

## Encapsulation of Surface Impurities by Silicon Wafer-Bonding

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Residual impurities on cleaned silicon wafers are encapsulated in the interface made by wafer-bonding and analysed by SIMS depth profiling. H. C. N. O. F and Cl with high concentrations are detected and their diffusions with increasing temperature are also observed. It is confirmed by IR absorption that oxygen in CZ crystals out-diffuses into the bonded interface and produces a  $\text{SiO}_2$  layer. The elements such as F and Cl contained in the final cleaning chemicals are detected in the bonded interfaces.

### 1. INTRODUCTION

The concentrations of heavy metal impurities<sup>1)</sup> on silicon wafers used for ULSI processes have been reduced extensively. This is owing to a new sampling method<sup>2)</sup> for the heavy metal impurities with the extremely low concentration. Although the effects of light elements on the device fabrications have been noticed recently, there is no proper sampling method existed. Even SIMS which is one of the most sensitive technique is used, it has been believed that the direct measurement on surface impurities is difficult due to the reason which is the evaporation from the surface until the stabilization of the secondary beam. In order to prevent such disadvantage, a-Si in a vacuum chamber<sup>3)</sup> or poly Si by CVD<sup>4)</sup> at 600C are coated for the encapsulation of the impurities. However, the contaminations from the chamber or during CVD are worried about in the former and the latter case, respectively.

To avoid the above problems, the specimens which are bonded by two wafers are used and the behavior of the encapsulated impurities at high temperature are studied also in this paper.

### 2. EXPERIMENTS

Figure 1 shows schematically the wafer bonding

process for bipolar devices made with the SOI structure<sup>5)</sup> as an example. The base wafer as denoted is brought in contact with the bonded wafer without the use of external pressure, AC voltage or adhesives. These are annealed at various temperatures for 2 hrs. in

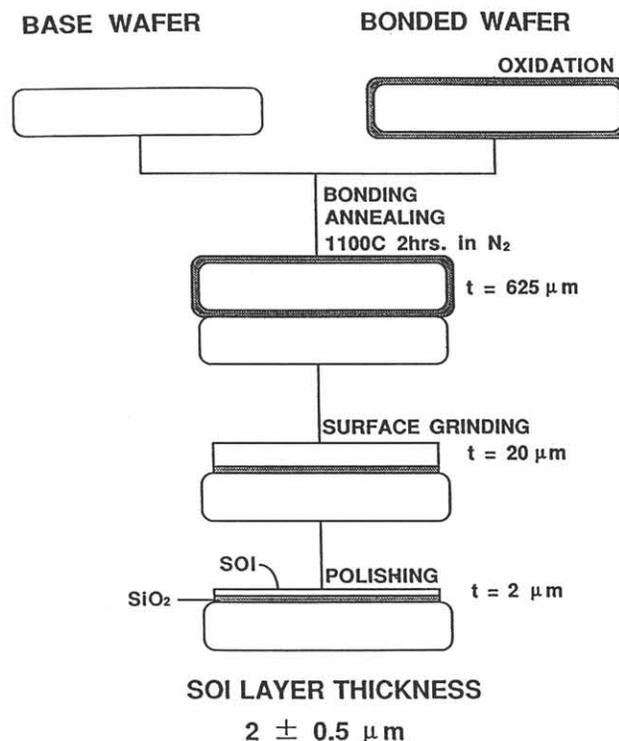


Fig. 1 Schematic of silicon wafer bonding process with SOI structure.

a nitrogen ambient. The tight binding specimens annealed over 800C are thinned by surface grinding and etching and the loose binding specimens annealed under 600C are etched for obtaining the thin SOI layer.

CZ and FZ wafers with the diameter of 4 inches and the thickness of 525 $\mu$ m, which are (100) orientation, p-type  $\sim 10 \Omega$ cm in resistivity are used. The concentration of oxygen in CZ crystals is  $1 \times 10^{18} / \text{cm}^3$ . Two different final cleaning processes, that is, dilute HF and HCl/H<sub>2</sub>O<sub>2</sub> of modified RCA cleaning are used. In the case of the former, both HF cleaning and bonding are proceeded in a complete nitrogen ambient.

SIMS depth profiles for the direct bonding (Si/Si) wafers are taken by CAMECA IMS-3f using Cs ion as a primary beam, but for the one side oxide bonding (SiO<sub>2</sub>/Si) by PHI 6300 with the quadropole type that is effective for insulator materials using Cs ion as a primary beam.

The variations of IR absorption<sup>6)</sup> at 1060cm<sup>-1</sup> with the increasing temperature are measured through the direct bonding FZ and CZ wafers separately. The thickness of an SiO<sub>2</sub> layer which are grown at the bonded interface in the CZ wafers is estimated using the FZ wafers as references.

### 3. RESULTS

Figure 2 shows the SIMS depth profiles of the specimens which are cleaned by a dilute HF and annealed at 800C and 1000C. The high concentration of hydrogen ( $5 \times 10^{18} / \text{cm}^3$ ) exists at 800C but under detection at 1000C. Carbon is also high concentration ( $5 \times 10^{18} / \text{cm}^3$ ) but no changed at 1000C. Nitrogen increases their concentrations with increasing temperature.

The diffusion of oxygen into the bonded interface with the increasing temperature is clearly observed and this is different from other impurities. The asymmetry of oxygen profiles at interface and the absolute value of oxygen cannot be described in detail here. The concentration of F does not change with temperature.

Figure 3 shows the profiles of the specimens cleaned by HCl/H<sub>2</sub>O<sub>2</sub> and annealed at 1000C and 1200C. Hydrogen disappears at 1200C. The high concentrations of carbon ( $1 \times 10^{19} / \text{cm}^3$ ) at 1000C is

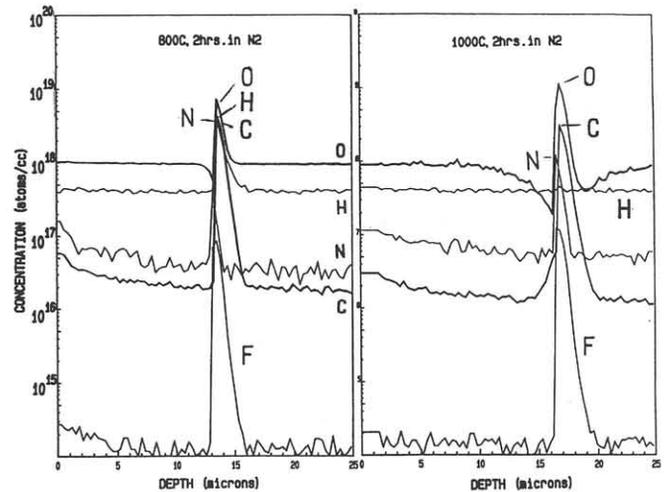


Fig. 2 SIMS depth profiles of the direct bonding wafers annealed at 800C (a) and 1000C (b). The dilute HF is used for the final cleaning of two wafers.

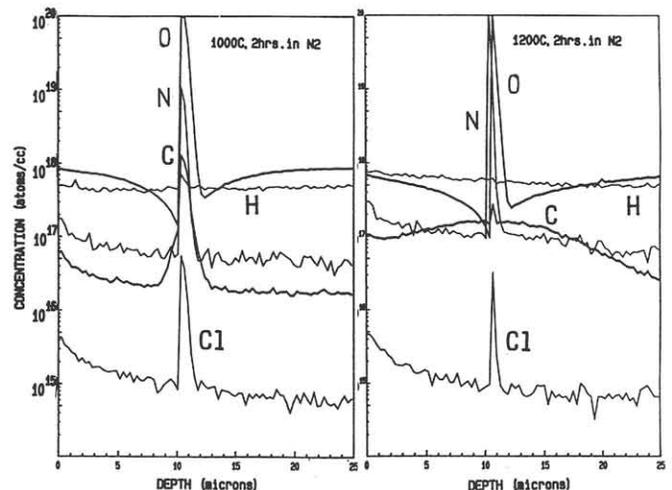


Fig. 3 SIMS depth profiles of the direct bonding wafers annealed at 1000C (a) and at 1200C (b). The HCl/H<sub>2</sub>O<sub>2</sub> solution is used for the final cleaning of two wafers.

dramatically decreased at 1200C, and carbon diffuses into bulk silicon. The concentrations of oxygen in both Fig.3 (a) and (b) overflow, but the large difference of out diffusion profiles are seen. The concentration of Cl does not change with temperature.

Figure 4 is the SIMS profiles of the specimen with the SiO<sub>2</sub> layer annealed with 1100C, 2hrs in a nitrogen ambient. In this figure P and Q show the thermally grown oxide interface and bonded interface, respectively. H, C and Cl exist at the bonded interface,

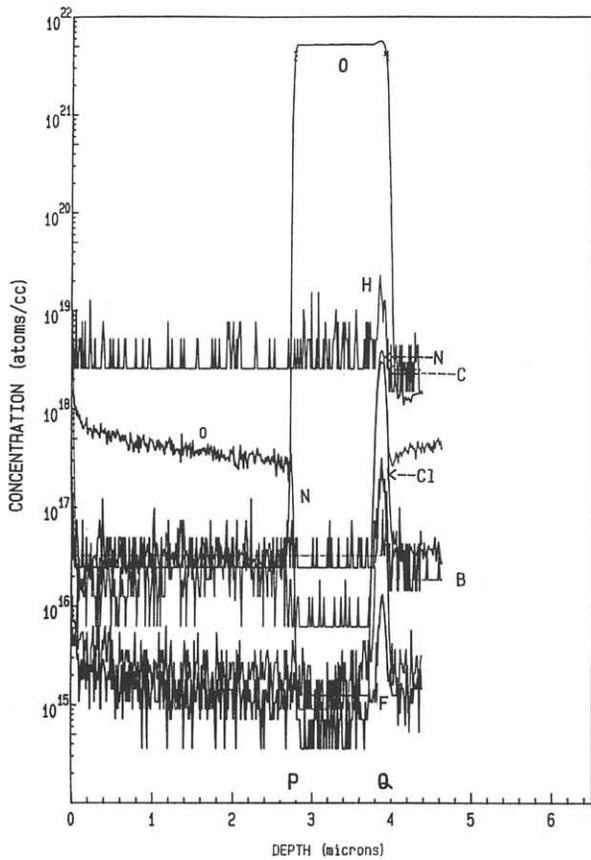


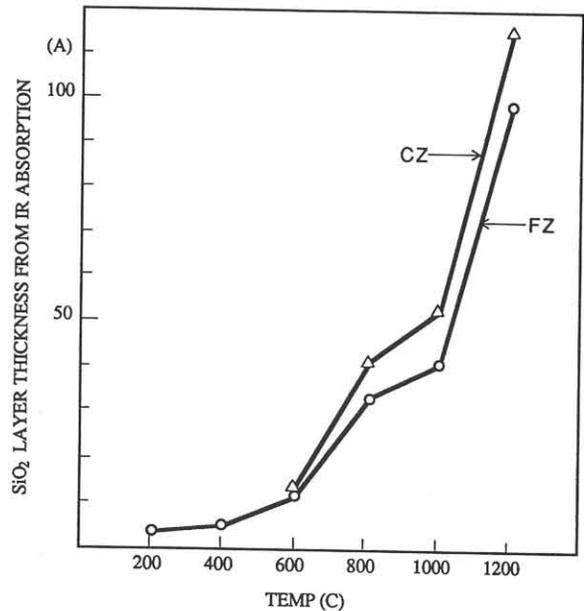
Fig. 4 SIMS depth profiles of the bonding wafer with the one side oxide. P and Q indicate the thermally grown oxide interface and bonded interface, respectively.

but nitrogen at both interfaces. It is observed that oxygen diffuses into the interface (P).

The total thickness (two surface-oxides and an interface oxide) variations of  $\text{SiO}_2$  layer based on the absorption of  $1060 \text{ cm}^{-1}$  with temperature are shown in Fig. 5. From the difference of  $\text{SiO}_2$  layer thickness between CZ and FZ crystals, it is expected that the oxide layer grows in the bonded CZ wafer over  $800^\circ\text{C}$ .

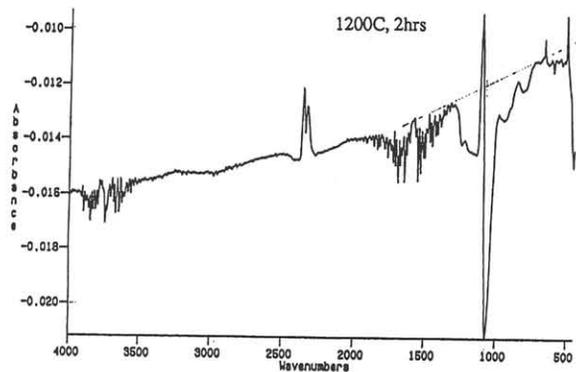
#### 4. DISCUSSION

From the fact of disappearance of hydrogen at high temperature it is speculated that higher concentration of hydrogen should be existed at low temperature. Silicon wafer surfaces used in this experiments are contaminated with the high concentrations of carbon and they seem to diffuse into the bulk with the larger diffusivity<sup>7)</sup> than that of known value. The diffused carbon affects as a harmful impurity in the device chips.



(a)

#### INFRA-RED ABSORPTION OF BONDED WAFER



(b)

Fig.5 Total thickness (surface oxide and interface oxide) of  $\text{SiO}_2$  layer IR absorption on temperature (a) and IR absorption spectrum of CZ crystal annealed at  $1200^\circ\text{C}$  (b).

However, the oxide layer as seen in Fig. 4 is a barrier for carbon diffusion to the active layer. Nitrogen behavior is well-understood by the reference(7), that is, nitrogen aggregates the lattice defects depending on the temperature and the volume of defects and never diffuse out like as a carbon. Nitrogen aggregation is an indication of the lattice defects.

In the both cases of the one side oxide and direct bonding, oxygen out-diffuses into their interfaces and then will enhance the growth of the oxide layers. The

thickness of oxide layer in the direct bonding CZ wafer at 1200 is estimated as 19 nm from the IR absorption as seen in Fig. 5. The oxide thickness of the bonding FZ wafer is assumed as zero according to the reference(8).

## 5. CONCLUSION

The elements such as F and Cl contained in the final cleaning chemicals are detected at the bonded interfaces. A quantitative explanation of the residual contaminations encapsulated requires the SIMS results of the specimens with the lower temperature annealing. The high concentrations of carbon exist and diffuse into the bulk. In the case of the SOI structure, SOI layer is protected by the oxide layer from C, F and Cl impurities. In the case of the direct bonding, if CZ wafers are used, the thick oxide layer will be formed.

## REFERENCES

- 1) T. Abe and T. Itoh, *Defect Control in Semiconductors*, edited by K. Sumino (North Holland, 1989 Yokohama) P. 297
- 2) A. Shimazaki et al., *Extend Abstracts of the 16th (1984 International) Conference on ssdm*, Kobe 1984 (J. Soc. Appl. Phys. Tokyo), P. 281
- 3) N. Yabumoto et al., *Jpn. J. Appl. Phys.* 29 (1990) L490
- 4) R. S. Hockett and J. C. Norberg, *Secondary Ion Mass Spectrometry SIMS VII*, edited by A. Benninghoven et al. (John Wiley, 1989) P. 491
- 5) T. Abe et al. *Silicon-Insulator Technology and Devices*, edited D. N. Schmidt (Electrochem. Soc. Pennington 1990) P. 61
- 6) I. W. Boyd and J. I. B. Wilson, *J. Appl. Phys.* 53 (1982) 4166
- 7) T. Itoh Y. Hayamizu and T. Abe, *Materials Science and Engineering*, B4 (1989) 309
- 8) K. Y. Ahn, R. Stengl, T. Y. Tan and U. Gosele, *J. Appl. Phys.* 55 (1989) 561