. As the annealing temperature is higher, the hole concentration decreases, while the boron concentration is constant. This indicates that the boron atoms in the precipitates have electrically inactive configuration.

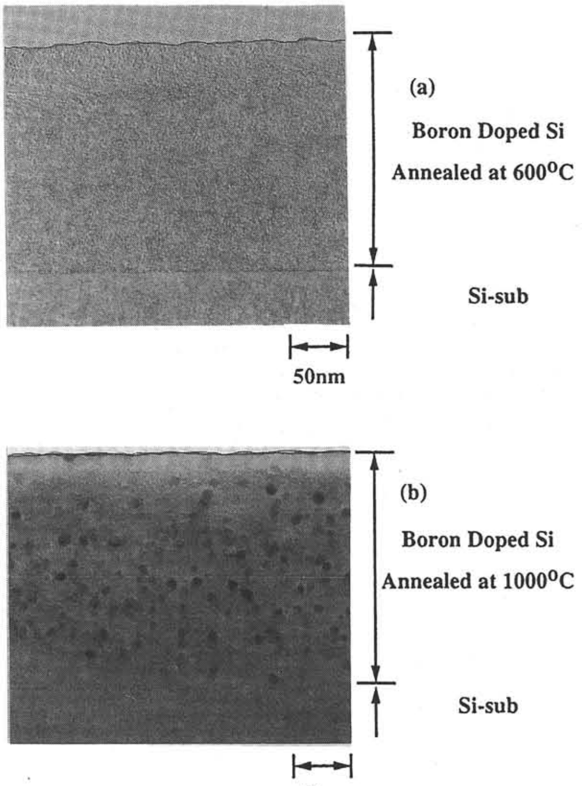

Fig. 1 Cross-sectional TEM for boron-doped Si films annealed (a) at 600°C for 1 hour and (b) at 1000°C for 1 hour.

4. Atomic Configuration of Boron Precipitate

XPS spectra for samples annealed at various temperatures clearly identified the configuration of boron in each sample. Figure 4 shows the B1s spectra for samples annealed at various temperatures. The B1s spectrum can be decomposed to 4 peaks. Each peak is attributed to 2-folded, 3-folded, 4-folded and clustered boron, from the lower energies, respectively[3,4]. The 2-folded and 3-folded boron are observed only for the as-deposited sample and the sample annealed at 400°C. This is the consequence of the fact that the deposited layer is amorphous in these samples. In the sample annealed at 600°C, most of the boron atoms are 4-folded, which indicates that most of the boron atoms substitute Si atoms in the lattice.

It should be noted that the clustered boron appeared for samples annealed at temperatures higher than 600°C. Higher annealing temperature tends to bring about higher concentration of boron cluster. Such an annealing temperature dependence suggests that the deactivation process of boron is the process that the boron atoms form their clusters.

Results of SIMS measurements of the clustered ions also indicate that the clustering occurs according with the deactivation of boron. B_2^+ ion intensity for the as-deposited and annealed samples are shown in Fig. 5. B_2^+ ion yield for samples annealed in the high temperature range, at which deactivation of boron occurs as shown in Fig.3, is much higher than the yield for the as-deposited and annealed at 600°C, even though the boron concentration is constant in every sample. This result also suggests that boron clusters are formed in the samples annealed at high temperatures.

5. Conclusion

A lot of precipitates including boron were observed in the samples, in which inactive boron exists. XPS analysis of chemical state of boron and the SIMS measurements of clustered ions revealed that the electrical deactivation of boron corresponds to the formation of clustered boron.

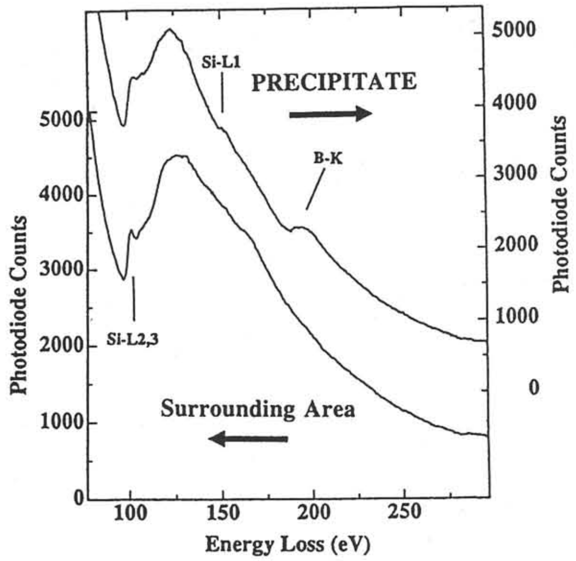

Fig.2 EELS spectra for the precipitate and the surrounding area.

Acknowledgment

The authors wish to thank Dr. K. Suguro and Y. Tsunashima for fruitful discussion.

References

1) A. Armigliato et al.: *Semiconductor Silicon 1977*, Electrochem. Soc. (1977) p. 638.
2) S. Solmi et al.: J. Appl. Phys. **68** (1990) 3250.
3) T. Kazahaya and M. Hirose: Jpn.J.Appl.Phys. **25** (1986) L75.
4) I. Mizushima et al.: Jpn. J. Appl. Phys. **33** (1994) 404.

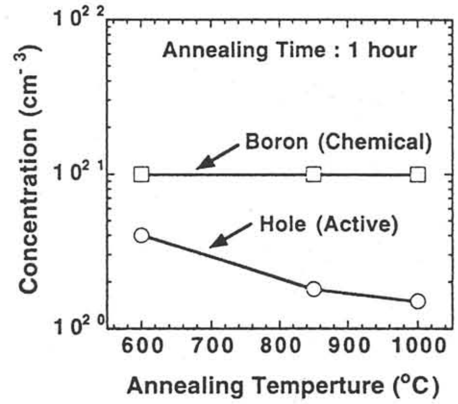

Fig.3 Annealing temperature dependence of the hole concentration and of the boron concentration.

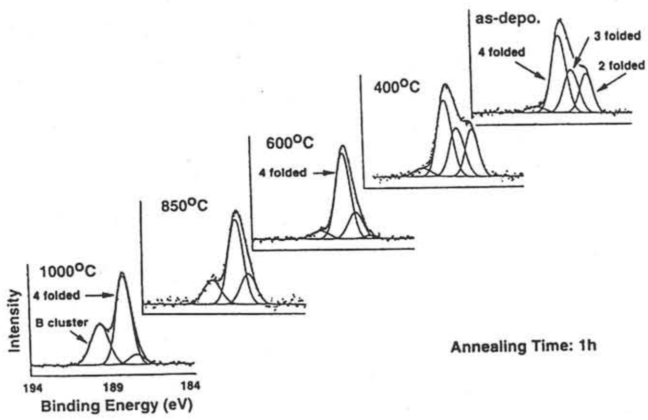

Fig.4 B1s spectra for samples annealed at various temperatures.

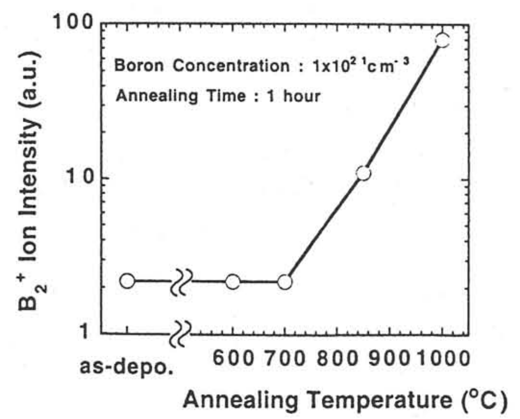

Fig.5 B_2^+ ion intensity for the as-deposited and annealed samples.