

CHAPTER FOUR

FABRICATION OF TWO DIMENSIONAL AIR-BRIDGE III-NITRIDE PHOTONIC CRYSTALS

4.1 Introduction

As demonstrated in Chapter 2, to achieve a PC with its band gap around the emission wavelength of GaN QDs, periodicity around 150 nm is requisite. Although there are plenty of fantastic features we could expect from 2D PC consisting of GaN QDs, the status quo, however, is not so optimistic. To achieve designed PC patterns into the III-nitride materials, especially in the case of pattern with periodicity of 150 nm or even smaller, abrupt vertical etching profiles and minimum degradation must be assured during each step of the nanofabrication process. On the other hand, since recent researches on III-nitride photonic crystal have been mainly focused on its application to light emitting diodes (LEDs) for enhancing light extraction efficiency, several work have been report on the fabrication of III-nitride photonic crystal with a high Ga content¹³⁻¹⁷ and little is known about the case of high Al content and periodicity as small as 150 nm. Therefore one of the most important parts of our study is to establish the suitable nanofabrication process for AlN-based photonic crystal with small periodicity. We carried out a series of systematic experiments to investigate the parameters and their effects on the fabricated sample during each process step and eventually established the suitable nanofabrication process for two dimensional AlN-based photonic crystal with the periodicity of 150 nm and smaller.

In the following section 4.2, reactive ion etching (RIE) system, which is an important technique employed for the etching of III-nitride material in this study will be demonstrated. Fabrication procedure will be demonstrated in section 4.3. Section 4.4, 4.5 and 4.6 show the optimization experiments for the photoresist developing, the fabrication of SiO₂ mask and etching of III-nitride, respectively. Finally conclusion remarks will be made in section 4.7.

4.2 Reactive Ion Etching (RIE)

III-nitride is chemically stable and very insoluble in most common etchants at room temperature. Wet chemical etching of III-nitride shows isotropic etching profiles and slower etching rates than the dry etching technique.⁵⁵ Therefore, dry etching is an attractive alternative in this respect, from which one can achieve controlled degrees of anisotropy, high etch rates, material selectivity, low damage, and the ability to control an etch stop. On the other hand, inductively coupled plasma (ICP) offers an alternative high-density plasma technique to etch III-nitrides.^{56,57} As widely recognized, ICP source is easier to scale up than the other dry etching system such as electron cyclotron resonance (ECR) and has the merits of relatively low cost and availability of truly automatic matching networks for tuning of the charge. In this study, etching of SiO₂ mask and III-nitride material were performed utilizing Samco RIE-101ip and Samco RIE-200ip reactive ion etching (RIE) systems, respectively. ICP are employed to generate the plasma.

Fig. 4.1 schematically depicts the reactor of RIE system used for the etching of III-nitride. Noting that RIE used for SiO₂ mask etching is similar. The RIE system used in this study is a load-locked stainless-steel chamber system. The substrate is placed inside the reactor in which several gases are introduced. ICP plasmas are formed in a

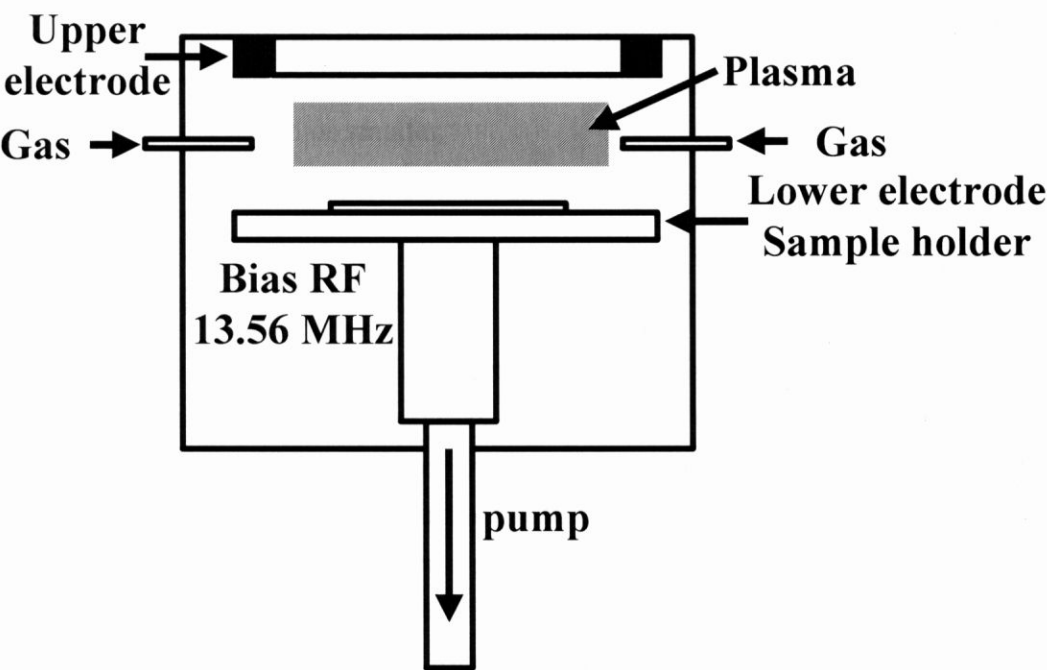


Fig. 4.1 Schematic diagram of RIE reactor

dielectric vessel encircled by an inductive coil into which RF power is applied, breaking the gas molecules into ions. A strong magnetic field is induced in the center of the chamber that generates a high-density plasma due to the circular region of the electric field that exists concentric to the water cooled inductive coil. And the substrate is cooled by He gas flowing from the electrostatic chuck. The inductive source is an 11 cm-diam copper coil connected to a 1 KW rf generator operating at 13.56 MHz via an autotuning matching network.

Generally in a RIE system, the ions are accelerated towards, and reacts at, the surface of the material being etched, forming another gaseous material. This is known as the chemical part of RIE. There is also a physical part which is similar in nature to the sputtering deposition process. If the ions have high enough energy, they can knock atoms out of the material to be etched without a chemical reaction. It is a very complex task to develop dry etch processes that balance chemical and physical etching, since there are many parameters to adjust. By changing the balance it is possible to influence the anisotropy of the etching, since the chemical part is isotropic and the physical part is highly anisotropic. The combination between chemical and physical etching will directly yield influence to the shapes of etched sidewalls. In this particular study, we carried out a throughout investigation of the parameters and the roles they are playing during the nanofabrication process. Also, since our goal is to optimize the dry etching process for III-nitride PC with periodicity as small as 150 nm or even smaller, the behavior of gas flux during the etching process may be different from the ones with bigger size. Taking all of these possibilities into consideration, we carried out a systematic investigation seeking for the optimal fabrication condition for III-nitride PC with periodicity of 150 nm or smaller.

4.3 Fabrication Procedure

Samples used for optimization were 120 nm thick AlN films deposited on SiC substrates. The thickness is appropriately the same with that of the sample consisting of GaN QDs. Also, since Al content of the samples containing GaN QDs is higher than 90%, we consider the condition optimized based on AlN samples can be applied to QDs samples as well. The AlN films were grown by MOCVD. Trimethylaluminum (TMA) and NH_3 were used as the source materials for Al and N, respectively. The optimization experiments were carried out by the following procedure:

1. Deposition of SiO_2 with various thickness values of 130 nm, 195 nm and

- 260 nm by sputtering upon AlN films.
- Coating of photoresist over the sample surface homogeneously using a spin coater.
 - Fabricating pattern onto photoresist layer utilizing electron beam (EB) lithography.
 - Photoresist developing to transfer pattern into photoresist layer (as shown in Fig. 4.2(a)).
 - Transfer of pattern into SiO₂ layer by RIE etching of SiO₂ that is not protected by photoresist (as shown in Fig. 4.2(b)).
 - Transfer of pattern into III-nitride layer by RIE etching (as shown in Fig. 4.2(c)).
 - Removal of remaining SiO₂ mask using HF.
- The purpose of our optimization experiment is to establish the suitable fabrication

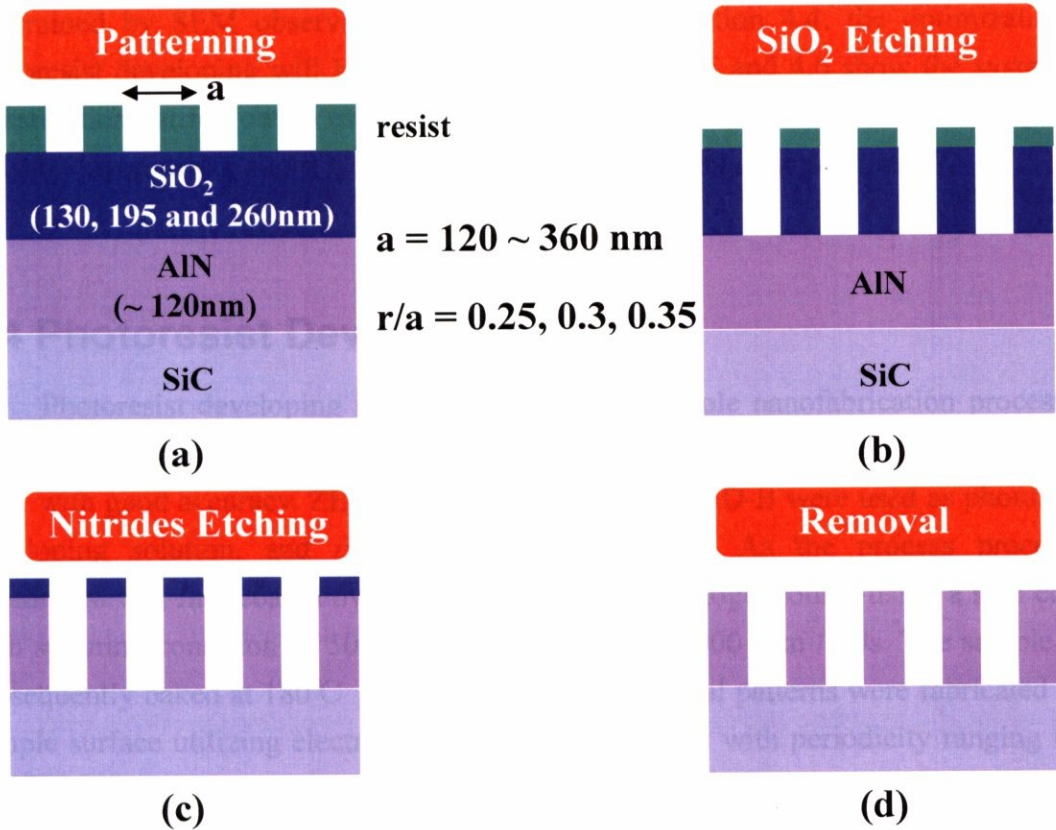


Fig. 4.2 Schematic description of fabrication procedure: (a) patterning, (b) SiO₂ etching, (c) III-nitride etching and (d) removal of SiO₂ mask.

process for AlN-based two dimensional PC with periodicity of 150 nm or smaller

utilizing RIE dry etching technique. During the experiment, we must find out the optimal conditions for the following three processes, respectively:

1. The developing condition for photoresist.
2. The etching condition for SiO₂ mask.
3. The etching condition for AlN layer.

To establish the optimal condition for photoresist developing, the effects of developing temperature and developing time on the developed pattern morphology have been investigated. The common purpose for the dry etching of SiO₂ mask and AlN layer is to find out the suitable conditions that promise **abrupt vertical etching profile** and **smooth etching morphology**. The etching of SiO₂ and III-nitrides were carried out using RIE in the CF₄ (C₄F₈) / Ar / O₂ and Cl₂ / Ar (Xe) chemistry, respectively. There are several parameters that play key roles during the RIE etching process: The **source power** and **bias power** of RIE system, **the mixing ratio** and **the pressure** of the etching gases. A series of systematic study has been carried out to investigate the effects of the parameters mentioned above on the vertical profile and etched morphology determined by SEM observation. In the following section 4.4, the optimization of photoresist developing will be demonstrated. Section 4.5 and 4.6 show the systematic investigation carried out to establish the suitable dry etching conditions for SiO₂ mask and AlN layer, respectively. Conclusion remarks will be made in section 4.7.

4.4 Photoresist Developing

Photoresist developing is the first step of the whole nanofabrication process. In this step, we must make sure the designed patterns can be transferred into photoresist layer with good accuracy. ZEP 520-22, ZEP-N50 and ZMD-B were used as photoresist, developing solution, and rinse solution, respectively. As the process procedure, photoresist was first coated over the sample surface homogeneously using a spin coater with spinning condition of 500 rpm / 5s followed by 4000 rpm / 60s. The sample was subsequently baked at 180°C for 20 min. Photonic crystal patterns were fabricated onto sample surface utilizing electron beam (EB) lithography with periodicity ranging from 120 nm to 360 nm and r/a ratios of 0.25, 0.3 and 0.325, respectively. Our EB lithography technique promises accurate pattern transfer even to the periodicity as small as 120 nm. The developing of photoresist was first carried out at room temperature. We found it difficult to control the developing time precisely due to the too fast developing speed. We therefore decreased the developing temperature to 10°C, expecting more

feasibility of temperature controllability. By optimizing the developing time and rinse

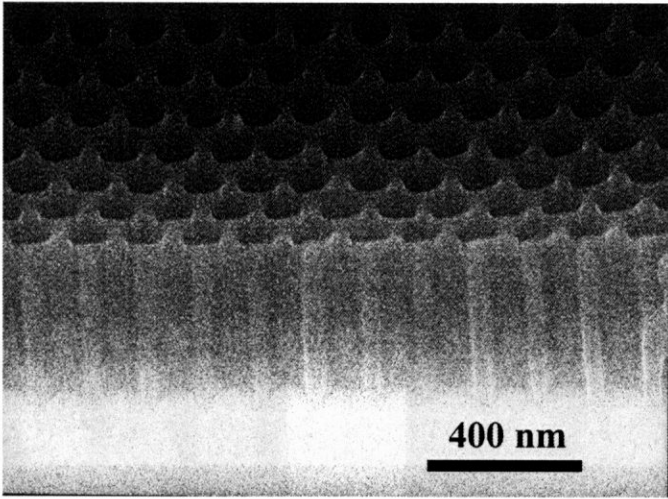


Fig. 4.3 Cross-sectional SEM image of pattern transferred into photoresist with periodicity of 140 nm and r/a ratio of 0.325.

time, we could transfer the patterns with periodicity as small as 140 nm and r/a ratio up to 0.3 into photoresist layer accurately. To the pattern with r/a ratio of 0.325, we succeeded to transfer the pattern with periodicity as small as 150 nm. Figure 4.3 shows the cross-sectional SEM image of sample with periodicity of 140 nm and r/a of 0.3. The thickness of photoresist is approximately 380 nm. One can observe the pattern was transferred into photoresist layer with abrupt vertical profile and good accuracy.

4.5 Fabrication of SiO₂ mask

4.5.1 Alternative Gas Supply Method

The abrupt vertical etching profile of SiO₂ mask is crucial since any deterioration caused in this step will yield critical influence to the subsequent III-nitride etching. The etching of SiO₂ was carried out utilizing CF₄ (C₄F₈) / Ar / O₂ chemistry by RIE. SiO₂ films with thickness of 130 nm, 195 nm and 260 nm were used for optimization experiments. We started from the following condition that has been employed for SiO₂ etching until then:

Source power 300 W, bias power 200 W, C₄F₈ 5 cc, Ar 5 cc, O₂ 3 cc and gas pressure 0.75 Pa.

The first improvement employed is to adopt CF₄ instead of C₄F₈ as etching gas. Since during the etching of C₄F₈-based chemistry polymer is generated as etching residues, which is difficult to dissolve at the sample surface. Another trend found under

the above condition is the significant damage to the photoresist. This is due to the continuous introduction of O₂ gas. Taking these issues into considering, we carried out the SiO₂ etching under the following condition 1: **Source power 125 W, bias power 300 W, CF₄ 5 cc, Ar 8 cc and gas pressure 0.75 Pa.**

SEM observation revealed significant appearance of etching residues inside the

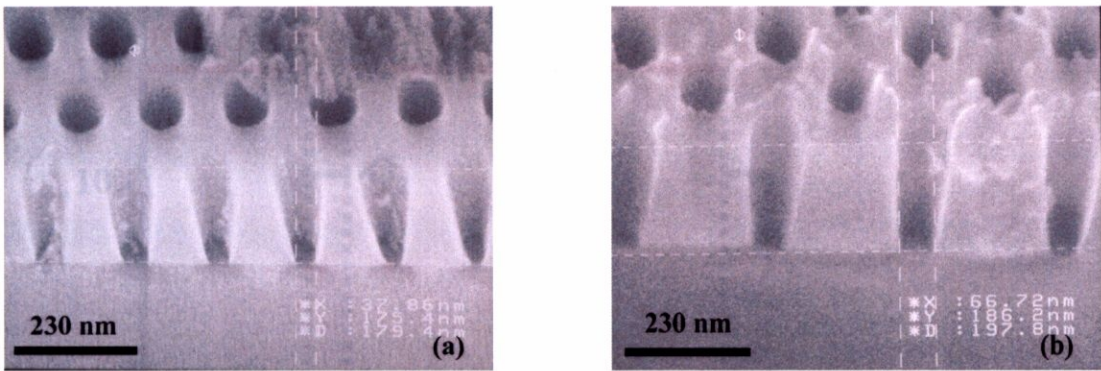


Fig. 4.4 (a) Cross-sectional SEM image of SiO₂ mask with periodicity of 150 nm and r/a ratio of 0.25 fabricated under continuous gas supply condition 1 and 15 sec O₂ ashing. (b) Cross-sectional SEM image of SiO₂ mask with periodicity of 160 nm and r/a ratio of 0.25 fabricated under alternate gas supply of reactive gas and O₂.

airholes and the deterioration of vertical etching profile especially to the periodicity smaller than 200 nm. We consider that in the case of a 2D PC with small periodicity, the removal of etching residues becomes more difficult with the progress of etching, eventually resulting in the isotropic etching of SiO₂ mask. The residues could not dissolve completely even under an additional 15 seconds of ashing under O₂ with the flux of 10 cc. Figure 4.4 (a) shows the cross-sectional SEM image of SiO₂ mask with periodicity of 150 nm and r/a ratio of 0.25 under condition 1 followed by 15 seconds O₂ ashing. As mentioned in section 4.2, the balance between the highly anisotropic physical part and the highly isotropic chemical part is essential upon the seeking for the suitable condition. To improve the vertical profile of the airhole sidewall, an increase in bias power is one solution. Since the enhancement of ion energy by the increased bias power will yield an enhancement of physical etching, eventually resulting in the improvement of vertical etching profile. However, we found it not sufficient enough in this case due to the limitation of our equipment. On instead, we developed an etching process by supplying O₂ and reactive gases (CF₄/ Ar) alternatively with a time interval. Figure 4.5 schematically demonstrates the recipe of this alternate gas supply method named condition 2: The parameters of source power, bias power, reactive gases (CF₄/ Ar) and gas pressure are the same with those of condition 1, in stead of an introduction of 5 sec

ashing by O₂ gas for three times with a interval of 50 seconds. Figure 4.4 (b) shows the

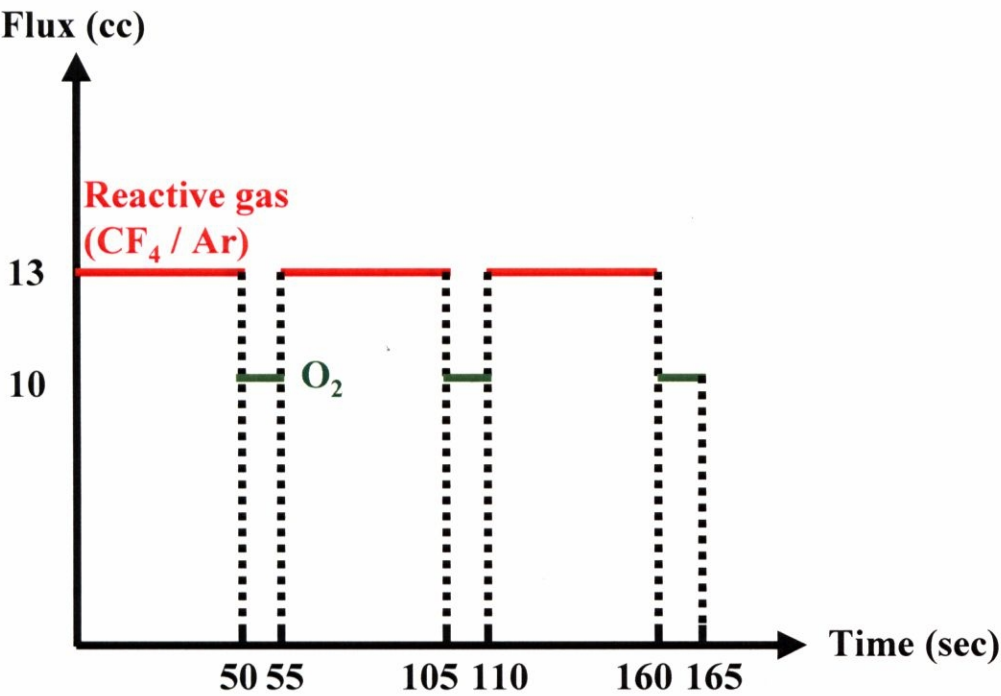


Fig. 4.5 Schematic demonstration of the alternate gas supply method.

cross-sectional image of the fabricated sample under this condition. One can observe that the introduction of this process drastically improved the removal of etching residues, hence promised the anisotropic etching profile of SiO₂ mask. This can also be demonstrated quantitatively from the result of SEM observation. In fig. 4.4 (a), the diameter of the bottom part of airhole is 37 nm, which is merely 49% of the designed value (75 nm). In contrast, in fig. 4.4 (b), the diameter of the bottom part of airhole is 66 nm, which is approximately 82% of the designed value. Note that at this moment further optimization was still required for the other etching parameters such as source power, bias power and gas ratio, hence the etching profile was still far from perfection. However, an improvement from 49% to 82% is truly a striking development. Also we found this method is effective especially to the patterns with periodicity smaller than 200 nm. As mentioned before, in the case of patterns with small periodicities, the removal of etching residues becomes more difficult with the progress of etching, eventually resulting in the deterioration of vertical etching profile. In general, O₂ is widely used for the removal of residues in the dry etching of SiO₂. However, a continuous introduction of O₂ into the RIE chamber will cause severe damage to photoresist mask, leading to the unexpected isotropic etching profile of SiO₂. In stead of the continuous supply, the intermittent introduction of O₂ during the etching process can

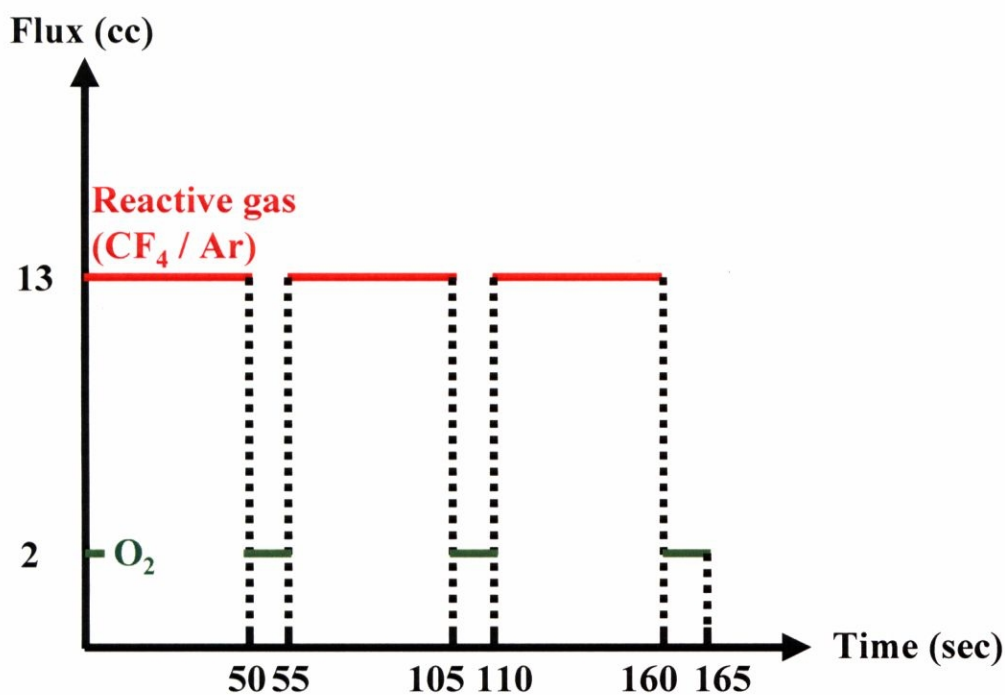


Fig. 4.6 Schematic demonstration of the optimized alternate gas supply method.

remove the etching residues effectively with the moderate damage yielded to photoresist. Therefore, we adopted this alternate gas supply method for SiO₂ etching. We subsequently carried out the optimization for O₂ flux. In the condition demonstrated in fig. 4.5, O₂ is introduced into chamber for the first time with the elapsed time of 50 seconds. We found in the first supply of O₂, in spite of the input flux value of 10 cc, the supplied value into chamber fluctuated significantly with the maximum value up to 20 cc. This fluctuation is very much undesirable since an introduction of extremely excessive amount of O₂ into chamber will yield significant damage to the photoresist. As the solution to this problem, we introduced O₂ into chamber for a very short time interval of 2 seconds from the very beginning, followed by the interruption until the designated time elapse. This is due to the following reason: 1. Our equipment will not introduce the gases into chamber until their fluxes are stable enough before the etching process starts; 2. Once the gas flux reaches a stable state, no more fluctuation will occur even with an interruption. This problem was solved by a small ingenuity considering the features of our equipment. Also a systematic study showed that the flux value of 2 cc was sufficient enough to remove the etching residue and promised the most moderate extent of damage to photoresist. As summary, the optimized condition is schematically shown in fig. 4.6. Note that the etching parameter of gas flux shown in the diagram has not been optimized yet at present moment.