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# Chemical Analysis of Ultratrace Impurities in $SiO_2$ Films

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A new method for analyzing the ultratrace impurities in silicon wafers is developed. The vapor phase decomposition method (VPD) involves oxidizing the wafers and decomposing them by hydrofluoric acid vapor. The sensitivity of VPD is better than other methods; the iron concentration of $10^9$ atoms/cm$^2$ and the sodium concentration of $10^8$ atoms/cm$^2$ in 50 nm silicon dioxide film can be detected. VPD is efficient and reliable method for measuring ultratrace impurities of the wafers. It is proved that this method is useful for the quick on-line cleanness monitor of wafer surface and the device manufacturing field.

## 1. Introduction

Recently, the size of active cells and the dimension of interconnection lines have been reduced remarkably with the development of very large scale integrated circuits (VLSI's), and this requires more reliable oxide layers as insulators of VLSI's. It also is required that the oxide layers be as thin as possible without lowering the breakdown voltage. The breakdown failure is mainly determined by impurities in the silicon wafer and the cleanness of the wafer surface. It has been reported that the contamination of the silicon wafer surface by particulates[1),2)] and ionic impurities, particularly sodium[3),4)], significantly reduces the breakdown voltage yield of thin $SiO_2$ films, and that microdefects in the silicon substrate caused by oxygen precipitates and impurities also affect the breakdown properties[5)]. While impurities such as carbon and oxygen in the silicon substrate have been studied in detail, other kinds of impurities, however, have not been investigated closely. It should be noted that it is important to analyze the ultratrace impurities in the $SiO_2$ films quantitatively in order to investigate the mechanism of the breakdown failure[6)].

Beam analysis methods, such as AES and SIMS, and electrical measurement methods are generally used to detect the metal impurities both in silicon substrates and on the surface of the silicon wafers. We have successfully developed a new measurement method with high sensitivity for ultratrace chemical impurities using the flameless atomic absorption spectrophotometry with a vapor phase decomposition method (VPD). The identification limits of the VPD and other methods are compared in Table 1. The figures show the detecting limits for Na and Fe in 50 nm $SiO_2$ film on a 100 mm diameter wafer surface. The VPD has higher sensitivity than other methods since the number of sample wafer pieces can be increased in the VPD. The method is very simple for analyzing many wafers simultaneously without any additional preparation such as cutting.

The experimental methods and the practical application of VPD analysis will be reported in this paper. We believe that this method is most useful for the evaluation of the wafer surface cleanness and the substrates in the device manufacturing field.

Table 1. Detection limit (atoms/cm$^2$)

| Analysis method | Na | Fe |
|---|---|---|
| This method | $10^8$ | $10^9$ |
| Secondary Ion Mass Spectroscopy | $10^8$ | $10^9$ |
| Neutron Activation Analysis | $10^{12}$ | $10^{14}$ |

## 2. Vapor Phase Decomposition Method

The VPD analysis instrument is illustrated in Fig. 1. The vessel, all the carriers and fixtures of the instrument are made of tephlon and are cleaned with a mixture of high grade hydrofluoric acid, hydrochloric acid and nitric acid for 4 hours at 200°C before the analysis is performed. Specimen wafers are cleaned with high grade chemicals and then they are oxidized in purified dry oxygen atmosphere at 1000°C until several tens nm thick oxide is formed. After oxidation, the wafers are placed perpendicularly in a wafer carrier in the vessel in order to decompose the oxides. Then the solution for decomposing silicon dioxide (50 ml hydrofluoric acid) is prepared in a beaker. The vessel is closed tightly for 3 hours to allow complete decomposition of the oxides by hydrofluoric acid vapor. The decomposed solutions drop into a sampling saucer and are collected by a micro pipet for the flameless atomic absorption spectrophotometry. The solution is stirred, weighed and then injected into a graphite furnace of the spectrophotometer, in which the solution is heated so that all the atoms are dissociated to ground states. The state is determined by measuring light absorption intensities of characteristic resonant wavelengths of the specific atoms. A hollow cathode lamp is used as a light source. The concentration of the atom is obtained by measuring the absorbed intensity. This method features high sensitivity and accuracy (Na: $\pm$1%, Fe: $\pm$2%), because the sample solutions are highly condensed in the atomizing furnace. The dissolution process is conducted in the closed vessel and all the analyzing procedure are performed in a highly clean environment.

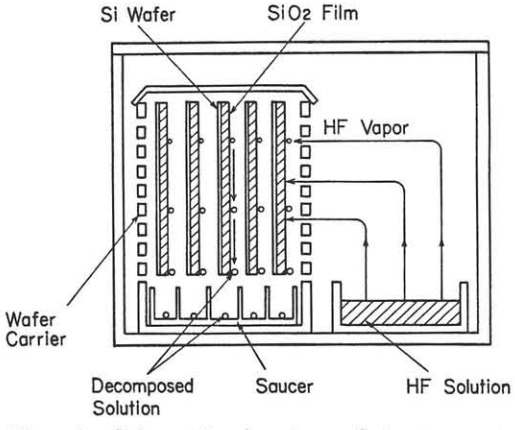



Fig. 1 Schematic drawing of instrument.

## 3. Practical applications in VLSI process

Following analyses are performed to examine the contamination in each process related to the breakdown voltage.

(1) Treatment conditions

Wafers prepared from the same lot are cleaned by various treatments (A-E) and oxidized in the same furnace, then impurity concentrations in the oxides are examined. The result is shown in Fig. 2. It can be seen that impurity concentrations vary with the treatments. This result shows that the surface contamination is apparently influenced by the surface cleaning conditions.

(2) Evaluation of wafer surface contamination

Experiments were made with the objective of examining the relation between the surface impurities and impurities in the cleaning solutions. The wafer was dipped into the specific cleaning solution with identified concentration of metal impurity, namely 0.1, 1, 10 ppm Na or Fe, for one minute and oxidized in the same furnace. Figure 3 shows that measured Na and Fe concentrations increase proportionally with the impurity concentration in the solution. This result shows that the impurity level in the solution must be reduced as low as possible in order to keep the wafer surface clean.

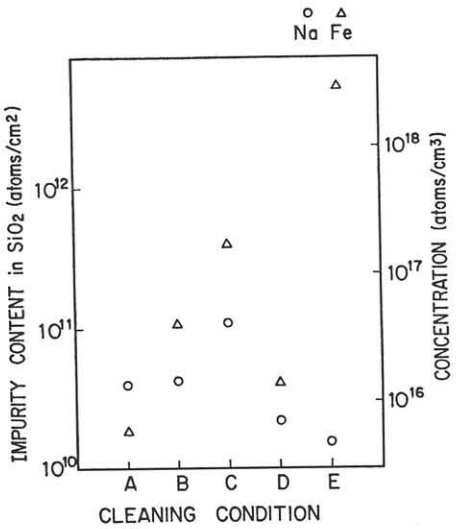



Fig. 2 Impurity content in $SiO_2$ vs cleaning conditions.

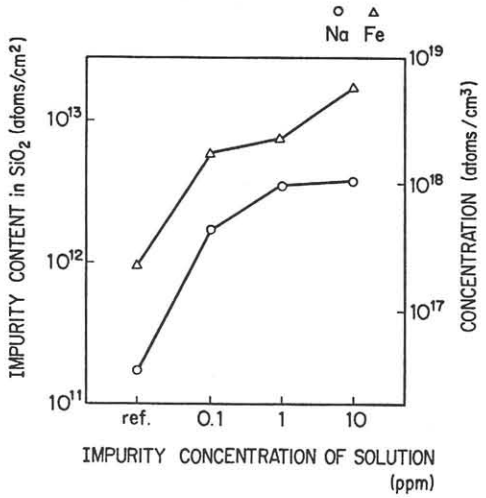



Fig. 3 Impurity content in $SiO_2$ vs impurity concentration of solutions.

(3) Evaluation of venders' wafers

We evaluated several venders' wafers by the VPD. All the samples were Si wafers which were CZ, (100), p type with several Ω - cm resistivity. They were cleaned and oxidized under the same condition. The result is shown in Fig. 4. It shows that the impurity concentration of each wafer varies from $10^{10}$ to $10^{12}$ atoms/cm$^2$ and it was estimated that each vender had different method of surface cleaning and impurity control in ingot fabrication process.

(4) Evaluation of impurity distribution in an ingot

We analyzed the impurity in the top, center and tail portions in an ingot in order to examine the impurity distribution of ingots. The result is shown in Fig. 5. The distribution of Na and Fe do not depend on the position. The concentrations of Na and Fe were expected to be higher for the ingot tail because the each segregation coefficient is less than 1 , Na: $1.65 \times 10^{-3}$, Fe: $8 \times 10^{-6}$, respectively. However, Na concentration is nearly the same throughout the ingot, and Fe concentration does not increase monotonously toward the tail position. It should be noted that these impurity distributions are caused by an accidental contamination in the ingot fabrication.

(5) Analysis of shallow pits in epitaxial wafers

The experiments described above are examples of surface impurity analysis. This method was also applied for the analysis of shallow pits. A micrograph of epitaxial wafer is shown in Fig. 6. Several shallow pits on the wafer are observed after 40 minutes' Dash etching. It has been reported that these shallow pits were formed by the impurities or silicon clusters caused by impurities, and that 'thermal oxidation + oxide removal' is efficient for eliminating them[7]. Based on this result, the following experiment was performed. Three samples, namely a wafer piece annealed in an epitaxial furnace under hydrogen atmosphere, an epitaxial wafer (both of them have $10^7$/cm$^2$ shallow pit density) and a raw wafer without shallow pits as a reference, were analyzed. The result is shown in Fig. 7. Iron and Cr were proved to exist more in hydrogen annealed wafer and epitaxial wafer than in the raw wafer. Thus it is concluded that metal impurity such as Fe and Cr probably cause shallow pits and silicon clusters.

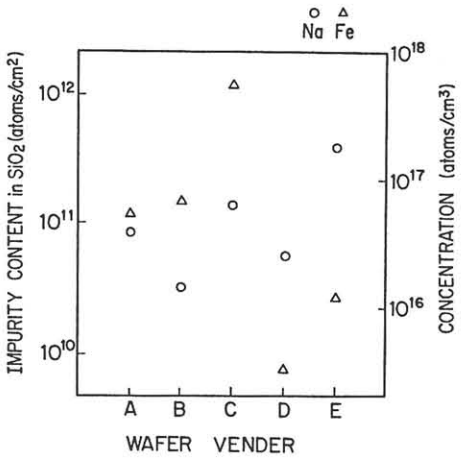



Fig. 4 Impurity content in $SiO_2$ vs wafer venders.

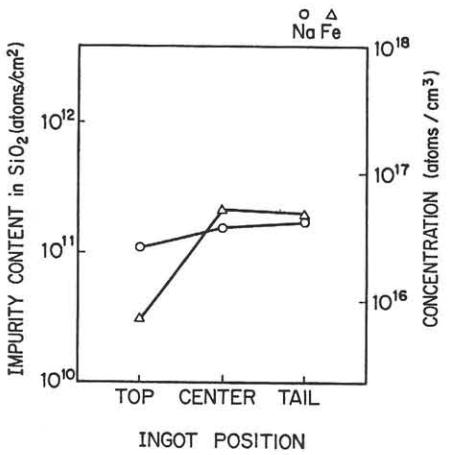
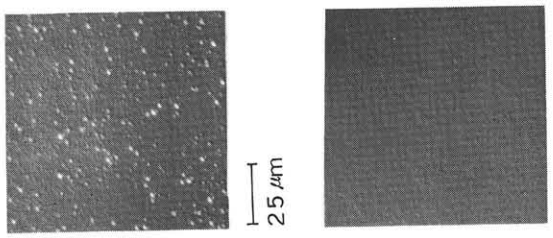



Fig. 5 Impurity distribution in an ingot.




a) Epi wafer (Dash etching 40 min.) shallow pit density ≃ $10^6/cm^2$

b) Raw wafer (Dash etching 40 min.) without shallow pit

Fig. 6 Optical micrographs of wafer surface.

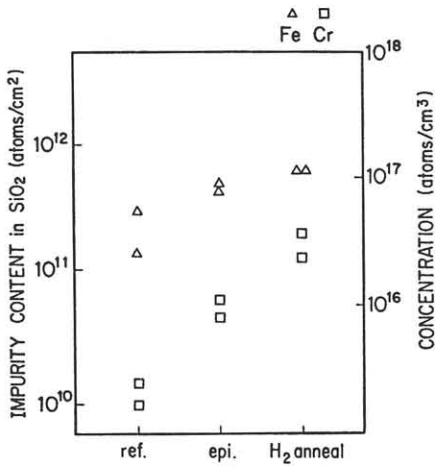



Fig. 7 Contamination during epitaxial process.

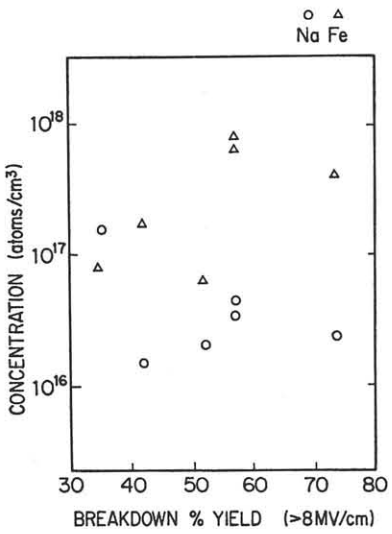



Fig. 8 Concentration in $SiO_2$ as a function of breakdown % yield.

(6) Oxide layer breakdown voltage

The dependence of oxide layer breakdown voltage on impurity concentrations was examined. The samples (A-E) were prepared using various cleaning chemicals and under various oxidation conditions. The result is illustrated in Fig. 8. This shows that Na atoms apparently decrease the breakdown yield while Fe atoms have different effects. The role of Fe atoms is not clear yet, however, it is possible that they may contribute to the suppression of the breakdown failure.

## 4. Conclusion

It has been proved that the VPD is the most efficient and reliable method for analyzing the ultratrace impurities both in the bulk substrate and on the wafer surface. In this method, the material is oxidized and decomposed by hydrofluoric acid vapor. It is applicable to the practical analysis and the evaluation of materials and the environment. This method is also suitable for monitoring wafer surface cleanness in LSI manufacturing process.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