

# Development of Batch Type Isotropic Gas SiO<sub>2</sub> Etching System Using HF Gas

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We have developed a new batch-type isotropic gas etching system that does not utilize H radicals. The isotropic gas etching process is used in semiconductor manufacturing to etch pattern structures and requires high aspect ratio etching without causing damage to the underlying layer. Our previous release, RISE-300, was a batch-type gas etching tool that utilized H radicals and was easy to handle due to the absence of highly corrosive gases like HF. However, it was difficult to control the etching distribution within each batch. In recent years, conventional processes have become insufficient to meet the performance requirements of device manufacturers. Our new batch-type isotropic gas etching process, which does not utilize H radicals, outperforms conventional methods in terms of wafer-to-wafer uniformity and step coverage. Additionally, this new process allows for precise control of etching distribution within the wafer plane.

## 1. Introduction

NAND and DRAM technologies have continued to evolve through the development of 3D device structures and the integration of transistor structures with high density. In the case of 3D NAND, the number of layers in the device structure is being increased to further enlarge capacity. Isotropic gas etching, a process that utilizes the chemical reaction between HF and NH<sub>3</sub> to perform tasks such as removing natural oxide films on silicon, can be used as a means of uniformly processing 3D devices and other structures with high aspect ratios. In 3D NAND devices, the isotropic gas etching process is used to remove the natural oxide film formed on the bottom surface of channel holes. As 3D NAND structures evolve, requirements are increasing not only for coverage performance, but also for wafer-to-wafer uniformity of etching amount distribution as well as in-wafer uniformity of the etching amount. This paper describes the development of a batch-type isotropic gas etching process to achieve higher process performance.

## 2. Batch-type isotropic gas etching process for SiO<sub>2</sub>

This section describes the differences between the

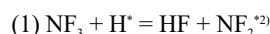
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conventional batch-type isotropic gas etching process and the new method, and compares the results of a basic evaluation of process performance.

### 2.1 Conventional process using hydrogen radicals

In the conventional process, hydrogen radicals are utilized for the generation of the etchant<sup>(1)</sup>. To be specific, the chemical reaction formulas for the process are as follows:



In formulas (1) to (3) above, hydrogen radicals play a role in producing the HF molecules depicted in formula (1). In formula (2), the produced HF molecules react with NH<sub>3</sub> molecules to form NH<sub>4</sub>F molecules. The NH<sub>4</sub>F molecules react with SiO<sub>2</sub> as an etchant and transform into SiF<sub>6</sub>(NH<sub>4</sub>)<sub>2</sub>. The SiF<sub>6</sub>(NH<sub>4</sub>)<sub>2</sub> is evaporated by heating in a vacuum chamber and removed from the wafer surface. At this stage, the etching of SiO<sub>2</sub> is completed. The equipment configuration for this process is shown in Fig. 1. To ensure that the reactions mentioned in (1) to (3) occur either in the gas phase or on the wafer surface within the reaction chamber, the system is designed in a way that the mixed gas containing hydrogen radicals, introduced from the applicator, is conveyed into the reaction chamber through a dispersion mechanism, where it is mixed with NF<sub>3</sub> gas introduced from a separate system. The vertical boat hosts 57 wafers, each with its own gas

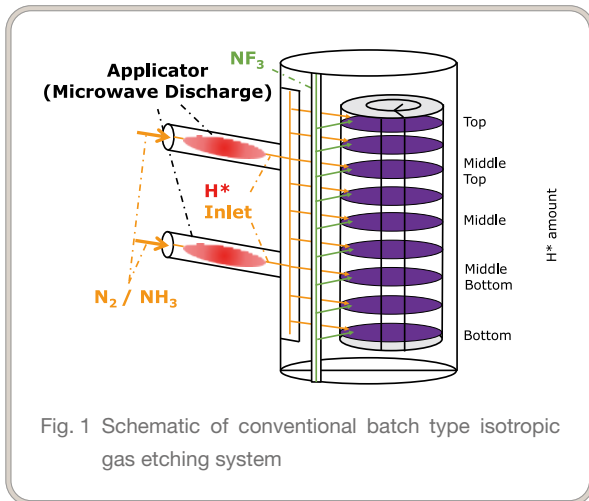


Fig. 1 Schematic of conventional batch type isotropic gas etching system

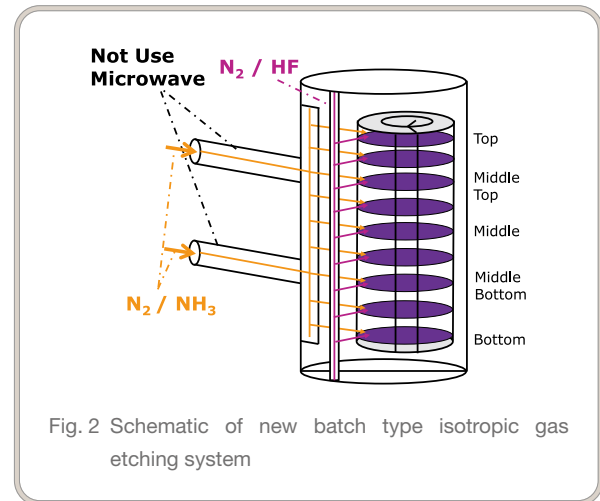


Fig. 2 Schematic of new batch type isotropic gas etching system

inlet. The 57 wafers are organized into the following five regions, from top to the bottom: Top, Middle Top, Center, Middle Bottom, and Bottom. The Middle Top and Middle Bottom are the regions located in front of the applicator. In the aforementioned conventional process, issues arise when hydrogen radicals are directly sprayed onto the wafer. We will describe the details below in sections 2.3 and 2.4.

## 2.2 New process using no hydrogen radicals

Our new process utilizes HF gas as the etchant generation method. To be more specific, the chemical reaction formulas for the process are as follows:



Formulae (4) and (5) are identical to formulae (2) and (3) in the conventional process. The key difference from the conventional process is the absence of a reaction equivalent to formula (1) which involves the use of hydrogen radicals. The equipment configuration for our new process is shown in Fig. 2. HF molecules are supplied directly as a gas, eliminating the need to supply hydrogen radicals. The etchant is produced through the reaction of HF gas and NH<sub>3</sub> gas introduced separately either in the gas phase or on the wafer surface within the processing chamber. As in the conventional process, 57 wafers and their gas inlets are arranged. In the aforementioned new process, hydrogen radicals are not sprayed directly onto the wafers.

## 2.3 Hydrogen radicals and wafer temperature rise

The difference between the conventional and new systems described in sections 2.1 and 2.2 is the presence of hydrogen

radicals. In the conventional process, when hydrogen radicals are sprayed onto the wafer surface in an active state, heat transfer occurs during deactivation, leading to an increase in the wafer temperature. The rate of temperature increase is proportional to the quantity of hydrogen radicals, and the wafer temperature during etching rises in regions where more hydrogen radicals are sprayed. Fig. 3 shows a schematic diagram of the distribution of hydrogen radicals sprayed in each region. In the Middle Top and Middle Bottom regions, which are located in front of the applicator, more hydrogen radicals are supplied than in the other regions. This causes etching to be performed at a relatively high temperature relative to the other regions, which adversely affects process performance. In the new process, in contrast, since there is no supply of hydrogen radicals, there is no temperature distribution caused by hydrogen radicals. Fig. 4 shows the actual measured values of wafer temperature during etching for both processes. In the conventional process, a temperature

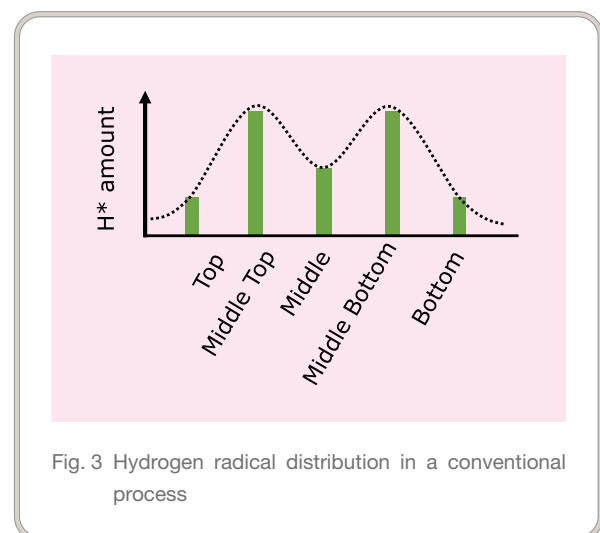


Fig. 3 Hydrogen radical distribution in a conventional process

difference was observed between the regions in front of the applicator and the other regions, indicating the influence of the hydrogen radicals.

### 2.4 Wafer-to-wafer temperature and etching rate distributions

This process is operated within a temperature range where the adsorption rate of  $\text{NH}_4\text{F}$  molecules, utilized as the etchant, becomes the rate-limiting factor for etching rate. As the temperature rises, the etching rate decreases. Fig. 5 shows the relationship between the temperature and the etching rate in this process. Based on the results shown in Fig. 4 and the relationship shown in Fig. 5, Based on the results depicted in Figure 4 and the relationship presented in Figure 5, it can be anticipated that the new process, which exhibits a lower distribution of temperatures from wafer to wafer, will provide improved uniformity in the etching rate across wafers. A comparison of the wafer-to-wafer etching amount distribution is shown in Fig. 6. The figure shows that the new process improves uniformity by increasing the amount of etching in front of the applicator.

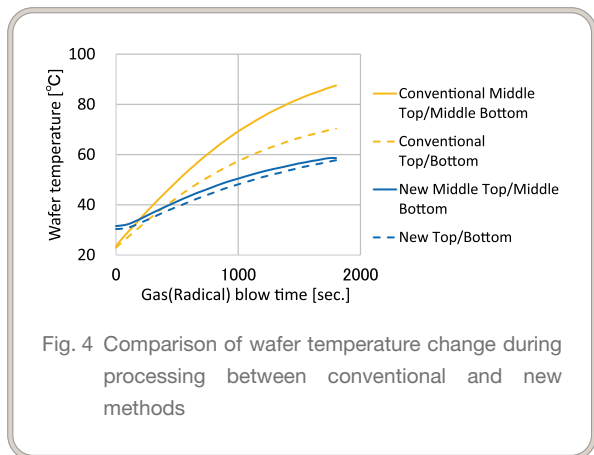


Fig. 4 Comparison of wafer temperature change during processing between conventional and new methods

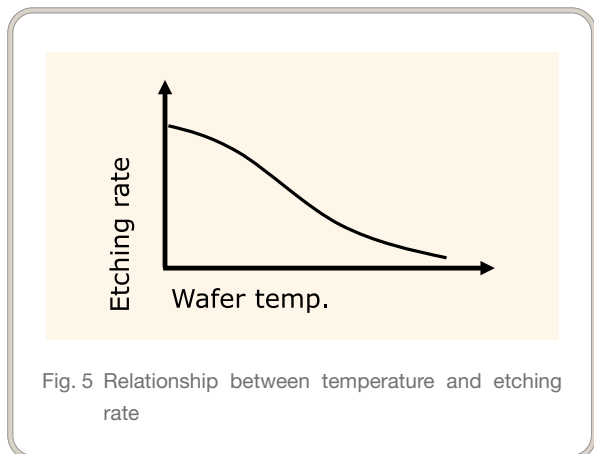


Fig. 5 Relationship between temperature and etching rate

### 2.5 Film type selectivity of etching rate

Fig. 7 shows the etching selectivity between SiN films and poly-Si film under the same conditions as in Fig. 6. The figure shows that the new process etch a higher selectivity the  $\text{SiO}_2$  film compared to the conventional process. This indicates that the active by-product molecules containing F in formula (1) act as an etchant for the SiN film and poly-Si film. In processes that use isotropic gas etching, it is sometimes required to etch a small amount of Si at the same time as etching  $\text{SiO}_2$ , and in these cases, combining the conventional process and our new process can provide a process with a wide margin.

## 3. Step coverage when processing high aspect ratio structures

Since this process is commonly employed for handling high aspect ratio structures, achieving good step coverage of the etching amount is crucial for process performance.

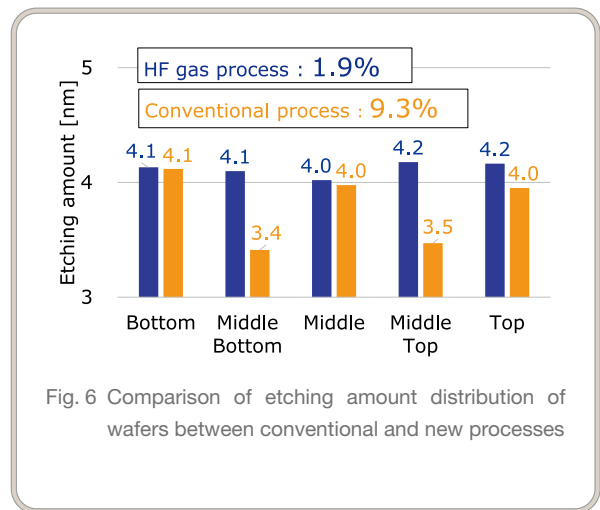


Fig. 6 Comparison of etching amount distribution of wafers between conventional and new processes

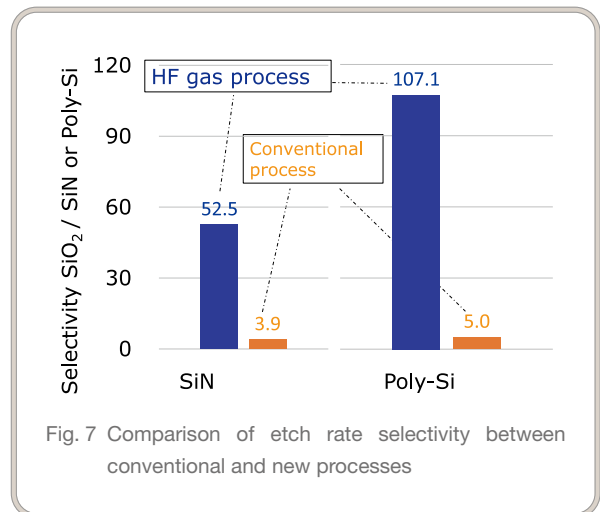
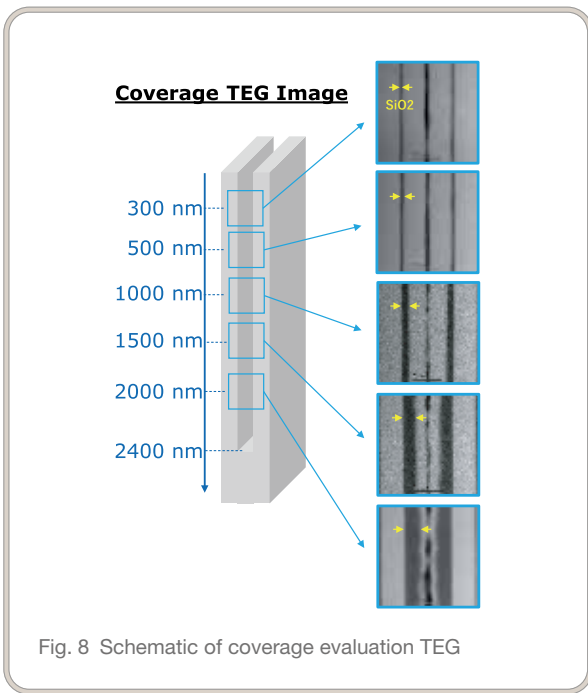


Fig. 7 Comparison of etch rate selectivity between conventional and new processes

This section presents the step coverage performance of both the conventional process and the new process utilizing HF gas. Additionally, methods for enhancing step coverage are introduced.

### 3.1 Step coverage performance of the conventional and new processes

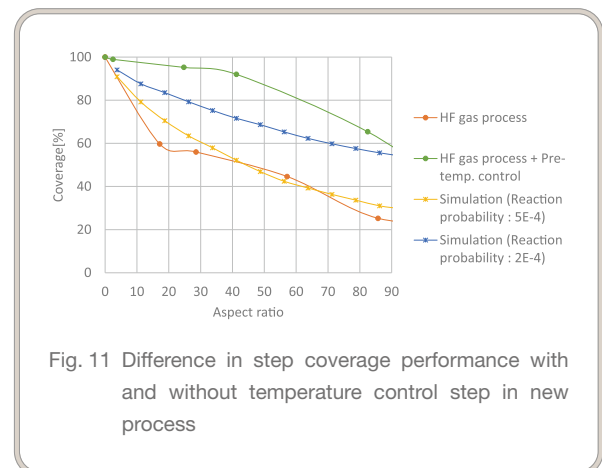
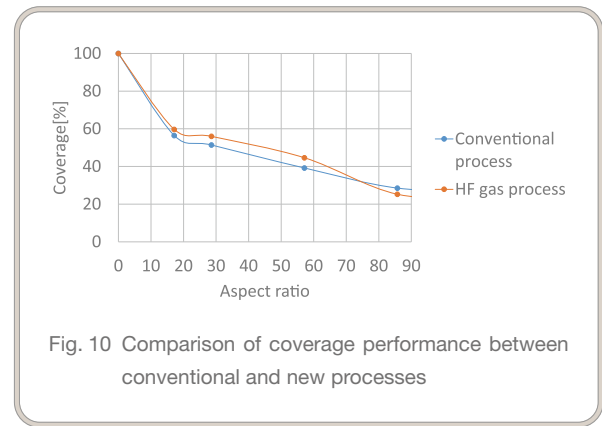
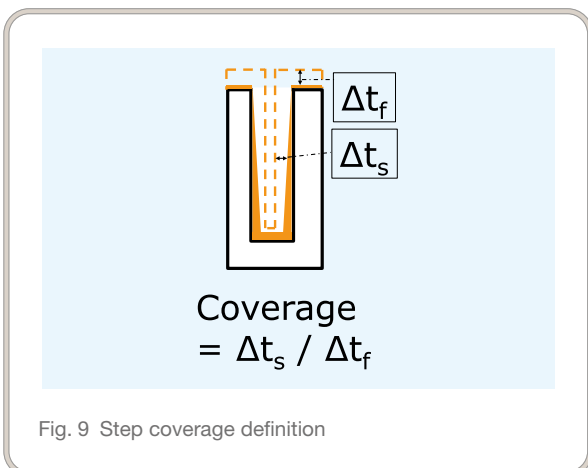
To evaluate coverage performance, we fabricated a TEG featuring high-aspect trench geometry. Fig. 8 shows a schematic diagram of the TEG and cross-sectional TEM image of the etched TEG utilized for the evaluation. The TEM image reveals an increase in SiO<sub>2</sub> film thickness in the direction of the trench depth, indicating a decrease in etching amount with increasing pattern depth. By quantifying this reduction relative to the etching depth direction, the



performance of step coverage can be evaluated. In this paper, we define the coverage performance as the ratio of the etching amount  $t_s$  at a given trench depth to the etching amount  $t_f$  outside the trench area, as shown in Fig. 9. Fig. 10 compares the results of the coverage performance under the same conditions as the results shown in Fig. 6. The results show no difference in coverage performance. Although the two processes differ in terms of whether the HF molecules are generated from hydrogen radicals or are directly supplied as HF gas, it is thought that the reason the coverage performance is the same is because the chemical reaction of the etching is the same.

### 3.2 Improving step coverage

We have developed a method to improve the step coverage of this process. In this method, the wafer temperature is adjusted to a predetermined temperature before the etching process is initiated, which improves step coverage by adjusting the probability of the etchant adsorbing onto the wafer. The results of evaluating this technique are shown in Fig. 11. The figure clearly shows that the inclusion of the temperature control step leads to improved coverage. Furthermore, when



comparing the step coverage results with those predicted by Monte Carlo simulations, the results without the temperature control step align closely with the simulation results where the adsorption probability is set to  $5 \times 10^{-4}$ . This shows that the coverage depends on the adsorption probability of the etchant. Meanwhile, when the temperature control step is added, the results exhibit a trend similar to a decreasing curve seen in Monte Carlo simulations with an adsorption probability of  $2 \times 10^{-4}$ . Although the shapes of the curves may vary slightly, this suggests that the adsorption probability of the etchant in the presence of the temperature control step is likely to be less than half compared to the process without the temperature control step. As mentioned earlier, coverage performance varies with temperature, so temperature control is important. As described in Section 2, in the conventional process, it is difficult to control the etching temperature due to the effect of the hydrogen radicals. That being the case, the new process is superior in terms of step coverage performance.

#### 4. New hardware development: In-plane distribution adjustment mechanism

In this section, we introduce a mechanism we developed for our new isotropic gas etching process that adjusts the etching distribution within the wafer plane. This mechanism is an effective countermeasure against the pattern loading effect, which is always a problem in batch-type systems.

#### 4.1 Pattern loading effect

In a batch-type isotropic gas etching system, etching gas is sprayed from the side onto wafers placed on a rotating boat, as shown in Fig. 1 and Fig. 2. Because the boat is rotating, the etching distribution is rotationally symmetrical within the wafer plane, but a distribution in the etching amount occurs between the outer periphery and the center. This is caused by a change in the partial pressure of the etchant gas within the wafer surface as the etchant is consumed while advancing towards the exhaust port. Naturally, this non-uniformity in the distribution increases as the surface area of the wafer consuming the etchant enlarges. This phenomenon is referred to as the pattern loading effect, as shown schematically in Fig. 12. Given that wafers with diverse pattern shapes are processed in the device fabrication process, the extent of this effect varies depending on the specific processing target. Consequently, it is crucial to implement a countermeasure that can be adjusted according to the magnitude of the effect.

#### 4.2 In-plane distribution adjustment mechanism

For our new etching process utilizing HF gas, we have developed a method for continuously adjusting the partial pressure of the etchant within the wafer plane. A schematic is shown in Fig. 13. This approach capitalizes on a key characteristic of our process, which involves mixing the raw material gases for the etchant within the processing chamber. By changing the point where the raw material gases are mixed, it is possible to adjust the partial pressure

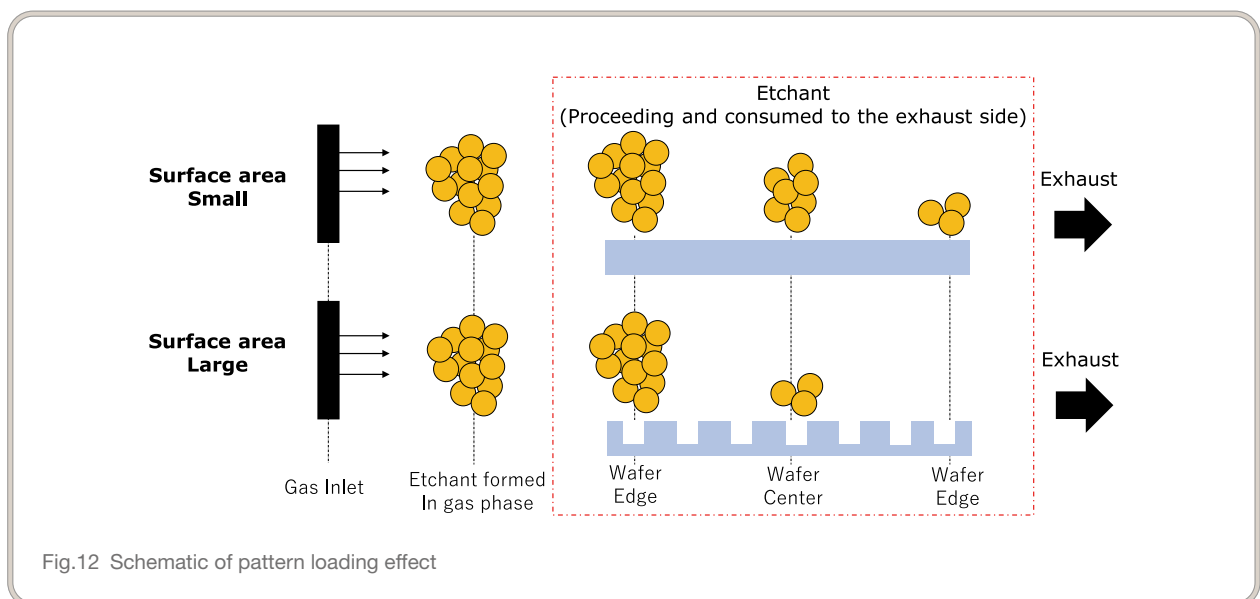


Fig.12 Schematic of pattern loading effect

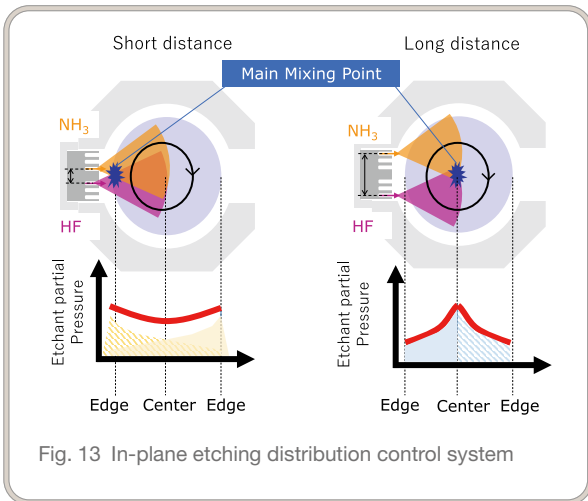


Fig. 13 In-plane etching distribution control system

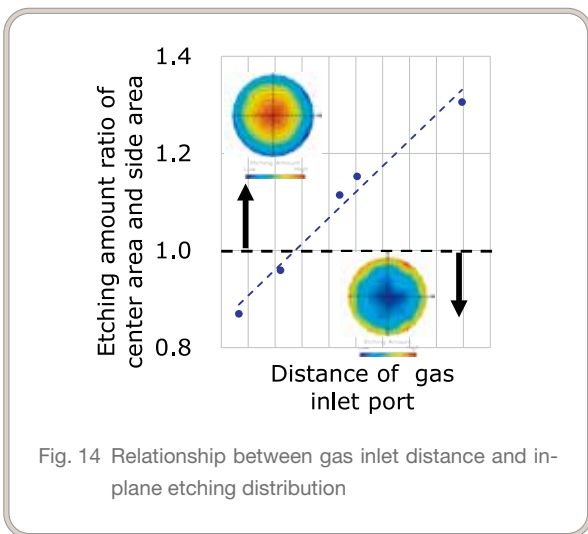


Fig. 14 Relationship between gas inlet distance and in-plane etching distribution

of the etchant within the wafer plane. Specifically, in the new process, we continuously adjust the peak position of the partial pressure of the  $NH_4F$  gas within the wafer plane by continuously changing the distance between the HF gas inlet and the  $NH_3$  gas inlet, which are arranged parallel to each other. Fig. 14 shows the relationship between the distance between the HF and  $NH_3$  gas inlets and the ratio of the etching amount at the center to the periphery. The figure shows that the in-plane etching amount distribution changes linearly relative to the distance between the gas inlets. By utilizing this mechanism to control the partial pressure of the etchant within the wafer plane to match the magnitude of the pattern loading effect, various patterned wafers with different surface areas can be uniformly etched.

## 5. Summary

We have developed a new batch-type isotropic gas etching system that does not use hydrogen radicals. Upon evaluating our new method and comparing it to the conventional approach, we observed superior results in terms of uniformity of wafer-to-wafer etching amounts and coverage. In addition, we also developed a new method to control the etching distribution within the substrate plane as necessary.

## References

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- 2) A. Matsugi et al.: "Gas-phase reaction mechanism in chemical dry etching using  $NF_3$  and remotely discharged  $NH_3/N_2$  mixture." RSC Advances 10.51 (2020): 30806-30814.