Cleaning Technology and Analysis Technology for Hydrocarbon Contamination on Si Wafer Surface

Naomichi YONEKAWA, Sinichi YASUI and Tadahiro OHMI
Department of Electronics, Faculty of Engineering, Tohoku University
Aza Aoba, Aramaki, Aoba-ku, Sendai, Japan, 980

This report describes our study on the single-wafer–dynamic–cleaning–technology. The dynamic cleaning process was evaluated in comparison with the batch process. The organic impurities can be removed perfectly. The dynamic cleaning efficiency has been found dependent on rotation speed. The spinning method is more effective in removing organic impurities from the wafer surface. And then, hydrocarbons are detected by FT-IR-ATR.

Previoufly, FT-IR-ATR is not calibrated. However, we can develop the calibration method which is the Langmuir–Blodgett monolayer.

1. INTRODUCTION

When Si wafer is exposed to the atmosphere, the growth of native oxide is generally known. Moreover, a great amount of organic impurities adhere onto Si wafer surface easily. Si wafer, therefore, must not be exposed to the ambience. For that reason, advanced N$_2$ sealed wet station is required.

Previously, hydrocarbons on the Si wafer surface are analyzed by FT-IR-ATR. The FT-IR-ATR method can detect the hydrocarbons directly. However, that method is not calibrated. Therefore, we have developed calibration method with Langmuir–Blodgett–monolayer.

2. SYSTEM DESCRIPTION

Figure 1 shows the structure of the Dynamic–cleaning system. When the wafer is cleaned, the wafer is mounted onto a special chuck in the cleaning chamber. Inside of the chamber is constantly purged with high purity N$_2$ gas in order to prevent contamination from the air. Cleaning chemicals, ozonized ultrapure water and ultrapure water are introduced onto the Si wafer through a mobile nozzle while the wafer is being rotated. Using ozonize is advantageous for the environment and the air condition of the cleanroom, because ozonized ultrapure water is not necessary for recovery of waste. Moreover, ozonized ultrapure water is a low temperature process.

It has been found that a previous data demonstrates effect of ozonized ultrapure water for organic impurities removal in dipping mode. We showed that dynamic cleaning method can perfectly eliminate for metallic impurities like as Cu. Similarly, the effectiveness of the removal for organic contaminants is proven by the experimental results in this report. The experimental results demonstrate that the dynamic cleaning method is more effective for removal of organic impurities from the wafer surface than the conventional dipping cleaning.

For the analysis of organic contaminants on wafer surfaces, we use the FT-IR-ATR method (Fig. 2). Generally, the method of using both–side–polished wafers as ATR–prism is used. In case of this method, peaks are high and sharp. However, this method can not confirm a very small amount of organic contaminants. This is because background spectrum for measurement is influenced by the Si wafer itself. This problem is solved by using an ATR–prism made from other materials, like as germanium. Using other materials as ATR–prism can correct exact background spectrum. Therefore, a very small amount of organic impurities can be detected.

3. CALIBRATION FOR FT-IR-ATR METHOD

Previously, FT-IR-ATR method could not be calibrated. Therefore, it is difficult to estimate the amount of organic impurities. However, we have developed the calibration method which is measurement of Langmuir–Blodgett monolayer (Arachidic acid). Some kind of Langmuir–Blodgett monolayer are measured by FT-IR-ATR, such as monolayer, 1/2 layer, 1/4 layer and 1/8 layer. These molecule–films have a good linearity and a good reproducibility. Therefore, we can calibrate the FT-IR–ATR method.

Figure 3 shows the FT–IR spectrum of monolayer, 1/2 layer, 1/4 layer and 1/8 layer. Figure 4 shows the calibration curves for FT-IR-ATR of each polarization by Langmuir–Blodgett monolayer. Linearity of absorbance of each layer is confirmed by this figure. Therefore, these results demonstrate that the calibration of FT-IR-ATR has been established.

4. REMOVAL OF ORGANIC IMPURITIES

Figure 5 shows the FT–IR spectrum of hydrocarbons. These wafers were unintentionally contaminated by organic impurities. As–received wafers were treated by each cleaning methods and agents. This figure demonstrate that as–received wafer is
contaminated. Moreover, the conventional dipping cleaning can not remove organic contaminants, because hydrocarbon remains on the wafer surface. However, the combination of the dynamic cleaning with ozonized ultrapure water can completely remove the hydrocarbons from the wafer surface.

Figure 6 shows the spectrum of intentionally contaminated wafers and the spectrum of after cleaned wafers. For this experiment of cleaning efficiency, intentionally contaminated wafers with each surfactant as organic contaminants were used. This result demonstrates that the SPM solution and the ozonized ultrapure water have almost the same cleaning efficiency. And these two oxidizing agents can not remove organic impurities in dipping mode perfectly. However, organic impurities can be completely removed by a combination of dynamic cleaning method with ozonized ultrapure water. This is because the reaction is accelerated by chemical mixing and formation of reaction products, and which are removed immediately by the constant flow of chemicals induced by the centrifugal force.

In these cases, contaminated level of each wafers from figure 5 are:

As-received wafer is about 0.1 molecule layer of Arachidic acid. Intentionally contaminated wafer with non-ionic surfactant is about 1.7 molecule layer of Arachidic acid.

5. CONCLUSIONS

The very small amount of hydrocarbons can be detected by FT-IR-ATR method and the calibration method for FT-IR-ATR could be established by using of Langmuir-Blodgett monolayer. Therefore, it is possible to confirm cleanliness level of organic impurities on Si wafer surface.

The organic contamination free Si wafer surface for next generation can be realized by combination of Dynamic cleaning system with the ozonized ultrapure water. And it is essential to realize the advanced cleaning process to make the ultraclean wafer surface. It is necessary, therefore, to develop a new cleaning method and a new cleaning system. Following the results have been obtained by a simulation test. ;

1. The method of measurement for a very small amount of organic impurities on Si wafer surface was established.
2. The calibration method for FT-IR-ATR is established by the measurement of Langmuir-Blodgett monolayer.
3. Dynamic cleaning can effectively remove the organic contaminants which are difficult to remove by conventional dipping cleaning.
4. Combination the dynamic cleaning method with ozonized ultrapure water is very effective and environment friendly.

The dynamic cleaning method has excellent characteristic for the removal of organic impurities. The analysis of hydrocarbons has become possible. Therefore, the efficiency of dynamic cleaning method can be confirmed.

6. ACKNOWLEDGMENTS

The authors would like to express their sincere thanks to Nisso Engineering Co., Ltd. and M.T.C Japan Co., Ltd. for supplying "Advanced Chemical Distribution System" and "Advanced Spinner System" respectively.

7. REFERENCES

Fig. 1 Dynamic Cleaning System

Fig. 2 FT-IR-ATR method

Fig. 3 FT-IR spectrum of Langmuir-Blodgett monolayer (1/8, 1/4, 1/2, mono)

Fig. 4 The calibration curve for FT-IR-ATR by Langmuir-Blodgett monolayer

Fig. 5 Comparison of removal efficiency of various cleaning method for unintentionally contaminated wafer

Fig. 6 Cleaning efficiency of each cleaning method for the removal organic impurities (wafer were intentionally contaminated by each surfactant)