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Study on Dry Etching for Profile and Selectivity Control in ULSI (Ultra-Large Scale Integrated Circuits) Manufacturing

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1. Introduction

1.1 Introduction

Since the realization of MOS (Metal-Oxide-Semiconductor) transistor in 1960s, silicon integrated circuits have made a tremendous progress and become indispensable components for our modern society with advanced information technology. The progress of the silicon integrated circuits has been accomplished by that of the fine fabrication technology which enables the higher integration and higher speed operation of the circuits, basically with lower power consumption and lower production cost. Up to the present, ULSI (Ultra-Large Scale Integrated circuits) having the smallest dimension of patterning below 100 nm are mass-produced. On the research and development, devices with further smaller dimension patterning, sub-50 ~ 5 nm have been fabricated. In the production of such very small size devices, the fine patterning technology is very important in order to manufacture the detailed device design based on the principle of the device operation. The fine patterning of the films is accomplished by photolithography technique which contains the following several process steps as shown in Fig. 1.1. First the film of semiconductor, metal or insulator, which is to be patterned, is coated by resist. Next the resist is exposed to light or electron beam through a photomask to make a resist pattern. The following development removes the exposed region of the resist (for positive type resist), which results in the patterned resist mask of the film for etching. After patterned mask formation, un-masked region of the film is etched off to obtain the desired profile. Finally, the remained resist pattern is removed. The etching process carried out in gas

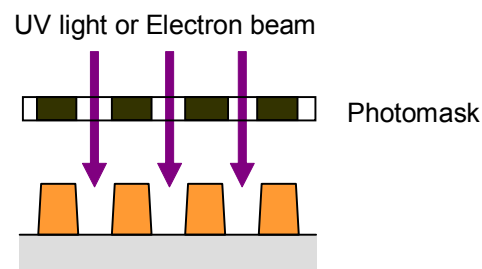
and/or plasma phase is called dry etching, which yields finer patterns than wet etching. Thus, dry etching is used for most of the integrated circuits fabrication steps. More than 30 photolithographies are necessary for recent ULSI fabrications, and even 5 to 10 are required for TFT-LCD (Thin Film Transistor-Liquid Crystal Display) devices. As an example, fine patterned structures used in the manufacturing CMOS (Complementary MOS) logic device with trench capacitors are schematically shown in Fig. 1.2. In addition, the photolithography is also used to make the photomask itself.

Resist Coating

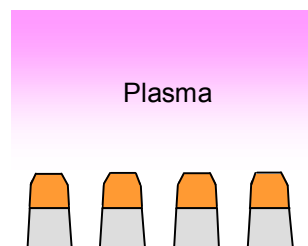


Photolithography

(Exposure and Developing)



Dry Etching



Resist Removal



Fig. 1.1. Schematic view of fine patterning process.

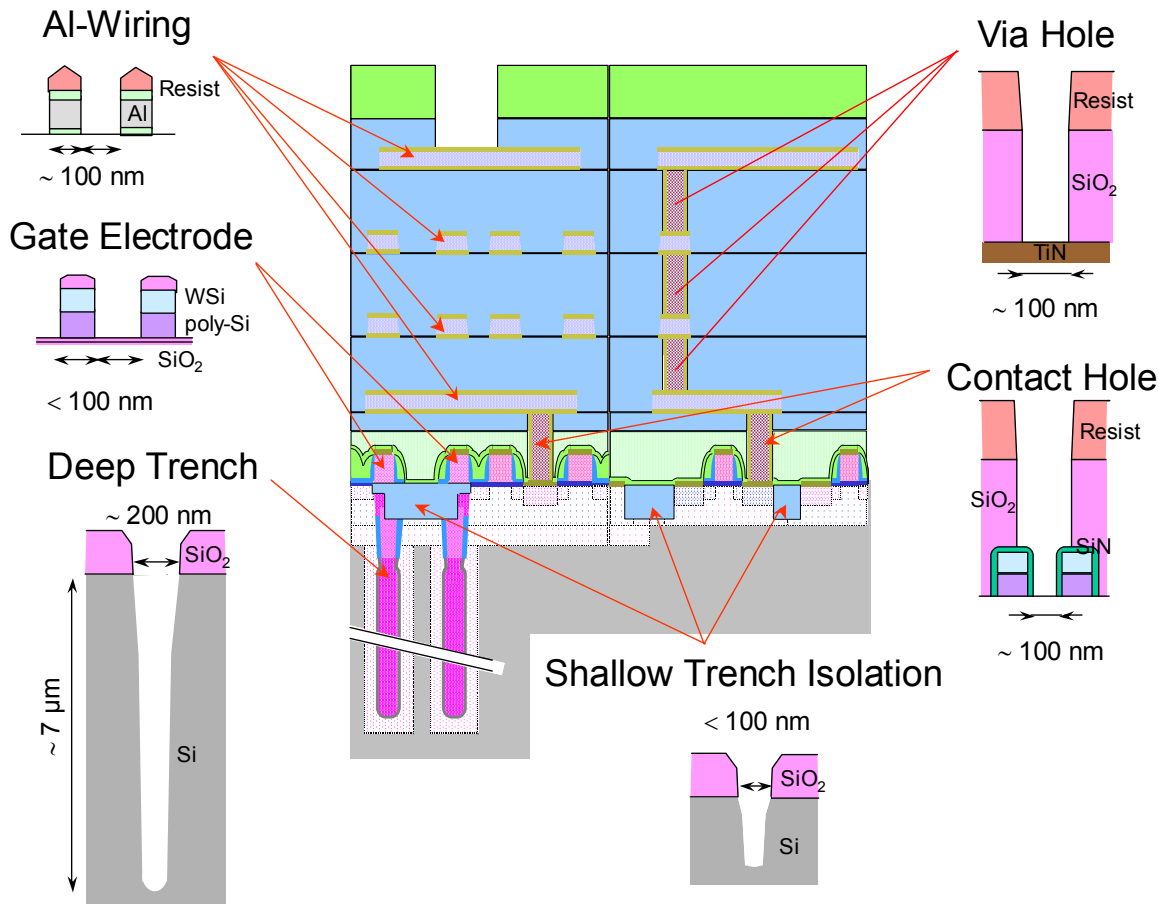


Fig. 1.2. A typical device cross-section and fine patterning processes.

The studies described in this thesis are concerned about the dry etching technology which is a key of the fine patterning. The mechanisms of controlling the dry etching profile and selectivity are experimentally investigated for various films used in ULSI devices such as Al, TiN, TaN, AlO_x , $\text{Cr}_2\text{O}_3/\text{Cr}$, ZrO_2 and Gd_2O_3 . In particular, this thesis focuses on the behavior of etching reaction products which play an important role in the etching profile and selectivity control.

1.2 Background

1.2.1 Silicon Device Trend

Silicon devices, especially LSI (Large-Scale Integrated circuits) have made a great progress over 30 years by the miniaturization of their components guided by the scaling rule [1.1]. The basic scaling rule requires the downsizing of the device in both horizontal and vertical dimensions, which enhances the performance of the devices. However, the continuous device shrinking has been facing the following limitations [1.2]. First, the gate SiO_2 film thickness has been continuously scaled down to 1.2 nm for recent most advanced logic LSI products. Such an ultra-thin SiO_2 film consists of only a few atomic layers, causing a large direct-tunneling current through the film, and resulting in significant increase of power consumption. Therefore, high-k gate insulator has been investigated extensively to replace the SiO_2 film [1.3]. This is because high-k gate insulator has an advantage to obtain the same capacitance with larger film thickness than SiO_2 film, which can reduce the tunneling-leakage current as shown in Fig. 1.3. Second, although polysilicon (poly-crystalline silicon) has been used for 30 years as the gate electrode material to allow the source and drain regions to be self-aligned to the gate, the depletion layer formation at the bottom of polysilicon gate under higher gate bias is becoming a serious problem [1.3] [1.4]. The gate depletion results in an additional capacitance in series with the gate insulator as shown in Fig. 1.4, which lowers the total capacitance between the gate and Si channel, resulting in an increase in the equivalent gate oxide thickness and hence a decrease in MOSFET (MOS Field Effect Transistor) drain current. Metal gate electrode which does not suffer from the depletion layer formation is effective to solve the problem.

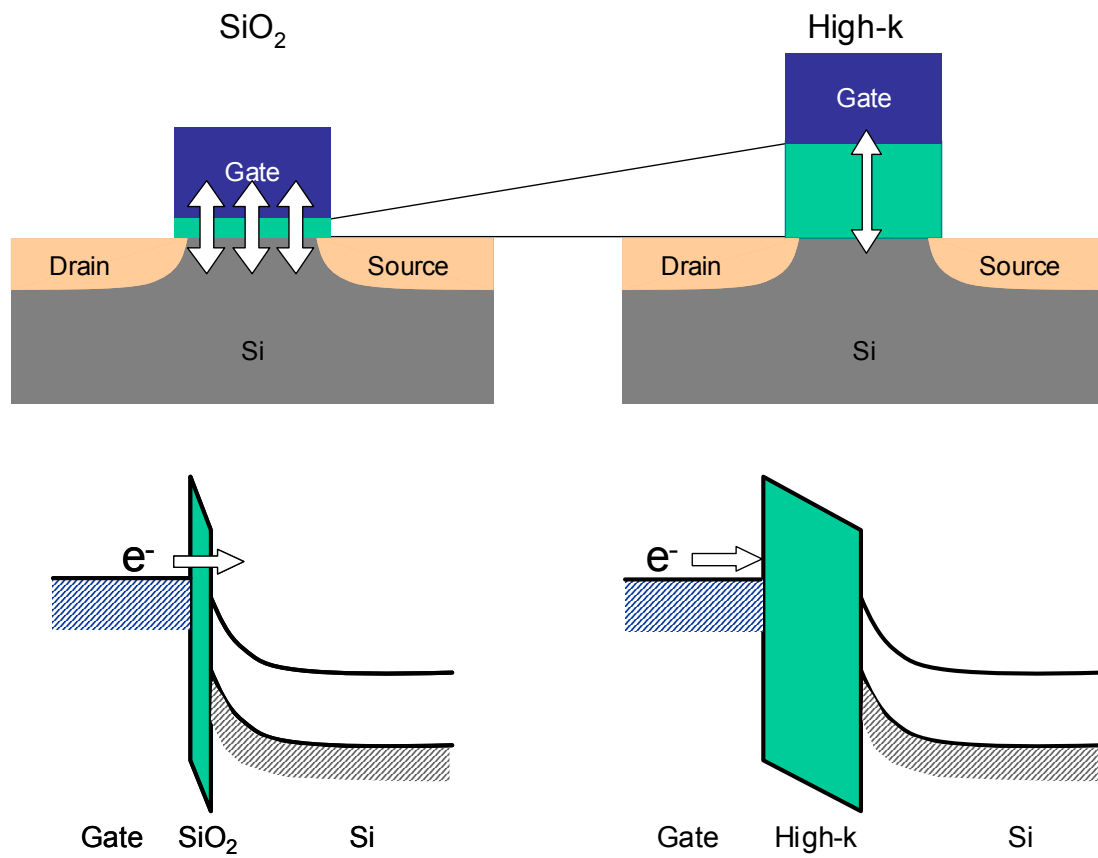


Fig. 1.3. Reduction of leakage current in high-k gate insulator.

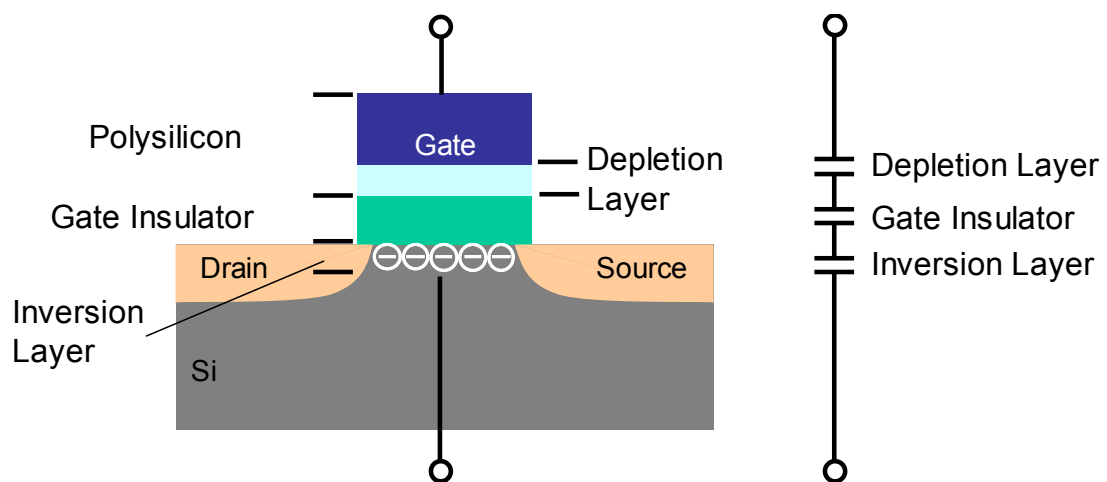


Fig. 1.4. Polysilicon gate depletion phenomenon.

Third, for downsized Al interconnects, a stacked film such as TiN/Ti/Al/TiN/Ti has been used in order to improve the electromigration reliability [1.5]. In that case, etching profile control of the complex stack film tends to be difficult. The precise control of the profile is required for the following ILD (Inter-Layer Dielectric) deposition step coverage of the interconnects.

Thus, in the downscaled devices, brand-new materials such as high-k films and metal gate electrode are required to be patterned, and also the complicated stack film such as TiN/Ti/Al/TiN/Ti should be patterned with precise profile control.

1.2.2 Dry Etching Technology

In the fine patterning processes of ULSI device manufacturing, it is required that the feature sizes of the etching mask defined by photolithography are precisely transferred by etching to the film to be patterned. Figure 1.5 schematically illustrates the typical three etching profiles: isotropic, anisotropic and completely anisotropic (vertical). In order to transfer the etching mask pattern accurately to the film to be etched, anisotropic etching is preferable to be isotropic one in which etching rates are equal in all directions. Furthermore, in such an extreme case that the mask width is less than the thickness of the film to be etched, it is impossible to conduct the pattern transfer by isotropic etching. In the etching process, selectivities against the etching mask and the underlayer are required. That is, the mask must remain throughout the etching and the underlayer must not be etched after etching-off the film to be etched. The selectivity is defined as the ratio of the etching rate of the film to be etched of that of the mask or the underlayer. Thus, the fine patterning

process is desired to have an anisotropic etching profile with sufficient selectivity.

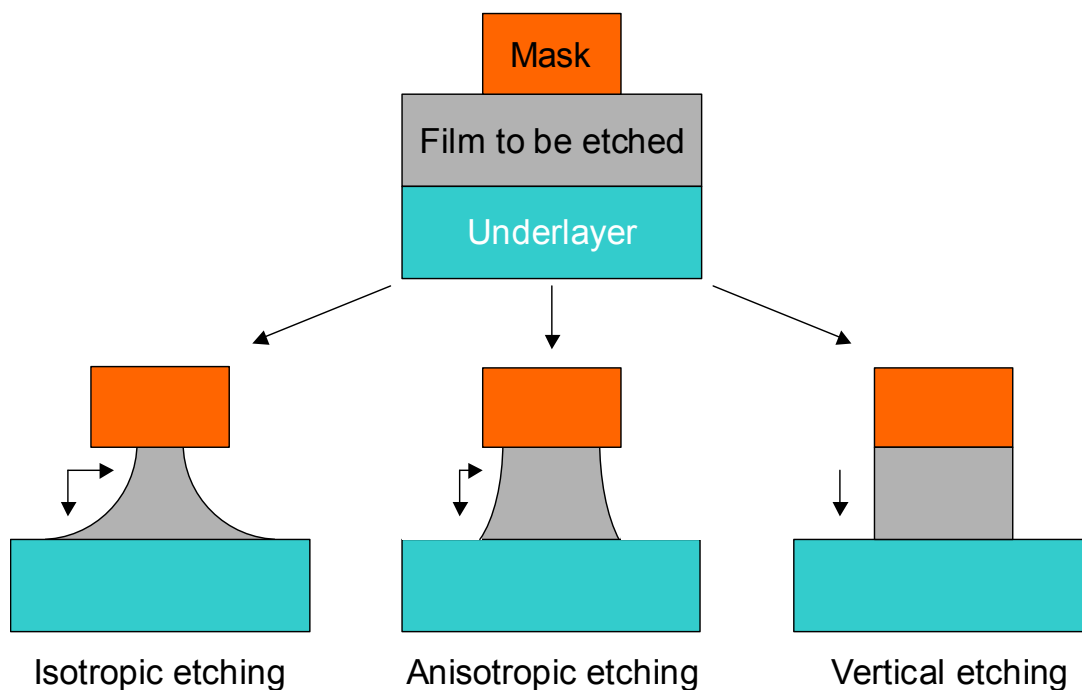


Fig. 1.5. Schematic illustration of typical etching profiles.

Etching is usually carried out using liquid phase or gas phase etchants. The liquid phase etching is called ‘wet etching’ where reaction products must be soluble in solvent or gaseous. The gas phase etching is called ‘dry etching’ where reaction products must be gaseous or have a low sublimation temperature. In wet etching, reactions between etchants and the film to be etched occur completely chemically. Therefore, wet etching leads isotropic etching profile while high selectivity can be obtained because it is based on chemical processes. In addition to the isotropic etching profile, bubbling formation during the etching reaction is a disadvantage of wet etching [1.6]. That is, gaseous bubbles generated by

the etching reaction adhere to the surface to be etched. The etching reaction cannot take place on the regions masked by bubbles, which results in poor surface morphology, inhomogeneous etching, and etching stop especially for small a hole patterning. Thus, wet etching is not much suited for the fine patterning in ULSI manufacturing.

In dry etching, gas and/or plasma are used for etching. If a film to be etched is put far from plasma and only reactive chemical species reach the film, the etching is purely chemical called ‘chemical dry etching’ [1.7]. Chemical dry etching is very selective because it uses purely chemical reaction which can be very specific. However, similar to wet etching, chemical dry etching causes an isotropic etching profile because the reactive chemical species, namely molecular and/or atomic radicals have isotropic thermal velocities of the order of 10^4 cm/s. Thus, chemical dry etching is not suitable for patterning of small feature sizes in advanced ULSI devices.

Therefore, plasma etching has largely replaced wet etching and chemical dry etching in ULSI manufacturing because the directional etching is possible. Plasma for dry etching is usually generated by RF (Radio Frequency) or microwave power application to the gaseous molecules and atoms inlet into the etching chamber. By the application of electric field, molecules and atoms are ionized, producing ions (mainly positive) and free electrons, creating plasma. Figure 1.6 shows a schematic illustration of the plasma usually used for dry etching. The pressure of the mixture of the generated plasma and source gas in the chamber is typically 0.1 ~ 100 Pa. The generated plasma is weakly ionized to have the electron density $10^9 \sim 10^{12}$ cm⁻³. In the chamber, free electrons with enough energy to cause ionization, dissociation and

excitation collide inelastically with the gaseous molecules or atoms, resulting in the generation of both reactive and non-reactive molecules, atoms and ions as shown in Fig. 1.6.

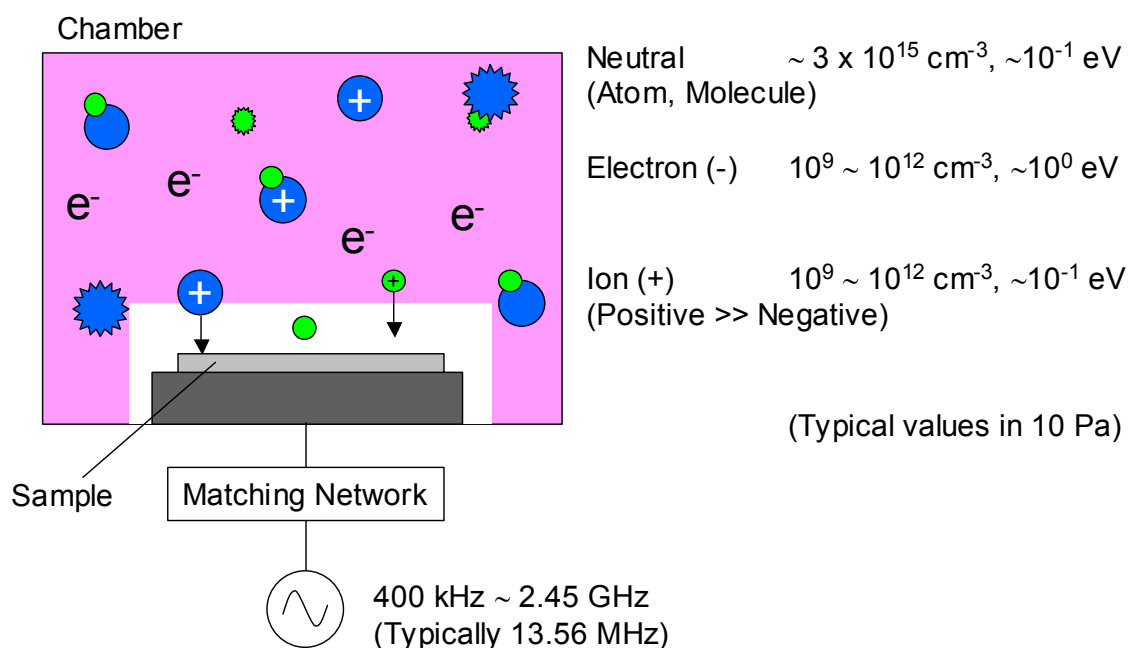


Fig. 1.6. Schematic view of the plasma used for dry etching.

Part of such reactive fragments is transported to the surface of the film, and the film is etched by two types of species: free energetic molecular or atomic radicals and atomic or molecular ions. For the electrically neutral species such as free energetic molecular or atomic radicals, incident energy and direction to the film to be etched are determined by their thermal velocities, that is the order of 10^4 cm/s and isotropic. Therefore, if only neutral species contribute to the etching, the etching becomes isotropic like chemical dry etching and wet etching. In contrast, ions are accelerated along an electric field near the film to be etched if it exists. Typical plasma etching equipment has at least one electrode applied with RF power

and coupled capacitively with the plasma. For such capacitive coupling, because the electron mobility is much higher than the ion mobility, the plasma potential cannot be less than the potential of any surface in contact with the plasma [1.8] [1.9]. The region where the voltage drop exists is called ion sheath. If the film to be etched is placed on the small electrode applied with RF power, large voltage bias develops in ion sheath near the film as illustrated in Fig. 1.7.

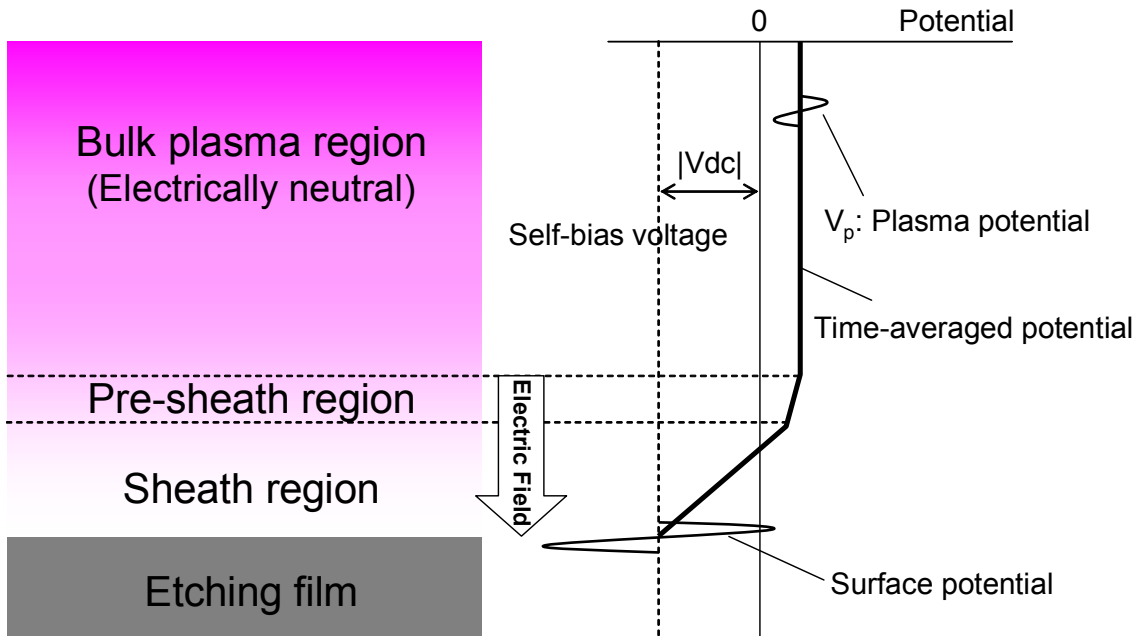


Fig. 1.7. Schematic view of ion sheath.

Thus, ions are accelerated toward the film to be etched in the plasma etching. The ionic species strike the film surface with high momentum resulting in the physical component of etching. Since the ions are directional due to the electric field in the sheath region, etching becomes anisotropic. Furthermore, the etching becomes completely anisotropic or

vertical if only the ions contribute the etching physically without any chemical components from ions, molecules and atoms. However, purely physical etching causes poor etching selectivity, which is not suited for the patterning of thin films in ULSI manufacturing. Thus, chemical etching component causes isotropic etching with high selectivity and physical etching component leads to anisotropic etching with poor selectivity.

It has been well known that if a combination of ionic and chemically reactive species is used simultaneously, they act in a synergistic manner leading to an etching rate that is much faster than the sum of individual etching rates when they are acting alone [1.10]. The synergy of the chemically reactive species and ions are considered that ion bombardment enhances at least one of the steps in chemical etching process such as surface absorption, etching reaction, reaction product formation, reaction product removal and removal of un-reacted etchants. The etching utilizing both components is called ion enhanced etching or RIE (Reactive Ion Etching) and has been the major way of fine patterning of ULSI devices because RIE provides a good anisotropic etching profile and selectivity. In RIE, it is important to carefully optimize both the etching gas chemistry to determine chemical actions and the ion fluxes to generate physical actions. In addition, the etching profile and selectivity depend on the behavior of reaction products which are generated by both chemical and physical actions. Part of the reaction products evaporates to be exhausted and the rest is deposited on the etching sample and/or the etching chamber as shown in Fig. 1.8. The area where reaction products are deposited is not etched faster than that not deposited. Thus, by optimizing the reaction products deposition and the ion bombardment effect, the etching profile and selectivity can be tuned.

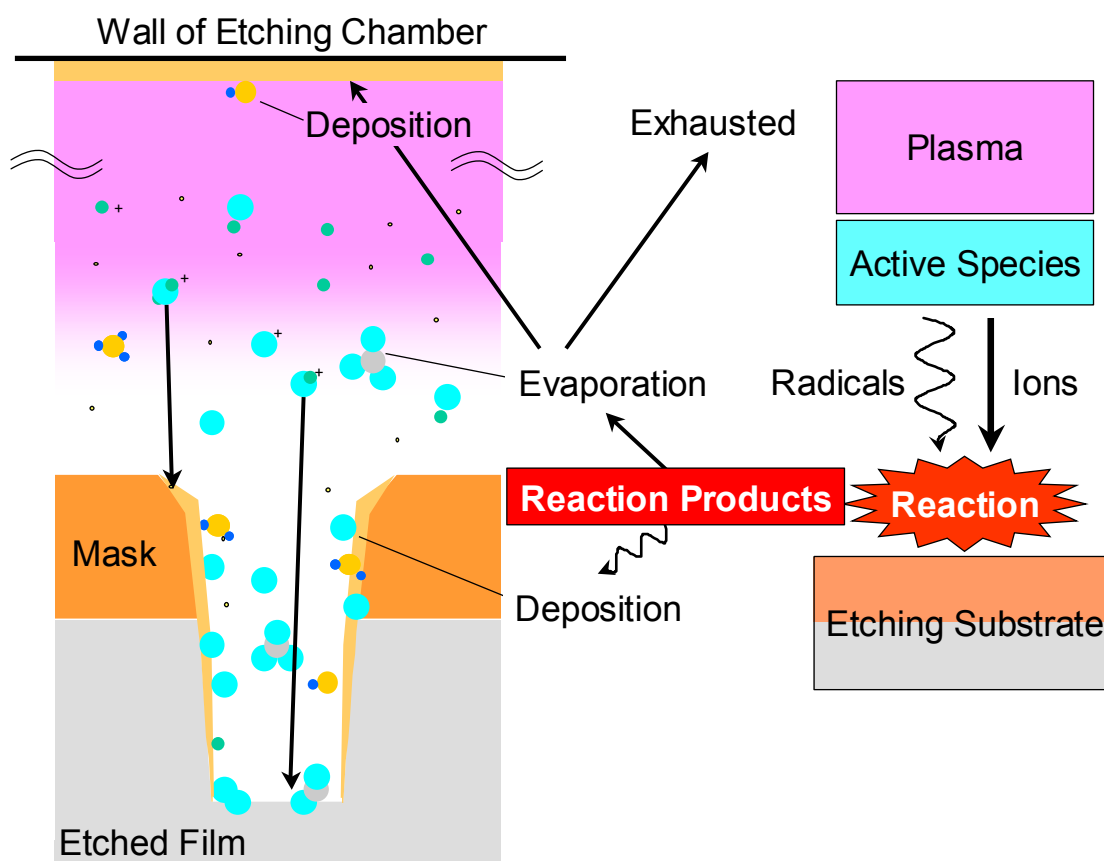


Fig. 1.8. Behavior of reaction products.

1.2.3 Etching Profile Control

Etching profile is desired to be vertical in order to realize the designed mask dimensions, but on the other hand smooth tapered profile is required for improving the step coverage in the deposition processes followed the etching. In most cases, the profile with definite taper angle ranging $30^\circ \sim 90^\circ$ is requested. Thus, dry etching should be carried out controlling the taper angle. Generally, the taper angle control in dry etching is possible to adjust etching mask erosion and deposition of reaction products on the sidewall of the etched pattern as shown in Fig. 1.9.

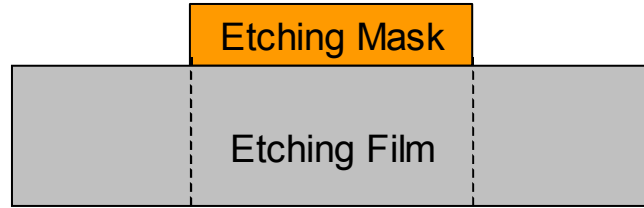
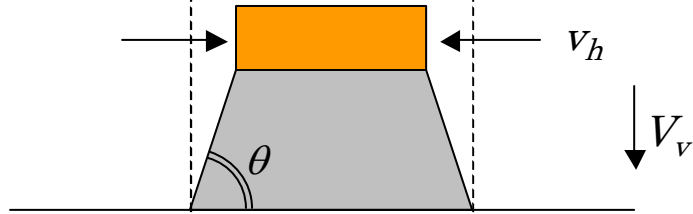
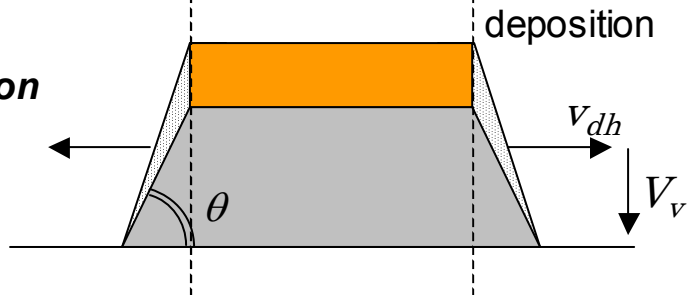
Before Etching**Etching with Resist Erosion****Etching with Sidewall Deposition**

Fig. 1.9. Two ways of controlling taper profile by dry etching.

In the etching mask erosion, if the horizontal erosion velocity of the etching mask is v_h and if the etching occurs only vertically with the velocity V_v , the taper angle θ is given by

$$\tan \theta = V_v / v_h. \quad (1.1)$$

In reality, the simple equation (1.1) is not valid exactly because not only the vertical velocity V_v but also horizontal velocity exists and V_v is not

always constant during the etching. However, in the etching system where the two velocities can be estimated as a constant value, one can estimate and control the taper angle θ by adjusting the ratio of the two velocities V_v and v_h . For example, in the etching with organic resist mask, since the etching of the resist depends on chemical etching by oxygen atoms in the plasma and on physical etching by incident ions from the plasma, the taper angle of the etched film can be controlled by adjusting the following values: the oxygen atom concentration in the plasma, the etched film temperature, bias voltage between the plasma and the etched film and the etching rate of the etched film.

In the deposition of reaction products on the sidewall of the etched pattern, if the horizontal deposition velocity on the sidewall of the etched pattern is v_{dh} and if the etching occurs only vertically with the velocity V_v , the taper angle θ is given by

$$\tan \theta = V_v / v_{dh}. \quad (1.2)$$

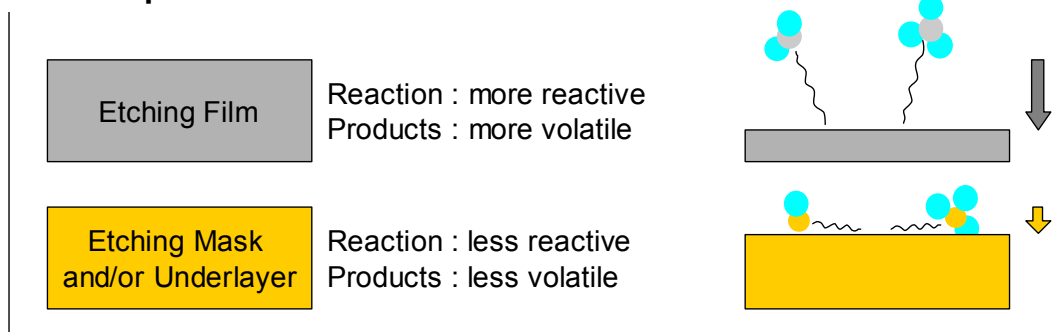
Although this equation (1.2) is the same form as equation (1.1), wider pattern is obtained with the sidewall deposition while narrower pattern is obtained with the etching mask erosion. In the way of sidewall deposition, it is difficult to find the deposition velocity v_{dh} experimentally. In addition, it is difficult to identify the deposit itself in most cases. This is because the deposition is the result from the deposition of reactive fragments in the plasma, the re-deposition of the reaction products of the etching mask and the re-deposition of the reaction products of the film to be etched [1.5]. This means that the deposition phenomenon depends strongly on the etching system and the etching condition. From a different point of view,

since the three deposition sources always exist in the etching, every actual dry etching process involves the sidewall deposition phenomenon with each effect on the profile. Therefore, it must be understood that such a sidewall deposition phenomenon in order to control the etching profile precisely. There have been several studies focusing on the analysis of the sidewall deposit by using FE-AES (Field Emission-Auger Electron Spectroscopy) [1.11] [1.12] and SIMS (Secondary Ion Mass Spectroscopy) [1.13]. However, it is difficult to obtain the detailed information on the chemical bonding state because FE-AES and SIMS analyses give us only the kind and concentration of chemical elements. Thus, the detailed analysis of the sidewall deposition has not been studied extensively, and hence the author can safely say that the etching profile control with the sidewall deposition has not been well-established.

1.2.4 Etching Selectivity Control

If the etching rates of the film to be etched and the film desired not to be etched are V and v , respectively, the etching selectivity is defined by as V/v , where the film desired not to be etched is etching mask and/or the underlayer of the film to be etched. For example, the underlayer gate oxide SiO_2 in the polysilicon RIE for gate electrode formation, the etching mask SiN or SiO_2 in the Si trench RIE, the resist mask in the Al-wiring RIE, the underlayers Si, NiSi, TiN or Cu in the RIE of ILD film, etc. Generally, there are two ways of obtaining the etching selectivity as shown in Fig. 1.10; one is to use the difference of the reactivity between the active species and the film to be etched, the other is to cause deposition of an etch-inhibiting layer only on the film desired not to be etched.

Using the difference of the reactivity and/or volatility of the reaction products



Using the selective deposition of etch-inhibiting layer

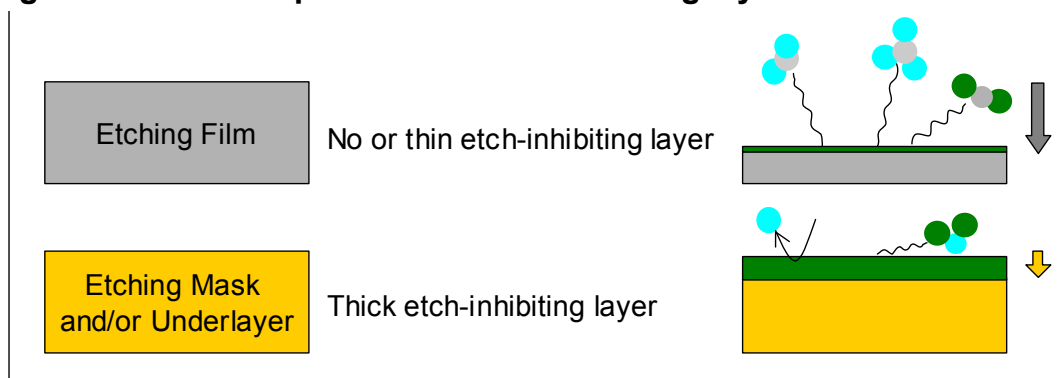


Fig. 1.10. Two ways of obtaining dry etching selectivity.

In the former method, it is important to choose the proper etching gas chemistry; the etching reaction products of the film to be etched is volatile and at the same time the reaction products of the film desired not to be etched is less volatile or even the reaction itself does not occur. This method is used in a basic process such as silicon patterning with the organic resist mask. In the Si etching, the Si/resist selectivity is obtained by using fluorine containing gas chemistry. In the following resist ashing, resist/patterned Si selectivity is obtained by using oxygen-based plasma. The same concept has also been used for the polysilicon RIE with using

HBr containing gas chemistry to obtain the etching selectivity against the SiO₂ underlayer. As described above, this method is so simple and effective that it is widely applied to the selective etching. However, it is sometimes difficult to use because it depends on the chemical reactivity between the active species in the plasma and the materials and on the structure of the etching sample which is already decided from the device design.

The latter method, which uses the deposition of the etch-inhibiting layer, is often used for the layer structures to which the former method is difficult to apply. The typical process is SiO₂ RIE in the ILD film patterning where it is required to have the high etching selectivity against the underlayer Si. The key to have the high etching selectivity in this process is CF_x deposition on Si surface by using CF_x gas chemistry and by adjusting the incident ion energy and the substrate temperature. The CF_x film deposited on Si functions as the etch-inhibiting layer, and hence the SiO₂/Si selective etching is possible. The mechanism and the controllability have been thoroughly studied [1.14] [1.15] [1.16]. The outline of the mechanism is that although CF_x deposition is suppressed by oxygen generated on the SiO₂ film surface due to the etching, thick CF_x film deposition occurs on Si surface where no oxygen is supplied. For the future device and etching process developments, the author considers that it is important to examine the applicability of such an excellent mechanism to the selective etching of brand-new materials and the compound films.

1.3 Purpose of the Thesis

As described above, RIE is suitable for fine patterning and hence widely used in ULSI manufacturing because the resist mask pattern can be accurately transferred to the film to be patterned due to the anisotropic etching. Furthermore, RIE enables the control of the etching profile and selectivity to the underlayer by utilizing the etching reaction products. The downscaling of ULSI devices requires more precise control of the etching profile and selectivity. For example, the underlayer films become thinner with the downscaling, and higher etching selectivity is required. In addition, the introduction of new material and complicated stack film structure into the advanced ULSI requires the development of new RIE technique to treat such materials and structures with precise control of the underlayer selectivity and etching profile. In the study described in this thesis, the author has investigated the individual dry etching processes used in manufacturing recent ULSI devices of mainly 180 nm technology node and below. In the study, the etching profile and selectivity have been especially focused on.

This study has two purposes; one is to clarify the dry etching mechanism underlying the individual dry etching phenomena, and second is to contribute the semiconductor manufacturing by developing and providing suitable dry etching processes for advanced ULSI devices. In order to clarify the mechanism determining the etching profile and selectivity, the author investigated the mechanism of etching reaction on the surface of the film. In particular, the behavior of the etching reaction products has been investigated by experiments and chemical analyses.

1.4 Outline of the Thesis

This thesis consists of five chapters. Figure 1.11 illustrates the outline of the thesis. In this chapter, the background of this study, the dry etching technology in manufacturing the downscaled ULSI and the purpose of this study are described.

In chapter 2, the control of dry etching profile in Al-wiring fabrication is described. First, in the Al-wiring dry etching using $\text{BCl}_3 + \text{Cl}_2$ based gas chemistries, the author investigates the analyzing method of sidewall deposit on the Al-wiring pattern. On the basis of the method named ‘imitation sidewall method’ in this study, the mechanism of the sidewall protection is clarified. It is shown that N_2 gas addition to $\text{BCl}_3 + \text{Cl}_2$ gas mixture generates a thick sidewall deposit which contains ammonium salts of Al and Al-chloride in addition to carbon-based compounds. It is also clarified that CH_2F_2 gas addition causes the sidewall deposit containing AlF_x among carbon-based compounds. Both additional gases lead to the tapering the Al-wiring profile.

Second, the author describes the dry etching characteristics of TiN which is used together with Al and clarifies the mechanism of the etching profile control. Experimental results show that vertical etching profile of TiN is obtained by the RIE using Cl radicals and that BCl_3 gas addition generates the sidewall deposit containing BN-containing compounds. The result indicates that the taper profile control is possible by the amount of BCl_3 addition.

Third, it is suggested that the endpoint detection is possible for TiN RIE by monitoring the emission intensity of Ti atoms in the plasma. The endpoint detection is adopted to the patterning of Al-wiring consisting of TiN/Ti/Al/TiN/Ti stacked layers to stabilize the etching profile.

In chapter 3, two kinds of selective etching processes are described. One is the process existing in resist ashing using oxygen plasma after dry etching of $\text{Cr}_2\text{O}_3/\text{Cr}$ stacked film used as a light blocking film in photomasks. Since it was newly found that the $\text{Cr}_2\text{O}_3/\text{Cr}$ film was etched during the ashing, the author investigates the mechanism of the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by oxygen plasma. It is found that the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching occurs when the film temperature is higher than $200\text{ }^\circ\text{C}$ due to CrO_x ($2 \leq x \leq 3$) generation and evaporation. It is concluded that $\text{Cr}_2\text{O}_3/\text{Cr}$ etching can be suppressed by keeping the film temperature below $200\text{ }^\circ\text{C}$ to prevent CrO_x ($2 \leq x \leq 3$) from evaporating. The results provide a proper ashing process and apparatus in photomask manufacturing.

Next the selective etching of AlO_x against Al is studied for decreasing process steps in the formation of contact holes to underlayer Al in TFT-LCD manufacturing. The selective deposition of etch-inhibiting layer on Al surface is investigated to obtain the etching selectivity. It is turned out that $\text{BCl}_3 + \text{CH}_3\text{OH}$ or $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$ gas chemistry generates carbon-rich deposition much more on Al surface than AlO_x surface. By using the selective deposition phenomenon, AlO_x/Al selective dry etching, which is usually considered difficult, is realized with the selectivity more than 5.

In chapter 4, on the basis of the techniques developed in the previous chapters, the dry etchings of new materials currently studied for the future CMOS devices are described. TaN as the metal gate electrode material and high-k gate insulators such as ZrO_2 and Gd_2O_3 are investigated. In the TaN dry etching, it is found that the native oxide layer of TaN surface should be initially etched by BCl_3 -based gas chemistry. After the surface oxide removal, chlorine-based chemistry is found suitable for the gate

electrode patterning in the respect of the higher etching rate than fluorine-based chemistry. Furthermore, it is shown that the etching profile tends to be tapered due to the sidewall deposition of the reaction products. For ZrO_2 and Gd_2O_3 , it is found that the etching rates of Gd_2O_3 are the lowest and that the etching rates of ZrO_2 are higher than that of Gd_2O_3 but lower than that of SiO_2 . This indicates that, in the gate electrode etching, the high etching selectivity to the under-layer high-k film can be obtained. As far as the selective removal of the high-k film against Si substrate is concerned, ZrO_2/Si selective etching is possible by using the selective deposition of CF_x on Si surface. However, the $\text{Gd}_2\text{O}_3/\text{Si}$ selective etching is considered difficult. As a conclusion, MOSFET consisting of TaN gate electrode and ZrO_2 insulator can be fabricated by using dry etching. However, when a rare-earth metal oxide is used as a high-k insulator, the selective wet etching against Si might be suitable if the selective dry etching is not realized.

In chapter 5, the content of the thesis is summarized and the conclusions are stated with further problems and expectation in the future.

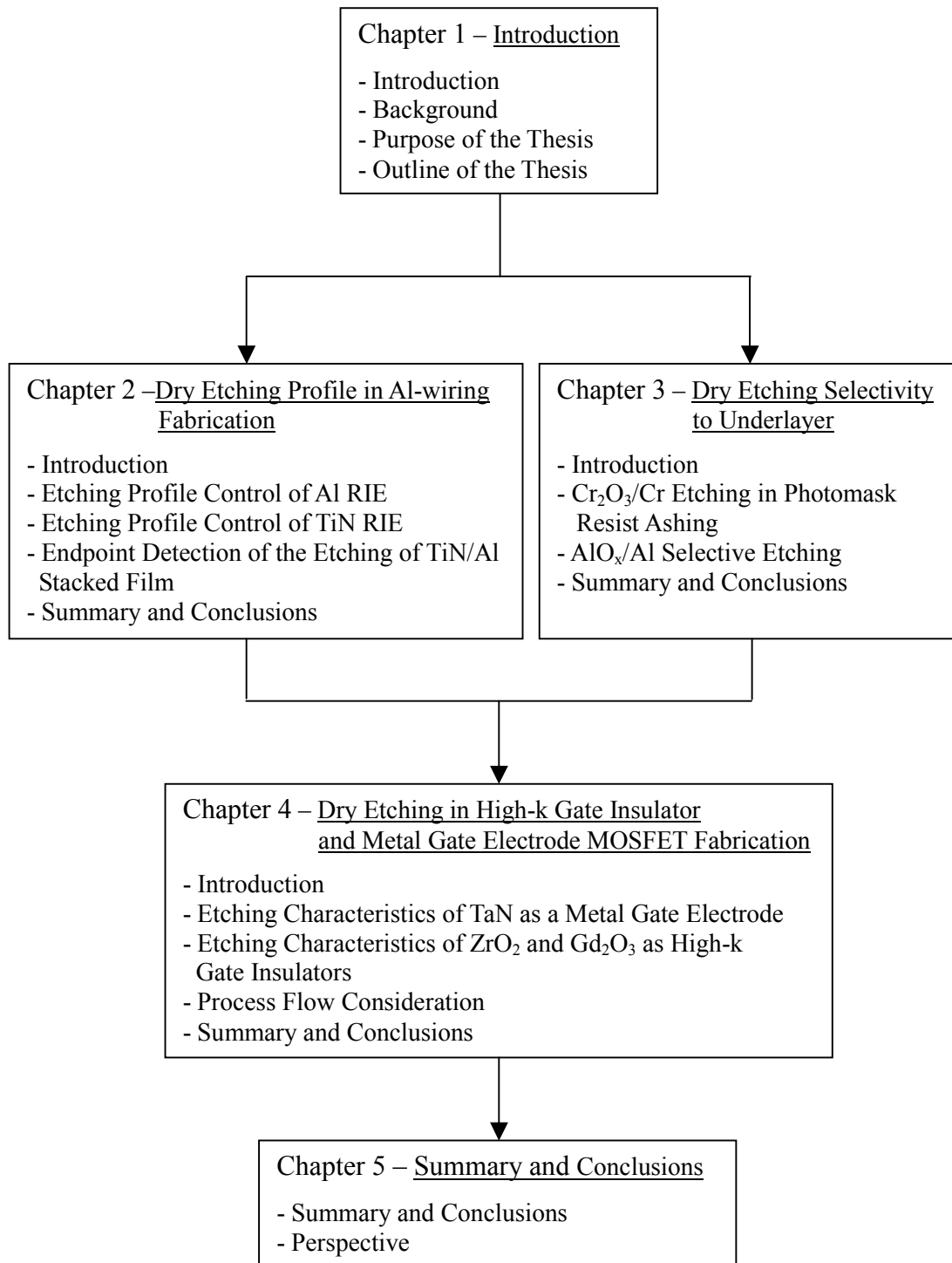


Fig. 1.11. Outline of the thesis.

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2. Dry Etching Profile in Al-Wiring Fabrication

In this chapter, the results of the investigation for dry etching profile control of the major materials forming the interconnects wiring of ULSI, Al and TiN are described. Since the 'sidewall deposition phenomenon' is used for the profile control, the method named 'imitation sidewall method' is contrived in order to analyze the sidewall deposits in detail. The method enables us to understand the sidewall deposition phenomenon, which leads to establish models determining the etching profile of Al by $\text{BCl}_3 + \text{Cl}_2$ gas with N_2 or CH_2F_2 addition. It is found that the N_2 gas addition causes a thick sidewall deposit which contains ammonium compounds in addition to carbon-based compounds. In the CH_2F_2 gas addition, the sidewall deposit contains AlF_x among carbon-based compounds. From the consideration of the sidewall deposition mechanism for the two gas additions, it is turned out that the CH_2F_2 gas addition is better than the N_2 addition in the point of the resist selectivity. Similarly, TiN etching profile is studied and the mechanism is proposed. Finally, in order to stabilize the etching profile of the wiring such as stacked TiN/Ti/Al/TiN/Ti-wiring, the endpoint of TiN etching is detected by using the plasma emission change. The etching process with the endpoint detection can provide a good and smooth profile in the stacked wiring and can also show good electric characteristics.

The study described in this chapter has contributed to productivity improvements of CMOS devices (180 nm technology node and below) by fine-tuning the etching profile of the stacked wiring of the interconnects.

2.1 Introduction

Although Cu interconnects have been introduced to high-speed logic devices, Al interconnects are still used for the majority of LSI. In the interconnects consisting of Al-wiring and SiO₂ ILD, the metal stack structure TiN/Ti/Al/TiN/Ti has been widely used, because the TiN layers prevent the interconnects from electromigration failures [2.1] and also because the bottom TiN layer prevents the metal-to-Si contact from short-circuit failures due to the formation of Al alloy spikes in the Si substrate [2.2]. In addition, the bottom TiN layer enhances the crystallinity of sputtered Al [2.3] and the top TiN layer reduces the standing wave and notching effects on the photoresist pattern due to the reflection of the exposure light in photolithography [2.4] [2.5]. In the TiN/Ti/Al/TiN/Ti-wiring manufacturing process, RIE of the each film is one of the key technologies because it determines the width and profile of Al-wiring which are important for both electrical property and the following process such as dielectric film deposition.

In the Al RIE, a gas chemistry containing Cl such as BCl₃+Cl₂ has been generally used [2.6] [2.7] because Al is easily etched by the Cl atoms and molecules. This is due to the high reactivity between Al and Cl, which results in volatile compounds such as AlCl₃ or Al₂Cl₆. In order to obtain the desired etched profile of Al, the method of Al sidewall protection is used. The sidewall protection is realized by making deposition of etching reaction products on the sidewall. In fact, in the Al RIE with the organic resist mask, BCl₃+Cl₂ gas chemistry causes C-Cl_x deposition on the patterned sidewall [2.8]. Furthermore, CHF₃ and CH₃Cl are often used as additional gases to BCl₃+Cl₂ in order to control the taper angle more precisely. N₂ addition to BCl₃+Cl₂ gas mixture has also been carried out, which is found

effective to form the protection layer on the Al sidewalls resulting in preventing side-etch or notch [2.9] [2.10]. It has been reported that in the cases of CHF_3 and CH_3Cl , the deposit on the Al sidewall consists mainly of carbon and chlorine [2.11] [2.12]. However, the details of the sidewall deposit have not been understood well. Thus, the mechanisms of the sidewall deposition formation of N_2 and CH_2F_2 gas additions to BCl_3+Cl_2 are investigated for fabricating the Al-wiring. In order to clarify the composition and structure of the sidewall deposit a new method ‘imitation sidewall method’ is newly proposed. By using the imitation sidewall method, the sidewall protection phenomena for $\text{BCl}_3+\text{Cl}_2+\text{N}_2$ and $\text{BCl}_3+\text{Cl}_2+\text{CH}_2\text{F}_2$ gas chemistries are investigated.

As far as TiN RIE is concerned, it has been often regarded as the accompanying process to Al RIE because the TiN layers are thin compared to the Al layer and BCl_3+Cl_2 gas chemistry can etch the TiN layers. With the downsizing of the interconnects, however, the etched profile of the TiN layer may cause a large shift in the linewidth of the wiring. In fact, there have been several reports that the etching performance of the metal stack structure is dependent on that of the top TiN layer [2.5] [2.7]. Therefore, the control of the etched profile of TiN and/or Ti layer is becoming increasingly important for forming the interconnects as the design rule is reduced. Several authors have reported studies on the dry etching of TiN [2.6] [2.7] [2.13] [2.14] [2.15]. However, there have not been many reports on the controllability of the etched profile of the top TiN layer. Thus, the profile controllability of TiN RIE is investigated and the optimum etching condition is suggested.

In general, the proper etching conditions for Al and TiN/Ti are different each other, which requires the change of the condition at the

2. Dry Etching Profile in Al-Wiring Fabrication

interface. In order to avoid the irregular profile due to the improper change, endpoint detection of the TiN/Ti etching step is investigated by using optical emission of the plasma. The change of the etching step using endpoint detection is applied to the TiN/Ti/Al/TiN/Ti-wiring fabrication.

2.2 Etching Profile Control of Al RIE

2.2.1 Experimental Procedure

800-nm-thick Al, which is an alloy containing Si (1%) and Cu (0.5%), is sputter deposited on thermal oxide of 6 inch Si (100) wafer. Then 1.3- μm -thick resist is coated and patterned with lines and spaces equal to 0.8 μm . Figure 2.1 schematically shows the Al etching sample. Figure 2.2 shows another Al sample which consists of 4- μm -thick Al, 500-nm-thick thermal SiO_2 patterned by using resist mask. Figure 2.3 is the schematic view of the experimental apparatus used in this study. The etching chamber system consists of quartz tube, stainless steel process chamber and exhaust manifold. The etching gases such as BCl_3 , Cl_2 , N_2 , CH_2F_2 and Ar are introduced to the etching chamber after controlled its flow rate by mass flow controllers and are exhausted by TMP (Turbo Molecular Pump). The pressure of the chamber system is controlled at desired value by the valuable gate valve between the chamber system and the TMP. An etching sample is placed on the stage electrode to which 13.56 MHz RF power is supplied through the matching network. Typical etching condition for N_2 addition case is as follows; $\text{BCl}_3 + \text{Cl}_2 = 60 + 20$ sccm, $\text{N}_2 = 0, 20$ and 40 sccm, the pressure = 33 Pa, the RF power = 270 W, and the electrode temperature = 25 °C. For the CH_2F_2 addition experiment, the total gas flow rate = 120 sccm, the pressure = 1.0 or 2.0 Pa, the RF power = 320 W, and the electrode temperature = 35 °C. In both cases, the endpoint of the Al etching was detected by the optical emission change at Al (396.2 nm) and 30% over-etching was carried out after the endpoint time. The etched profile of Al was observed by using SEM (Scanning Electron Microscopy). The sidewall deposit on etched Al lines was analyzed directly by FE-AES. The deionized water rinsing the etched wafer was analyzed by Ion

Chromatography. Furthermore, a Si chip was placed near the etched sample during the etching and the deposit was obtained on the Si chip. The deposit was analyzed by XPS (X-ray Photoelectron Spectroscopy), FT-IR (Fourier Transform Infra Red spectroscopy) and TDS (Thermal Desorption Spectroscopy). In addition, the plasma during the etching was monitored by optical emission spectroscopy.

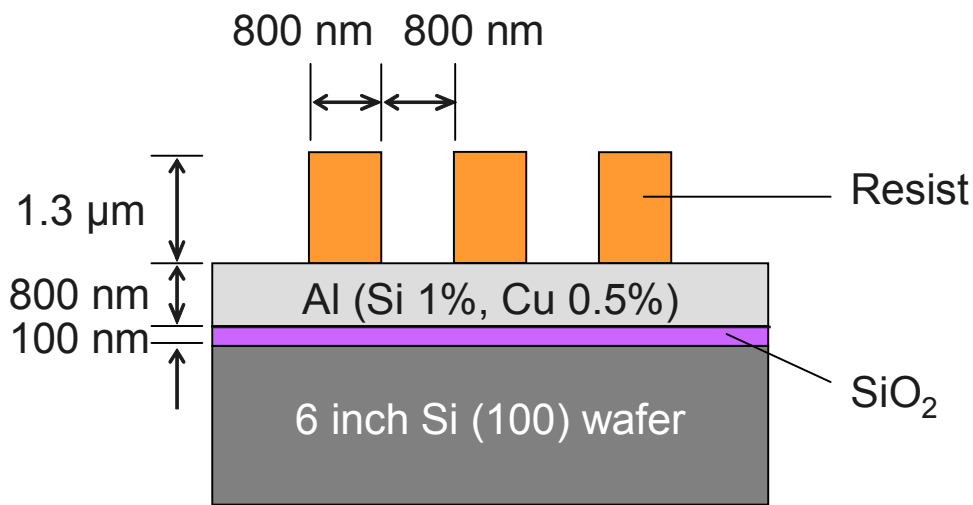


Fig. 2.1. Cross-sectional view of Al etching sample for N_2 gas addition experiments.

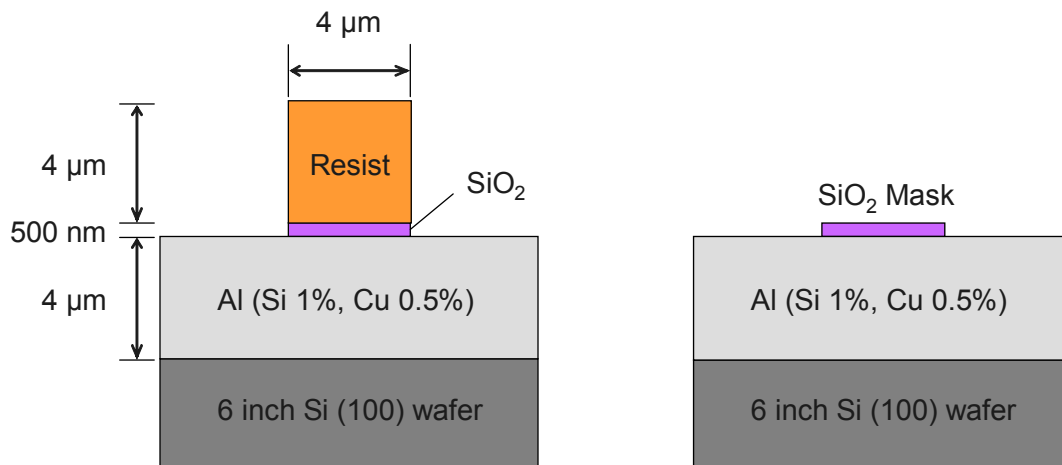


Fig. 2.2. Cross-sectional view of Al etching sample with SiO_2 mask for CH_2F_2 gas addition experiments.

2. Dry Etching Profile in Al-Wiring Fabrication

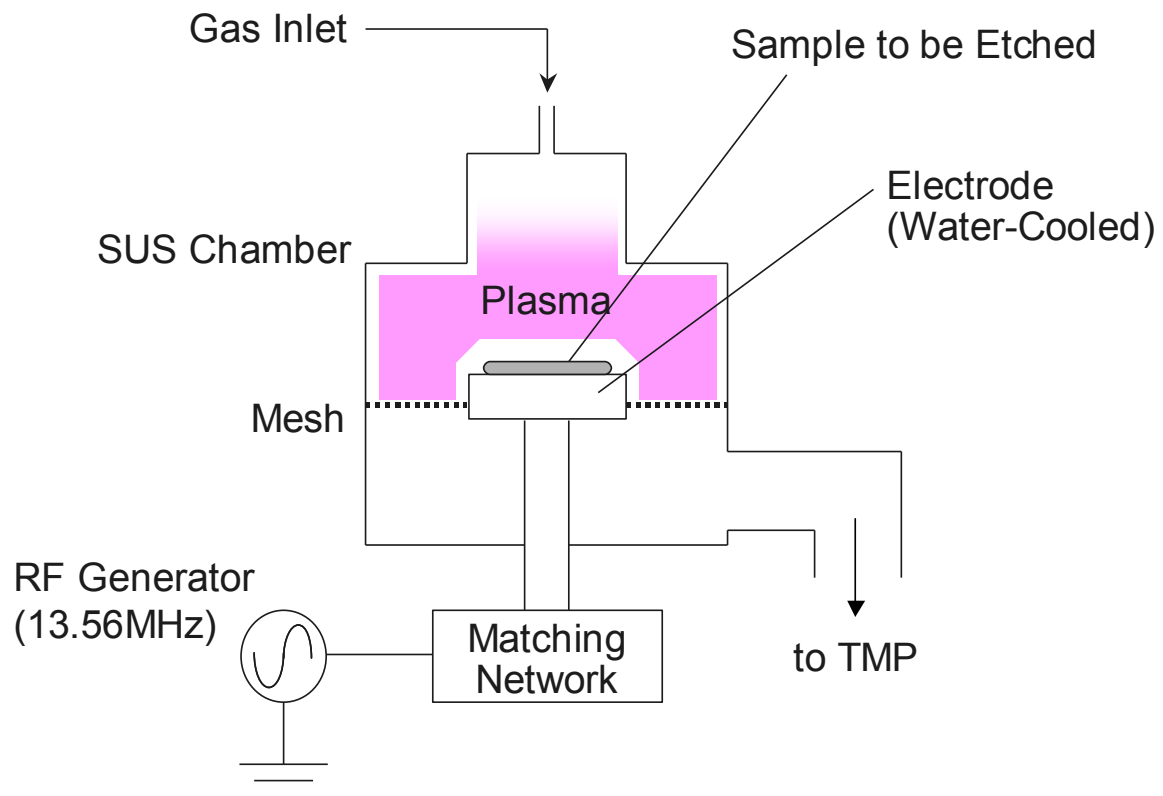


Fig. 2.3. Schematic view of dry etching apparatus.

2.2.2 Results and Discussion

A Etching Profile of Al RIE

The change of the etched Al profile with N_2 gas addition to BCl_3+Cl_2 gas mixture has been examined. The etching condition was fixed except N_2 gas flow; $BCl_3+Cl_2 = 60+20$ sccm, the pressure = 33 Pa, the RF power = 270 W and the electrode temperature = 25 °C. Figure 2.4 shows the cross-sectional micrographs after the RIE of the sample as illustrated in Fig. 2.1. When the N_2 gas flow rate is increased, the etched profile changes from anti-tapered to straight and the line width increases. Figure 2.5 shows another etching profile comparison: BCl_3+Cl_2+Ar gas chemistry ($BCl_3+Cl_2+Ar = 50+30+20$ sccm, 1.0 Pa) with the resist mask, BCl_3+Cl_2+Ar ($BCl_3+Cl_2+Ar = 50+30+20$ sccm, 1.0 Pa) without the resist mask and $BCl_3+Cl_2+Ar+CH_2F_2$ ($BCl_3+Cl_2+Ar+CH_2F_2 = 45+27+20+8$ sccm, 2.0 Pa) without the resist mask. It is clearly found that the resist mask and/or CH_2F_2 gas is necessary to obtain Al profiles without any side-etch. In both Figs. 2.4 and 2.5, it should be noted that the lateral erosion of the resist or SiO_2 mask does not occur at all. Thus, the profile change is accounted for a sidewall deposition phenomenon.

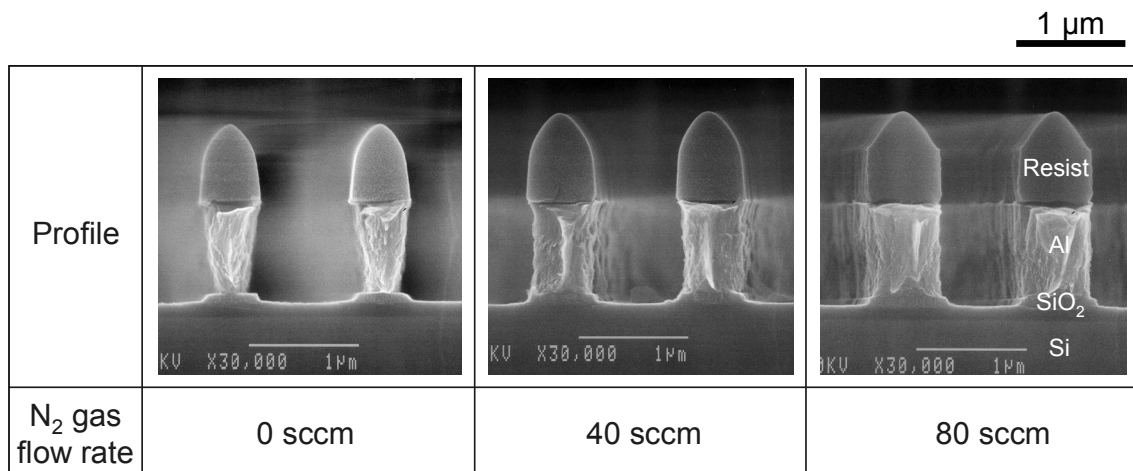


Fig. 2.4. Al RIE profile change by N_2 gas addition.

2. Dry Etching Profile in Al-Wiring Fabrication

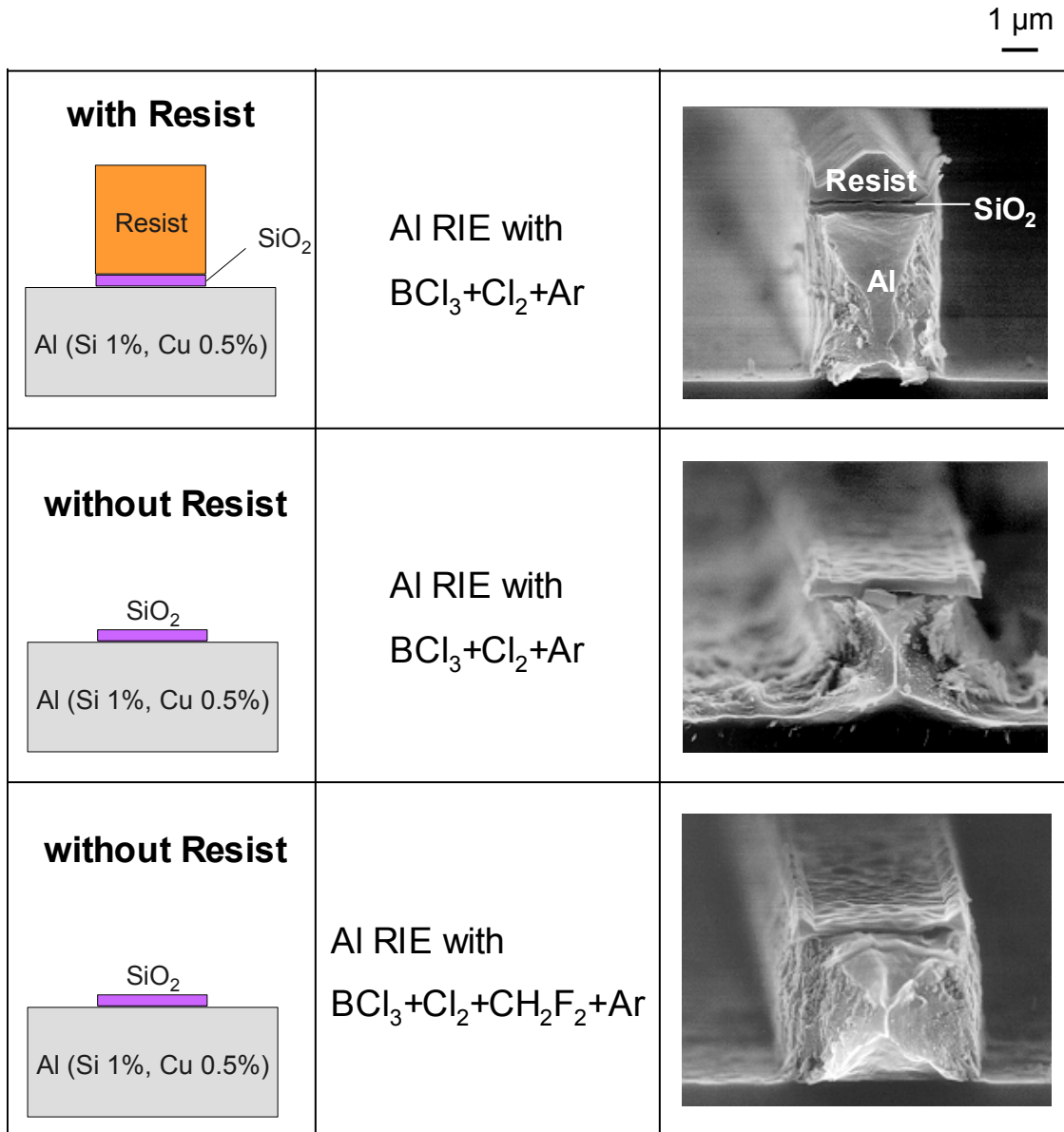


Fig. 2.5. Al RIE profiles comparison between $\text{BCl}_3 + \text{Cl}_2 + \text{Ar}$ chemistry with resist mask, $\text{BCl}_3 + \text{Cl}_2 + \text{Ar}$ chemistry with SiO_2 mask and $\text{BCl}_3 + \text{Cl}_2 + \text{Ar} + \text{CH}_2\text{F}_2$ chemistry with SiO_2 mask.

B Analysis of Sidewall Deposition

In order to investigate the sidewall-deposited film during Al RIE, the sidewall was directly analyzed by FE-AES, where the probing electron beam spot is small sufficiently to exclude the resist region as shown in Fig. 2.6. Table 2.1 shows the composition of the surface of the Al sidewall deposits obtained by FE-AES analysis after etching with and without N₂ gas addition. Carbon is the main ingredient in the sidewall deposits independent on the amount of additional N₂ gas. It is found that N and Cl are slightly increased in the case of N₂ gas addition. As another direct analysis of the sidewall deposit, Ion Chromatography analysis was conducted for the deionized water which was used for rinsing the etched wafer. The procedure of the water rinsing is shown in Fig. 2.7. Table 2.2 shows the Ion Chromatography result. It is found that chlorine ions, ammonium ions and aluminum ions are detected in the deionized water. Since the deposition occurs almost on the sidewalls, it is considered that these ions are present in the sidewall deposit. From the above results, it is expected that in the deposit on the sidewall, N is involved forming ammonium compounds.

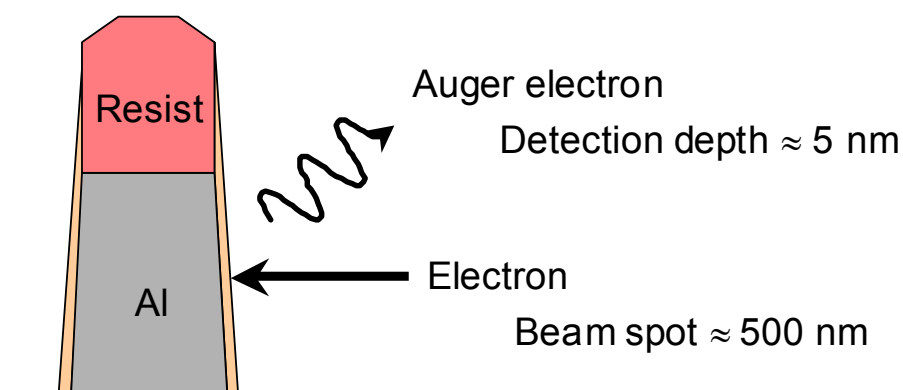


Fig. 2.6. Schematic view of FE-AES analysis of the Al sidewall surface.

Table 2.1 Concentrations of elements on the surface of the Al sidewall after Al RIE as determined by FE-AES.

N ₂ gas flow rate	Al	Cl	C	N	O
[sccm]	[%]	[%]	[%]	[%]	[%]
0	16	1	71	1	10
40	15	3	70	5	7

unit: atomic %

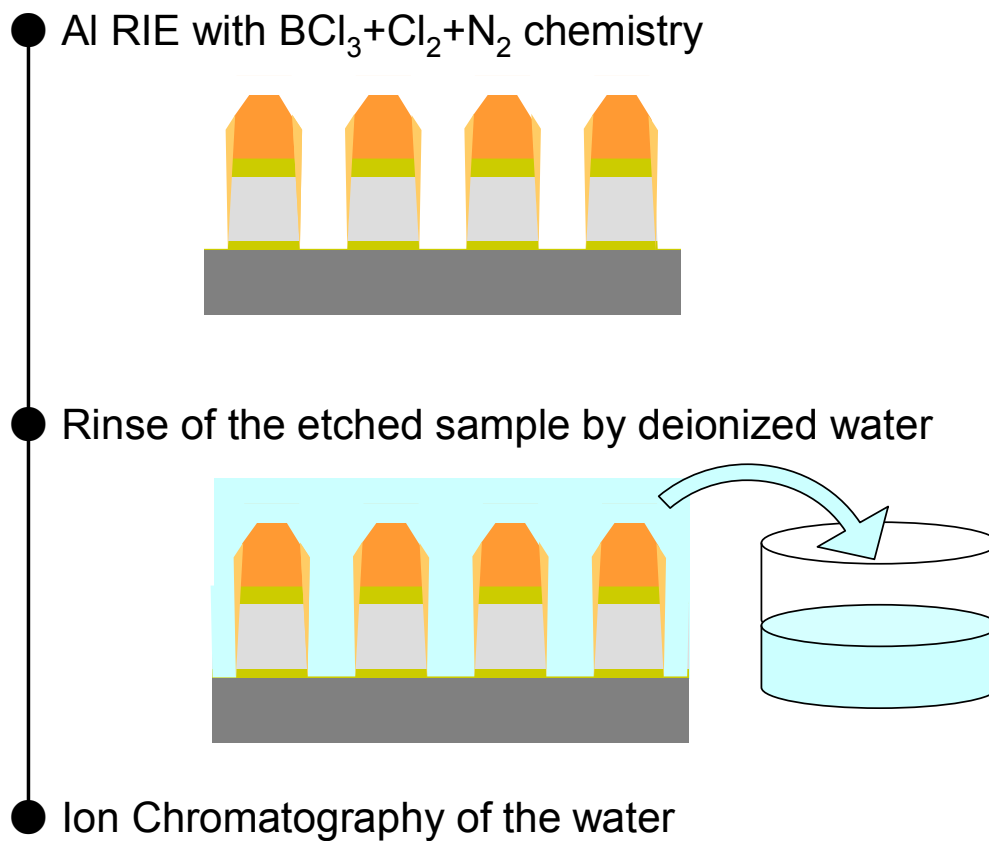


Fig. 2.7. Procedure of sample making for Ion Chromatography.

Table 2.2 Ions on etched wafer as determined by Ion Chromatography.

Cl^-	NH_4^+	Al^{3+}
[μg]	[μg]	[μg]
57	3.0	4.0

unit: $\mu\text{g}/\text{wafer}$

The direct analysis of the sidewall deposit described above can give us a certain amount of information about it. In order to clarify the deposit, however, there should be analyzing area large enough to carry out such analyses as XPS, IR, etc. Therefore, the author prepared and placed a Si chip near the etched sample as shown in Fig. 2.8; the Si chip is put on the vertical plane of the Al cubic which is placed near the etched wafer. After finishing the Al RIE, the Si chip is extracted from the etching chamber to analyze the deposit on the chip. In the ‘imitation sidewall method’, it is assumed that the Si chip can be regarded as the Al sidewall in point of less ion bombardment because it is set perpendicularly to the bias electrode. Table 2.3 shows the surface concentrations of each element of the deposits on the Si chip as determined by XPS. In the case without the N_2 addition, the deposit on the Si chip is considered thin because the concentrations are not different between the Si chips after the Al RIE and that as a control. In the case of N_2 addition, however, it is found that Si chips are covered with thick depositions, which is confirmed by the fact that Si is not detected at all. The deposition thickness is estimated more than 10 nm from electron escape depth of XPS. The composition obtained from the XPS analysis of the deposit on the Si chip is similar to that from direct FE-AES analysis to

the Al sidewalls explained above; carbon is the main component and Al, B, Cl, N and O are detected in it. Furthermore, both concentrations of nitrogen and chlorine are increased in the case of the N₂ addition. Therefore, the author considers the imitation sidewall method as qualitatively valid method to analyze the sidewall deposit in detail. More precisely, however, the real sidewall and the imitation sidewall are completely different in the distance from the etching surface and in the location whether or not the sidewall is in the ion sheath region around the bias electrode. During the transport of a fragment of the reaction products, the number of collisions the fragment suffers along the way is considered different. After the deposition, the energy and flux of ion bombardments is different. Therefore, the chemical bonding structure of the deposit can be different between the actual and imitation sidewalls. Nevertheless, the author considers that the imitation sidewall method is reliable at least qualitatively because XPS result for the deposits on the Si chip agrees with the FE-AES result of the actual sidewall.

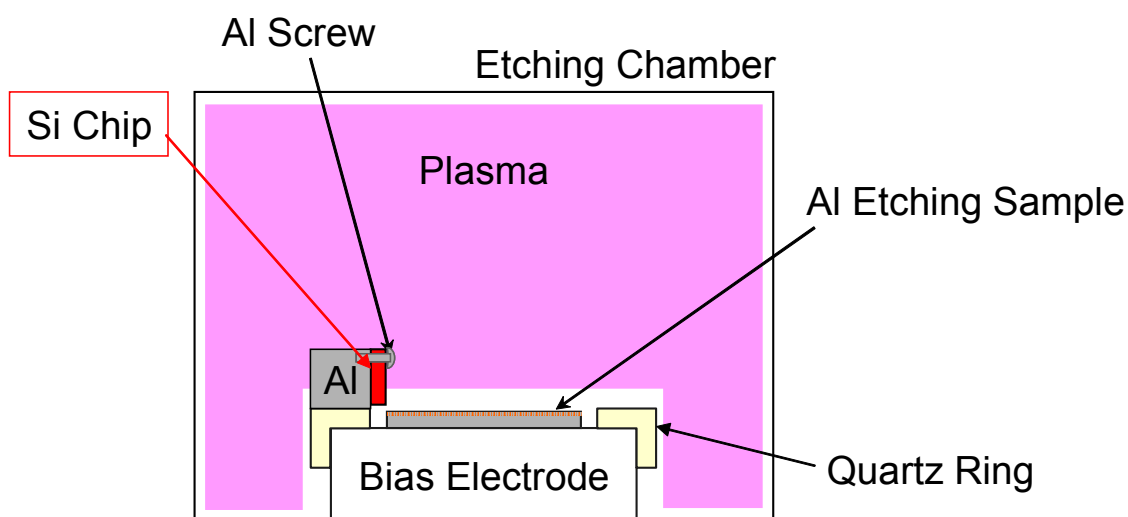


Fig. 2.8. Schematic view of the 'imitation sidewall method' by which the reaction product is obtained for the detail analyses.

Table 2.3 Concentrations of elements on the Si chip surface after Al RIE as determined by XPS.

N ₂ gas flow rate [sccm]	Al [%]	Si [%]	B [%]	Cl [%]	C [%]	N [%]	O [%]
0	0	37.5	0	2.6	16.9	0	43.0
40	4.4	0	1.7	21.1	42.8	12.0	18.1
80	4.9	0	2.0	22.9	44.2	9.5	16.6

unit: atomic %

Figures 2.9, 2.10 and 2.11 show the C 1s, Cl 2p and N 1s XPS narrow-scan spectra of the deposits on the Si chips, respectively. It should be noted that the each main peak for the N₂ addition case is much stronger than that for the N₂ addition, which suggests that the thick deposition occurs with the N₂ addition. In C 1s spectra shown in Fig. 2.9, the peak at 284.6 eV due to C-C and/or C-H bonds and sub peaks attributed to C-Cl_x (x = 1 ~ 3) bonds are recognized in the case of the N₂ addition. From Cl 2p spectra shown in Fig. 2.10, it is confirmed that the deposit contains Cl bonding with C (200 eV and 202 eV) and Cl bonding with Al (198 eV). In Fig. 2.11, the main peak of N 1s is located at slightly higher than 400 eV, which implies that N combines with H by considering the result of ion chromatography described above.

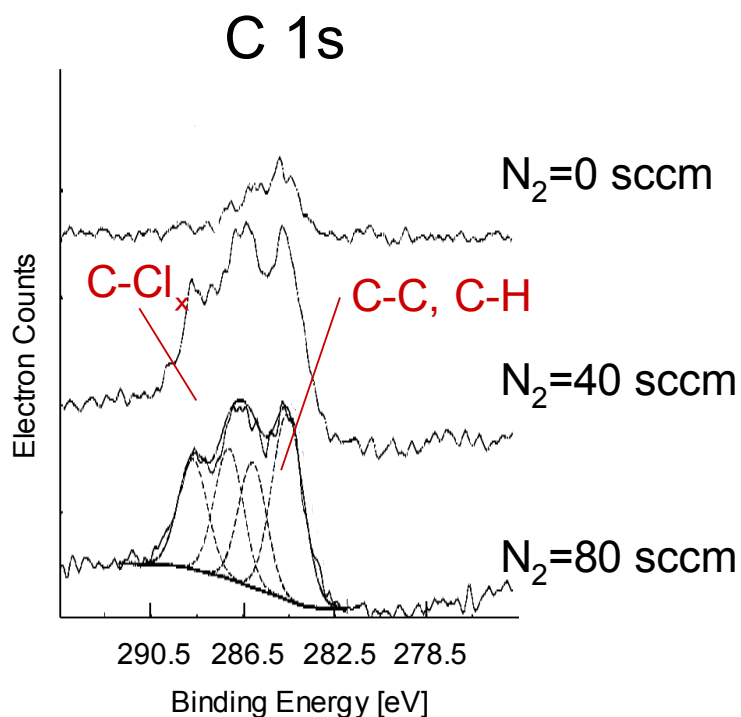


Fig. 2.9. C 1s spectra of the reaction products deposited on the Si chip.

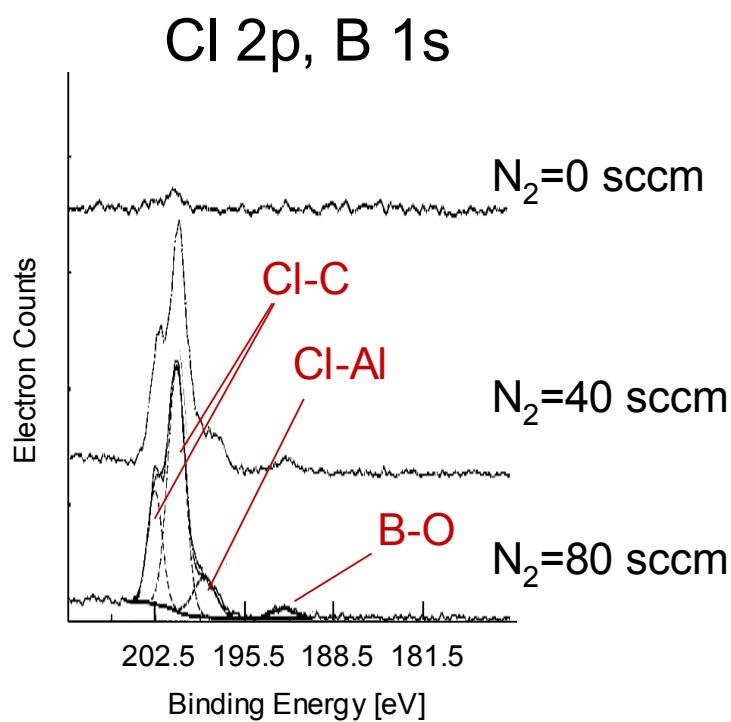


Fig. 2.10. Cl 2p and B 1s spectra of the reaction products deposited on the Si chip.

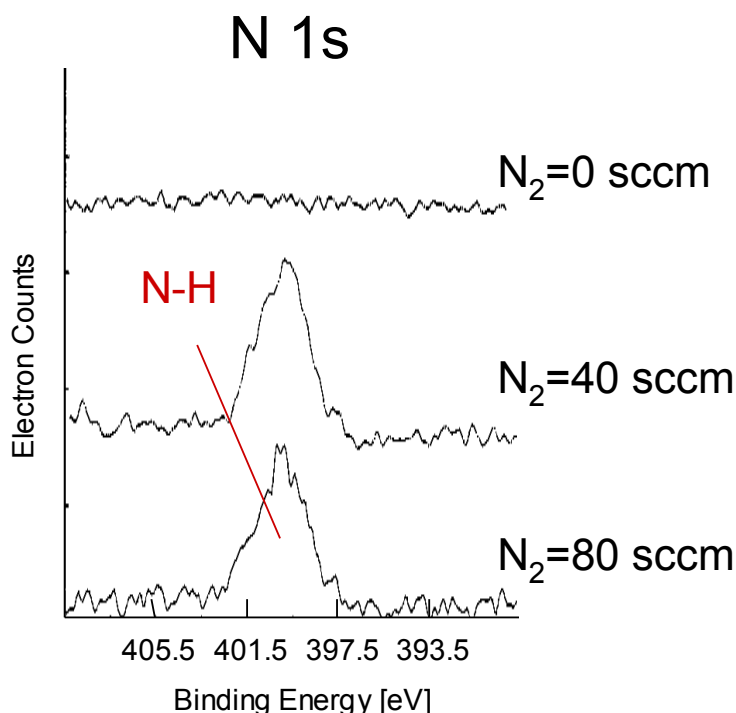


Fig. 2.11. N 1s spectra of the reaction products deposited on the Si chip.

In order to obtain more information about the chemical structure of the deposit, FT-IR analysis of the deposits were carried out. Figure 2.12 shows the spectrum of the deposit on the Si chip when the amount of the N_2 addition is varied in the Al RIE. Since two peaks due to N-H stretching vibration newly appear at 3300 cm^{-1} and 1410 cm^{-1} , the nitrogen was confirmed to exist in the form of ammonium ion NH_4^+ [2.15] [2.16] [2.17]. It should also be noted in the Fig. 2.12 that peaks originated from boron acid are observed, which is consistent with the XPS result.

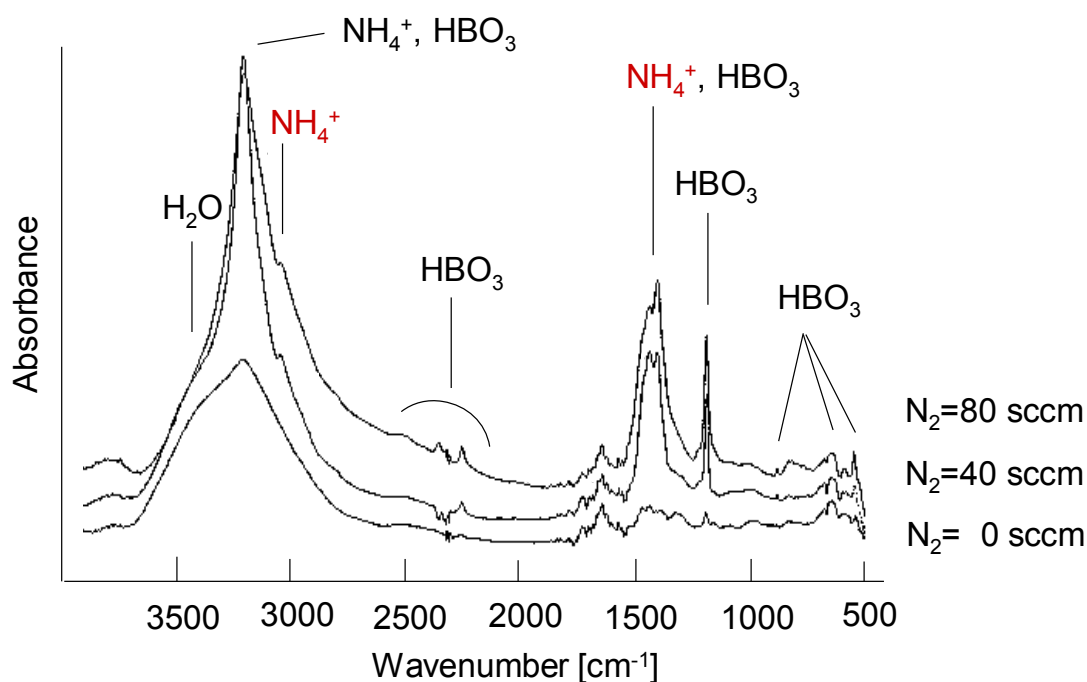


Fig. 2.12. IR result of the reaction products deposited on the Si chip.

TDS analysis was carried out for the Si chip used for the imitation sidewall method in order to know the form of the ammonium compound. Figures 2.13 and 2.14 show the TDS result for BCl_3+Cl_2 condition and $\text{BCl}_3+\text{Cl}_2+\text{N}_2$ condition, respectively. In the case of BCl_3+Cl_2 condition, Al ($M/e = 27$), Cl ($M/e = 35$), CH ($M/e = 15$), C_2H_5 ($M/e = 29$) and CO_2 ($M/e = 44$) evaporate at around 400°C . On the other hand, in the case of $\text{BCl}_3+\text{Cl}_2+\text{N}_2$ condition, NH_3 ($M/e = 17$), NH ($M/e = 15$), Al and Cl are desorbed at around 200°C , in addition to the desorptions at about 400°C . Therefore, it is considered that ammonium ion exists in the form of ammonium chloride (NH_4Cl) and/or ammonium Al-chloride (NH_4AlCl_4) which does not combine with carbon directly.

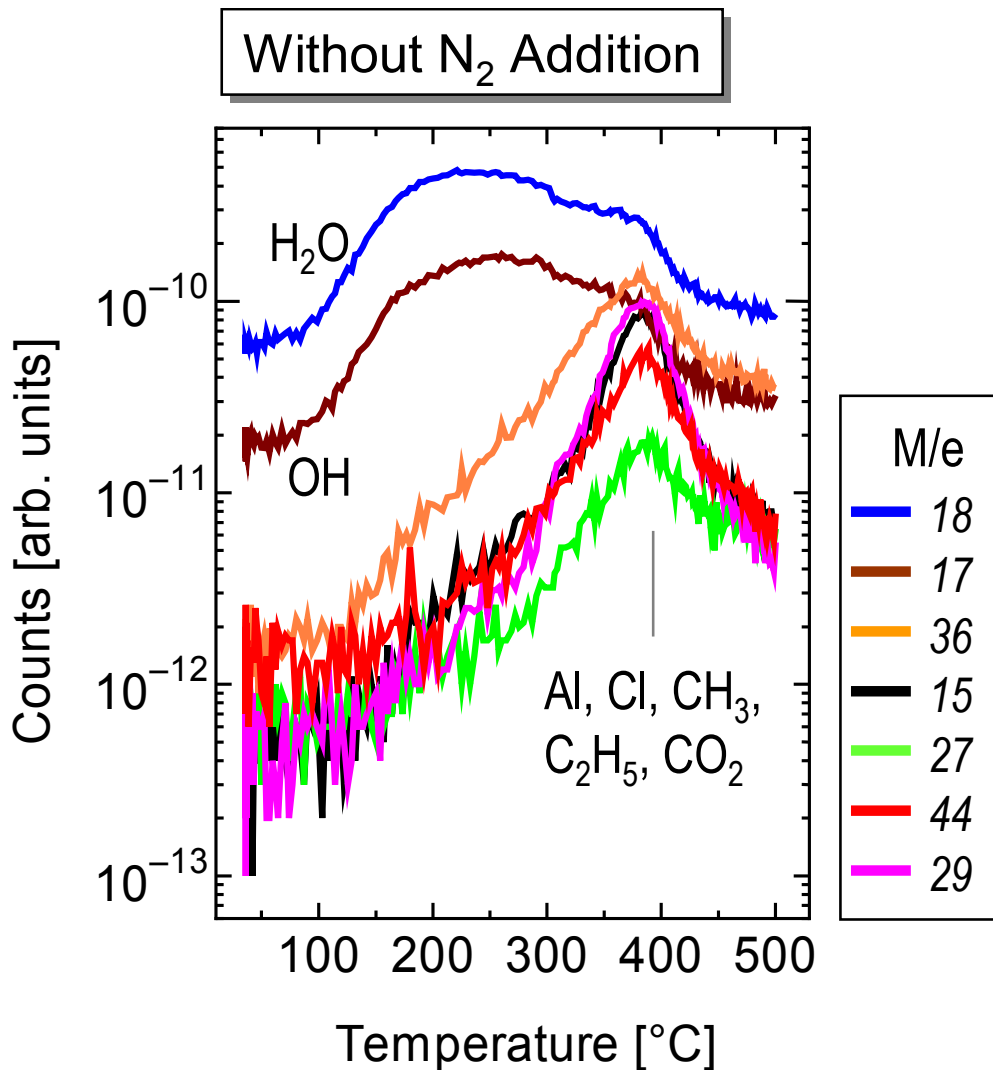


Fig. 2.13. TDS result of the reaction products deposited on the Si chip without N₂ addition.

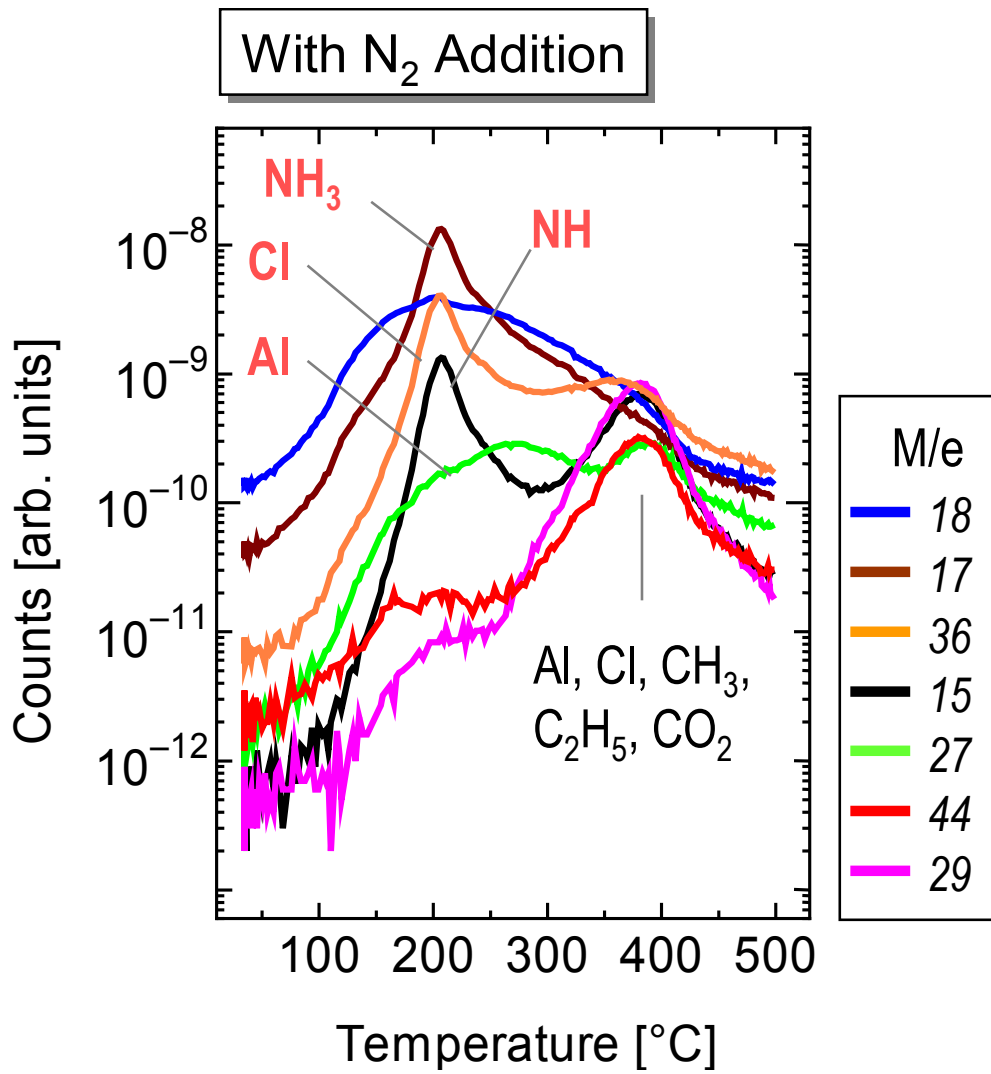


Fig. 2.14. TDS result of the reaction product deposited on the Si chip with N₂ addition.

For the formation of the ammonium compounds, the presence of H is necessary in addition to N. In order to clarify the origin of the H, plasma emission spectra during Al RIE were examined. Figure 2.15 shows the spectra in the case of $\text{BCl}_3 + \text{Cl}_2$ gas chemistry with and without the organic resist mask. It is clearly shown that hydrogen emission is not observed without the resist mask and that a sharp spectrum of H (656.3 nm) is observed in the case of using the resist mask. This indicates that the organic resist is supplying H into the plasma during the etching.

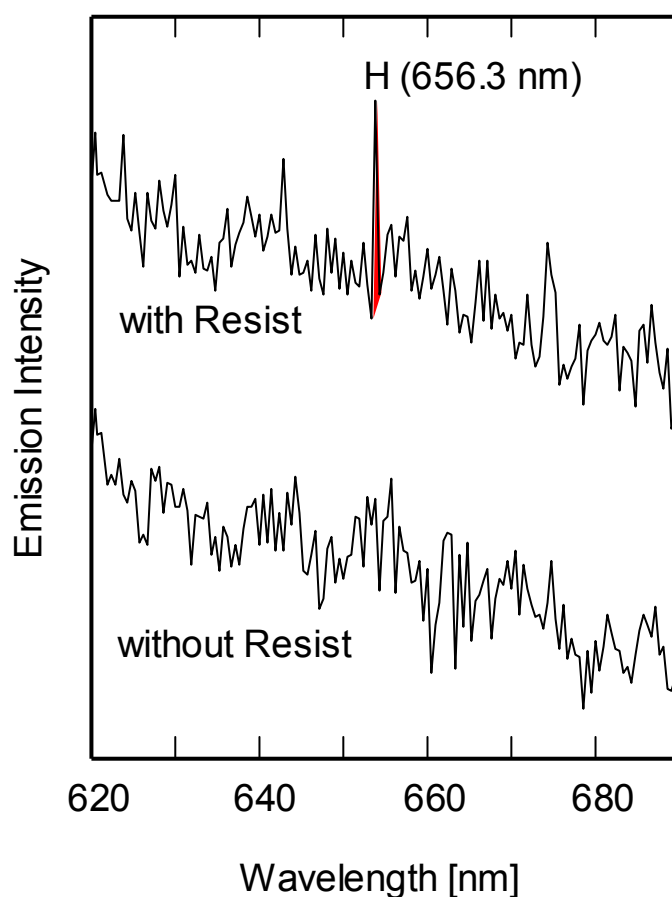


Fig. 2.15. Optical emission spectra ranging 620-690 nm of the plasma during etching Al sample with and without an organic resist mask.

Figure 2.16 shows the spectra of the plasma during the Al RIE with the organic resist mask for the various amount of additional N_2 gas flow rate. It is clearly observed that H (656.3 nm) emission decreases remarkably when N_2 gas is added. It is considered that H supplied from the organic resist reacts with N from N_2 dissociation, resulting in ammonium compounds formation. In addition, it should be noted that CN (388.3 nm) emission intensity increases with increasing the amount of additional N_2 gas flow rate as shown in Fig. 2.17.

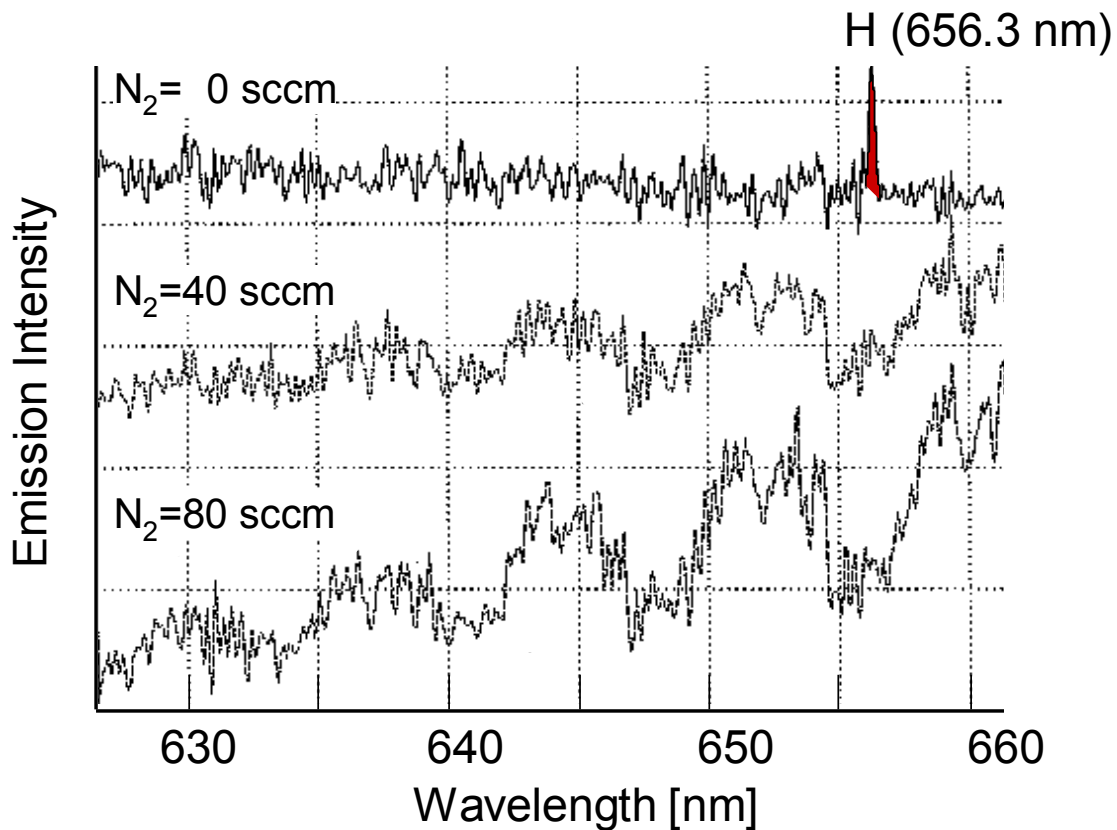


Fig. 2.16. Optical emission spectra ranging 627-662 nm of the plasma during etching Al sample with an organic resist mask in the case of N_2 gas addition.

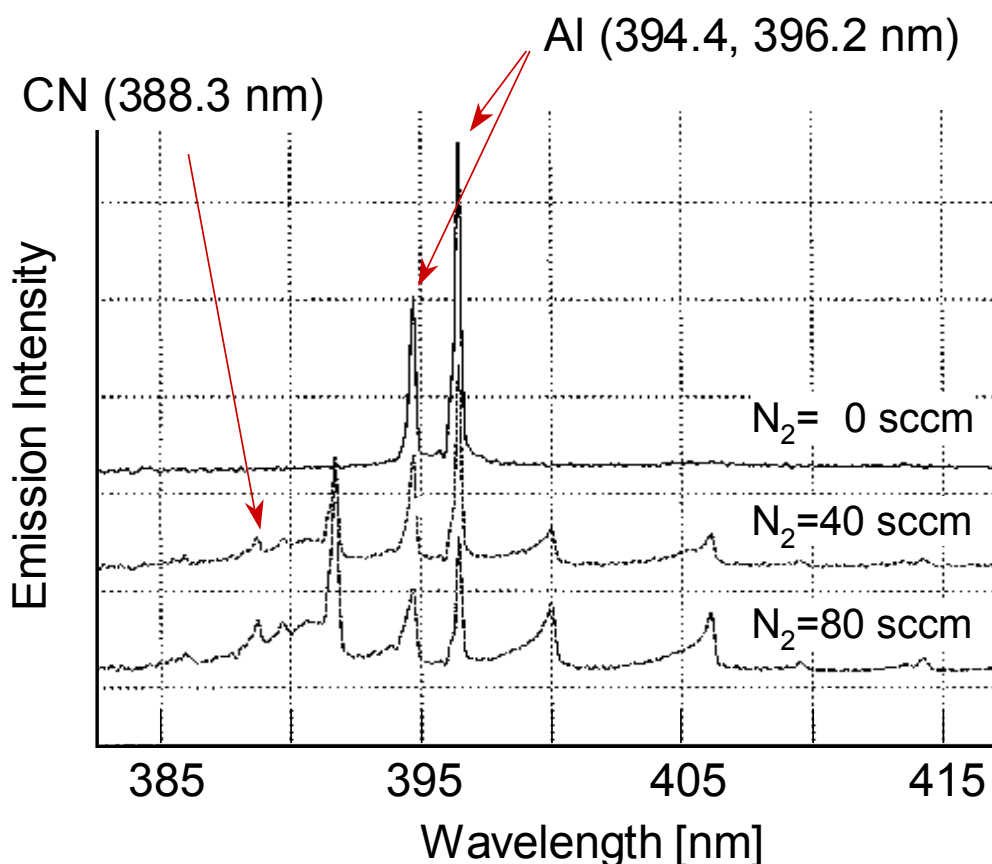


Fig. 2.17. Optical emission spectra ranging 383-418 nm of the plasma during etching Al sample with an organic resist mask in the case of N₂ gas addition.

By using the ‘imitation sidewall method’, the sidewall deposits have been analyzed for the CH₂F₂ gas addition case. Table 2.4 and Fig. 2.18 show XPS results of the reaction product on SiO₂ chip for BCl₃+Cl₂+CH₂F₂ gas chemistry. SiO₂ chip was used here in order to distinguish Si in the deposit from that from the chip for imitation sidewall. In the case of the resist mask without CH₂F₂ addition and the SiO₂ mask with CH₂F₂ addition,

which leads to non side-etch Al profile as shown in Fig. 2.5, a deposition is found on SiO₂ chip. It is found from the Table 2.4 that the deposit contains Al, C, B and Cl for the two cases and that in addition, F only for the SiO₂ mask with CH₂F₂ addition. It is not considered that Si is included in the deposit from the result that Si 2p peak of the SiO₂ chip after RIE is the same as that of SiO₂ as a control. From the narrow-scan spectra of C 1s, Cl 2p and Al 2p shown in Fig. 2.18, it is evident that both cases of the resist mask without CH₂F₂ addition and the SiO₂ mask with CH₂F₂ cause almost same deposits including carbon compounds with C-C, C-H and C-Cl_x bonds, AlCl_x and BO_x. However, the existence of AlF_x compound is almost only different between the two cases.

Table 2.4 Concentrations of elements on the SiO₂ chip surface after Al RIE as determined by XPS.

Mask	Ratio of CH ₂ F ₂ [%]	Al [%]	Si [%]	B [%]	Cl [%]	C [%]	O [%]	F [%]
Resist	0	11.2	23.4	0.4	3.4	18.2	43.5	0
SiO ₂	10	16.7	17.9	0.7	4.7	11.9	43.9	4.2
SiO ₂ chip as a control		0	38.3	0	0	1.8	59.9	0

unit: atomic %

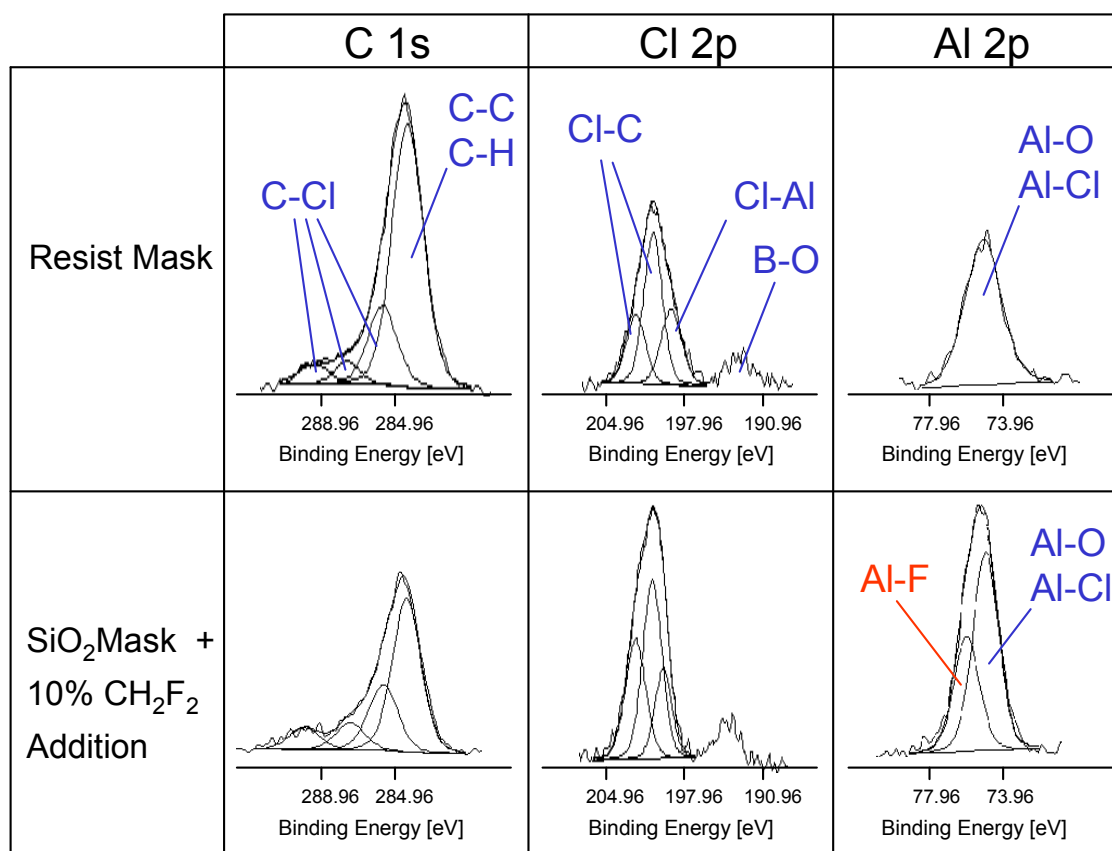


Fig. 2.18. XPS narrow-scan spectra of the reaction products deposited on the SiO₂ chip during Al RIE with resist mask without CH₂F₂ addition and with SiO₂ mask with CH₂F₂ addition.

C Mechanism of Etching Profile Control of Al RIE

On the basis of the results obtained up to present, the author considers the mechanism of sidewall deposition determining the Al etching profile in the case of the N₂ and CH₂F₂ gas additions to BCl₃+Cl₂ gas mixture. Figure 2.19 shows the schematic view of the Al RIE model of the N₂ gas addition case. In the plasma, BCl_x, B, Cl₂, Cl, N₂ and N are supplied from the etching gas and its dissociations. Those fragments are transported to

the surface of the etching sample to cause the etching. On the surface, Al is etched forming volatile compounds AlCl_x and the resist mask is also etched generating CH_x and H mainly by ion sputtering. Those etching reaction products return into the plasma. Due to the existence of N in the case of the N_2 addition, H reacts with N to generate ammonium radicals NH_x in the plasma and/or the etching surface. Parts of these etching reaction products are exhausted out of the etching chamber. The rest are attached to the Al sidewall or decomposed first and attached to the sidewall second. The attached reaction products become the deposit on the Al sidewall after all. The deposit consists of a large amount of carbon compounds, in which carbon is combining with C, Cl and H and a small amount of ammonium compounds. Probably due to the ion bombardment effect to extract H and Cl from the carbon compounds, the majority of the carbon bond is considered C-C bonds. Ammonium compounds taking the form of NH_4Cl and NH_4AlCl_4 are considered to exist in the volume spaces of the carbon compounds. The reason has not been clarified why the amount of the carbon-rich deposition increases by the N_2 gas addition. Two possible explanations are considered as follows. One is the existence of CN-containing compounds on the sidewall surface, which is inferred from the result of plasma emission spectra shown in Fig. 2.17. CN-containing compounds are considered to enhance the sticking coefficient of the deposition fragment to the sidewall surface due to the existence of a lone pair of N. Another idea is that the low concentration of H in the plasma makes much more carbon deposition because the deposited carbon has more dangling bonds instead of C-H bonds.

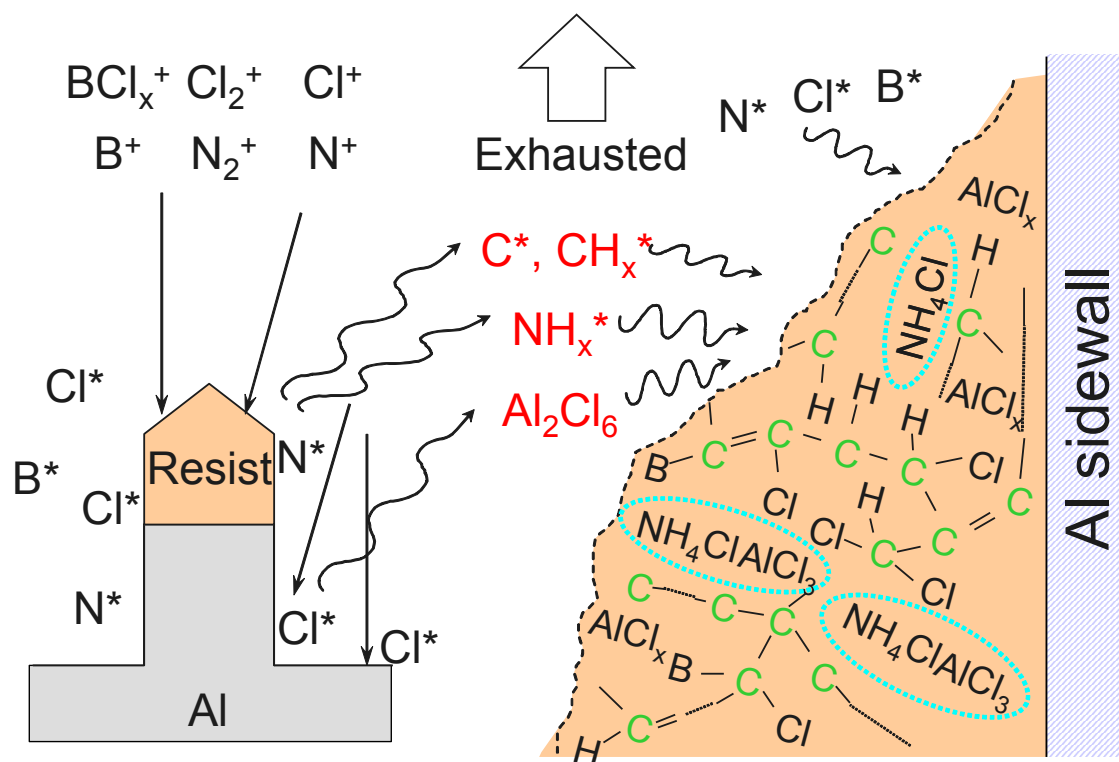


Fig. 2.19. Model of Al RIE with N_2 gas addition.

Figure 2.20 shows the Al RIE model in the case of the CH_2F_2 gas addition with the SiO_2 mask. The dissociations of CH_2F_2 gas leads to supply CH_x fragments, which contributes the protection layer formation on the Al sidewall. This is different from the case of the organic resist mask in which CH_x is supplied by the resist etching and decomposition. In addition to the etching reaction forming $AlCl_x$, new etching reactions should be considered such as the formation of SiF_x on the SiO_2 mask surface and AlF_x on the etched Al surface. Although SiF_x is volatile, AlF_x is non-volatile and hence remained in the sidewall deposit. Such CH_x and AlF_x are considered major ingredients of the sidewall deposit.

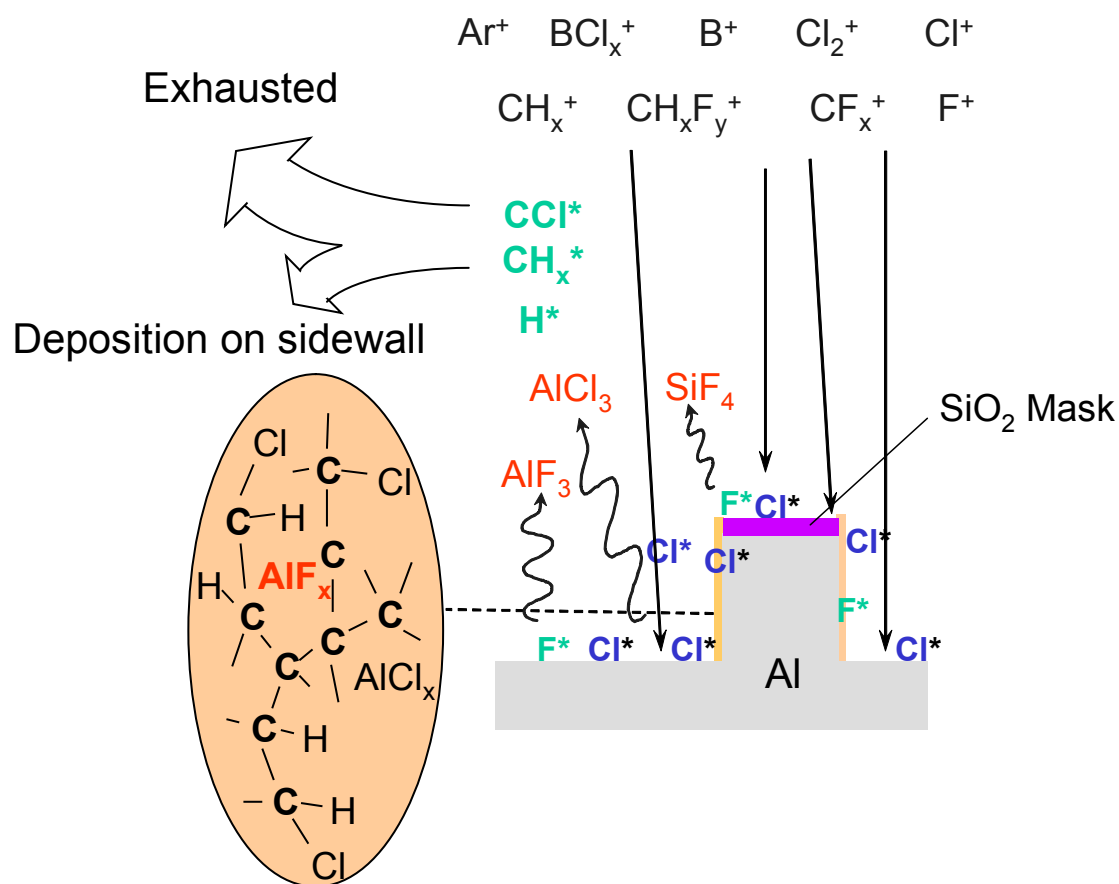


Fig. 2.20. Model of Al RIE with CH_2F_2 gas addition with SiO_2 mask instead of an organic resist mask.

As described above, the sidewall protection with N_2 gas addition requires H to from the ammonium compounds. H is supplied from the etched resist during the Al RIE, which means that the resist etching is necessary for the N_2 gas addition case. However, the resist should be etched as little as possible because the resist mask for advanced devices becomes thin due to keeping the photolithography capability. Therefore, the N_2 addition method cannot meet both the sidewall protection and the resist selectivity

in principle. On the other hand, CF_x -containing gas addition does not always need H from the etched resist to form the enough sidewall protection to avoid a side-etch. This mechanism is suitable especially for the thin resist mask used in the fine patterning of Al-interconnects.

2.2.3 Summary and Conclusions

Profile control of Al RIE has been investigated. Two cases were focused on: $\text{BCl}_3+\text{Cl}_2+\text{N}_2$ gas chemistry with an organic resist mask and $\text{BCl}_3+\text{Cl}_2+\text{Ar}+\text{CH}_2\text{F}_2$ with SiO_2 mask. The Al profile changes from side-etched to non side-etched and vertical when N_2 or CH_2F_2 gas is added to BCl_3+Cl_2 gas mixture. In both cases, the sidewall deposition determines the taper profile. In order to analyze the sidewall deposit in detail, 'imitation sidewall method' has been proposed. Although the imitation sidewall method does not have quantitative validity to identify the sidewall deposit, it is turned out useful for the qualitative analysis of the sidewall deposit because of the large analyzing area. The sidewall protection film in the case of the N_2 gas addition consists mainly of carbon-based compounds bonding with C, Cl and H with ammonium compounds such as NH_4Cl and NH_4AlCl_4 . In the case of the CH_2F_2 addition, the deposit on the Al sidewall is thinner than that in the case of the N_2 addition and the deposit consists of a mixture of carbon-based compounds bonding with C, Cl and H and Al compounds such as AlF_x and AlCl_x . It has also been found in the N_2 gas addition case that H generated from the organic resist reacts with N resulting in the formation of the ammonium compounds. The low concentration of H in the plasma has a possibility to cause the thick carbon-rich deposition because deposited carbon does not bond with H but has much dangling bonds. Another

speculation for explaining the thick carbon-rich deposition is based on the existence of CN bonds in the sidewall surface. CN bonds are considered to enhance the sticking coefficient of the deposition fragment due to the existence of a lone pair of N.

From the sidewall deposition mechanisms clarified thus far, one can compare the two additional gases. Since the N_2 addition needs the resist mask etching to form the sidewall protection including ammonium compounds, it is not suitable for the thin resist used in the fine Al patterning. Thus, the N_2 addition method cannot meet the requirements, the sidewall protection and the resist selectivity in principle. On the other hand, the CF_x -containing gas addition does not always need H from the etched resist to form the enough sidewall protection to avoid a side-etch. This mechanism is suitable especially for the thin resist mask case. This is one reason why N_2 is not major additional gas to tune the Al profile at the present time. On the basis of those considerations, Al RIE process has been improved. In particular, it is possible to find the proper process condition at the early stage of the next generation device development. In addition, the clarification of the etching reaction products leads to another benefit. In the case of N_2 addition process, a large amount of deposition occurs on the etching chamber wall surface. The thick deposit can peel off resulting in particle defects on the device, which is more and more serious in the downscaled device. In the case of CF_x -containing gas addition process, a certain amount of AlF_x are deposited on the etching chamber wall. The AlF_x film can also be a source of the particle defect. In order to prevent the deposition film from peeling to cause particle defects, the material, roughness and temperature of the etching chamber wall should be properly chosen for example.

2.3 Etching Profile Control of TiN RIE

2.3.1 Experimental Procedure

100-nm-thick TiN films were prepared by reactively sputtering a Ti metal target onto 300-nm-thick SiO₂, which is deposited on an 8 inch (100) Si wafer by CVD (Chemical Vapor Deposition) using TEOS (Tetraethoxysilane) as a source. Then, 1.5-μm-thick resist (PFR IX410, JSR) was coated with BARC (Bottom Anti-Reflection Coating) and patterned by KrF lithography. A metal etcher (Centura-DPS, Applied Materials Inc.) was used for the TiN RIE experiments. Figure 2.21 shows the schematic view of the etcher, which has an ICP (Inductively Coupled Plasma) source excited by 13.56 MHz power through the upper electrode. 13.56 MHz power is also supplied to the lower electrode in order to control the DC self-bias voltage between the plasma and the surface of the etching sample. During the RIE, the total gas flow = 120 sccm, the pressure = 1.1 Pa, the RF power for the upper electrode = 1000 W, the RF power for the lower electrode = 85 W and the temperature of the lower electrode = 85 °C. The endpoint of the TiN film etching was detected by monitoring the intensity of the Ti (337.5 nm) spectral line from the plasma. After the detection of the endpoint of the etching, the sample was overetched for 50% of the etching time. The etched profile of patterned TiN was observed using a SEM. FE-AES was used for analyzing the sidewall surfaces after RIE of the patterned TiN. In the experiment blanket TiN films without the resist mask were etched as a control. The etched depth of the blanket TiN was determined by the use of X-ray fluorescence, by which the number of Ti atoms in the film can be counted. After half etching of the blanket TiN, the surface was analyzed by XPS.

2. Dry Etching Profile in Al-Wiring Fabrication

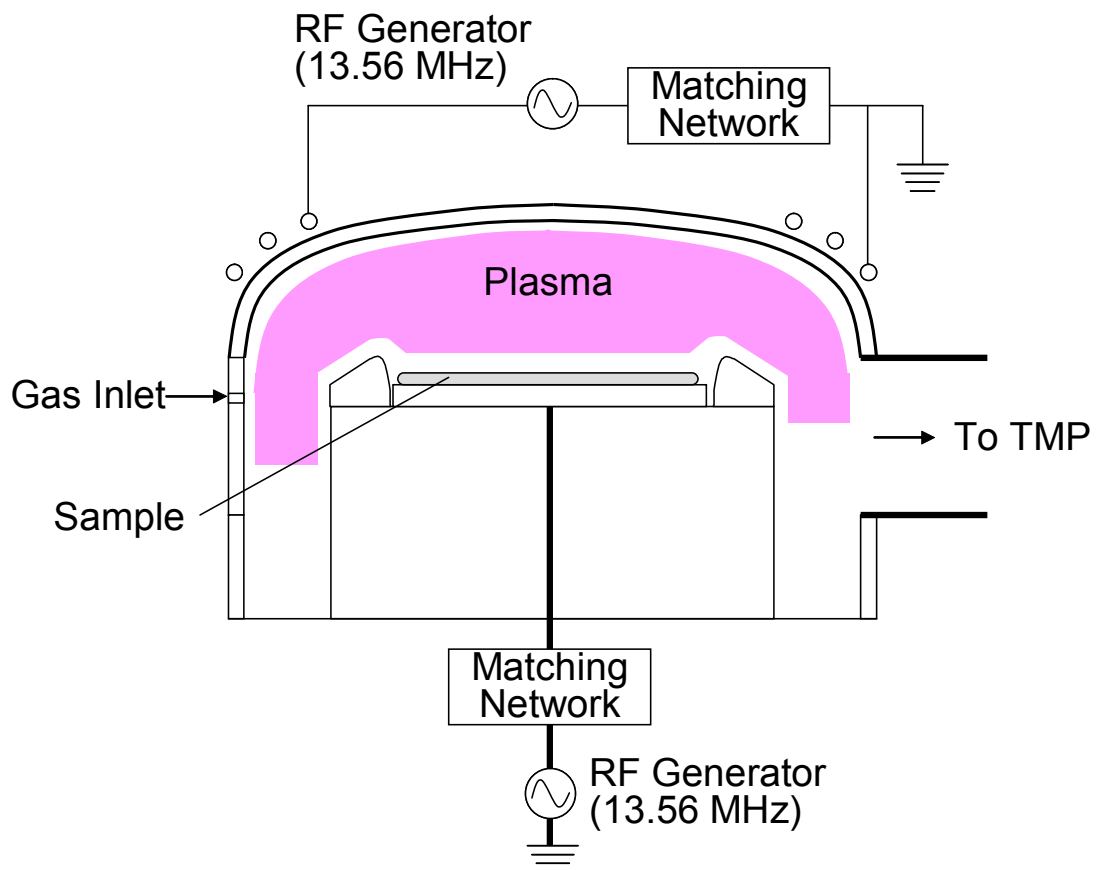


Fig. 2.21. Schematic view of dry etching apparatus.

2.3.2 Results and Discussion

A Etching Rate and Profile of TiN RIE

The etching rate of blanket TiN is shown as a function of the ratio of additional gas to Ar in Fig. 2.22. First, it is noted that Ar plasma without any additional gas cannot etch the TiN film at all. The reason for this is considered to be as follows; there is no chemical effect in the Ar plasma and the sample is not exposed to strong ion bombardment induced by a DC self-bias voltage in this experiment. In contrast to Ar plasma, any additional gas such as CHF_3 , BCl_3 or Cl_2 enhances the etching rate proportionally to the additional gas flow rate ratio. The increase in the etching rate is quite different for each of the three additional gases; it is maximum for Cl_2 addition (188 nm/min), minimum for CHF_3 addition (10 nm/min) and slightly more for BCl_3 addition (30 nm/min) than for CHF_3 .

The profiles after etching of TiN samples with resist were observed by SEM and are shown in Fig. 2.23. The film was not etched at all in the case of Ar without any additional gas as shown in Fig. 2.23 (a). The profiles of the samples etched with the addition of 30% CHF_3 , BCl_3 or Cl_2 flow of the total are shown in Figs. 2.23 (b), (c), and (d), respectively. In the case of CHF_3 addition (Fig. 2.23 (b)), TiN was not etched off in the etching time of 95 s due to the very low etching rate, and the profile is rather tapered with some deposition on the sidewall of the and TiN films, as indicated by an arrow in the figure. In the cases of BCl_3 (Fig. 2.23 (c)) and Cl_2 (Fig. 2.23 (d)) additions, etching times were fixed at 204 s and 48 s, respectively, which correspond to 50% overetching. Cl_2 addition resulted in an almost completely non-tapered profile of etched TiN, whereas a tapered profile with a low taper angle was obtained by BCl_3 addition.

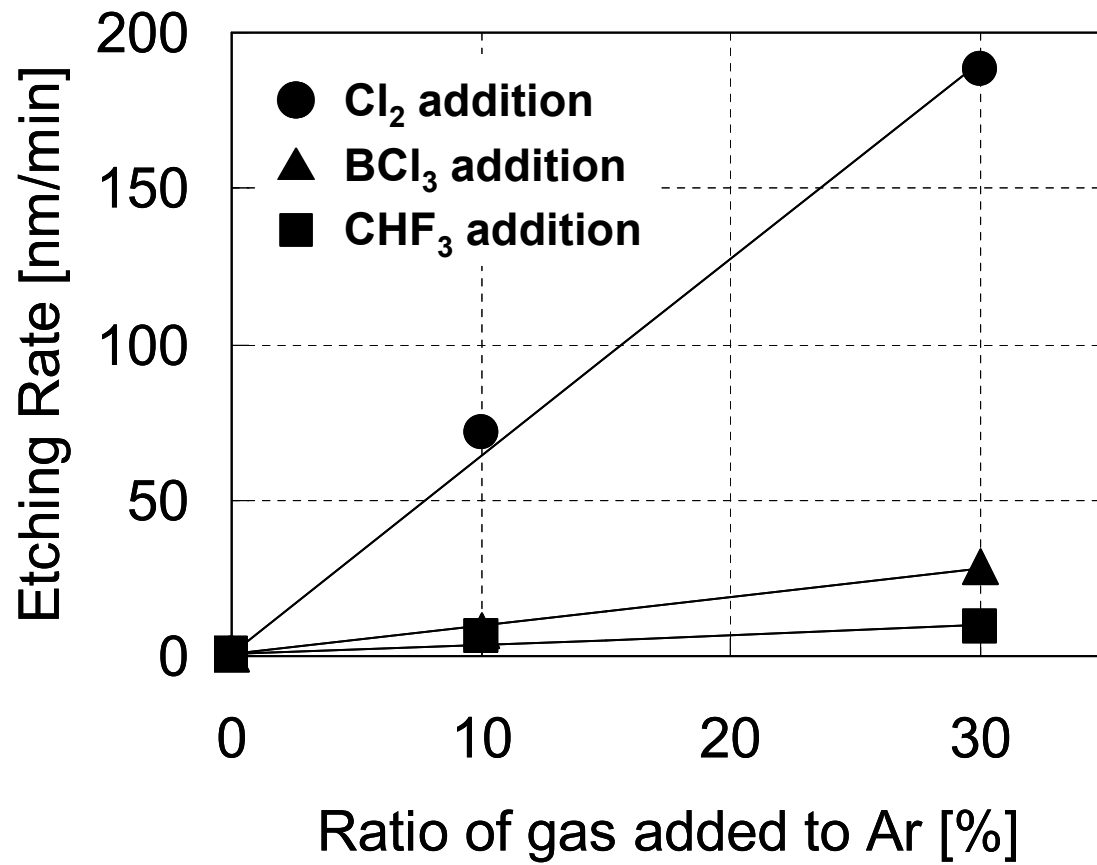


Fig. 2.22. TiN etching rates as a function of the ratio of additional gas such as CHF₃, BCl₃ or Cl₂ to Ar.

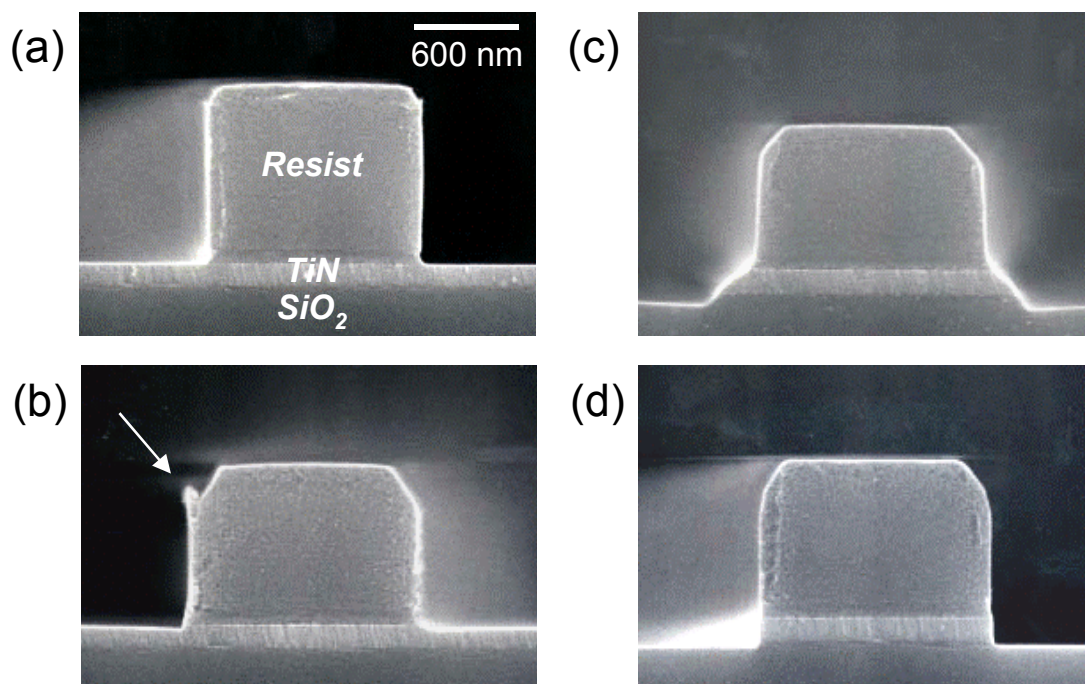


Fig. 2.23. TiN etching profiles for different gas chemistries; (a) Ar, (b) Ar+CHF₃, (c) Ar+BCl₃, and (d) Ar+Cl₂.

In order to distinguish the cause of the tapered profile of etched TiN in the case of BCl₃ addition, etching experiments with varying the additional BCl₃/Cl₂ gas flow ratio were carried out. The resultant profiles and their features are shown in Fig. 2.24 and Table 2.5, respectively. It is clearly evident in the figure and table that the taper angle of etched TiN decreases with increasing the BCl₃ flow rate. With increasing the BCl₃ flow rate, the etching rate of the TiN film decreased and the etching time of the experiment increased. In spite of the longer etching time and smaller resist etching selectivity in the cases of BCl₃ involvement, the top TiN width after the etching did not decrease as shown in the table. This suggests that the resist is hardly side-etched in this experiment for all the

cases, (a), (b), and (c). Thus, the deposition of some materials on the TiN sidewall is supposed to be the cause of the tapering. The materials are supposed to be reaction products of the resist and TiN with the fragments generated from BCl_3 and Cl_2 . In the comparison between cases (b) and (c), the taper angles were quite different while the remaining resist thicknesses were not significantly different. This suggests a possibility that reaction products of TiN with fragments of BCl_3 plasma are the major material for decreasing the taper angle.

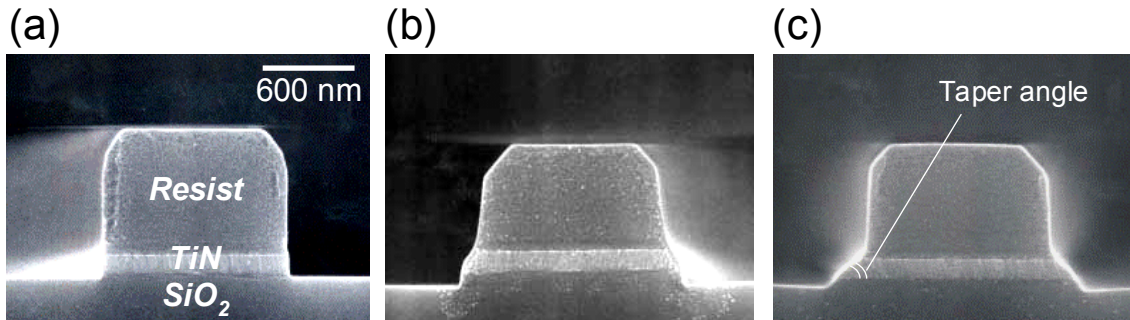


Fig. 2.24. TiN profiles after RIE with conditions for BCl_3+Cl_2 addition to Ar in varying the BCl_3/Cl_2 ratios; (a) Cl_2 100%, (b) $\text{BCl}_3:\text{Cl}_2=1:1$, and (c) BCl_3 100%.

Table 2.5 Features of TiN profiles after RIE with conditions for BCl_3+Cl_2 addition to Ar in varying the BCl_3/Cl_2 ratios.

Case	Gas			Etching rate [nm/min]	Etching time [s]	Top TiN width [μm]	TiN taper angle [$^\circ$]	Selectivity to resist
	Ar	BCl_3	Cl_2					
	[sccm]							
a	84	0	36	230	48	1.00	88	1.73
b	84	18	18	61	159	1.03	59	0.70
c	84	36	0	36	204	1.06	38	0.79

B Analysis of Etched Surface and Sidewall of TiN

In order to clarify the above etching characteristics of TiN RIE, at first XPS analyses were carried out for the blanket TiN surface before and after the half etching by Ar only, Ar+CHF₃, Ar+BCl₃, and Ar+Cl₂, respectively. The ratio of each additional gas flow rate to the total was 30%. Table 2.6 shows the surface concentrations of each element, as obtained by the XPS. The surface concentrations were calculated by the area ratios of the spectrum corrected by the elemental sensitivities. The surfaces of all the samples were somehow oxidized and contaminated with carbon before the XPS measurements as shown in the table. Small amounts of Cl and F were detected after Ar only half etching. These halogen elements are thought to come from contamination in the etching chamber. On the surface after half RIE with Ar+CHF₃ plasma, nearly three times more F than Ar plasma was detected, which was naturally expected. It is found that BCl₃ addition causes B to remain on the etched surface and an increase in the N concentration.

Table 2.6 Concentrations of elements on TiN surface before and after RIEs as determined by XPS.

TiN sample	Ti [%]	N [%]	B [%]	Cl [%]	C [%]	O [%]	F [%]
before RIE	21.6	19.1	- ^a	-	22.5	36.9	-
after RIE with Ar	19.2	10.1	-	1.3	29.6	35.9	3.9
after RIE with Ar+CHF ₃	16.2	12.4	-	-	30.2	29.3	11.9
after RIE with Ar+BCl ₃	16.2	25.1	2.4	1.7	31.7	19.7	3.3
after RIE with Ar+Cl ₂	18.3	19.8	-	1.1	32.0	22.9	5.9

^a ‘-’ indicates below detection limit

unit: atomic %

Narrow-scan spectra obtained by the above XPS analyses are shown in Figs. 2.25 (a) and (b), Figs. 2.26 and 2.27, where peak shift corrections were made by using C 1s (284.6 eV) spectra. Figures 2.25 (a) and (b) show the Ti 2p and N 1s spectra, respectively, for all sample surfaces obtained in a previous RIE experiment. The TiN peaks were not clear before the etching while Ti-O-N peaks were dominant in Figs. 2.25 (a) and (b), but the TiN peak became clear after the etchings. It is found that TiF_x [2.13] [2.18] exists after half RIE using $\text{Ar}+\text{CHF}_3$ plasma in Fig. 2.25 (a). The existence of TiF_x is also supported by the spectrum in Fig. 2.26, where the peak position of F 1s is located at around 684.6 eV, indicating that F bonds with metal. In the case of BCl_3 addition, it should be noted that the TiO_2 peak was smaller and that the TiN peak was larger in comparison to the other gas addition cases, as shown in Fig. 2.25 (a). These results correspond to the O and N atomic concentrations shown in Table 2.6. It is also found that sub-peaks at around 398 ~ 400 eV are present in the case of BCl_3 addition, as shown in Fig. 2.25 (b). These peaks are attributed to boron oxynitrides and/or titanium oxynitrides [2.17] [2.18]. Furthermore, the B 1s peak at 191.4 eV found in Fig. 2.27 indicates the existence of boron oxynitrides [2.19], which is consistent with the consideration made based on the N 1s spectrum shown in Fig. 2.25 (b). It is considered that detected chemical bonds such as Ti-F_x and $\text{B-N}_y\text{-O}_z$ have been formed during TiN RIE and that they remained on the surface even after the half RIE of TiN. Since TiF_3 , B_2O_3 and BN are known as compounds which do not easily evaporate and have high boiling points, it is considered that the relatively low etching rates, in the case of CHF_3 or BCl_3 addition, are caused by those surface layers formed on TiN which include Ti-F_x bonds in CHF_3 addition or $\text{B-N}_y\text{-O}_z$ bonds in the case of BCl_3 addition.

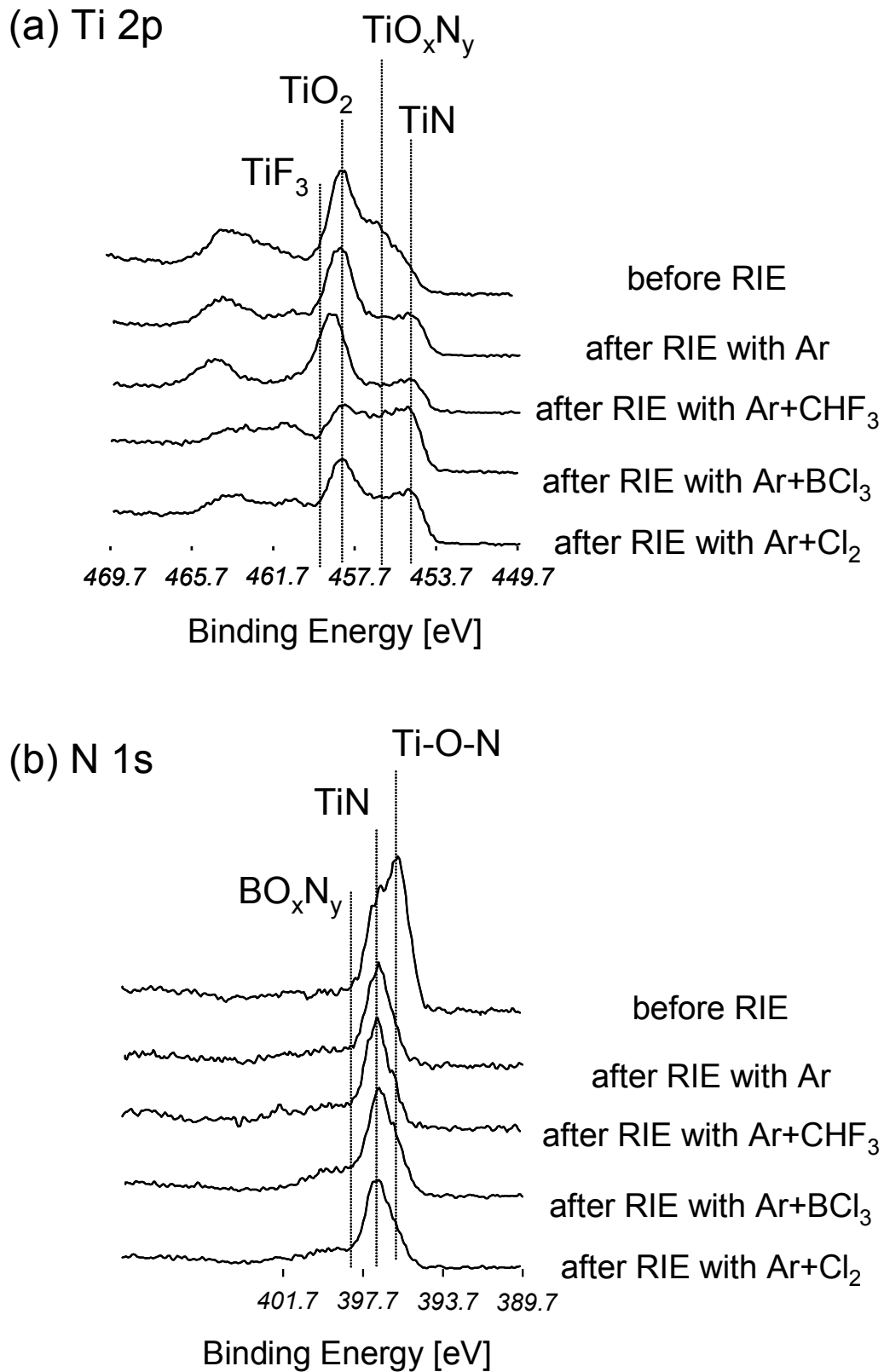


Fig. 2.25. XPS narrow-scan spectra of (a) Ti 2p and (b) N 1s for TiN half-etched surface after various RIE gas chemistries.

F 1s

after RIE with Ar+CHF₃

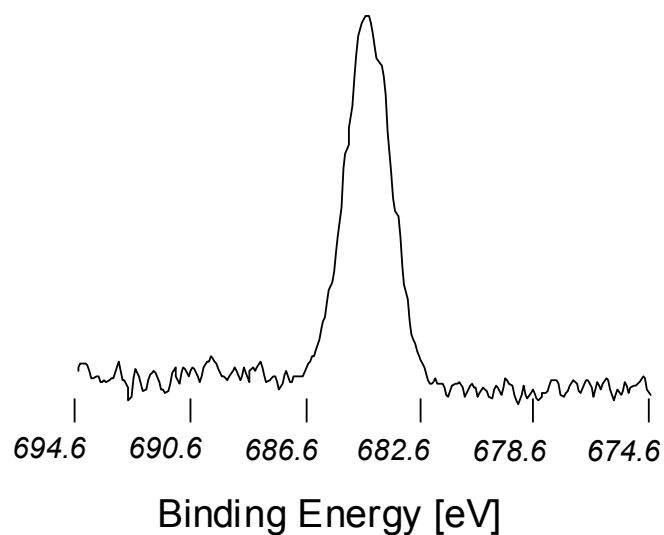


Fig. 2.26. XPS F 1s narrow-scan spectrum of TiN half-etched surface after RIE with Ar+CHF₃.

B 1s, Cl 2p

after RIE with Ar+BCl₃

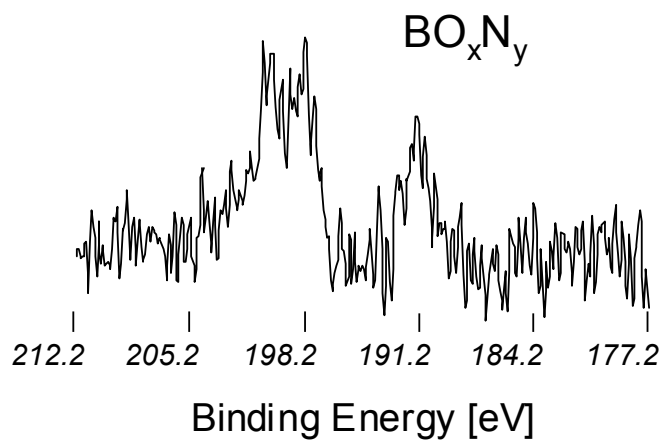


Fig. 2.27. XPS B 1s, Cl 2p narrow-scan spectra of TiN half-etched surface after RIE with Ar+BCl₃.

In order to investigate the effect of sidewall-deposited film during the RIE on the etching profile, FE-AES analyses were carried out on the sidewall of the resist pattern for TiN samples after the RIE. The analyzed samples are shown in the upper three micrographs of Fig. 2.28. The lower three micrographs show the states of the sidewall deposits themselves after O₂ plasma ashing to remove the resist mask. The spatial resolution of the Auger electron spectroscopy was 500 nm and this is sufficiently large to measure the resist sidewall region excluding TiN and SiO₂ substrate. The depth resolution of the Auger electron spectroscopy was 10 nm. The result of the FE-AES analyses is shown in Table 2.7. Similarly to the XPS analysis results, Cl and F from the etching machine were detected under the Ar-only plasma condition. The concentration of Ti decreases significantly in the cases where Cl is included in the etching ambient, i.e., Ar+BCl₃ and Ar+Cl₂, because titanium chlorides are volatile. The concentration of F in the case of Ar+CHF₃ was five times larger than those in other cases. Thus, it is expected that the resist sidewall of the Ar+CHF₃ case contains certain amounts of fluorocarbons and titanium fluorides. It is known that titanium fluorides and fluorocarbons are relatively nonvolatile. Probably, certain amounts of these fluorocarbons and titanium fluorides extend to the TiN sidewall. This would be the cause of the very small etching rate of TiN and also the tapering in the case of the Ar+CHF₃ gas chemistry.

In the case of the Ar+BCl₃ gas chemistry, certain amounts of B and N were detected at the resist sidewall. Boron nitrides are non-volatile and this would be the cause of the tapering in the case of Ar+BCl₃ etching.

2. Dry Etching Profile in Al-Wiring Fabrication

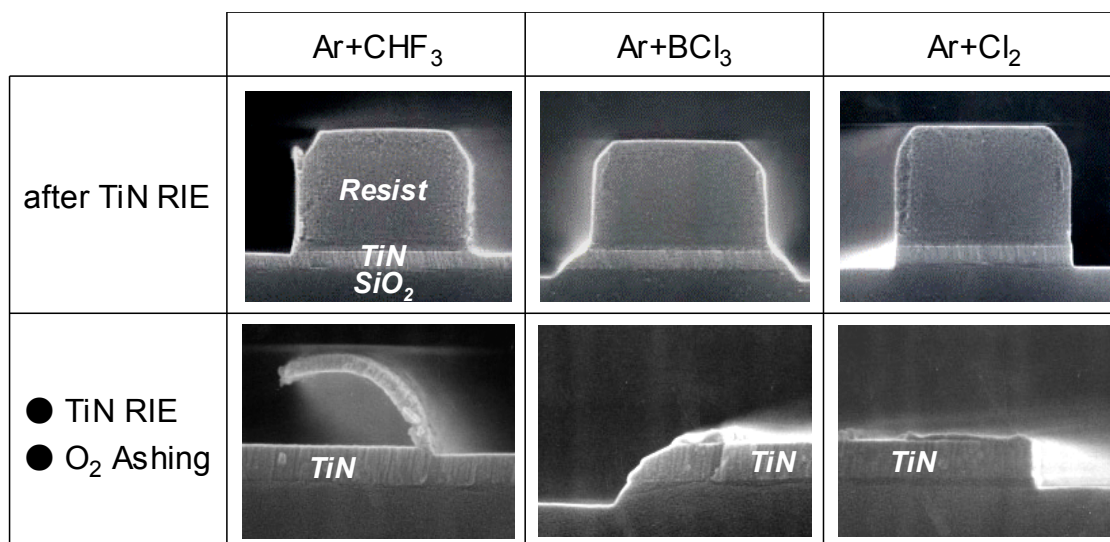


Fig. 2.28. TiN profiles after RIE and the sidewall deposit remaining after O₂ ashing for different TiN RIE gas chemistries.

Table 2.7 Concentrations of elements on the surface of resist sidewall after TiN RIE as determined by FE-AES.

TiN sample	Ti	N	B	Cl	C	O	F	Al	Si
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
after RIE with Ar	8	-	- ^a	0.2	75	16	1	-	-
after RIE with Ar+CHF ₃	12	-	-	-	69	14	5	-	-
after RIE with Ar+BCl ₃	2	7	5	-	69	11	1	3	2
after RIE with Ar+Cl ₂	1	5	-	0.3	79	8	1	2	5

^a '-' indicates below detection limit

unit: atomic %

Boron nitrides generated in the case of Ar+BCl₃ gas chemistry are considered one of the reasons for the slow etching rate of TiN, according to the XPS analysis. N in the TiN would be essential to form the boron nitrides during the RIE with Ar+BCl₃ gas chemistry. In order to confirm the role of boron nitrides for the slow etching rate, etching of Ti film (which does not include N as the component) was carried out and compared with that of TiN. In the case of Ti etching, boron nitrides formation is expected to be little and thus the etching rate is expected to be high. The results are shown in Table 2.8. In addition to the Ar+BCl₃ gas chemistry, the etching with the Ar+Cl₂ gas chemistry was carried out as control. It should be noted that the etching rate of TiN is higher than that of Ti in the case of the Ar+Cl₂ gas chemistry but it is lower than that of Ti in the case of the Ar+BCl₃ gas chemistry. This suggests that the formation of boron nitrides during the RIE with Ar+BCl₃ gas chemistry is the reason for the slow etching rate of TiN.

Table 2.8 Etching rates of Ti and TiN for different gas chemistries: Ar+BCl₃ and Ar+Cl₂.

Sample	Gas chemistry	Etching rate [nm/min]
Ti	Ar+BCl ₃	47
Ti	Ar+Cl ₂	138
TiN	Ar+BCl ₃	29
TiN	Ar+Cl ₂	188

C Etching Model of TiN RIE

On the basis of the results described above, it is possible to propose a TiN RIE model which will enable a consideration of the appropriate conditions for obtaining the desired etched profile of TiN. Figures 2.29, 2.30 and 2.31 show a schematic model of TiN RIE for Ar+CHF₃, Ar+Cl₂ and Ar+BCl₃ gas chemistry, respectively.

First, TiN is not etched at all under the Ar-only plasma condition. Thus the role of Ar in the case of additional gases is probably the removal of the deposited films and the enhancement of the etching reactions at the TiN surface by bombardments of the Ar ions in addition to other ions. Etching of the TiN film is accomplished by radicals such as F, CF_x, H, Cl, BCl_x, B generated from the gases.

In the Ar+CHF₃ case, Fig. 2.29, radicals containing F are the main etchants, and thus F reacts with Ti and N to produce TiF_x and NF_x as reaction products, respectively. At the same time, CH_xF_y becomes the precursor of fluorocarbon deposition. Among those reaction products, NF_x is considered to evaporate very easily because the boiling point of NF₃ is -128.8 °C and thus it is often used as a cleaning gas for the SiO₂ CVD chamber [2.20]. As far as titanium fluoride is concerned, however, it is known that TiF₄ is not difficult to evaporate as its sublimation temperature is 284 °C, but TiF₃ is a nonvolatile compound which has the very high boiling point of 1400 °C. Therefore, except NF_x and TiF₄, there are many compounds which cause deposition on the etched TiN surface and the sidewall. This is the reason why the etching rate of TiN is low and the etched profile has a low taper angle under the Ar+CHF₃ condition.

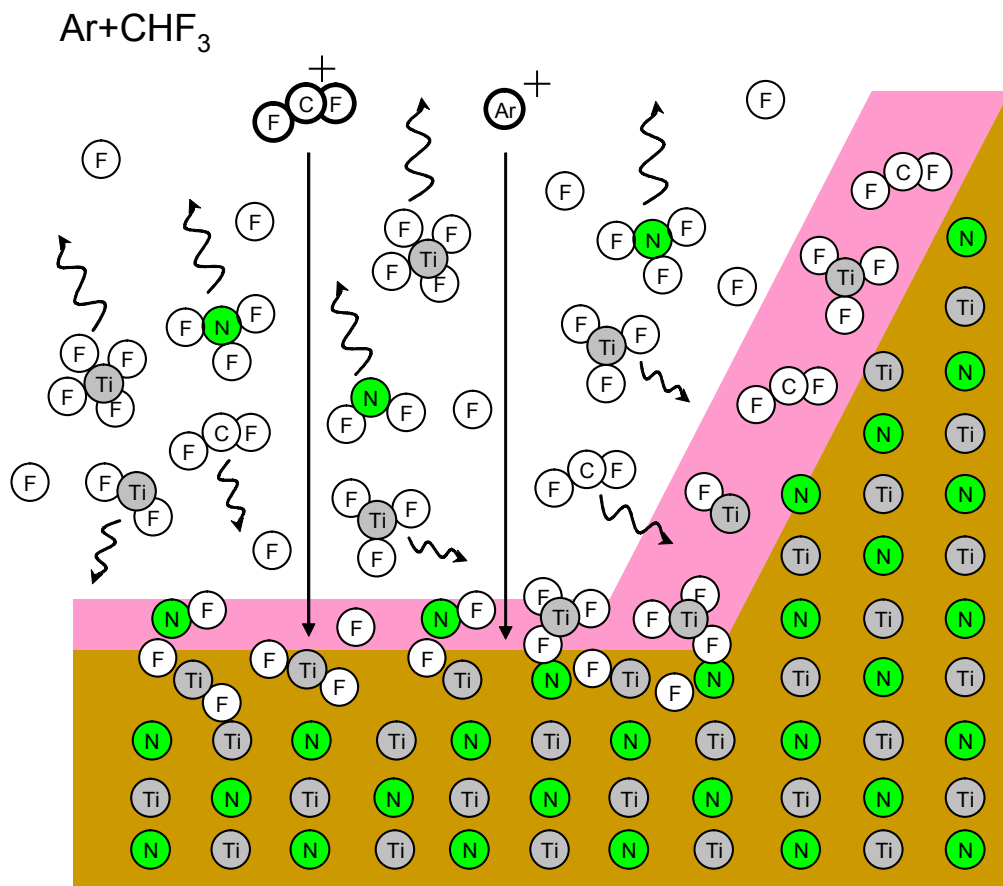


Fig. 2.29. Model of TiN RIE in the case of Ar+CHF₃ gas chemistry.

In the $\text{Ar}+\text{Cl}_2$ case, Fig. 2.29, large amounts of Cl and Cl_2 radicals exist and react with Ti and N to produce TiCl_x and NCl_x as reaction products. These reaction products do not have very high boiling points. For examples, the boiling points are as follows; NCl_3 : less than 71°C , TiCl_4 : 136.4°C , TiCl_2 : 475°C , TiCl_3 : 660°C . These compounds are not difficult to evaporate with the assistance of ion bombardments. Therefore, a high etching rate and non-tapered etched profile are obtained by Cl_2 addition.

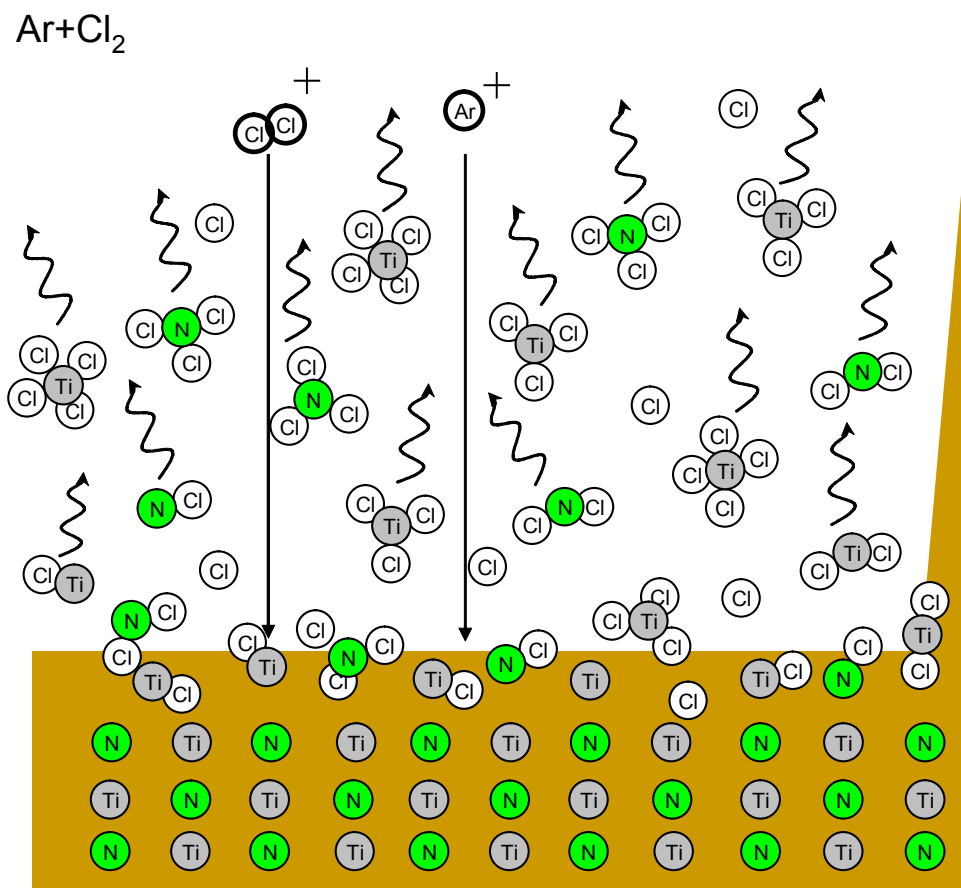


Fig. 2.30. Model of TiN RIE in the case of $\text{Ar}+\text{Cl}_2$ gas chemistry.

In the Ar+BCl₃ plasma, Fig. 2.30, Cl_x, BCl_x and B_x are generated by the dissociation of BCl₃. On the etching surface of TiN, a reaction between B and N should be taken into account [2.5] in addition to the same reactions as those for Ar+Cl₂ plasma. Here one does not think that it is necessary to consider a reaction between B and Ti because no TiB [2.18] is detected on the etched TiN surface by XPS analyses. Therefore, under the Ar+BCl₃ condition, reaction products are considered to consist of TiCl_x, NCl_x and BN_x. Since the boiling point of BN is 3000 °C it is inferred that BN_x are a nonvolatile compounds resulting in deposition on both the TiN surface and the TiN sidewall, which causes a lower etching rate than Cl₂ addition and a low taper angle of the etched profile.

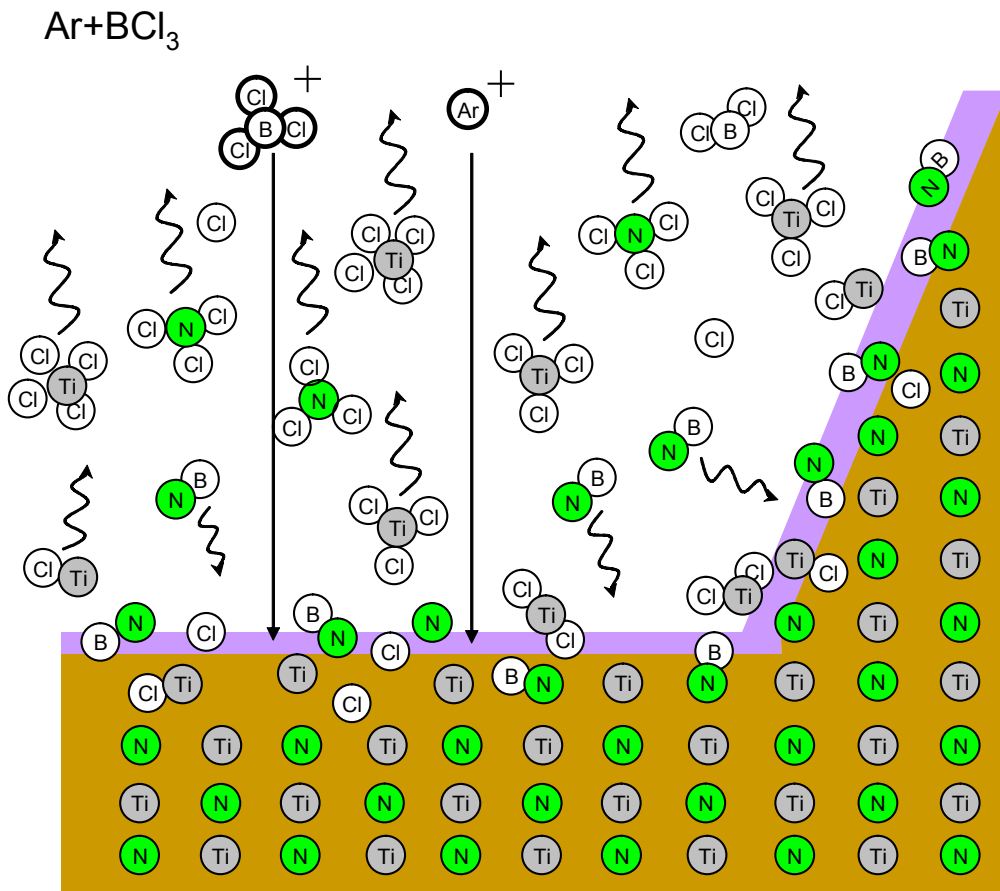


Fig. 2.31. Model of TiN RIE in the case of Ar+BCl₃ gas chemistry.

The above models are simple cases. In reality, the involvement of O and perhaps C as contaminants should be considered. For example, instead of boron nitrides, boron oxynitrides should be considered, as previously described with respect to the XPS results. Moreover, new etching mechanism should be considered in the case of the combination of Cl radicals and F radicals [2.21].

2.3.3 Summary and Conclusions

RIE characteristics of TiN film have been studied. Although TiN is not etched in the case of using Ar as the etching gas, the etching rate is increased by the addition of CHF₃, BCl₃ or Cl₂. The etching rates, however, differ among these additional gases as follows; Ar+CHF₃: 10 nm/min, Ar+BCl₃: 30 nm/min and Ar+Cl₂: 188 nm/min. It has also been found that the etching profile is non-tapered in the case of Cl₂ addition and tapered in the case of BCl₃ addition. Therefore, it is considered that Cl₂ addition is most effective for obtaining a high etching rate and non-tapered profile, and that BCl₃ or CHF₃ addition enables control of the taper angle of the etched profile. The difference in etching characteristics among the additional gases is inferred from the results of surface analyses for etched TiN samples. Although F or Cl radicals generated in the plasma enhance the etching rate of TiN by forming volatile compounds such as TiF₄, NF_x, TiCl_x and NCl_x, nonvolatile compounds such as TiF_x or BO_xN_y are produced in the case of CHF₃ or BCl₃ addition. Moreover, CHF₃ addition is considered to promote fluorocarbon deposition on the TiN surface during etching, which results in the lowest etching rate in this experiment.

2.4 Endpoint Detection of the Etching of TiN/Al Stacked Film

As described earlier, the proper etching conditions for Al and TiN/Ti are different each other in general. This indicates that the etching condition should be changed when the etching of one of the layers is accomplished. In particular, a careful change is required at the interface between top TiN/Ti and Al. This is because Al side-etching occurs more easily than TiN/Ti due to the high reactivity of Al with Cl. The side-etch might cause the poor step coverage of ILD deposition over patterned Al-wirings. Usually, the condition change from the TiN/Ti to Al layer is carried out by a fixed time calculated from the etching rate of the TiN/Ti, which sometimes causes the irregular profile due to fluctuations of the film thickness and/or the etching apparatus. To avoid the irregularity and to stabilize the patterning process of the stacked wiring, the author attempts to detect the etching endpoint by using the optical emission of the plasma. The through process flow of TiN/Ti/Al/TiN/Ti-wiring patterning is illustrated in Fig. 2.32. Figure 2.33 shows the change of 396.2 nm emission intensity with time and the emission spectra (wavelength range = 300 ~ 800 nm) at 35, 45 and 50 s. It is evident that many strong emissions of Ti atoms and ions are observed in the wavelength range 300 ~ 600 nm, which are very close and even overlap with Al emissions. Thus, it is easy to detect the endpoint of TiN/Ti etching by using the same detection system as that for Al RIE. In fact, TiN endpoint detection has been successfully applied to the TiN/Ti/Al/TiN/Ti-wiring patterning by using the intensity change at 396.2 nm as shown in the top graph in Fig. 2.33. Figure 2.34 shows the TiN/Ti/Al/TiN/Ti-wiring profile in case of using the endpoint detection of the top TiN/Ti layer. The cross-sectional micrograph was taken after the resist and sidewall deposit removal following the RIE. It is

found that a good profile with little side-etch of Al. It was also confirmed that a good result in electric open/short test are obtained although the data is not specified in this thesis. The applicability of the endpoint detection can lead to prevent the etching profile from fluctuating due to the variations of film thicknesses and etching chamber conditions.

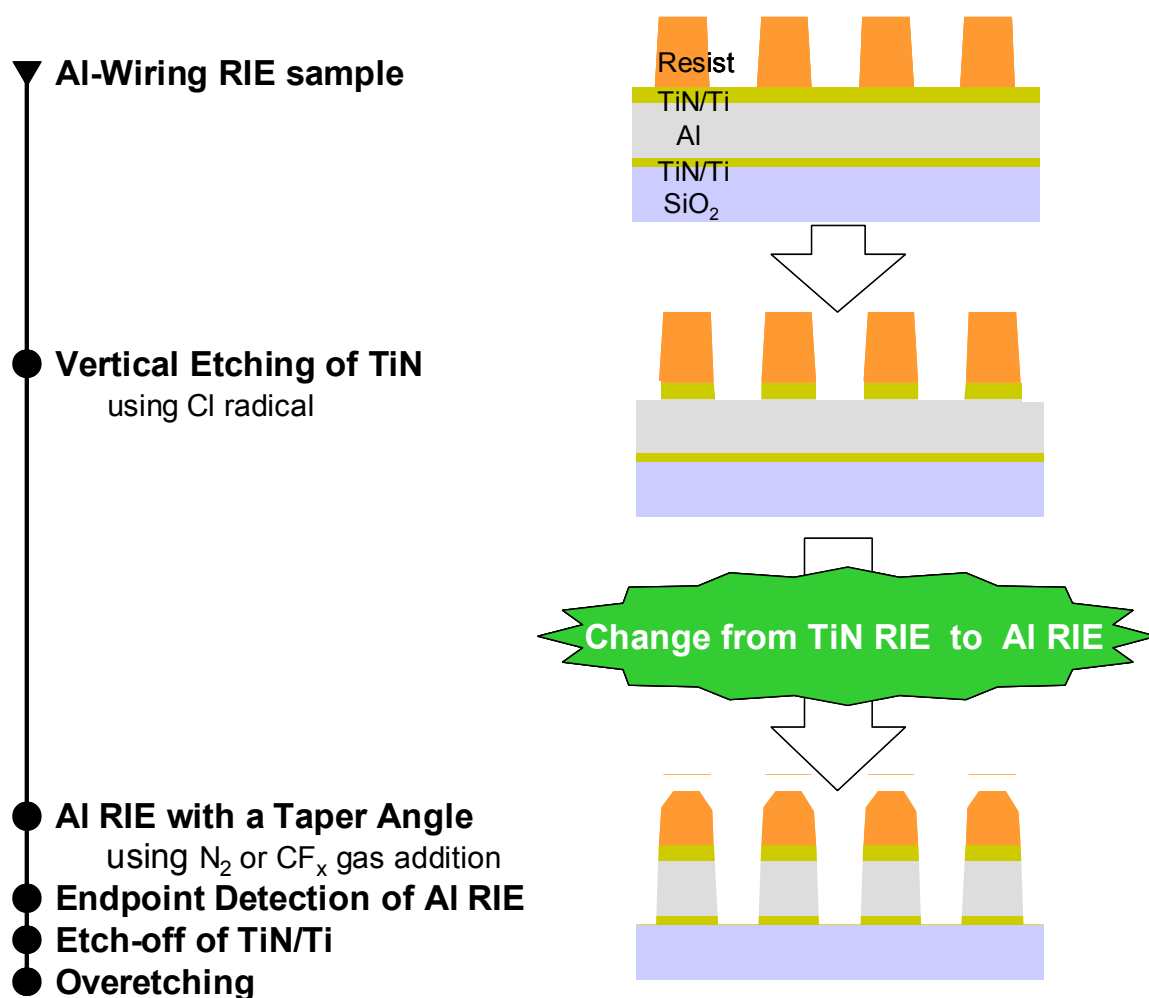


Fig. 2.32. Process flow of TiN/Ti/Al/TiN/Ti-wiring patterning.

2. Dry Etching Profile in Al-Wiring Fabrication

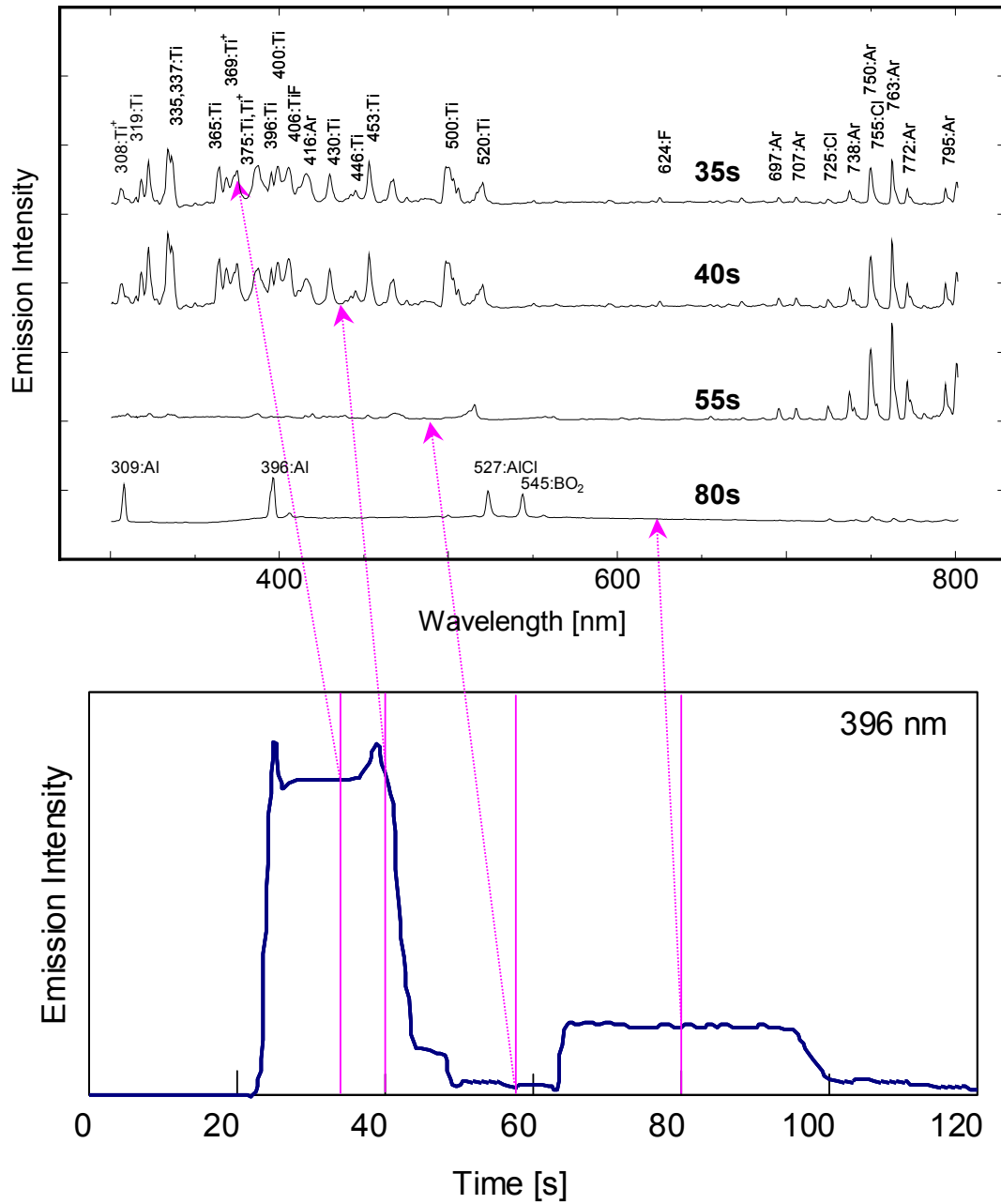


Fig. 2.33. Plasma optical emission spectra before and after the TiN RIE step and a 396 nm emission intensity change with time.

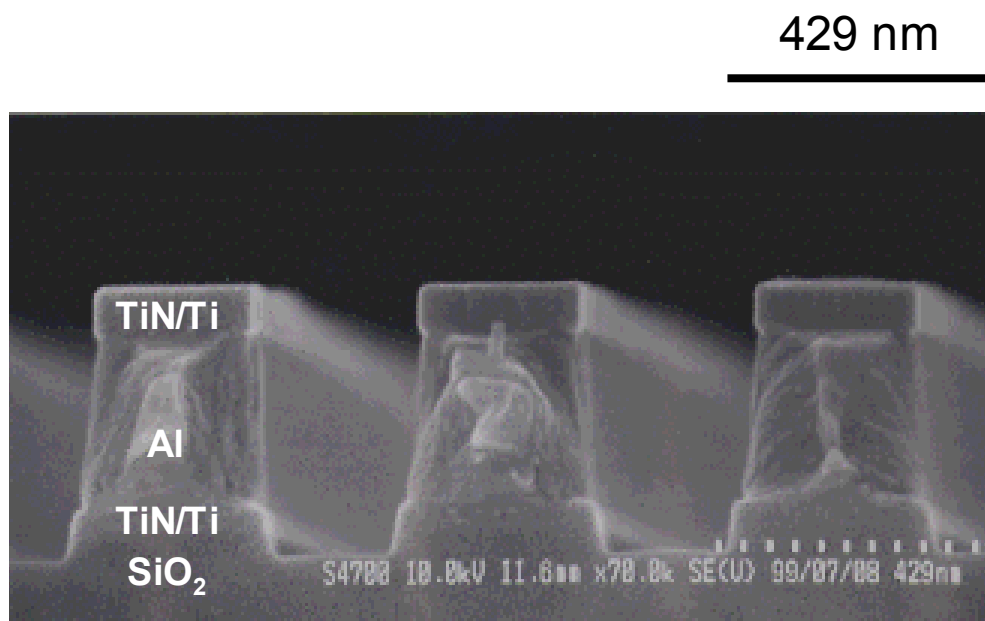


Fig. 2.34. TiN/Ti/Al/TiN/Ti-wiring profile after stripping the resist mask and sidewall deposits in case of using the endpoint detection of the etching of the top TiN/Ti layer.

2.5 Summary and Conclusions

The control of dry etching profile in Al-wiring fabrication has been described. In the Al-wiring RIE using BCl_3+Cl_2 -based gas chemistries, the author investigated the analyzing method of sidewall deposit on the Al-wiring pattern. On the basis of the method named ‘imitation sidewall method’ in this study, the mechanism of the sidewall protection was clarified. As a result, it is found that a N_2 gas addition to a BCl_3+Cl_2 gas mixture generates a thick sidewall deposit which contains ammonium salts of Cl (NH_4Cl) and Al-chloride (NH_4AlCl_4) in addition to carbon-based compounds. It was also clarified that the CH_2F_2 gas addition caused a sidewall deposit containing AlF_x among carbon-based compounds even without the organic resist mask.

The dry etching characteristics and the mechanism of the etching profile control of TiN have also been described. Experimental results have shown that vertical etching profile of TiN is obtained by the RIE using Cl radicals and that BCl_3 gas addition generates the sidewall deposit containing BN-containing compounds. The result indicates that the taper profile control is possible by adjusting the BCl_3/Cl_2 ratio.

Finally, it has been suggested that the endpoint detection is possible for TiN RIE by monitoring the emission intensity of Ti atoms and/or ions (for example 396.2 nm) in the plasma. The endpoint detection has been successfully adopted in the fabrication of the stacked TiN/Ti/Al/TiN/Ti-wiring, which leads to the smooth profile with good electrical testing result. The etching condition switching by using the endpoint detection is considered useful to obtain the smooth profile by absorbing the film thickness variations and the RIE apparatus fluctuations.

The sidewall deposition mechanisms clarified in this chapter

contribute the Al RIE process with the additional gases. For example, it is considered that N_2 addition method cannot meet both the sidewall protection and the resist selectivity in principle. This is because N_2 addition needs the resist mask etching to form the sidewall protection including ammonium compounds. Thus, it is confirmed that N_2 addition process is not suitable for the thin resist used in the fine Al patterning. On the other hand, CF_x -containing gas addition, which is considered as a generalized case from CH_2F_2 addition, is suitable for the thin resist mask case because H is not necessary to form the sidewall protection layer. This is one reason why N_2 is not major additional gas to tune the Al profile at the present time. On the basis of those considerations, Al RIE process has been improved. In fact, the mechanisms of the profile control of Al and TiN have contributed to productivity improvements of CMOS devices (180 nm technology node and below, the Emotion Engine™ [2.23] for PlayStation® 2, for example) by fine-tuning the etching profile.

2.6 References

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2. Dry Etching Profile in Al-Wiring Fabrication

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“A Microprocessor with 128b CPU, 10 Floating-Point MACs, 4
Floating-Point Dividers, and MPEG2 Decoder”, ISSCC (Int’l
Solid-States Circuit Conf.) Digest of Tech. Papers, p.p. 256-257,
February, 1999

2. Dry Etching Profile in Al-Wiring Fabrication

3. Dry Etching Selectivity to Underlayer

In this chapter, two kinds of selective dry etchings are described. One is suppression of $\text{Cr}_2\text{O}_3/\text{Cr}$ stacked film erosion during the resist ashing of a photomask. The necessity arises from the unexpected result that $\text{Cr}_2\text{O}_3/\text{Cr}$ film is etched during the oxygen plasma ashing. Several analyses clarify that CrO_x ($2 \leq x \leq 3$) evaporation leads to the etching and that low film temperature below 200 °C is effective to suppress the etching. Another is the etching of AlO_x film selectively against Al. The realization of the AlO_x/Al selective etching can reduce the process steps relating the contact-hole formation in TFT-LCD fabrication for example. In order to obtain a certain value of the selectivity, a method of 'etch-inhibiting layer deposition' has been investigated. By using $\text{BCl}_3 + \text{CH}_3\text{OH}$ or $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$ gas chemistry generating CH_x fragments in the plasma, carbon-rich film deposition occurs much more on Al surface than AlO_x surface. The use of this selective deposition leads to a good AlO_x/Al selectivity more than 5. It is also confirmed that the carbon-rich film is removed by ordinal processes such as oxygen plasma ashing and alkali wet treatment. Thus, AlO_x/Al selective dry etching is established by using the selective deposition of the etch-inhibiting film and can be adopted to the future devices including AlO_x/Al structure.

The photomask ashing process and apparatus optimized to suppress the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching have been put into practical use in manufacturing the photomasks for ULSI (180 nm technology node and below). Those design rules require the $\text{Cr}_2\text{O}_3/\text{Cr}$ pattern sizes below 1 μm , and thus $\text{Cr}_2\text{O}_3/\text{Cr}$ RIE is indispensable, which results in necessity of the resist ashing.

3.1 Introduction

In this chapter, two kinds of selective dry etchings are studied. In the first half, the suppression of $\text{Cr}_2\text{O}_3/\text{Cr}$ stacked film erosion during the resist ashing of photomasks is investigated. The $\text{Cr}_2\text{O}_3/\text{Cr}$ stacked film has been widely used as photomasks of photolithography in semiconductor device fabrication. In the patterning of the $\text{Cr}_2\text{O}_3/\text{Cr}$ films, dry etching is applied especially for the sub-micrometer patterns [3.1] [3.2] [3.3] [3.4]. After the etching, a resist used as the mask for the etching is conventionally removed by using an alkali solution. However, oxygen plasma ashing has started to be used for the removal of the resist because the alkali solution can result in residues, i.e., imperfect removal. Unexpectedly, the reduction of the $\text{Cr}_2\text{O}_3/\text{Cr}$ film thickness was observed by the oxygen plasma ashing of the resist as the mask for the $\text{Cr}_2\text{O}_3/\text{Cr}$ film etching. A photomask with the $\text{Cr}_2\text{O}_3/\text{Cr}$ erosion is one of the failures because of less light absorbance with the thinner Cr_2O_3 layer. Although the $\text{Cr}_2\text{O}_3/\text{Cr}$ surface should be oxidized by oxygen plasma exposure, Cr_2O_3 is known to be stable and non-volatile. Thus, it is possible to consider that other types of Cr oxides are generated by the oxygen plasma ashing, and that the oxides evaporate resulting in the reduction of the $\text{Cr}_2\text{O}_3/\text{Cr}$ film thickness. In this investigation, the Cr oxides formed on the $\text{Cr}_2\text{O}_3/\text{Cr}$ surface exposed to oxygen plasma are analyzed. Then, the author clarifies the reason why the $\text{Cr}_2\text{O}_3/\text{Cr}$ film thickness decreases during the oxygen plasma ashing of the resist and suggests a way of preventing the reduction of the $\text{Cr}_2\text{O}_3/\text{Cr}$ film thickness.

In the second half of this chapter, the selective etching of AlO_x against Al is investigated. Due to chemical stability and relatively high dielectric constant, AlO_x has been used in many devices as high-k gate insulator of

advanced CMOS [3.5] and tunneling dielectric film in MRAM (Magnetoresistive Random Access Memory) [3.6] [3.7], etc. In those cases, the patterning of AlO_x film is needed with high selectivity against the etching mask and/or the underlayer film. In this investigation, the author supposes the application of the AlO_x/Al selective etching to the high performance TFT-LCD fabrication with Al gate [3.8] [3.9]. During the fabrication process, the Al gate is difficult to handle because of its chemical and thermal instability; it can be eroded by acid or alkali and it can diffuse into an adjacent layer during heating [3.10]. Therefore, when Al gate lines or Al signal lines are used in TFT-LCDs, they should be covered by an AlO_x layer to protect them from chemical and thermal damage [3.11]. In the formation of contacts to Al gates with the AlO_x cover, AlO_x should be removed to expose Al surface. Thus, AlO_x/Al selective etching is required. However, the selective etching is difficult because AlO_x is more stable thermally and chemically than Al in general. Furthermore, only a few studies on the etching mechanism of AlO_x have been reported [3.12] [3.13]. Thus, the author attempts the selective deposition of etch-inhibiting layer much more on Al surface than AlO_x surface. This idea came from the principle of SiO_2/Si selective RIE where CF_x etch-inhibiting layer deposits much more on Si surface than SiO_2 [3.14]. As a result, $\text{BCl}_3+\text{CH}_3\text{OH}$ or $\text{BCl}_3+\text{CH}_2\text{Cl}_2$ gas chemistry generates carbon-rich deposition much more on Al surface than AlO_x surface. The chemical structure of the deposit is clarified and the selective deposition phenomenon is applied to selective etching of AlO_x against Al.

3.2 Cr₂O₃/Cr Etching in Photomask Resist Ashing

3.2.1 Experimental Procedure

The substrates used in this experiment were 6 × 6 inch Cr mask blanks (HOYA) for the use of photomasks. Figure 3.1 shows the schematic view of the layer structure of the Cr₂O₃/Cr film consisting of a 30-nm-thick Cr₂O₃ layer at the top surface and a 70-nm-thick-metallic Cr layer between the top surface and the quartz substrate. The Cr₂O₃/Cr mask blanks were cut into small chips as the etching samples. Figure 3.2 shows the schematic view of the oxygen plasma etching equipment, in which the plasma is generated by 2.45 GHz microwave power and the substrate holder can be heated up to 300 °C. Etching rates of the Cr₂O₃/Cr film were measured by using the step height between the etched and un-etched portion of the film using organic material tape as the mask for the etching. A resist (OFPR-800, Tokyo Ohka Kogyo) was used for the etching rate comparison. The oxygen plasma during the etching of the Cr₂O₃/Cr film was diagnosed by optical emission spectroscopy measurements. The Cr₂O₃/Cr surfaces before and after the etching were analyzed by XPS. Reaction products generated during the etching were gathered on the Si chip (2 × 2 cm²) placed at the inner wall of the etching chamber and were analyzed by XPS.

3. Dry Etching Selectivity to Underlayer

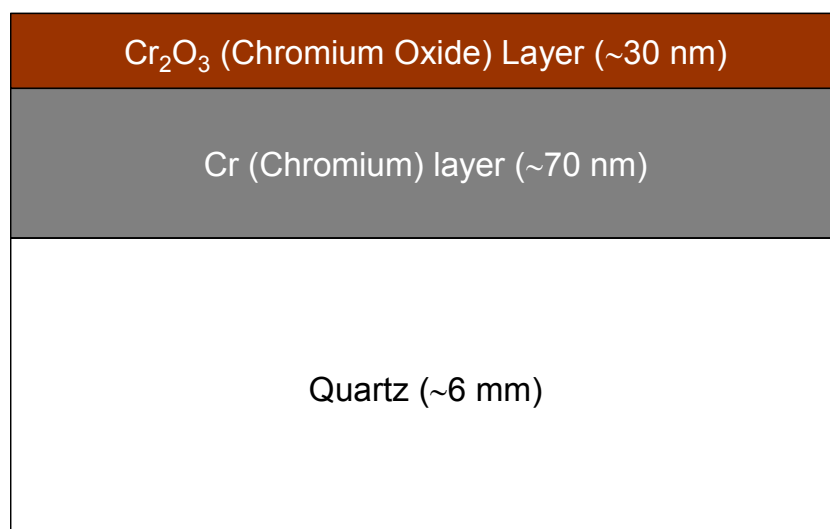


Fig. 3.1. Schematic view of the Cr₂O₃/Cr stacked film to be used.

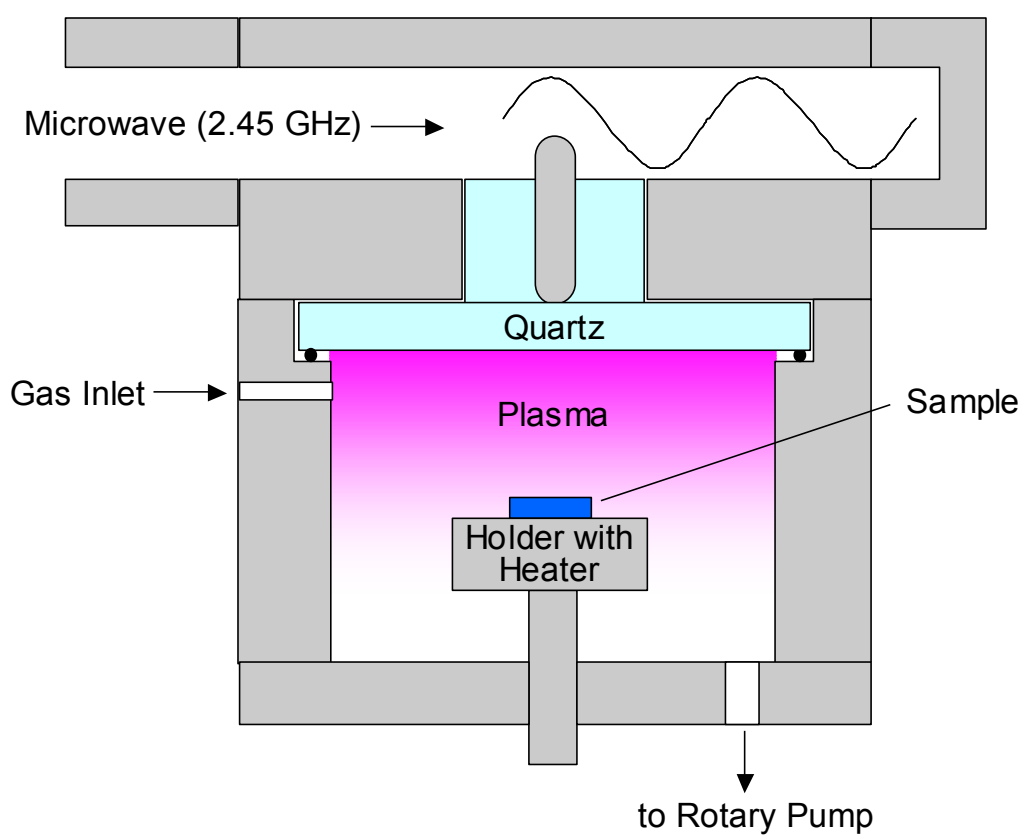


Fig. 3.2. Schematic view of O₂ plasma etching apparatus.

3.2.2 Results and Discussion

A $\text{Cr}_2\text{O}_3/\text{Cr}$ Etching by Oxygen Plasma

Prior to the experiment of the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by using oxygen plasma, it was first confirmed that the $\text{Cr}_2\text{O}_3/\text{Cr}$ film was not etched at all only by oxygen gas flow even if the substrate temperature was set to 250 °C. Figure 3.3 shows the dependence of the etching rates of the $\text{Cr}_2\text{O}_3/\text{Cr}$ film and the resist on the film temperature. During the oxygen plasma etching, the $\text{O}_2 = 200$ sccm, the pressure = 100 Pa, and the microwave power = 500 W. The etching rate of the $\text{Cr}_2\text{O}_3/\text{Cr}$ film increases with increasing the temperature above 200 °C, while it was not etched at all below 200 °C. Since the resist is etched below 200 °C, it should be considered that reactive fragments such as oxygen ions and radicals in the oxygen plasma reach the etched samples. Thus, it is confirmed that the $\text{Cr}_2\text{O}_3/\text{Cr}$ film is etched at higher temperature than 200 °C in the oxygen plasma.

The possibility of $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by oxygen radicals without ion bombardments is then examined. In the experimental system shown in Fig. 3.2, the $\text{Cr}_2\text{O}_3/\text{Cr}$ film on the substrate holder is exposed to not only oxygen radicals but also oxygen ions although the energies of the ion bombardments are considered small enough to be nearly equal to the plasma potential. In order to prevent the etching sample from receiving energies of the ion bombardments, a mesh plate made of Al was placed 50 mm below the quartz window as shown in Fig. 3.4. Figure 3.5 shows the dependence of the etching rates of the $\text{Cr}_2\text{O}_3/\text{Cr}$ film and the resist on the substrate temperature in the oxygen radical etching system with the mesh plate. During the etching, the $\text{O}_2 = 200$ sccm, the pressure = 100 Pa, and the microwave power = 500 W. Similarly to the result of the oxygen

3. Dry Etching Selectivity to Underlayer

plasma etching shown in Fig. 3.3, the $\text{Cr}_2\text{O}_3/\text{Cr}$ film was etched above 200 °C, although the etching rate decreased to one third. It was not etched below 200 °C.

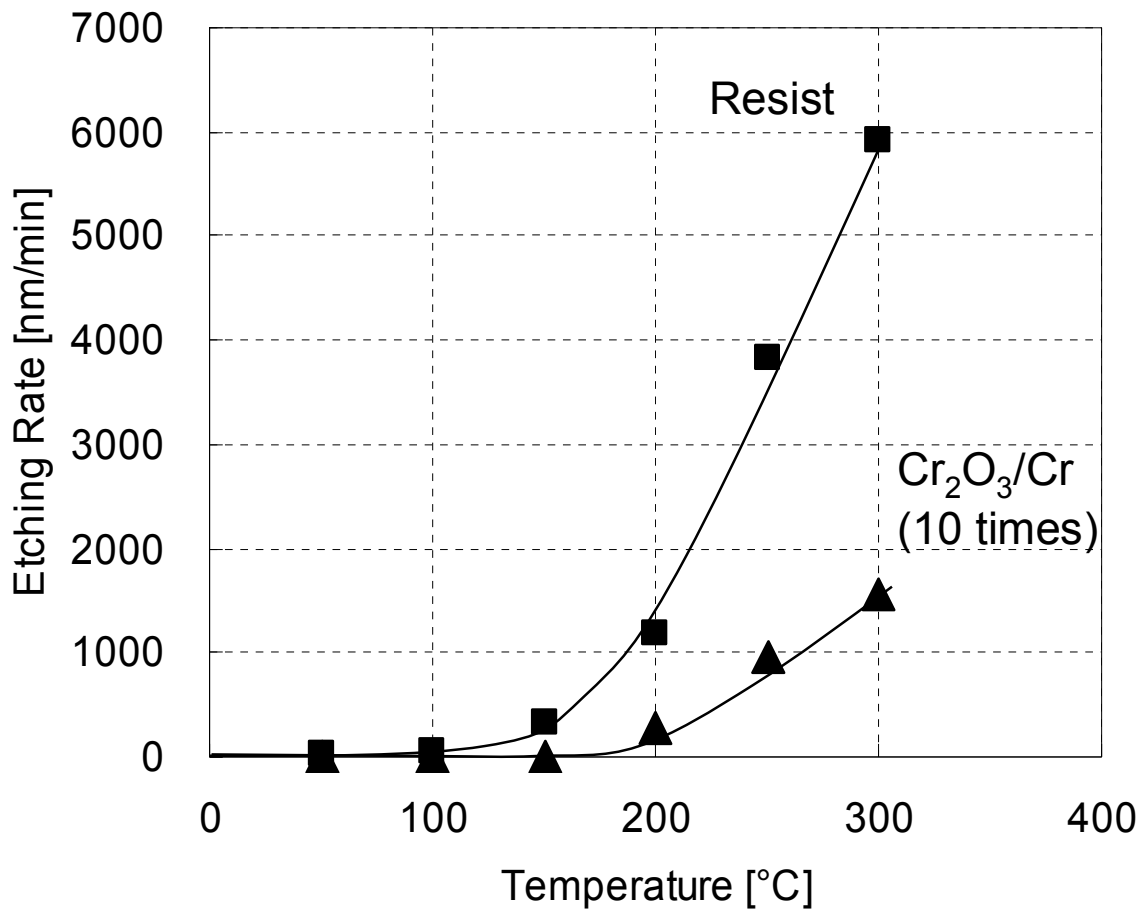


Fig. 3.3. Etching rates of $\text{Cr}_2\text{O}_3/\text{Cr}$ and resist by oxygen plasma as a function of the film temperature.

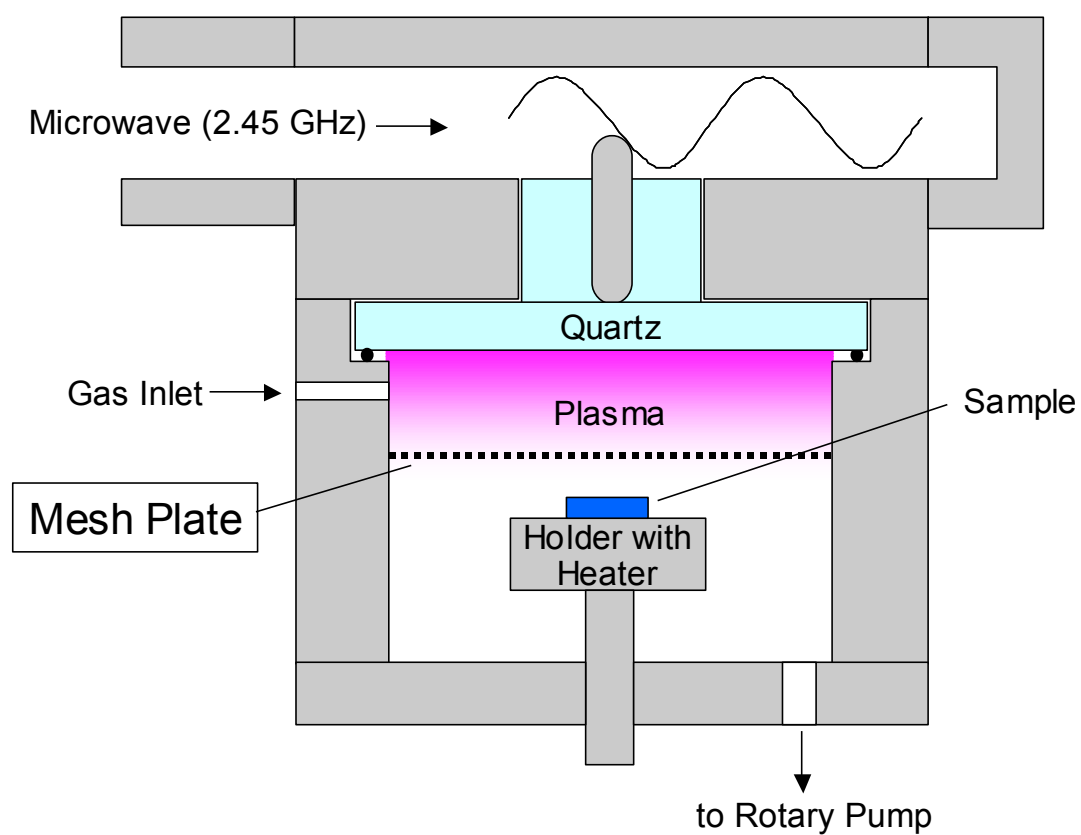


Fig. 3.4. Schematic view of the oxygen radical etching apparatus.

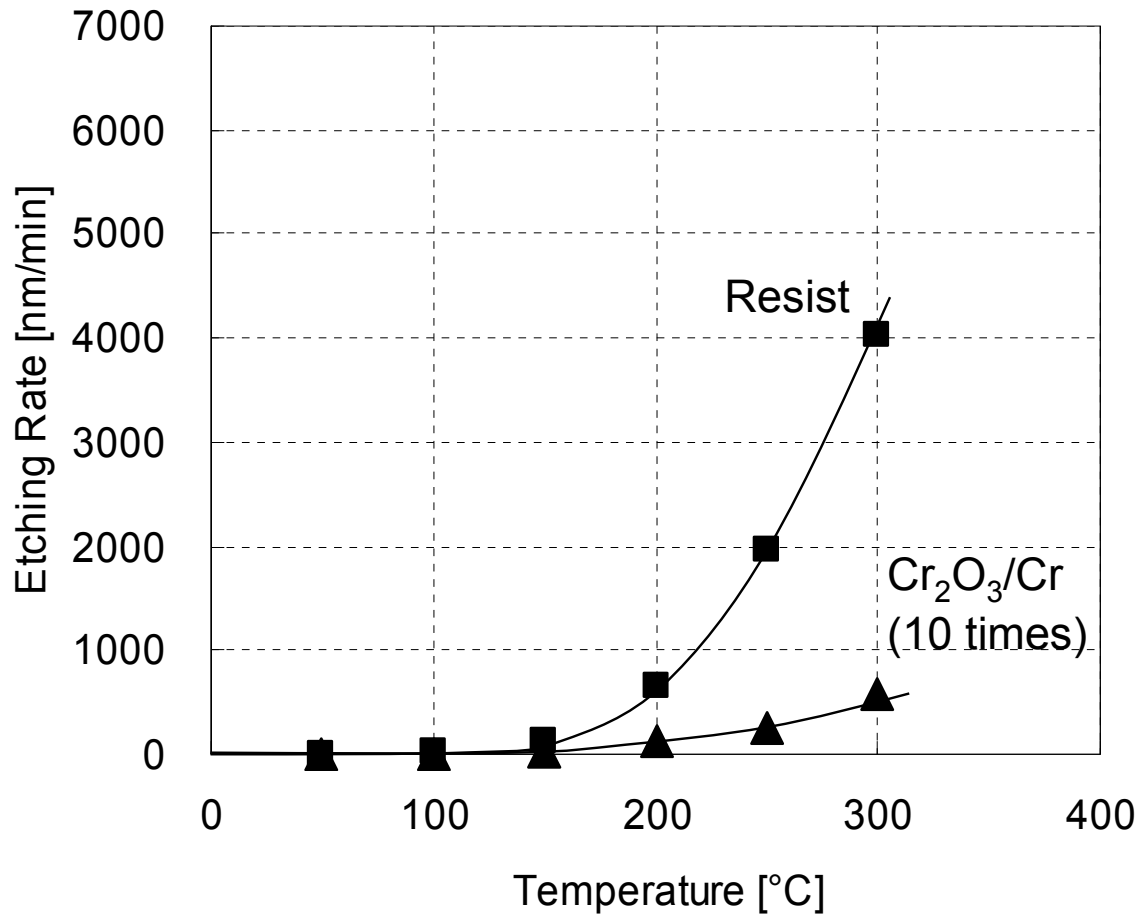


Fig. 3.5. Etching rates of Cr₂O₃/Cr and resist by oxygen radical as a function of the film temperature.

Figures 3.6 (a) and (b) are the Arrhenius plots of the results of the oxygen plasma etching (Fig. 3.3) and the oxygen radical etching (Fig. 3.5), respectively. The slope for the resist with the mesh plate shown in Fig. 3.6 (b) is almost the same as that for O radical down flow ashing of resist [3.15] [3.16]. This confirms that the mesh blocks the oxygen plasma completely and only neutral species such as oxygen radical and oxygen molecule flow down beyond the mesh.

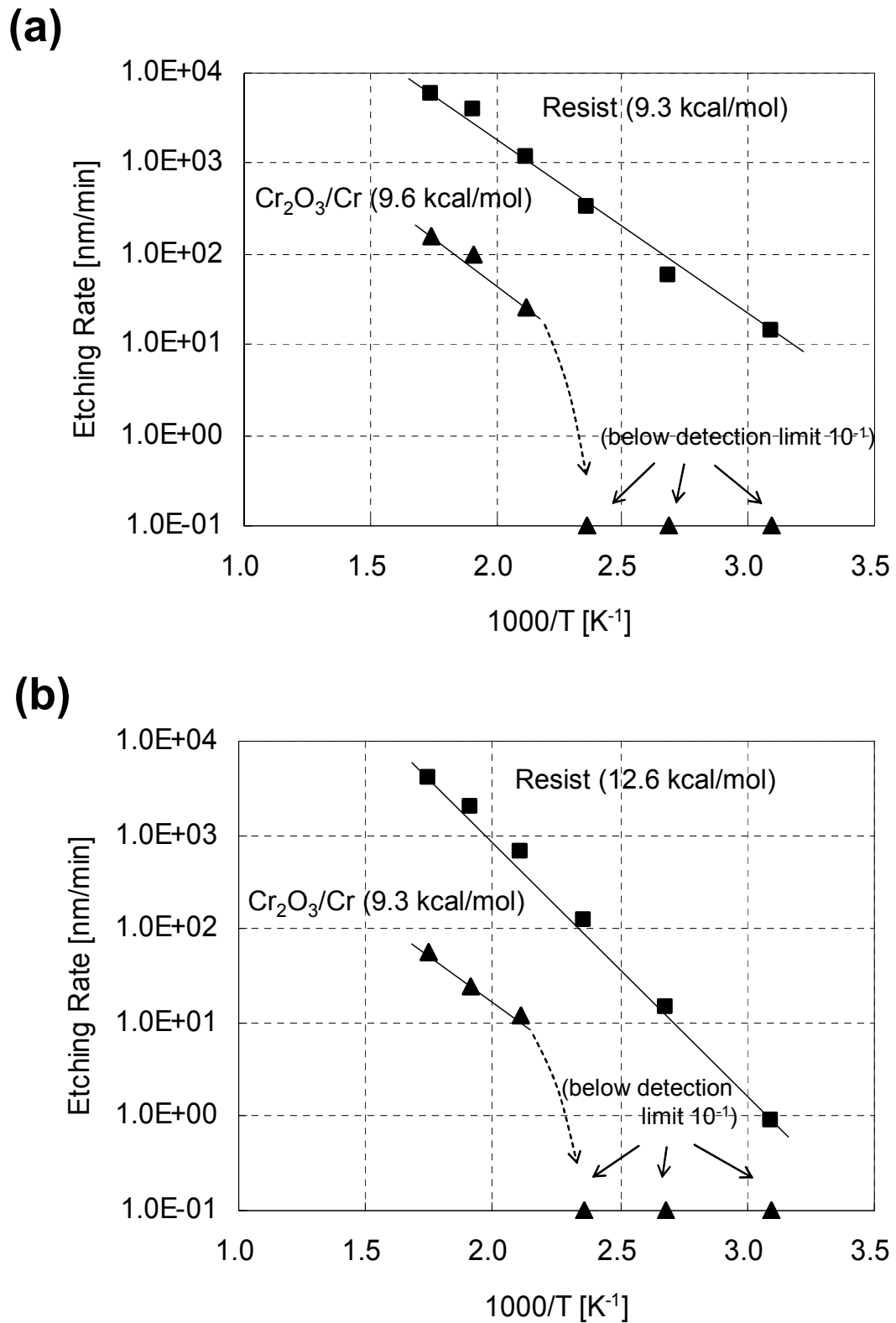


Fig. 3.6. Arrhenius plots for the oxygen plasma etching and oxygen radical etching of $\text{Cr}_2\text{O}_3/\text{Cr}$ film.

B Analysis of CrO_x Etching

In order to clarify the phenomenon of the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by oxygen plasma, optical emission analyses were carried first out for the oxygen plasma during the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching. In this analysis, the mesh plate shown in Fig. 3.4 was not used. Figures 3.7 and 3.8 show the optical emission spectra ranging from 322.5 nm to 367.5 nm and from 577.5 nm to 612.5 nm, respectively. During the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching, the $\text{O}_2 = 200$ sccm, the pressure = 100 Pa, the microwave power = 500 W, and the substrate temperature = 50 °C or 250 °C. It is clearly shown that the intensities of Cr (357.9, 359.8, and 360.5 nm) and CrO (579.4 and 605.1 nm) are significantly increased with increasing the temperature from 50 °C to 250 °C. Since the melting point of Cr is 2672 °C, those optical emissions of the Cr are considered not due to an evaporation of Cr itself but due to dissociations from CrO_x , which suggests that the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching progresses by the evaporation of its oxides.

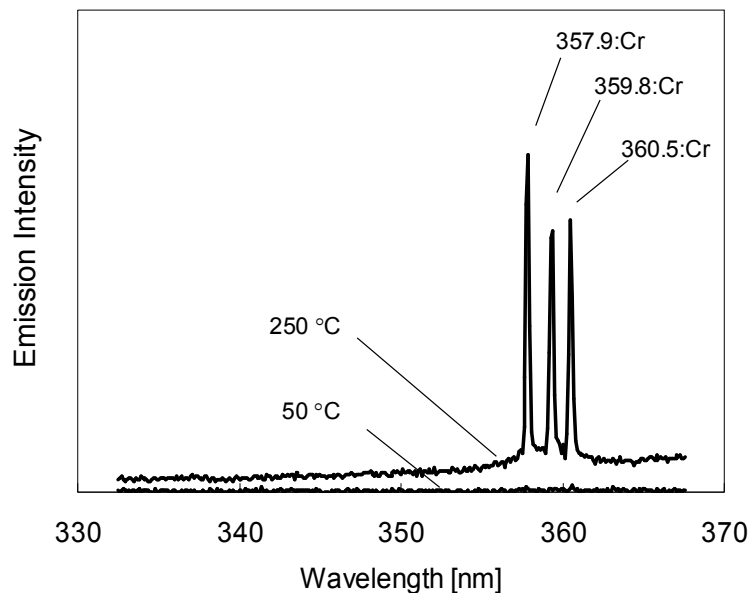


Fig. 3.7. Plasma optical emission spectra ranging 322.5-367.5 nm during $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by oxygen plasma for two temperatures.

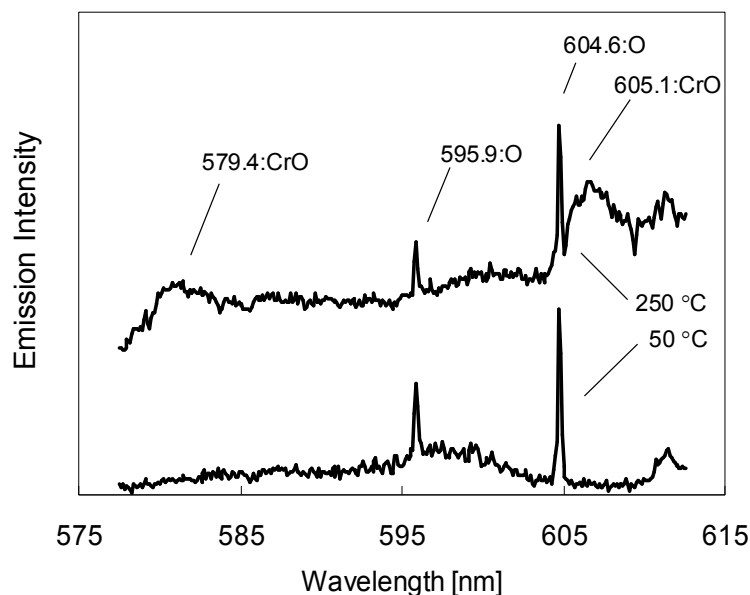


Fig. 3.8. Plasma optical emission spectra ranging 577.5-612.5 nm during $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by oxygen plasma for two temperatures.

XPS analyses were carried out for the $\text{Cr}_2\text{O}_3/\text{Cr}$ surfaces after the oxygen plasma half-etching at 250 °C. The mesh plate shown in Fig. 3.4 was not used during the etching of the $\text{Cr}_2\text{O}_3/\text{Cr}$ film for making the analyzing samples. Figure 3.9 shows the Cr 2p narrow-scan spectra for the $\text{Cr}_2\text{O}_3/\text{Cr}$ samples, where peak shift corrections were made by using C 1s (284.6 eV) spectra. The spectra for the $\text{Cr}_2\text{O}_3/\text{Cr}$ film without the oxygen plasma etching are also shown for comparison. The peak positions of Cr (metal) and CrO_x ($1.5 \leq x \leq 3$) are indicated according to the previous study [3.17]. It should be noted that the oxidation state of the $\text{Cr}_2\text{O}_3/\text{Cr}$ surface changes from low valence to high valence such as CrO_x ($2 \leq x \leq 3$) after the oxygen plasma half-etching at 250 °C.

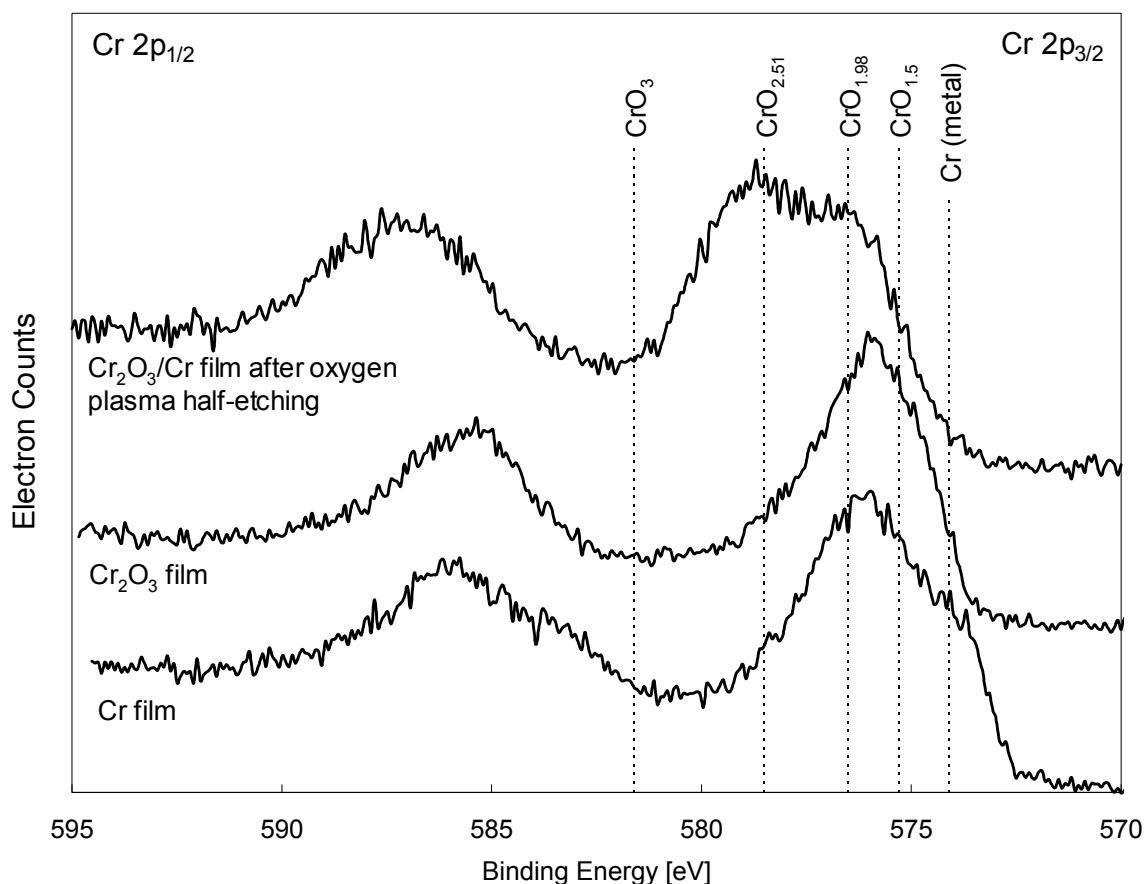


Fig. 3.9. XPS narrow-scan spectra of Cr₂O₃/Cr surfaces before and after oxygen plasma etching.

The etching reaction products of the Cr₂O₃/Cr film by the oxygen plasma etching at 250 °C are also analyzed by XPS. The etching reaction products were deposited on a small Si chip placed on the inner wall of the etching chamber as shown in Fig. 3.10. Figure 3.11 shows the Cr 2p narrow-scan spectra for the surface of the Si chip for the different conditions of the oxygen plasma etching. After the oxygen plasma etching at 50 °C, no etching reaction product containing Cr was detected on the surface of the Si chip. In the case of 250 °C, however, Cr oxides CrO_x

($2 \leq x \leq 3$) were found on the surface of the Si chip. It should be noted that the detection of the Cr oxides is the result from the evaporation and deposition of the etching reaction products. In Fig. 3.11, it is also found that the CrO_x ($2 \leq x \leq 3$) on the Si chip evaporates and/or changes to Cr_2O_3 after 600 °C annealing in a vacuum $\approx 10^{-5}$ Pa. Thus, it is concluded that not only CrO_3 but also other high valence oxides CrO_x ($2 \leq x < 3$) are easier to evaporate than low valence oxides.

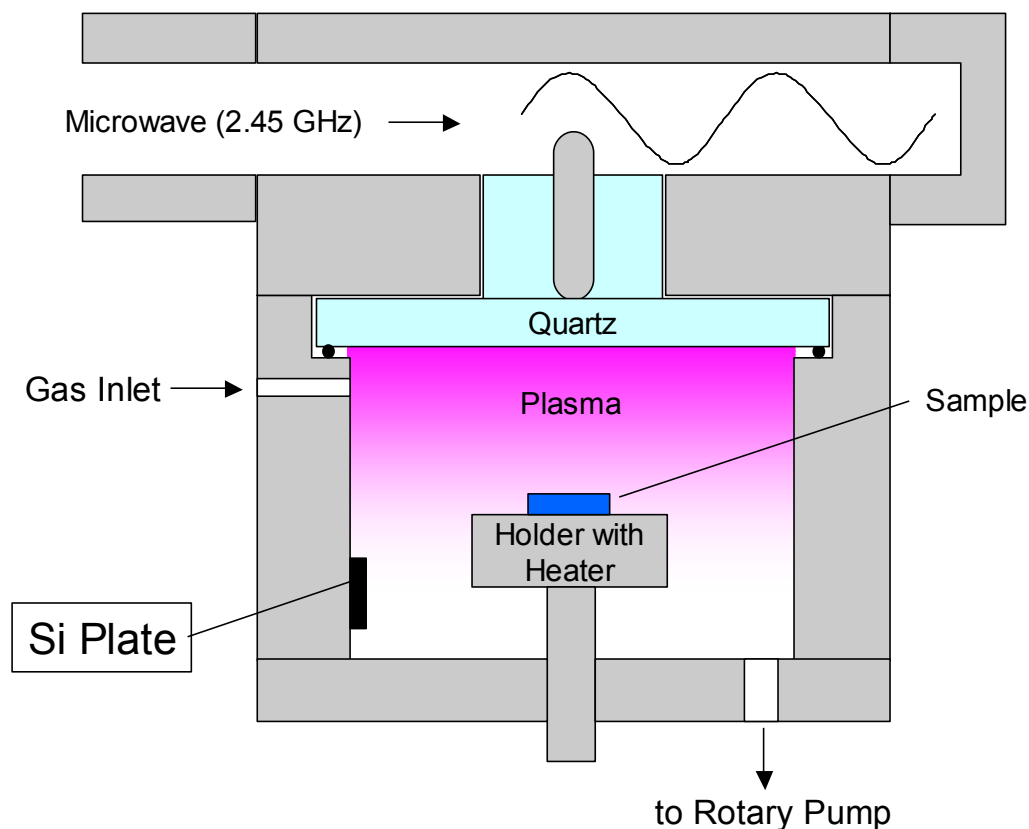


Fig. 3.10. Schematic view of the way of gathering the etching reaction products on a Si chip.

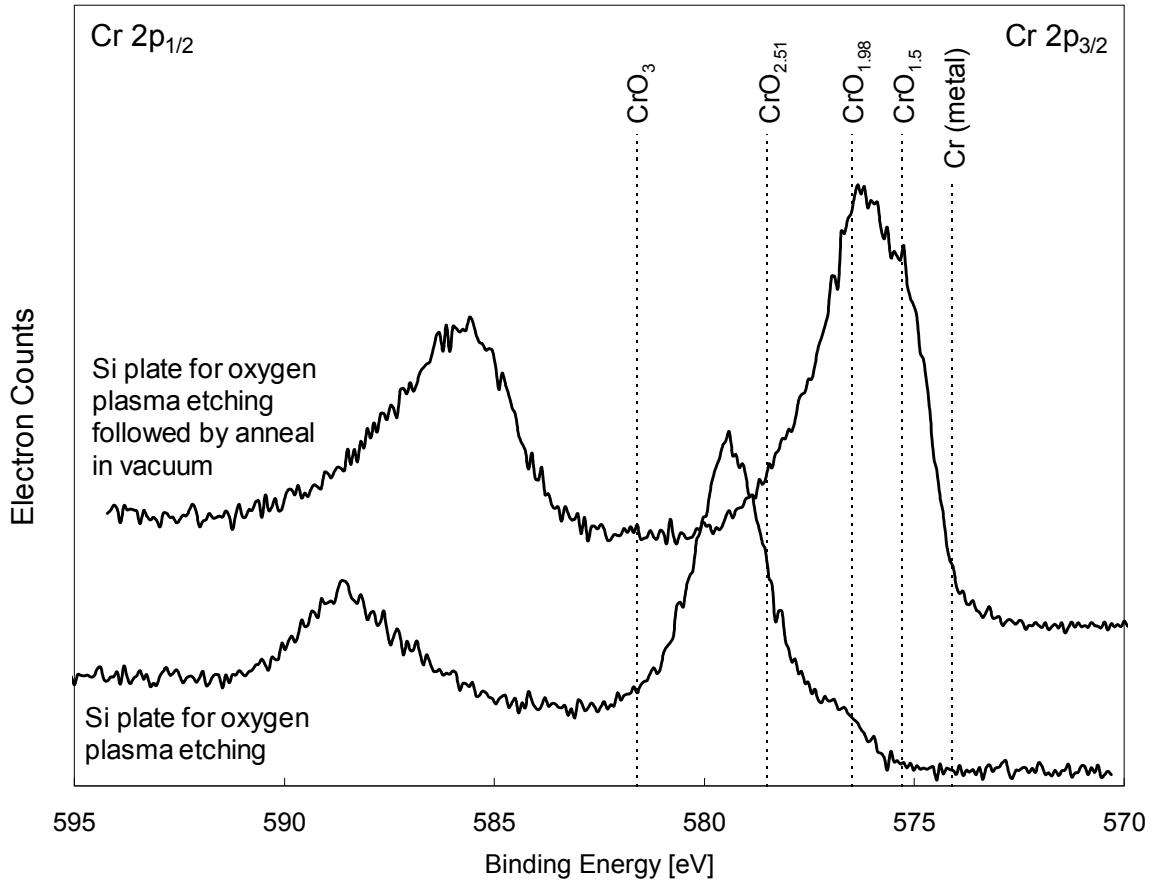


Fig. 3.11. XPS narrow-scan spectra of etching reaction products gathered on the Si chip during the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching.

C Model of $\text{Cr}_2\text{O}_3/\text{Cr}$ Etching by Oxygen Plasma

From the earlier result, a model of $\text{Cr}_2\text{O}_3/\text{Cr}$ etching using oxygen plasma is proposed as shown in Fig. 3.12. $\text{Cr}_2\text{O}_3/\text{Cr}$ film is oxidized by the oxygen plasma and forms various types of Cr oxides. The valence of the Cr in those Cr oxides ranges from +3 (Cr_2O_3) ~ +6 (CrO_3). At low Cr substrate temperature below about 200 °C, any Cr oxide does not evaporate. However, the Cr oxide CrO_x ($2 \leq x \leq 3$; $\text{Cr}^{+4} \sim \text{Cr}^{+6}$) evaporates at high temperature above about 200 °C. The difference in the evaporation of

those Cr oxides can be inferred by the boiling point (b.p.) data for Cr_2O_3 and CrO_3 ; the b.p. of Cr_2O_3 is 4000 °C, the b.p. of CrO_3 is 250 °C. From this model, it is considered that in order to avoid the reduction of the $\text{Cr}_2\text{O}_3/\text{Cr}$ film thickness in an oxygen-based plasma resist ashing, it is effective to keep the film at low temperature.

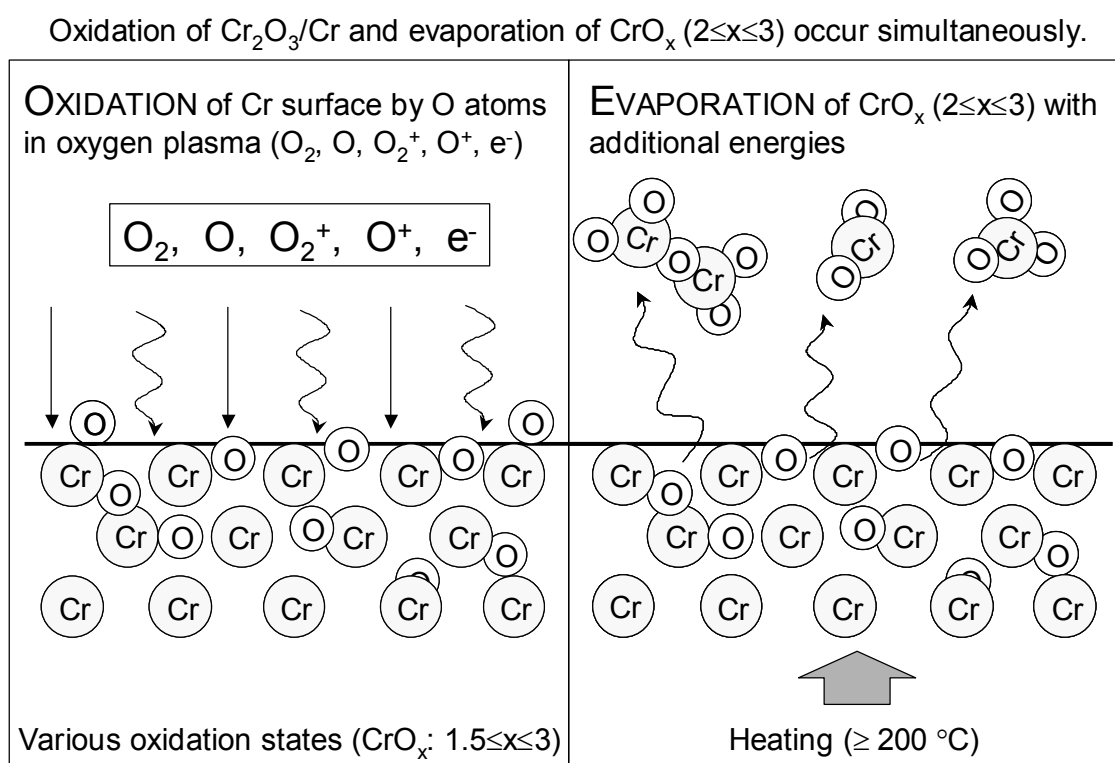


Fig. 3.12. Etching model of $\text{Cr}_2\text{O}_3/\text{Cr}$ film by oxygen plasma.

3.2.3 Summary and Conclusions

The $\text{Cr}_2\text{O}_3/\text{Cr}$ etching characteristics using oxygen plasma has been investigated. It has been newly found that $\text{Cr}_2\text{O}_3/\text{Cr}$ film can be etched by O atoms in the oxygen plasma when the film is heated above 200 °C. From the results of plasma optical emission analysis and XPS analyses of both the etched $\text{Cr}_2\text{O}_3/\text{Cr}$ surface and the evaporated reaction products, the etching model has been proposed as follows; $\text{Cr}_2\text{O}_3/\text{Cr}$ film is oxidized by the oxygen plasma and forms various kinds of Cr oxides CrO_x ($1.5 \leq x \leq 3$). Among the Cr oxides, CrO_x ($2 \leq x \leq 3$) are much less stable than the other Cr oxides such as Cr_2O_3 known as a stable oxide compound of Cr. Therefore, CrO_x ($2 \leq x \leq 3$) can evaporate when a certain amount of energy are supplied to the etching substrate by heating. This etching model can contribute to the improvement of a resist ashing process, especially for the resist which is remained on the $\text{Cr}_2\text{O}_3/\text{Cr}$ film as the etching mask. The mask substrate is easily heated up above 200 °C by oxygen plasma for usual case. Thus, suppression of the heating up by intentional cooling of the mask substrate or by keeping the distance between the mask substrate and plasma source is important.

3.3 AlO_x/Al Selective Etching

3.3.1 Experimental Procedure

Test samples were prepared using 6 inch Si (100) wafer with 100-nm-thick thermal silicon oxide layers. An Al film 350 or 400-nm-thick was deposited by magnetron sputtering (MCH-9000; ULVAC). Al oxide samples were produced by anodic oxidation of the Al top surface to form 100-nm-thick Al oxide layer. The sample making procedure is illustrated in Fig. 3.13. In the anodic oxidation, an aqueous solution of a mixture of ammonium tartrate and ethylene glycol was used as the electrolyte [3.12] [3.18] [3.19], and the current density between the Pt cathode and Al anode was kept at about 1 mA/cm². The etching chamber shown in Fig. 3.14 is of a magnetron-RIE type, where the magnetic field has a strength of about 200 gauss immediately beneath the magnet and about 50 gauss immediately above the electrode to which a RF power is applied. The wafer was cut into 3 × 3 cm² pieces. BCl₃+CH₃OH and BCl₃+CH₂Cl₂ gas mixtures were used as the etching gas. In this study, the process pressure, the applied RF power and the powered electrode temperature were kept constant at 2.0 Pa, 200 W (corresponding power/electrode area ratio is 1.5 W/cm²) and 20 °C, respectively. The etched depth was measured using a step measurement tool (DEKTAK; Veeco Instruments) after removing small pieces of organic tape or organic resist put on the test samples during the etching. Etched samples were analyzed by XPS, FT-IR, AES and Raman spectroscopy. In the IR-Johnson method for the FT-IR [3.20], KBr was used to collect the deposit on the samples. Optical emission spectroscopy of the plasma was also carried out. Peak intensities of species such as BCl, Cl, H, CH and OH were measured at various ratios of the gas flow rate.

▼ Si wafer

● Thermal oxidation of Si (100 nm)

● Al sputtering deposition (400 nm)

————— Al sample

● Anodic oxidation of Al (100 nm)

————— AlO_x sample

Fig. 3.13. AlO_x and Al sample making procedure.

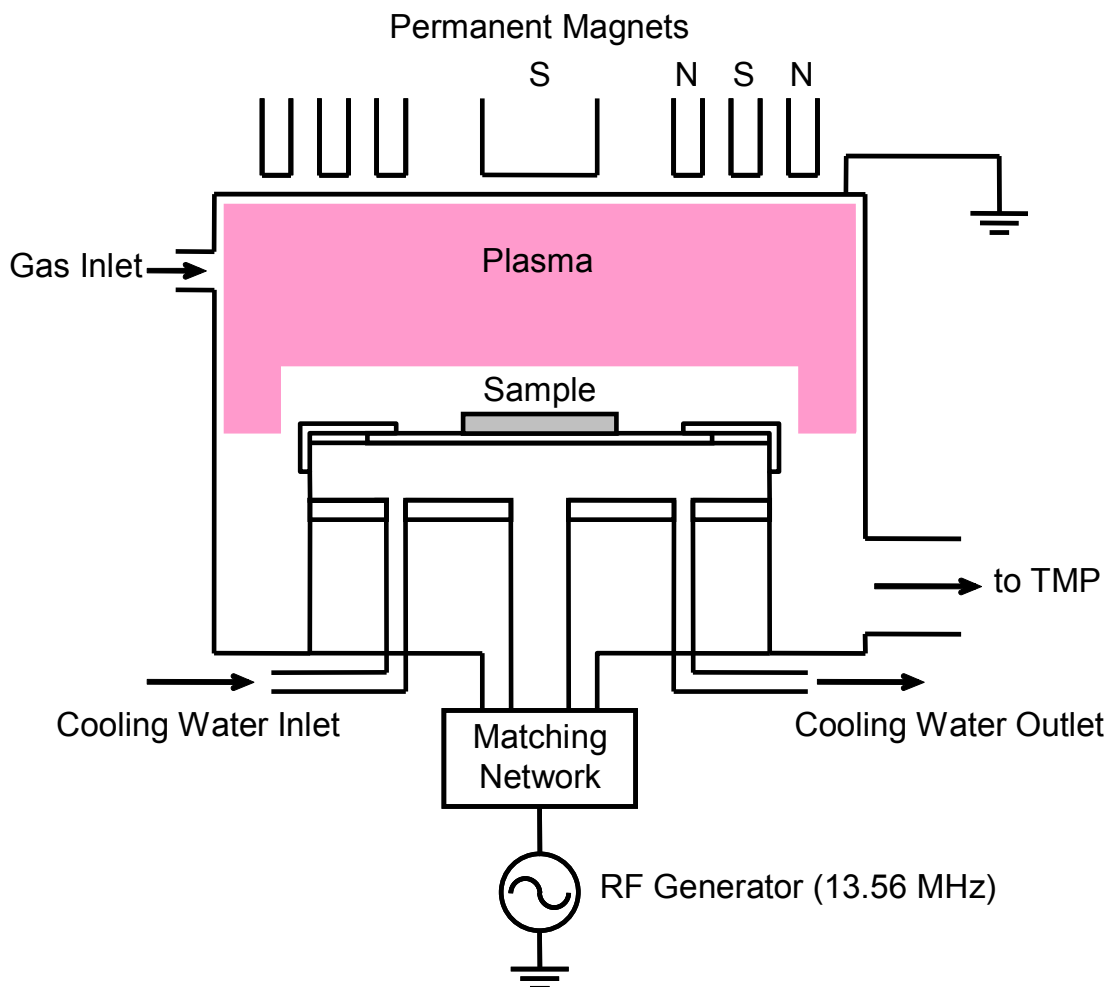


Fig. 3.14. Schematic view of dry etching apparatus.

3.3.2 Results and Discussion

A Selective Deposition of Carbon-Rich Film on Al Surface

The etched depths of Al and AlO_x after 4-min etching are shown as a function of $\text{BCl}_3 + \text{CH}_3\text{OH}$ flow rate ratio in Fig. 3.15. The etched depths of both Al and AlO_x decrease with increasing CH_3OH flow rate. Furthermore, when the CH_3OH flow rate is 66.7% of the total flow rate, the deposited films are observed by SEM. The SEM micrographs are shown in Fig. 3.16.

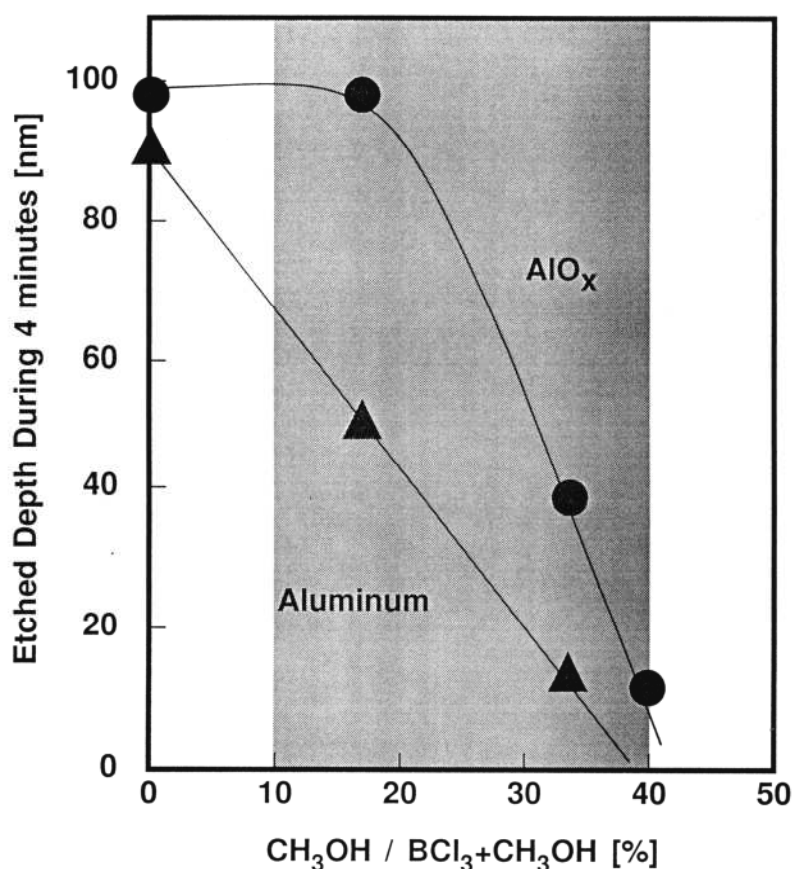


Fig. 3.15. Etched amount as a function of the ratio of CH_3OH addition to BCl_3 .

3. Dry Etching Selectivity to Underlayer

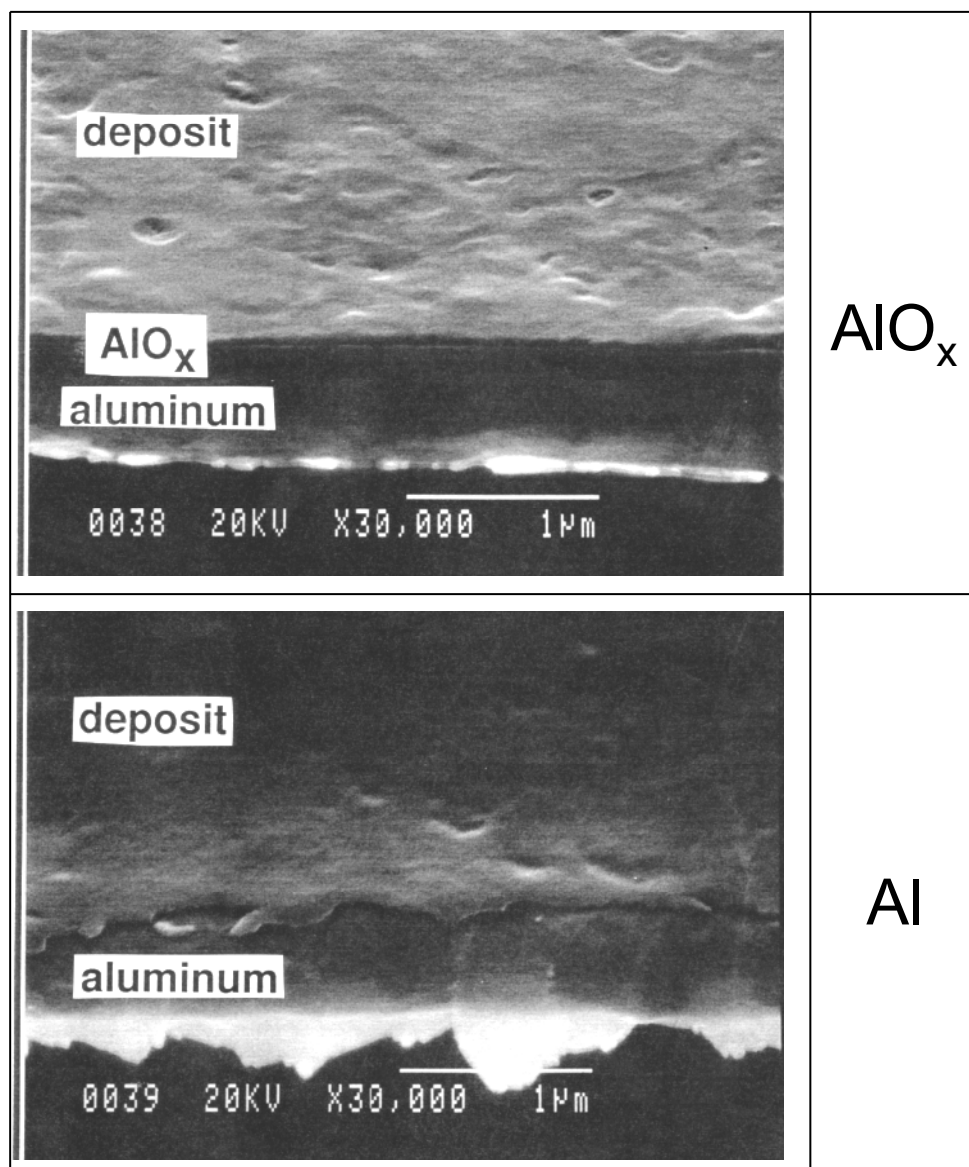


Fig. 3.16. Deposits on the etched AlO_x and Al film under the condition of 66.7% CH_3OH addition.

On the basis of Figs. 3.15 and 3.16, it is considered that the deposit resulting from $\text{BCl}_3 + \text{CH}_3\text{OH}$ gas chemistry leads to decrease the etched depths of both Al and AlO_x . The etched depth of Al decreases more rapidly than that of AlO_x as the CH_3OH flow rate increases. There are two possible reasons for this: one is the existence of a specific fragment in the $\text{BCl}_3 + \text{CH}_3\text{OH}$ plasma which decreases only the Al etched depth effectively, and the other is the difference in surface reactions with plasma fragment between Al and AlO_x . In order to clarify these phenomena, optical measurements of $\text{BCl}_3 + \text{CH}_3\text{OH}$ plasma and XPS analyses of the etched surfaces were carried out.

Figures 3.17 (a) and (b) show the emission intensities of the following species as a function of $\text{BCl}_3 + \text{CH}_3\text{OH}$ flow rate ratio: BCl (272.2 nm), Cl (754.7 nm), CH (431.4 nm), H (656.3 nm) and OH (306.9 nm). Figure 3.17 (a) shows that there is no significant decrease in the emission intensities of BCl_x ($x = 1 \sim 3$) and Cl fragments in the range of $\text{BCl}_3 + \text{CH}_3\text{OH}$ flow rate ratio where the decrease in Al etched depth has been recognized, as shown in Fig. 3.15. This means that chlorine-based fragments are little influenced by the addition of a small amount of CH_3OH to BCl_3 . It should be noted that the emission intensity of O (777.2 nm) is insignificant, as was shown in the previous study [3.21], and is not shown in Fig. 3.17 (b). These results confirm that the rapid decrease in Al etched depth is not due to the oxidation of Al. Fig. 3.17 (b) also shows that even in the range of 0% to about 40% of the CH_3OH flow rate, a large number of CH fragments exist (~ 60% of the maximum number). The existence of CH fragments suggests that other hydrocarbon fragments of CH_3OH such as CH_2 and CH_3 exist as well. These fragments are considered to be the precursors of hydrocarbon deposition [3.13].

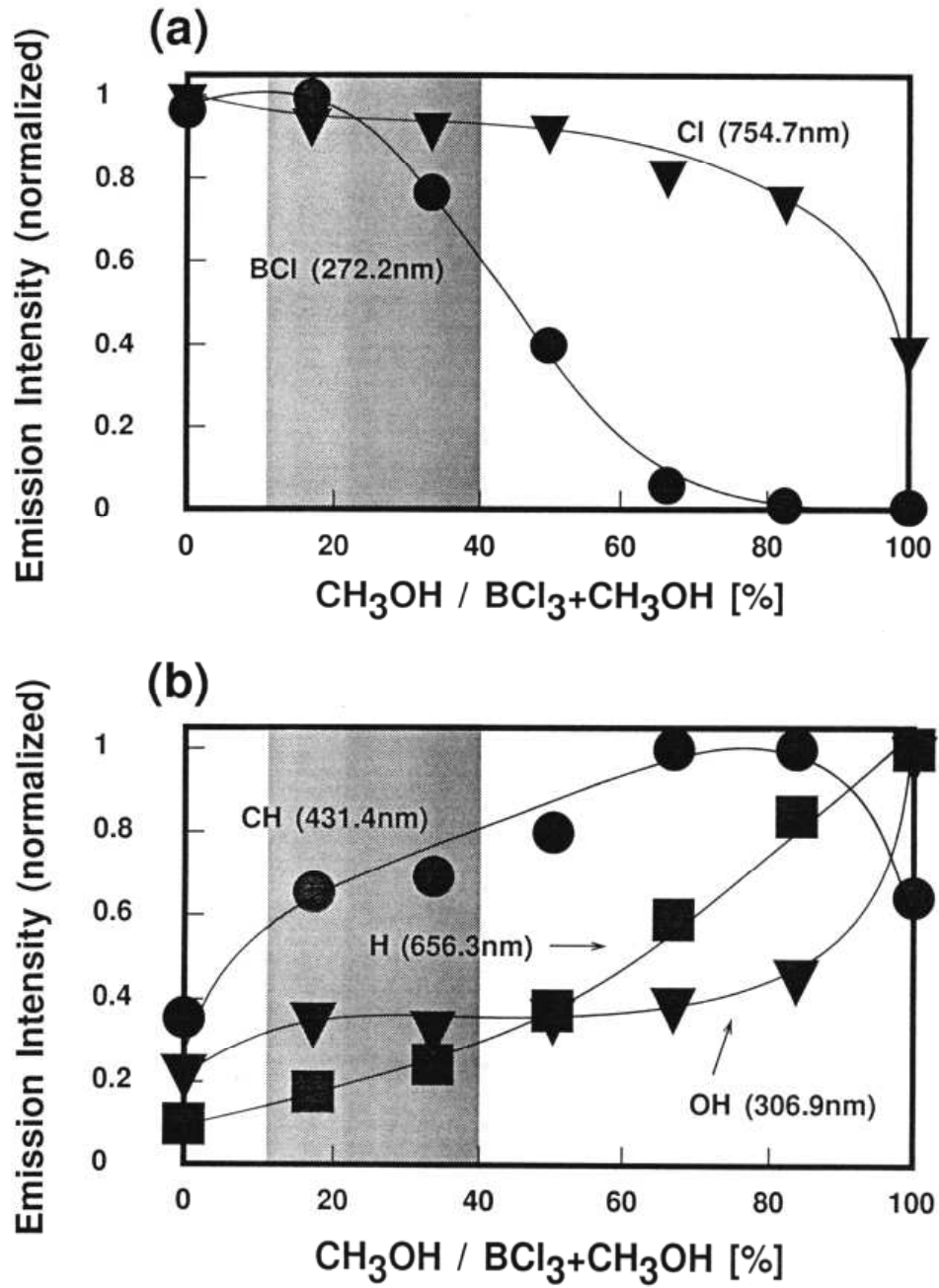


Fig. 3.17. Emission intensities of BCl, Cl, CH, H and OH fragments from the BCl₃+CH₃OH plasma.

Results of XPS analysis are shown in Fig. 3.18, where carbon concentrations on Al and AlO_x surfaces are plotted for various $\text{BCl}_3+\text{CH}_3\text{OH}$ flow rate ratios. When only BCl_3 is used as the etching gas, carbon concentrations on Al and AlO_x surfaces are nearly the same and are at a surface contamination level. As the CH_3OH flow rate is increased, the carbon concentrations on both Al and AlO_x surfaces exceed the surface contamination level, and reach $\sim 50\%$ at 66.7% of CH_3OH . However, at 33.3% of CH_3OH the carbon concentration on the Al surface is nearly twice that on the AlO_x surface. This difference in concentration is consistent with the difference in etched depth decrease between Al and AlO_x surfaces shown in Fig. 3.15. Therefore, from the results shown in Figs. 3.15, 3.17 (a) and (b) and 3.18, it is concluded that in $\text{BCl}_3+\text{CH}_3\text{OH}$ plasma, a carbon-rich film is deposited more easily on an Al surface than on an Al oxide surface, and that the deposit, which is considered to result from CH_x ($x = 1 \sim 3$) fragments in the plasma, considerably reduces the etched depth of Al compared with that of AlO_x .

To determine the structure of the deposit in detail, C 1s spectral data obtained by XPS are shown in Fig. 3.19. C 1s spectra of both Al and AlO_x surfaces for two different conditions, 33.3% and 66.7% of CH_3OH , in which the carbon-rich deposit is detected, are shown. It is found that the shape and binding energy for the four spectra are similar. This means that carbon in all the deposits exists in the same bonding state as C-C and/or C-H (284.6 eV, the main peak) and C-O (286.1 eV, the subsidiary peak). Table 3.1 gives surface concentrations of each element obtained by XPS. It should be noted that a number of boron atoms exist in the deposit. From the binding energy information for the B 1s spectra, it can be deduced that the boron atoms form bonds with oxygen or OH.

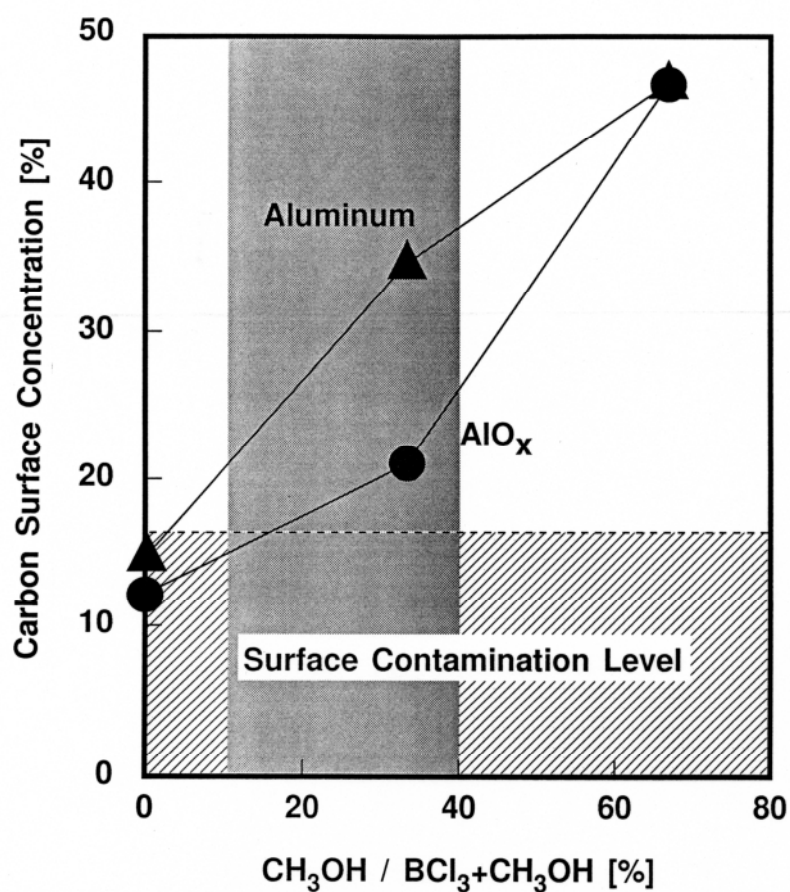


Fig. 3.18. Carbon concentrations on AlO_x and Al surfaces determined by XPS as a function of the ratio of CH_3OH addition to BCl_3 .

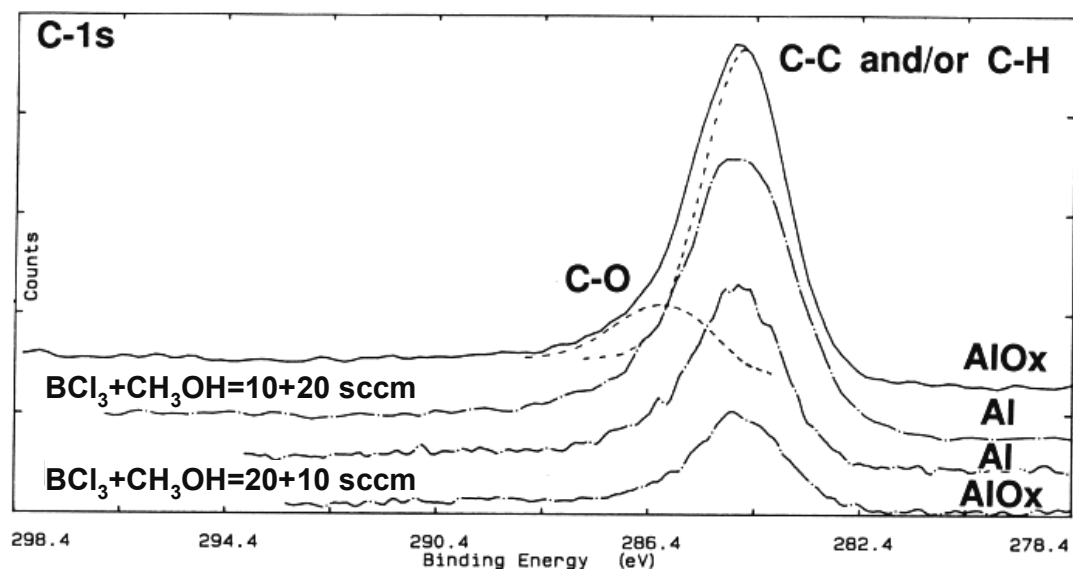


Fig. 3.19. XPS narrow-scan spectra of AlO_x and Al surfaces for different gas mixture ratio of CH_3OH and BCl_3 .

Table 3.1 Concentrations of elements on Al and AlO_x surface as determined by XPS.

$\text{BCl}_3+\text{CH}_3\text{OH}$ flow rate	Sample	Al [%]	B [%]	Cl [%]	C [%]	O [%]
10+20 sccm	AlO_x	-	21.0	1.0	46.5	31.6
	Al	-	20.4	1.0	46.3	32.3
20+10 sccm	AlO_x	17.6	12.9	2.5	21.1	45.9
	Al	7.8	17.8	3.7	34.5	36.1

^a '-' indicates below detection limit

unit: atomic %

In order to obtain information on the bonding state of carbon in the deposit, FT-IR analysis was carried out for the deposit on Al etched under the condition, $\text{BCl}_3 + \text{CH}_3\text{OH} = 10 + 20$ sccm, and the result is shown in Fig. 3.20. It is found that there are no strong peaks around 2800 cm^{-1} which represent C-H bonds. Peaks at 990 cm^{-1} , 1070 cm^{-1} and 1240 cm^{-1} suggest that C-O-C bonds also exist in the deposit. Therefore, it is concluded that a large number of C-C or C=C bonds and a small number of C-O-C bonds exist in the deposit. This is consistent with the result of Raman spectroscopy shown in Fig. 3.21, for the same deposit as for the FT-IR analysis. The Raman spectrum was measured at room temperature with 514.5 nm line of Ar^+ laser. In Fig. 3.21, the two Raman bands decomposed with Gaussian line shapes are shown. Since the Raman spectrum is similar to that of diamondlike amorphous carbon [3.22] [3.23], the deposit contains more C-C and C=C bonds than C-H bonds. The existence of a small number of C-H bonds is probably the result from the extraction of H due to ion bombardments on the deposit. Therefore, there should be more C-H bonds on the Al sidewalls than were observed in this investigation that is related to the surface exposed to ion bombardment. In addition, the IR peaks representing B-OH are consistent with the result of XPS analysis.

All of the results described above enable us to explain the mechanism of the carbon-rich film deposition on the Al surface and the reason why there are differences between the etching and deposition characteristics of Al and AlO_x under the condition of $\text{BCl}_3 + \text{CH}_3\text{OH} = 20 + 10$ sccm. Figure 3.22 shows a schematic model of Al etching and carbon-rich film deposition when a $\text{BCl}_3 + \text{CH}_3\text{OH}$ mixture is used as the etching gas. Ions and radicals of BCl_x ($x = 1 \sim 3$), Cl and Cl_2 etch Al, and each CH_x ($x = 1 \sim$

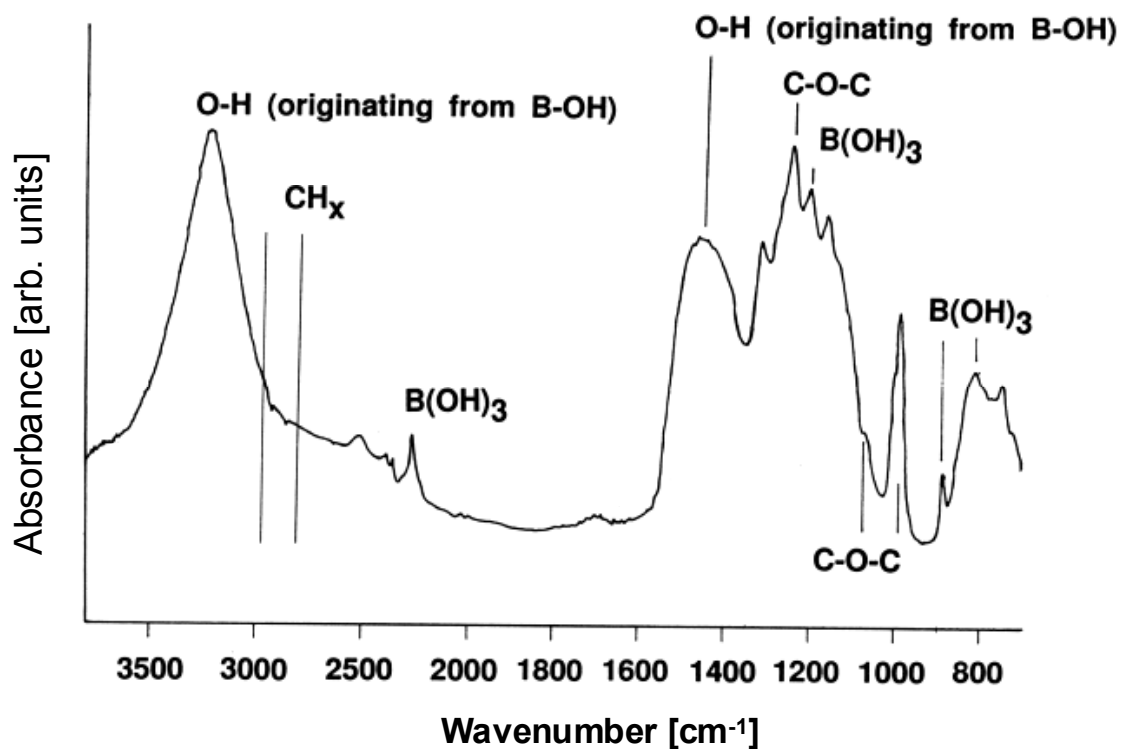


Fig. 3.20. FT-IR absorbance spectrum of the deposit on Al surface under the condition with BCl₃+CH₃OH = 10+20 sccm.

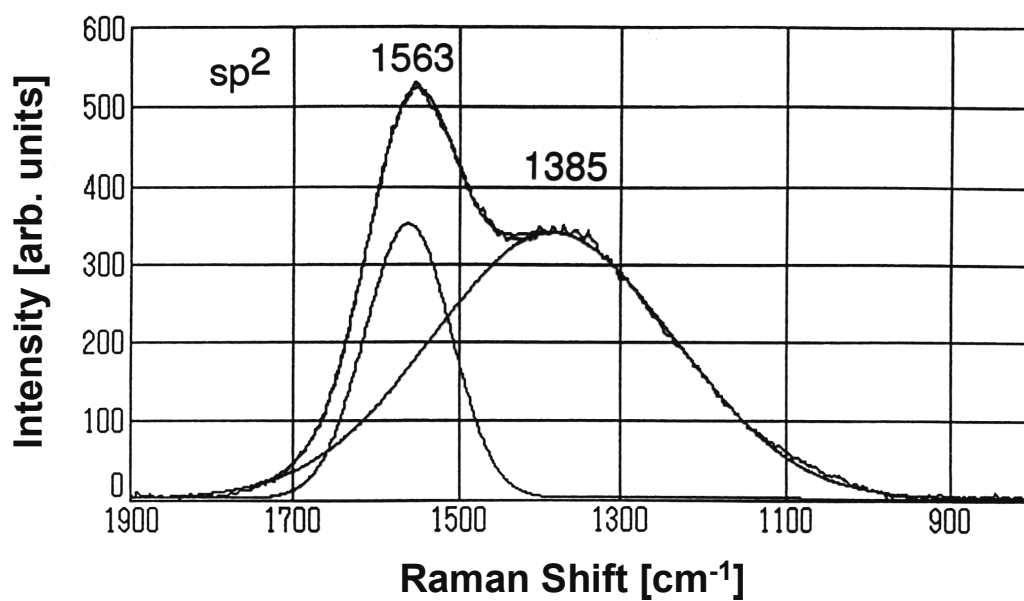


Fig. 3.21. Raman spectrum of the deposit on Al surface under the condition with BCl₃+CH₃OH = 10+20 sccm.

3) fragment is a precursor of the hydrocarbon deposit. On the Al surface, the deposition effect is dominant compared to the etching effect. On the other hand, on the AlO_x surface, oxidation of the hydrocarbon deposit, which is due to oxygen from the etched surface, hinders the deposition. This is why the AlO_x etching rate is not reduced considerably even when CH_3OH is added to BCl_3 .

B AlO_x/Al Selective Etching Capability

The carbon-rich film deposition phenomenon described earlier is used for realizing the selective etching of AlO_x against Al. Figure 3.23 shows the dependence of the etched depth on the etching time during the etching of the double-layer samples with a patterned resist mask. An AlO_x/Al double-layer sample is produced on glass in the same way as described in “Experimental Procedure” subsection; then a resist is coated and patterned. The $\text{BCl}_3+\text{CH}_3\text{OH}$ gas mixture ratio was set to 20+10 sccm, and other etching parameters were the same as those in previous sections. In the first 2 minutes of the etching, the etched depth is very small probably because of the existence of water vapor in the reactor [3.24]. During the next 4 minutes of the etching, AlO_x is etched at a rate of 25 nm/min. After an AlO_x layer 100-nm-thick has been etched off, the Al is etched, although, very slowly. From the graph in Fig. 3.23, the etching selectivity is estimated to be at least 10. Figure 3.24 shows the SEM micrographs and AES analysis results of the etching sample for different etching times; 5 min and 10 min. Although the surface is oxidized to a certain extent, it is confirmed that AlO_x etching is accomplished by 10 min.

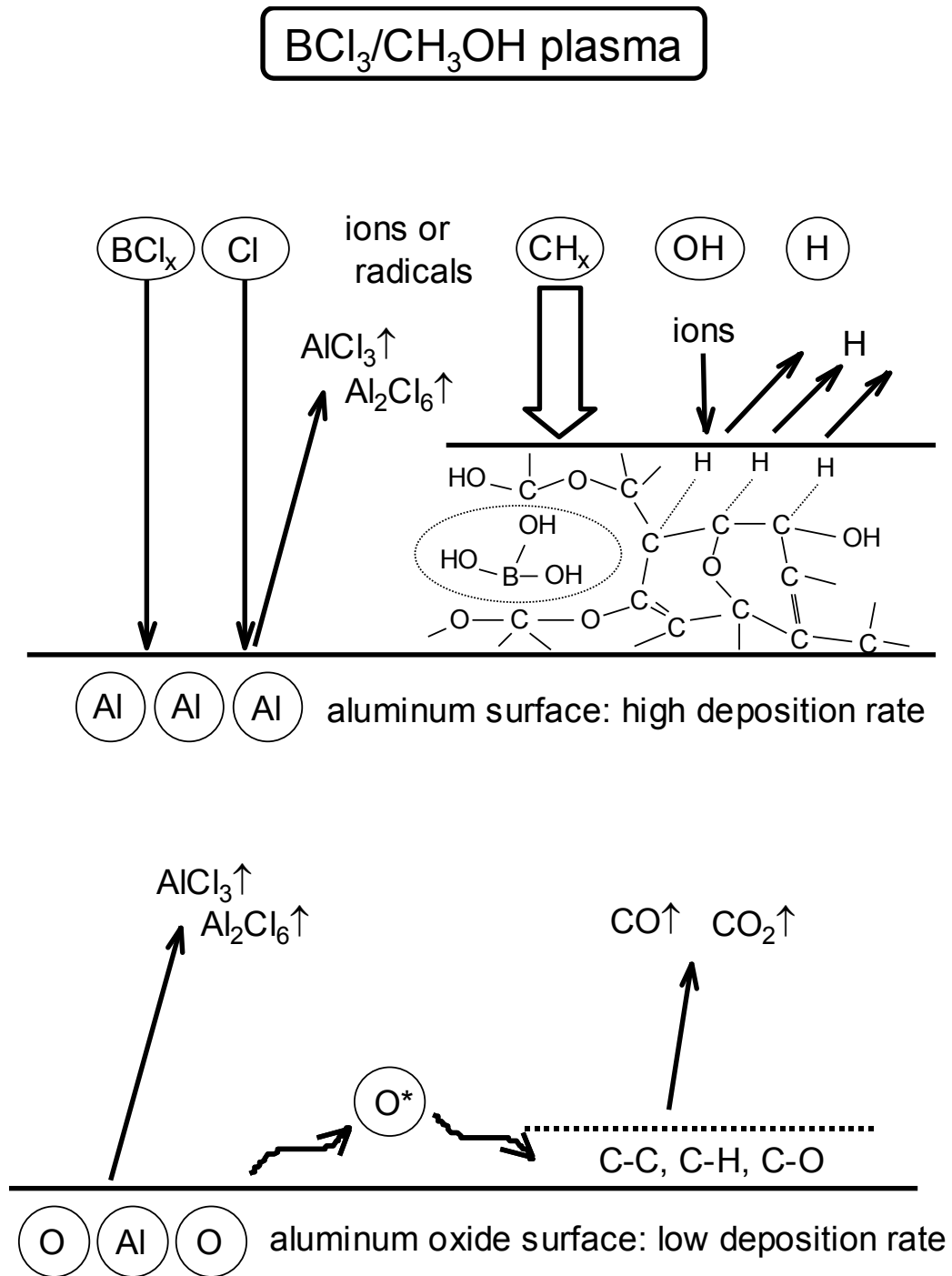


Fig. 3.22. Model of selective deposition of carbon-rich film on Al.

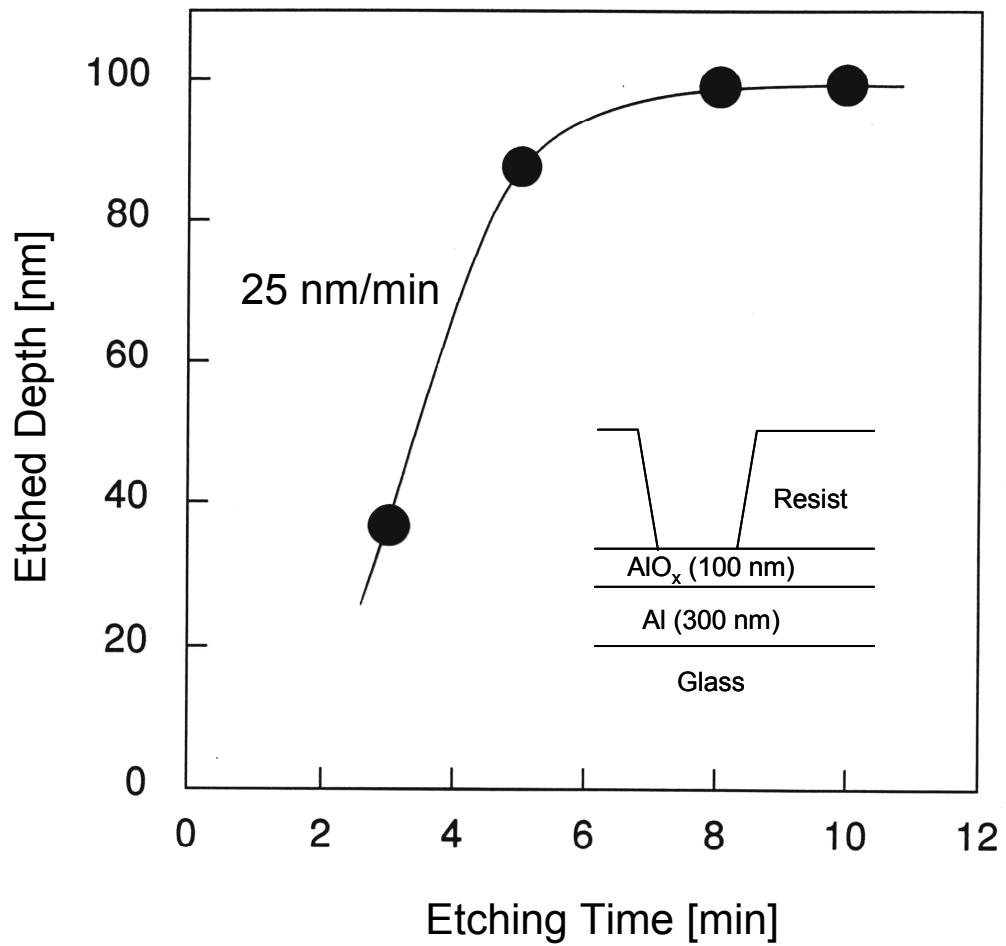


Fig. 3.23. Selective RIE of AlO_x against Al by using $\text{BCl}_3 + \text{CH}_3\text{OH}$ gas chemistry.

3. Dry Etching Selectivity to Underlayer

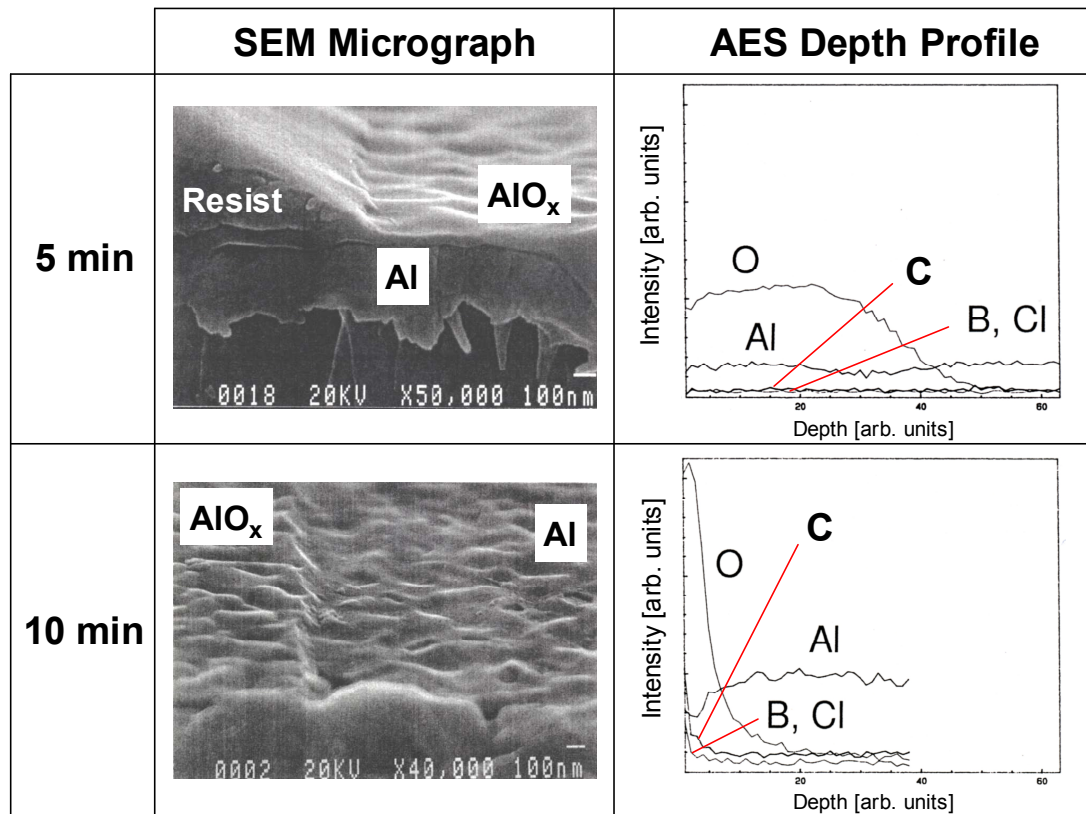


Fig. 3.24. SEM micrographs and AES depth analyses of the etched surfaces of the double-layer AlO_x/Al sample for different etching times: 5 and 10 min.

Similarly, $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$ gas chemistry has been examined for the selective AlO_x/Al etching. Figure 3.25 shows the etched depth vs. the etching time under the same condition as those in previous sections except $\text{BCl}_3 + \text{CH}_2\text{Cl}_2 = 27+3$ sccm. Compared to the $\text{BCl}_3 + \text{CH}_3\text{OH}$ case, two times faster etching rate of AlO_x 50 nm/min and half of the selectivity about 5 are obtained in the case of $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$. This is probably because more Cl radicals and less CH_x radicals are generated in the $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$ plasma than $\text{BCl}_3 + \text{CH}_3\text{OH}$. Figure 3.26 shows the result of AES depth analyses for the Al surfaces before the anodic oxidation, after the RIE using $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$ chemistry with 50% overetching and after the deposition removal processes. The SEM micrograph shown in Fig. 3.26 was taken after the deposition removal, which was the combination of the O_2 RIE ($\text{O}_2 = 50$ sccm, the pressure = 100 Pa, the RF power = 200 W in the same etching chamber shown in Fig. 3.14) and the 10-min organic alkali wet treatment (ELM-C30, Mitsubishi Gas Chemical). The depth profile after the deposition removal is almost same as that of Al as a control. Furthermore, the surface of Al after the deposition removal seems clean as can be seen in the micrograph in the Fig. 3.26. Thus, it is confirmed that the selective AlO_x/Al etching is established.

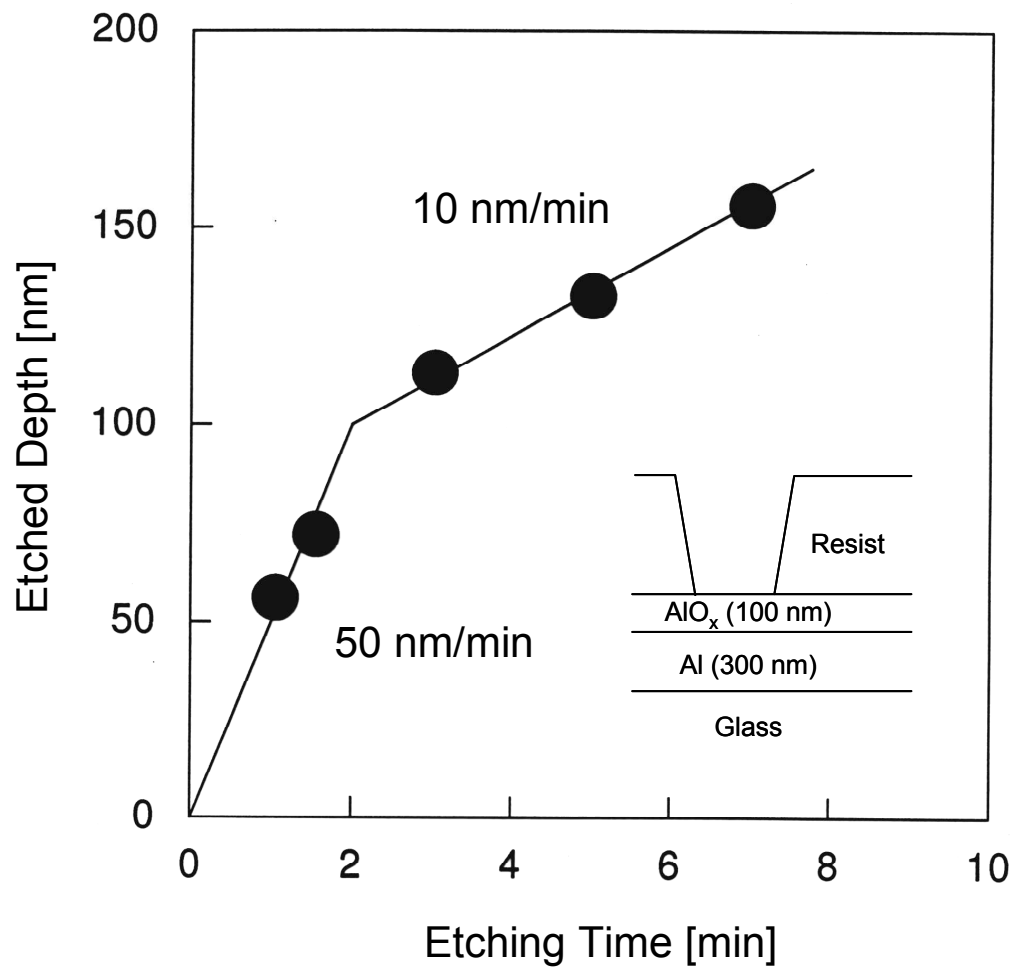


Fig. 3.25. Selective RIE of AlO_x against Al by using BCl₃+CH₂Cl₂ gas chemistry.

3. Dry Etching Selectivity to Underlayer

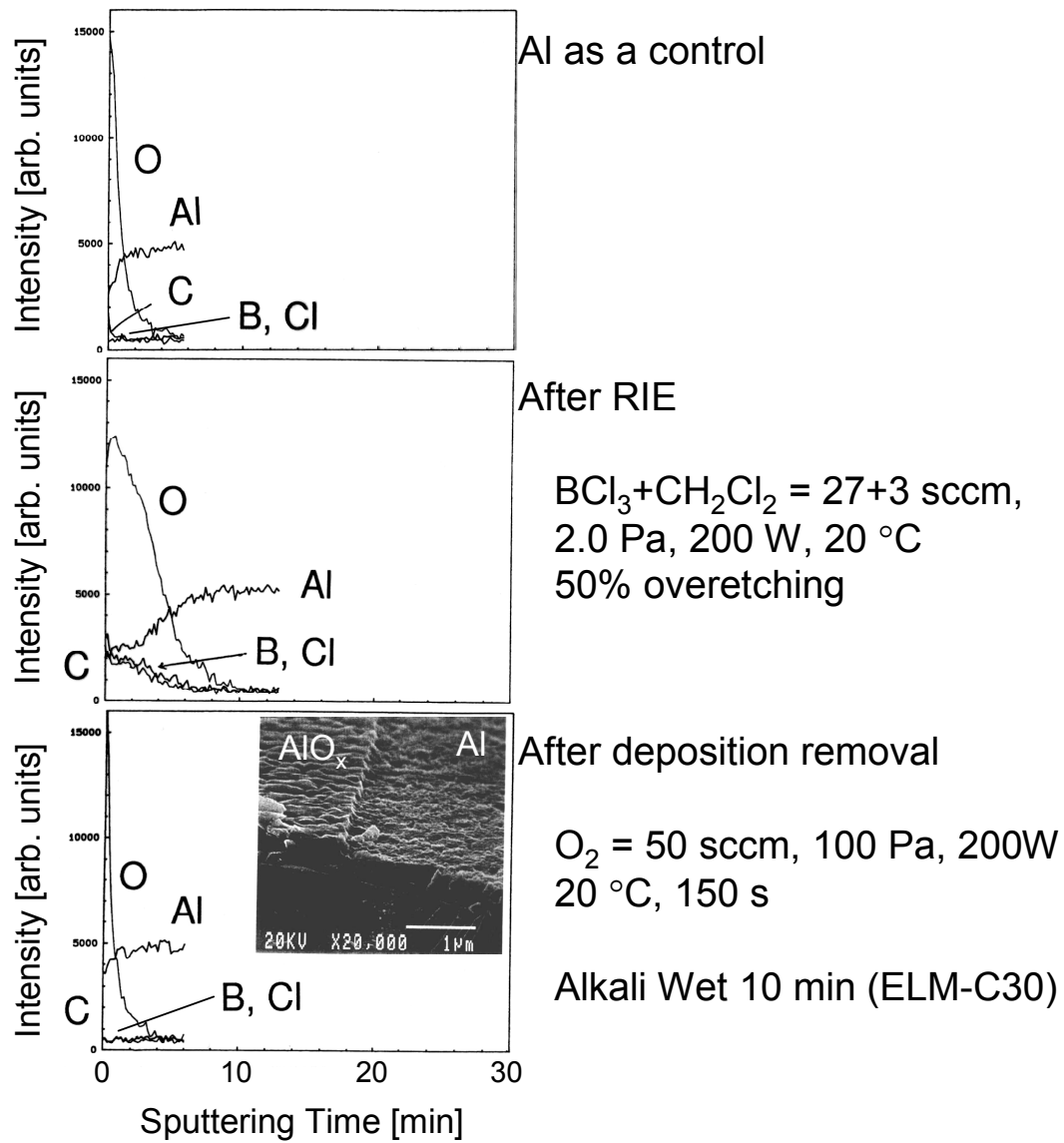


Fig. 3.26. AES depth analyses and SEM micrograph of the etched surface of the double-layer AlO_x/Al sample.

3.3.3 Summary and Conclusions

In order to realize AlO_x/Al selective etching, carbon-rich film deposition on Al and AlO_x surfaces during etching has been studied at first. When a $\text{BCl}_3+\text{CH}_3\text{OH}$ mixture is used as the etching gas in a magnetron-RIE reactor, a deposit is observed on the Al and AlO_x surfaces. Results of XPS, FT-IR and Raman spectroscopy show that the deposit consists mainly of carbon with C-C and C=C bonds. At $\text{BCl}_3+\text{CH}_3\text{OH} = 20+10$ sccm, the deposition occurs more easily on the Al surface than on the AlO_x surface, which accounts for the difference in etching rate of the two films. This difference in deposition characteristics is considered to be due to oxygen which does not exist in the Al film but exists in the AlO_x film. On the AlO_x surface, hydrocarbon which is about to be deposited is oxidized by oxygen originating from the surface during etching. However, on the Al surface, the deposition of a carbon-rich film is dominant because it is not disturbed by anything except ion bombardment. By applying these carbon-rich film deposition phenomena to the selective AlO_x/Al etching, good etching selectivity of at least 10 is obtained. Similarly, $\text{BCl}_3+\text{CH}_2\text{Cl}_2$ gas chemistry enables the selective etching with higher etching rate of AlO_x 50 nm/min and the lower selectivity 5. It has been also confirmed that the deposition film on Al surface can be removed by O_2 RIE and wet alkali treatment following the selective etching. Thus, the selective AlO_x/Al etching is established in principle. This selective AlO_x/Al etching has a possibility to decrease process steps in the formation of contact holes to underlayer Al in TFT-LCD manufacturing, for example.

3.4 Summary and Conclusions

Two kinds of selective etching processes have been studied. One is the process existing in the resist ashing using oxygen plasma after the dry etching of the $\text{Cr}_2\text{O}_3/\text{Cr}$ stacked film used as a light blocking film in photomasks. Unexpectedly, it was newly found that the $\text{Cr}_2\text{O}_3/\text{Cr}$ film was etched during the ashing. In order to clarify the mechanism underlying the phenomenon, the author has investigated the mechanism of the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by oxygen plasma. As a result, it is found that $\text{Cr}_2\text{O}_3/\text{Cr}$ etching occurs when the film temperature is higher than 200 °C due to CrO_x ($2 \leq x \leq 3$) generation and evaporation. The $\text{Cr}_2\text{O}_3/\text{Cr}$ etching is also recognized with oxygen atoms and molecules without ion bombardments above 200 °C. From the results of analyses of the etched $\text{Cr}_2\text{O}_3/\text{Cr}$ surface and etching reaction products, it has been concluded that $\text{Cr}_2\text{O}_3/\text{Cr}$ etching can be suppressed by keeping the film temperature below 200 °C to prevent CrO_x ($2 \leq x \leq 3$) from evaporating. This conclusion has provided an appropriate ashing process and apparatus in the photomask manufacturing.

Another selective etching is that of AlO_x against Al. Since AlO_x is more stable thermally and chemically than Al in general, the author attempted the selective deposition of etch-inhibiting layer on Al surface to obtain the etching selectivity. As a result, it is found that $\text{BCl}_3 + \text{CH}_3\text{OH}$ and $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$ gas chemistries generate carbon-rich film deposition much more on Al surface than AlO_x surface. The etch-inhibiting film is consisting of a carbon-rich compound in which C-C and C=C bonds are the majority. By using this selective deposition phenomenon, AlO_x/Al selective dry etching has been realized with the selectivity 5 and at least 10 for $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$ and $\text{BCl}_3 + \text{CH}_3\text{OH}$ chemistries, respectively. It has been

also examined that the deposition film can be removed by an ordinal process procedure following the selective etching such as oxygen plasma ashing and wet alkali treatment. Thus, the selective etching of AlO_x against Al has been established in principle. This suggests the possibility to decrease process steps in the formation of contact holes to Al-gate with AlO_x cover in TFT-LCD manufacturing. Furthermore, the mechanism of this AlO_x/Al selective etching can contribute to developments of AlO_x dry etching in the future device manufacturing.

On the basis of the study concerning the oxygen plasma ashing of $\text{Cr}_2\text{O}_3/\text{Cr}$ photomasks, both the ashing process and apparatus have been optimized to suppress the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by keeping the film at low temperature. In fact, the improved ashing process has been put into practical use in manufacturing the photomasks for ULSI (180 nm technology node and below). Since the pattern size of $\text{Cr}_2\text{O}_3/\text{Cr}$ is below 1 μm in those design rules, $\text{Cr}_2\text{O}_3/\text{Cr}$ RIE is indispensable, which makes the resist mask removal difficult due to the resist material change by RIE exposure. Thus, the oxygen plasma ashing has been very important to manufacture the high quality photomasks.

3.5 References

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4. Dry Etching in High-k Gate Insulator and Metal Gate Electrode MOSFET Fabrication

In the previous chapters, the studies about the dry etching profile and the selectivity have been described focusing on the behavior of etching reaction products. The method of analyzing the sidewall deposition in detail 'imitation sidewall method' was turned out to be useful. By using the new method in addition to the ordinal surface analyses and plasma emission analyses, dry etchings of Al, TiN, Cr₂O₃/Cr and AlO_x films were investigated in detail to clarify the etching mechanisms and to control the etching profiles and selectivities. In this chapter, dry etching of high-k insulator films and a metal gate electrode film, which are considered as new materials for the future advanced MOSFET, are studied by techniques used in the previous chapters. Although many researches of those films have been conducted focusing mainly on the MOSFET characteristics, it is also important to examine the dry etching characteristics because the process will be required in the manufacturing. In this chapter, the author investigates the etching profile of TaN and the etching selectivity of ZrO₂ and Gd₂O₃ against Si substrate. From the results of the etching characteristics, the process integration will be considered.

4.1 Introduction

High-k gate insulators such as Al_2O_3 , ZrO_2 , HfO_2 and rare earth metal oxides Ga_2O_3 , La_2O_3 , etc., have been extensively studied to overcome the leakage current issue of ultra-thin SiO_2 in sub 100 nm CMOS devices. Applications of a metal gate electrode to the CMOS devices have also been investigated to suppress the gate depletion in polysilicon gates. Most reports about high-k films and gate metal materials have been concerned about the comparison of the materials, the method of the film deposition, the control of the interfacial layer growth and the electrical characteristics [4.1] [4.2] [4.3] [4.4] [4.5] [4.6]. Needless to say, RIE of those materials is also important for the future CMOS fabrication. However, there are a few studies on the etching of the metal gate materials and high-k gate insulators thus far [4.7] [4.8] [4.9]. In this study, the author investigates the RIE characteristics of TaN as the metal gate material and ZrO_2 , Ga_2O_3 as the high-k gate insulators. TaN is one of the promising candidates as the mid-gap metal electrode. ZrO_2 is considered as a standard high-k gate insulator as well as HfO_2 and rare-earth metal oxides including Gd_2O_3 are the candidates for the CMOS devices of post-next generation. For the TaN RIE, the etching rate dependence on the halogen-containing gas chemistries such as CF_4 , Cl_2 and BCl_3 and the etching profile control were investigated. For ZrO_2 and Ga_2O_3 , the etching rate comparisons to SiO_2 were first carried out. Then, high-k/Si selective etching was focused on. On the basis of their RIE characteristics, the author makes consideration about the process flow of manufacturing the MOSFET gate structure.

4.2 Experimental Procedure

100-nm-thick TaN film was prepared by reactively sputtering a Ta metal target onto 4 inch n-Si (100) wafer. 100-nm-thick ZrO₂ film was prepared by conducting RF sputtering of a ZrO₂ target onto 4 inch n-Si (100) wafer. 50-nm-thick Ga₂O₃ film was prepared by electron beam evaporation onto n-Si (100) chip cut from the wafer. In addition, thermal oxide of 4 inch n-Si (100) wafer was prepared as a control for ZrO₂ and Gd₂O₃ etching. For measuring the etching rates of the films, an organic material tape is used as the mask for the etching. For evaluating the etched profile of TaN, a resist mask was coated on the TaN and was patterned by a photolithography process. The schematic view of the etching sample is illustrated in Fig. 4.1. Prepared TaN film was analyzed to know the depth composition by RBS (Rutherford BackScattering) and the sheet resistance was measured by four-point probe method. Figure 4.2 shows the schematic view of the dry etching apparatus used in this experiment. The etching chamber has a coil for the inductively coupled plasma generation and an electrode for the sample setting. A 13.56 MHz power is fed to both the coil and the electrode. SF₆, CF₄, CHF₃, Cl₂, BCl₃, and Ar were used as the etching gas. Etching rates of TaN, ZrO₂, Gd₂O₃, SiO₂ and Si were measured by using the step height between the etched and un-etched portion of the film. The etching profile of TaN was observed by SEM. After the half etching of the film, the surface was analyzed by XPS. The etching reaction products gathered by using the similar method of 'imitation sidewall method' were also analyzed by XPS. The plasma during the etching was analyzed by optical emission spectroscopy to estimate the dependence of radical amounts on the etching condition.

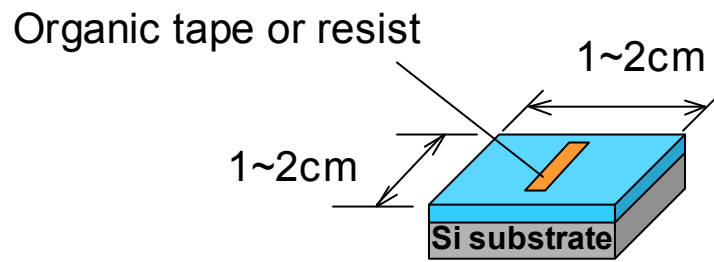


Fig. 4.1. Schematic view of etching sample.

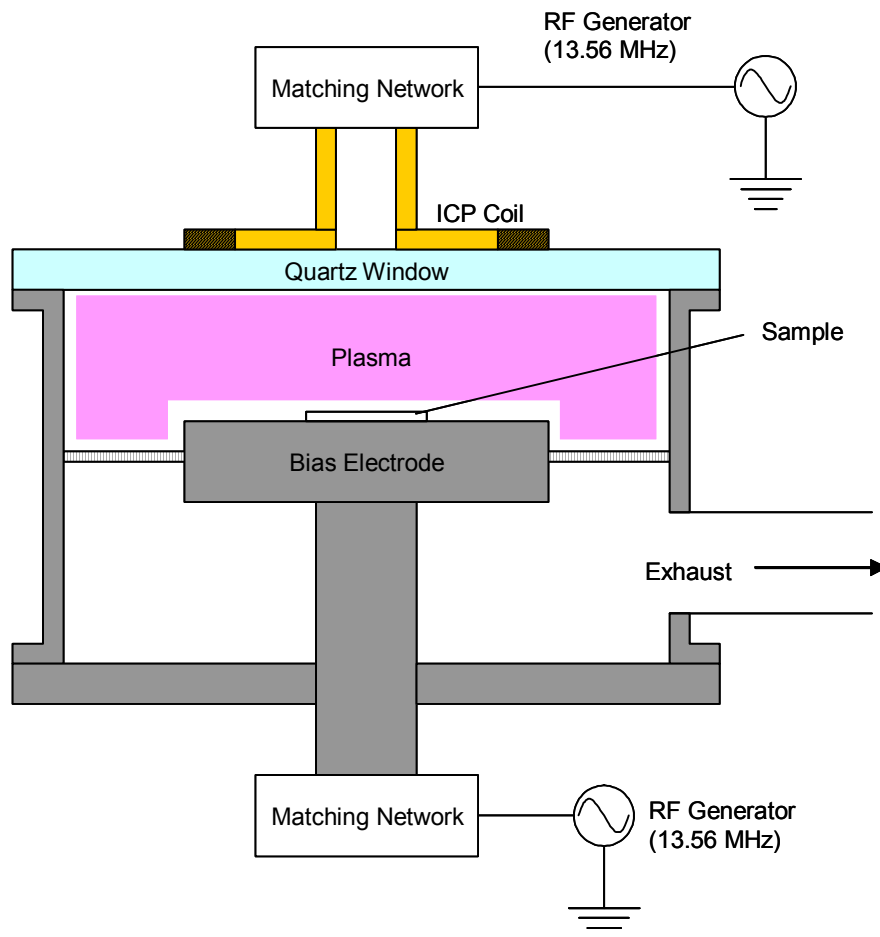


Fig. 4.2. Schematic view of etching apparatus.

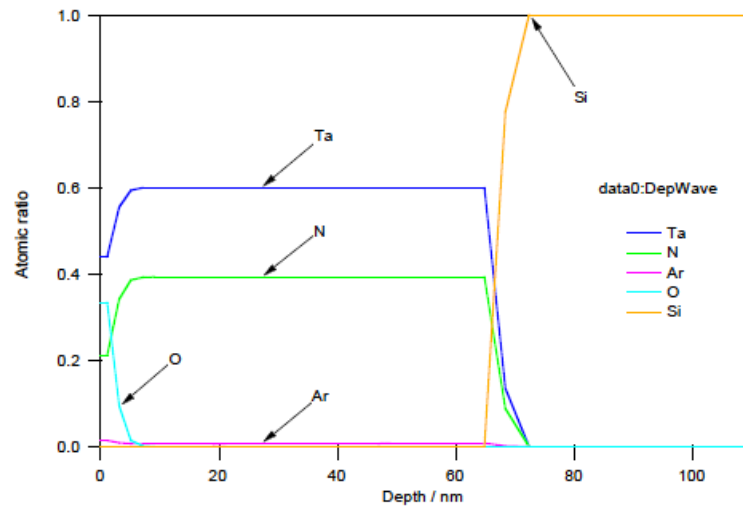
4.3 Results and Discussion

4.3.1 Etching Characteristics of TaN as a Metal Gate Electrode

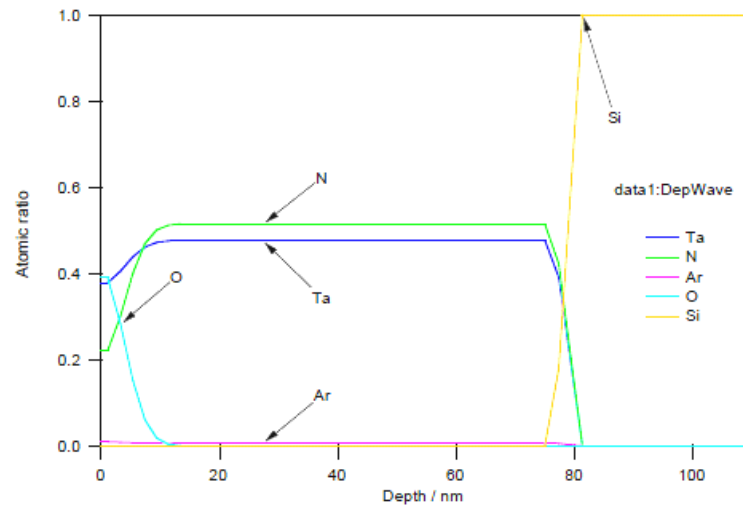
Figure 4.3 shows the depth profiles of three kinds of TaN films with different Ta/N ratios as determined by RBS. Tables 4.1 and 4.2 show the Ta/N ratios as determined by RBS and the sheet resistances of $Ta_{1-x}N_x$ ($x = 0 \sim 0.57$), respectively. Relatively low resistance $7.9 \Omega/\square$ is obtained in the case of $Ta_{0.6}N_{0.4}$ which is prepared by sputtering with the addition of 15% N_2 to the total $Ar+N_2$ gas mixture. In the following experiment, the $Ta_{0.6}N_{0.4}$ is used and is represented as TaN. It should be noted that 5 ~ 10-nm-thick native oxide on the TaN surface is recognized by RBS depth profile result.

Table 4.3 shows the etching rates of the TaN film for the three types of etching gas chemistries: CF_4+Ar , Cl_2+Ar , and BCl_3+Ar . During the etching, the total gas flow rate = 75 sccm in which Ar gas flow rate = 25 sccm, the pressure = 0.53 Pa, the power for the coil and the electrode = 200 W and 100 W, respectively. Prior to the etching, the native oxide layer on the TaN surface was removed by BCl_3+Cl_2+Ar condition. This is because TaN was not etched without the removal of the native oxide layers as reported for the Ta RIE [4.10]. During the pre-removal etching, $BCl_3+Cl_2+Ar = 25+25+25$ sccm, the pressure = 0.53 Pa, and the power for the coil and the electrode = 200 W and 100 W, respectively.

(a) N_2 15%



(b) N_2 30%



(c) N_2 50%

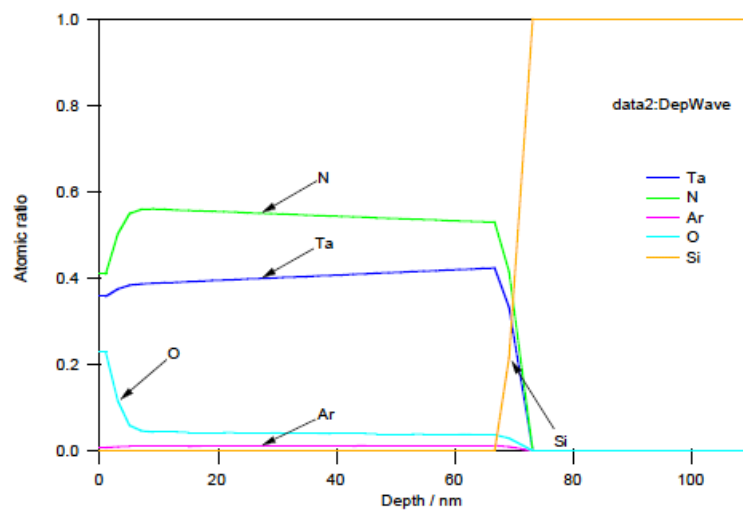


Fig. 4.3. RBS depth profiles of TaN deposited on Si by sputtering with (a) N_2 15%, (b) N_2 30% and (c) N_2 50%.

Table 4.1 Ratios of N/Ta for different gas mixtures in TaN sputtering as determined by RBS.

N ₂ gas ratio	N/Ta ratio
TaN (N ₂ =15%)	0.66
TaN (N ₂ =30%)	1.08
TaN (N ₂ =50%)	1.35

Table 4.2 Sheet resistances of three types of TaN and Ta measured by four-point probe method.

TaN _x	Sheet resistance [$\Omega/\square$]
Ta	7.17
Ta _{0.60} N _{0.40}	7.87
Ta _{0.48} N _{0.52}	20.6
Ta _{0.43} N _{0.57}	78.1

It is found that CF₄ or Cl₂ gas chemistry can not etch TaN without the native oxide removal whereas TaN is etched by BCl₃ or BCl₃+Cl₂ gas chemistry regardless the native oxide removal. This means that BCl₃ is necessary to remove the native oxide layer of the TaN surface. After the native oxide removal, the etching rate of TaN is lowest with CF₄+Ar plasma and that the existence of chlorine in the plasma leads to enhance the etching rate.

Table 4.3 TaN etching rates with different gas chemistries with and without native oxide removal prior to the etching.

Gas chemistry	TaN etching rate [nm/min]	
	Without native oxide removal	With native oxide removal
CF ₄	0	5.4
BCl ₃	19	19
BCl ₃ +Cl ₂	70	70
Cl ₂	0	86

Figure 4.4 shows the etching rates of TaN and Ta as a function of the gas mixture ratio of BCl₃ and Cl₂. It is evident that TaN is etched slower than Ta and that both the etching rates decrease monotonically with decreasing the Cl₂ ratio. The result of the emission analysis of the BCl₃+Cl₂ plasma is shown in Fig. 4.5, where the intensity ratio of Cl (725.4 nm) and Ar (750.4 nm), $I[\text{Cl}]/I[\text{Ar}]$, is plotted as a function of the gas mixture ratio of BCl₃ and Cl₂. The ratio $I[\text{Cl}]/I[\text{Ar}]$, which roughly represents the amount of chlorine atoms on the basis of actinometry, has the maximum at around 30% of BCl₃ to the total gas amount. From the results shown in Figs. 4.4 and 4.5, another factor of TaN RIE other than the amount of Cl radical should be considered.

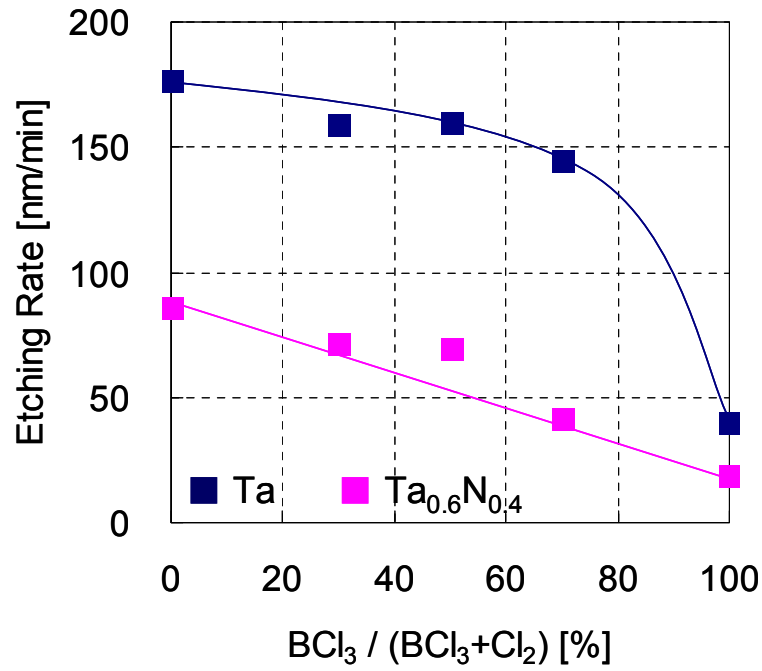


Fig. 4.4. Etching rates of TaN and Ta as a function of BCl₃/Cl₂ gas mixture ratio.

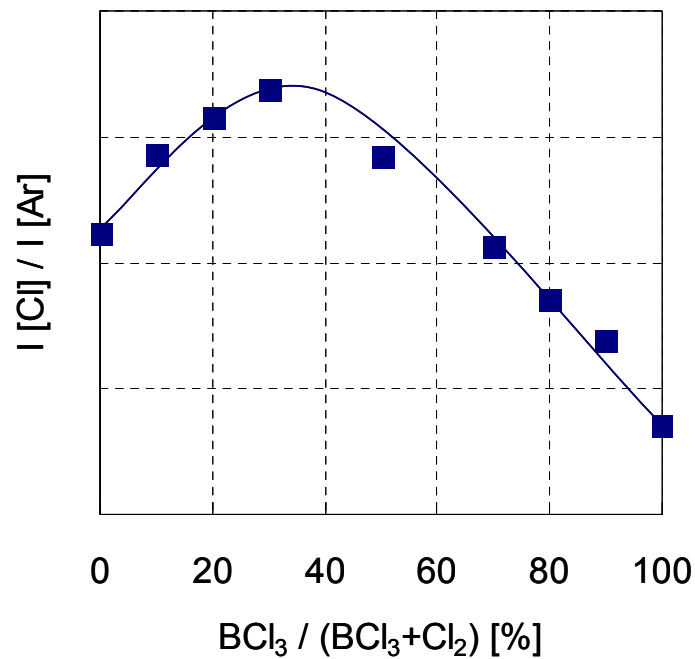


Fig. 4.5. Emission intensity ratio of Cl (725.4 nm) and Ar (750.4 nm) in BCl₃+Cl₂ plasma as a function of the mixture ratio.

In order to clarify the etching reaction of the TaN RIE, XPS analyses were conducted for the half-etched TaN surfaces. Figures 4.6 (a) and (b) show the Ta 4f, N 1s, and Ta 4p_{3/2} narrow-scan spectra of the TaN surfaces after the half etching following the pre-removal etching of the native oxide layers. In Fig. 4.6 (a), it is found that the dominant 4f_{7/2} peak consists of the sub-peaks which are attributed to TaF_x and TaO_x in the case of CF₄+Ar. In the case of Cl₂+Ar, the sub-peaks TaCl_x [4.11] and TaO_x are found. Considering the etching rate result, the author considers that the higher etching rate with Cl₂+Ar plasma than CF₄+Ar plasma is accounted for the higher volatility of TaCl_x than that of TaF_x under the etching condition. In addition, on the basis of a previous report [4.12], it can be considered that the TaN etching was prevented by oxygen generated from the quartz parts in the etching chamber under the CF₄+Ar plasma condition. In the BCl₃+Ar plasma, the dominant peak is shifted to lower binding energy, indicating less amount of TaO_x on the TaN surface. This is consistent with the result that BCl₃-containing gas chemistry is effective for removing the native oxide layer of the TaN surface. It is considered that B generated from BCl₃ play a role in reduction of the native oxide layer of the TaN surface.

From the above results, it is considered that in the RIE of a TaN gate electrode, the native oxide layer of the TaN surface should be removed by using BCl₃ containing gas chemistry at first. After the removal, chlorine-based gas chemistries are suitable because of the higher etching rate of TaN. Chlorine-based gas chemistries have another advantage in the respect of the etching selectivity to the under-layer high-k gate insulators as described later.

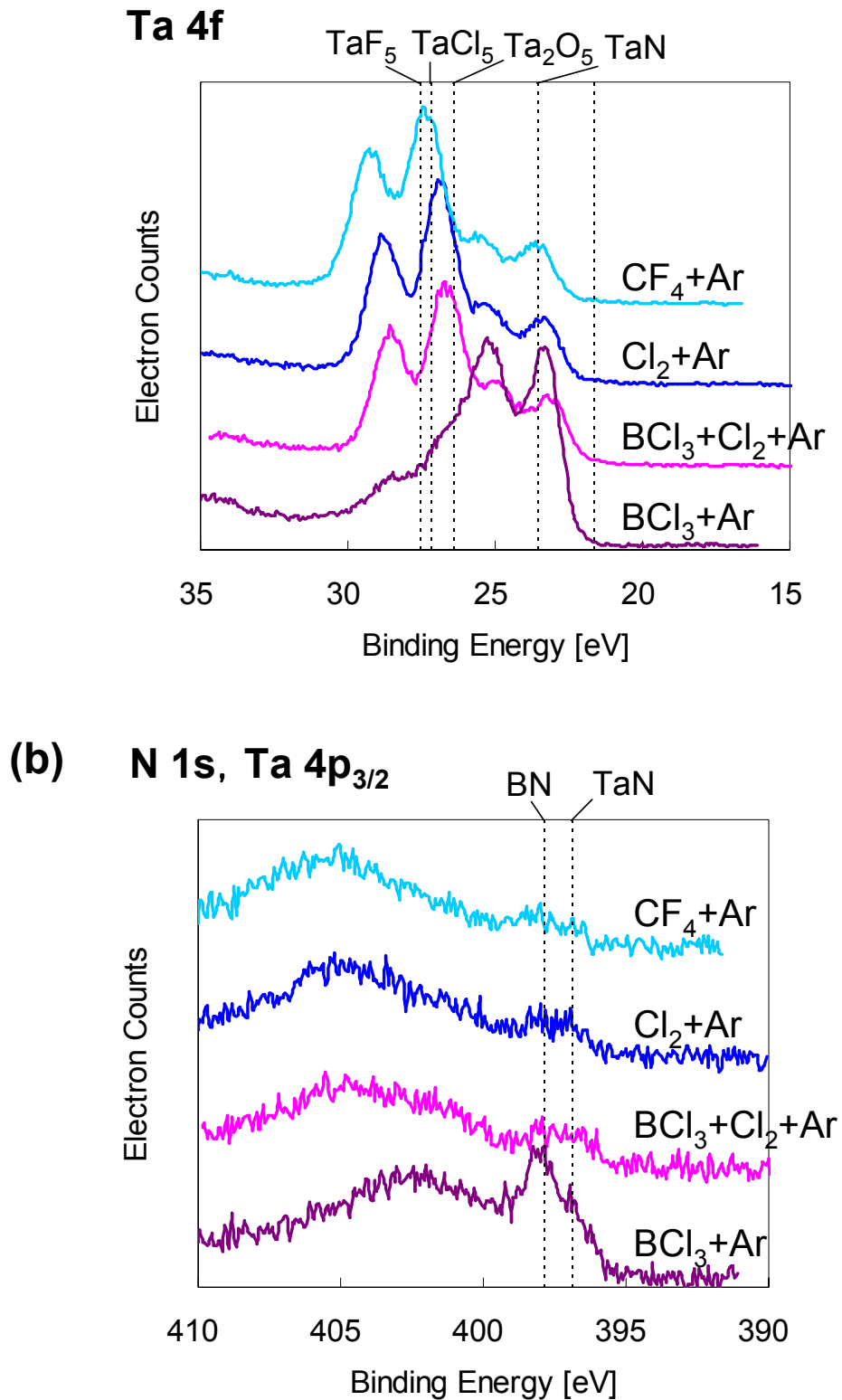


Fig. 4.6. XPS narrow-scan spectra of (a) Ta 4f and (b) N 1s for etched TaN surfaces by different gas chemistries.

In addition, in Fig. 4.6 (b), it should be noted that B-N bonds are detected on the half-etched TaN surface in the case of $\text{BCl}_3 + \text{Ar}$. At the same time, it is confirmed that B-N bonds are not detected for the Ta surface after the $\text{BCl}_3 + \text{Ar}$ half-etching, which is not shown in the figure. Similarly to the TiN RIE with BCl_3 -containing gas chemistries described in chapter 2, it is considered that compounds containing B-N bonds are less volatile and hence hinder the TaN RIE. These BN-containing compounds are considered to account for the lower etching rate of TaN than Ta shown in Fig. 4.4. Furthermore, the TaN etching rate increase despite of the Cl decrease below 30% BCl_3 concentration is also accounted for the inhibition of the etching of TaN due to the existence of the BN-containing compounds.

The etched profile of TaN with the resist mask has been evaluated in the case of chlorine-based plasma. Figure 4.7 shows the etched profile of TaN with varying the gas ratio of BCl_3 and Cl_2 , with the ratio of $\text{BCl}_3 + \text{Cl}_2$ to Ar kept constant. In addition, the features of the etched profiles are shown in Table 4.4. Before the etching, the native oxide layer of the TaN surface was removed with the same condition as described earlier. After the native oxide removal etching, the gas flow rate was set to 75 sccm in which Ar gas flow rate was set to 25 sccm, the pressure = 0.53 Pa, and the power for the coil and the electrode = 200 W and 100 W, respectively. It is clearly found that the tapered profile and the low etching selectivity against the resist mask are obtained with increasing the ratio BCl_3/Cl_2 in Fig. 4.7. The lower resist selectivity causes a larger amount of carbon fragments to lead the lower taper angle due to larger sidewall protection effect. In addition to the carbon fragments, BN-containing compounds are anticipated to lower the taper angle in the case of BCl_3 involvement.

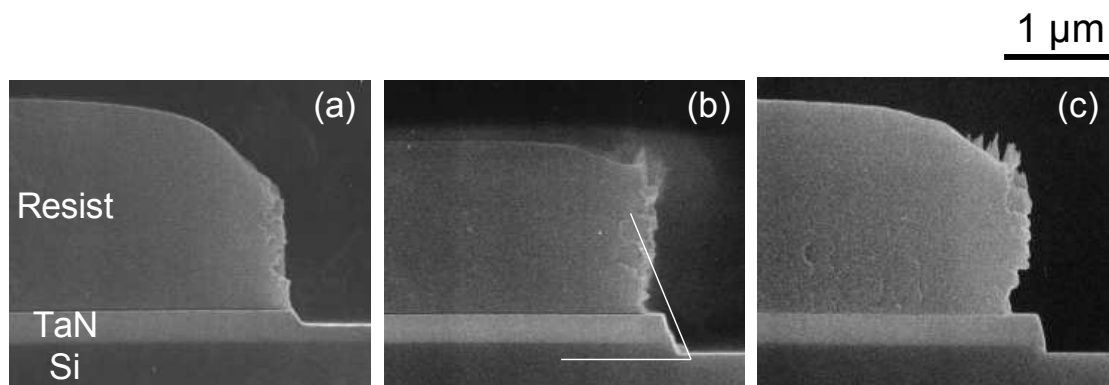


Fig. 4.7. Etching profiles of TaN after RIE with the gas mixture of Ar (25 sccm) + (a) $\text{BCl}_3 = 50$ sccm, (b) $\text{BCl}_3 + \text{Cl}_2 = 25 + 25$ sccm and (c) $\text{Cl}_2 = 50$ sccm.

Table 4.4 Features of TaN profiles after RIE with $\text{BCl}_3 + \text{Cl}_2 + \text{Ar}$ gas chemistries.

Gas			Etching time	Taper angle	Selectivity to resist
BCl_3	Cl_2	Ar			
	[sccm]		[s]	[°]	
50	0	25	600	53	0.26
25	25	25	240	70	0.51
0	50	25	180	76	0.62

Etching profile comparisons between TaN and Si, and between TaN and Al were conducted under the same RIE conditions for the respective cases; in the TaN and Si comparison, $\text{BCl}_3 + \text{Cl}_2 = 30 + 70$ sccm, the pressure = 1.3 Pa and the RF power for the ICP coil and the bias electrode = 500 W and 60 W, respectively. In the TaN and Al comparison, $\text{BCl}_3 + \text{Cl}_2 + \text{Ar} = 5 + 45 + 25$ sccm, the pressure = 0.53 Pa and the RF power for the ICP coil and the bias electrode = 200 W and 100 W, respectively. It should be noted that the comparing two samples such as 'TaN and Si' and 'TaN and Al' were simultaneously etched, respectively. The SEM micrographs are shown in Fig. 4.8. Compared to the profile of Si RIE, TaN is more tapered with thick deposition on its sidewall. Since the effect of the resist etching is not different between the Si RIE and TaN RIE, the difference in the profile must be caused by that of the behavior of the etching reaction products. Therefore, the etching reaction products of TaN such as TaCl_x , BN-containing compounds, etc. are less volatile than that of Si such as SiCl_x . As compared to the Al profile, TaN profile has less side-etch while Al profile has significant side-etch. This difference stems from that of the reactivity in the chlorination of Ta and Al and in the volatility of TaCl_x and AlCl_x . Thus, TaN etching profile tends to tapering. In order to obtain the vertical profile of TaN which is usually required in the gate electrode patterning, some improvement will be necessary such as high temperature process, much lower pressure condition, inorganic mask without an organic resist, etc.

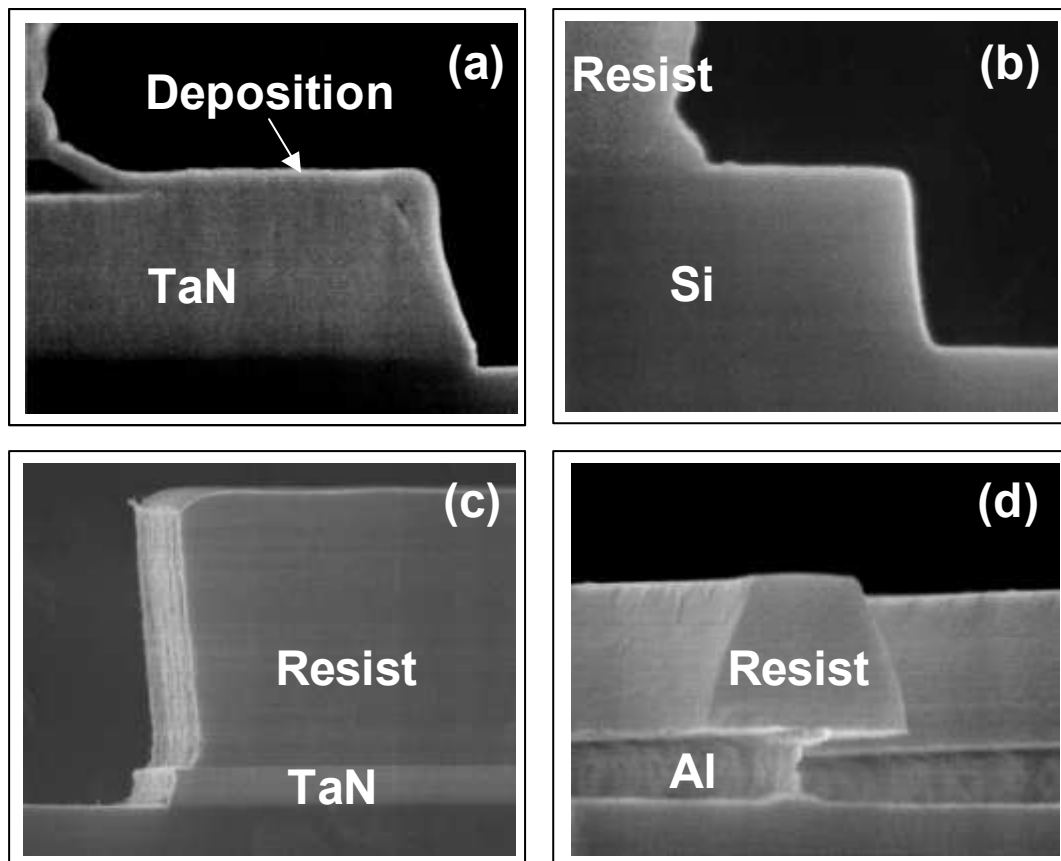


Fig. 4.8. Etching profiles comparisons between (a) TaN and (b) Si under the same RIE condition: $\text{BCl}_3 + \text{Cl}_2 = 30 + 70$ sccm, 1.3 Pa, $\text{RF}_{\text{ICP}} = 500$ W, $\text{RF}_{\text{Bias}} = 60$ W, and between (c) TaN and (d) Al under the condition: $\text{BCl}_3 + \text{Cl}_2 + \text{Ar} = 5 + 45 + 25$ sccm, 0.53 Pa, $\text{RF}_{\text{ICP}} = 200$ W, $\text{RF}_{\text{Bias}} = 100$ W.

In order to clarify the composition of sidewall deposition layer, XPS analysis of the etching reaction products was carried out by using the ‘imitation sidewall method’ shown in Fig. 4.9. In this experiment, TaN sample without an organic resist mask was used. Figure 4.10 shows the XPS wide-scan spectra of the SiO₂ surface. Upper two spectra indicate that the reaction products deposited during the TaN RIE. Figures 4.11 (a) and (b) show narrow-scan spectra of Ta 4f and N 1s for the SiO₂ chip surfaces, respectively. In the narrow-scan spectra, the peak shift correction was made by using C 1s (284.6 eV) spectrum. In the case of Cl₂+Ar plasma, it is found that the deposit on the SiO₂ surface involves TaO_x and TaCl_x. In addition, in the case of BCl₃+Ar plasma, compounds including B-N bonds (398.2 eV) [4.13] are found in the deposit on the SiO₂ chip surface. The generation of TaO_x is not only during the TaN RIE but also during the air exposure after the TaN RIE. However, the detections of Ta-Cl_x bonds and boron nitrides are accounted only for the evaporation and deposition on the ‘imitation sidewall’ SiO₂ chip surface. Thus, the TaN tapered profiles shown in Figs. 4.7 (a), (b) and 4.8 are caused by the deposit containing TaCl_x and BN-containing compounds on the sidewall.

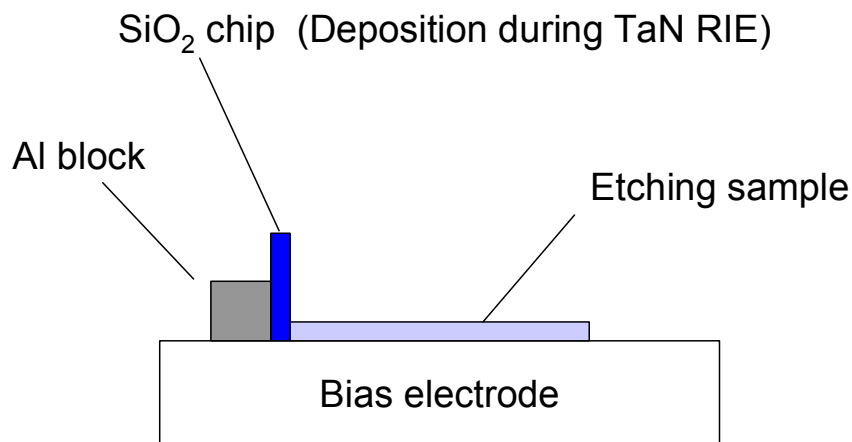


Fig. 4.9. Schematic view of the ‘imitation sidewall method’.

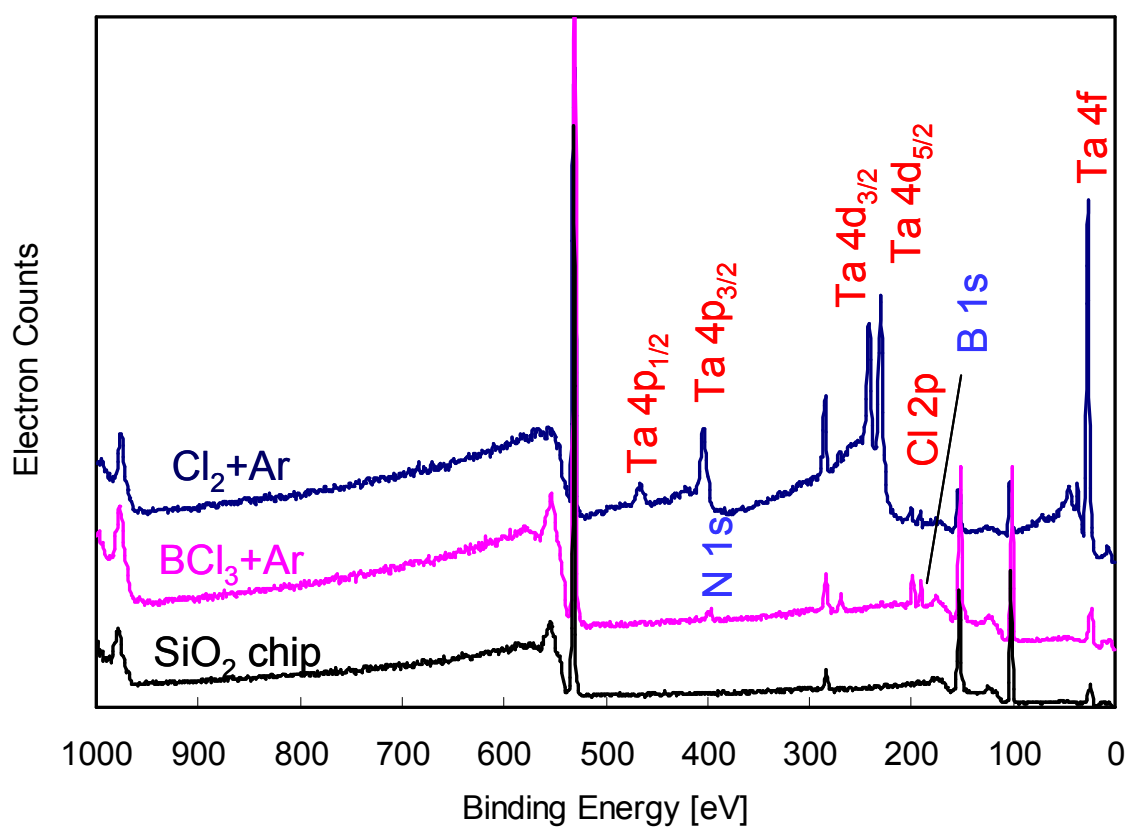
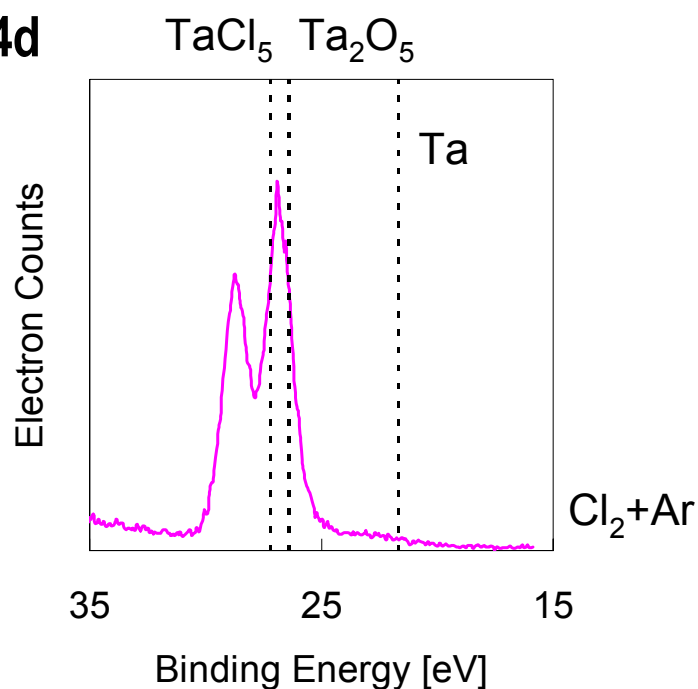


Fig. 4.10. XPS wide-scan spectra of the reaction products deposited on the SiO_2 chip.

(a) Ta 4d



(b) N 1s, Ta4p_{3/2}

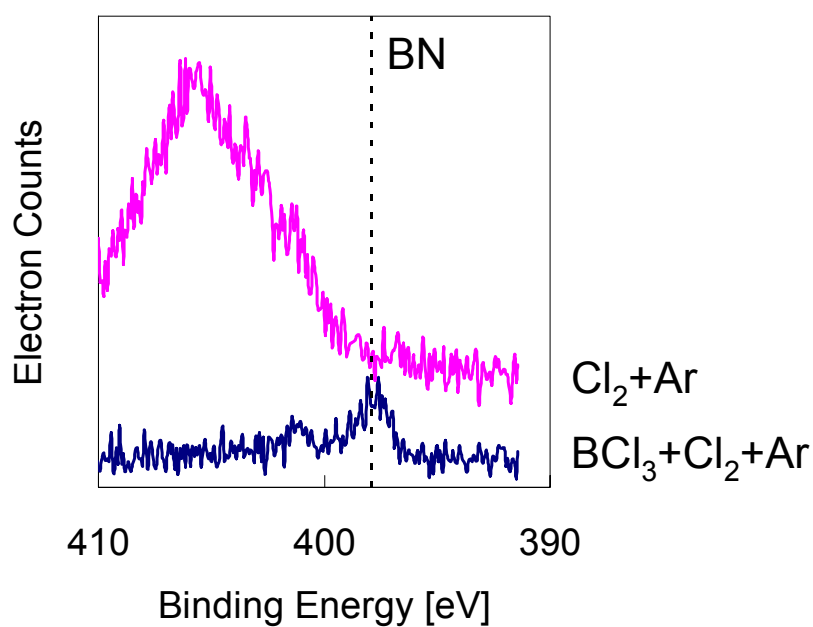
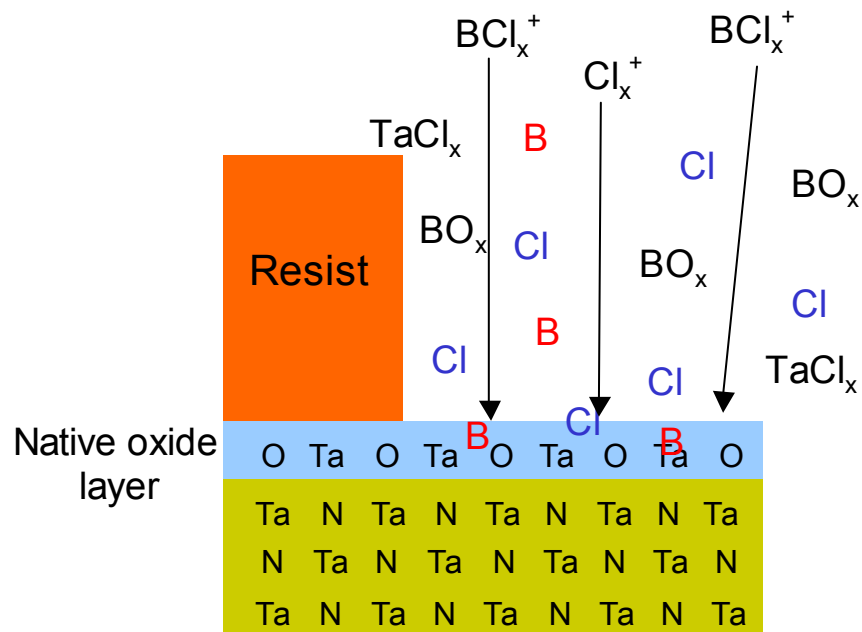


Fig. 4.11. XPS narrow-scan spectra of (a) Ta 4f and (b) N 1s for reaction product deposited on the SiO₂ during TaN RIE.

From the results obtained thus far, a model of TaN RIE is considered for both the native oxide removal and the main TaN etching with $\text{BCl}_3 + \text{Cl}_2$ gas chemistry. Figure 4.12 shows the model. Since the TaN surface is oxidized to a certain extent, the oxide layer should be removed. For the oxide removal, BCl_3 should be included in the etching gas probably because B generated from BCl_3 dissociations extracts oxygen effectively due to its reductive characteristics. After the native oxide layer removal from the TaN top surface, Ta and N are react with Cl, Cl_2 , B and BCl_x to form reaction products. Although NCl_x is volatile TaCl_x and compounds containing B-N bonds are considered less volatile, which causes to hinder the etching and to deposit on the sidewall. In addition to these sidewall deposits, carbon fragments stemmed from the resist etching make deposition on the sidewall and hence contribute to the tapering.

Native oxide removal



TaN etching after the native oxide removal

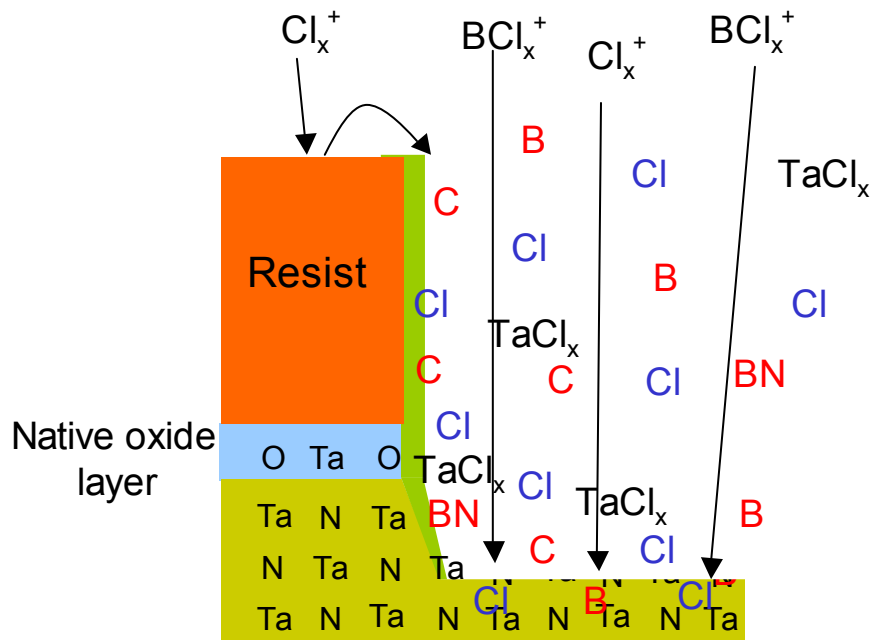


Fig. 4.12. Model of TaN RIE.

4.3.2 Etching Characteristics of ZrO_2 and Gd_2O_3 as High-k Gate Insulators

Figure 4.13 shows the etching rates of ZrO_2 , Gd_2O_3 , HfO_2 , SiO_2 , and Si under the following etching condition: the total gas flow = 100 sccm, the pressure = 4.0 Pa, and the power for the coil and the electrode = 0 W and 100 W, respectively, and the etching time was 5 minutes. It is found that Cl_2 addition to Ar enhances all the etching rates and that the etching rates of ZrO_2 , HfO_2 and Gd_2O_3 are lower than that of SiO_2 . In the Fig. 4.13, it is also found that the etching rates are quite different in the case of SF_6 addition; $\text{Gd}_2\text{O}_3 \ll \text{ZrO}_2 \approx \text{HfO}_2 \ll \text{SiO}_2 \ll \text{Si}$. In the case of CF_4 addition, the etching rates of the high-k films are higher than in the case of SF_6 addition. In the case of CHF_3 addition, the etching rates of all films except Gd_2O_3 become lower than in the case of CF_4 addition.

Figures 4.14 and 4.15 show the Zr 3d and Gd 4d narrow-scan spectra of XPS analyses for the half-etching surfaces of ZrO_2 and Gd_2O_3 , respectively. Figures 4.16 (a) and (b) show the F 1s spectra for ZrO_2 and Gd_2O_3 surface after half-etching with fluorine-containing gas chemistries, respectively. It is found that ZrCl_x and GdCl_x are formed on the etched surface in the case of Cl_2 50% condition. The low etching rates of ZrO_2 and Gd_2O_3 compared to SiO_2 are considered due to the formation of the non-volatile ZrCl_x and GdCl_x , respectively. As discussed earlier, chlorine-based plasma is suitable for the RIE of the TaN gate electrode. Therefore, the etching of gate electrode, which is deposited on the gate insulator film, will not be difficult in terms of the etching selectivity against the high-k film.

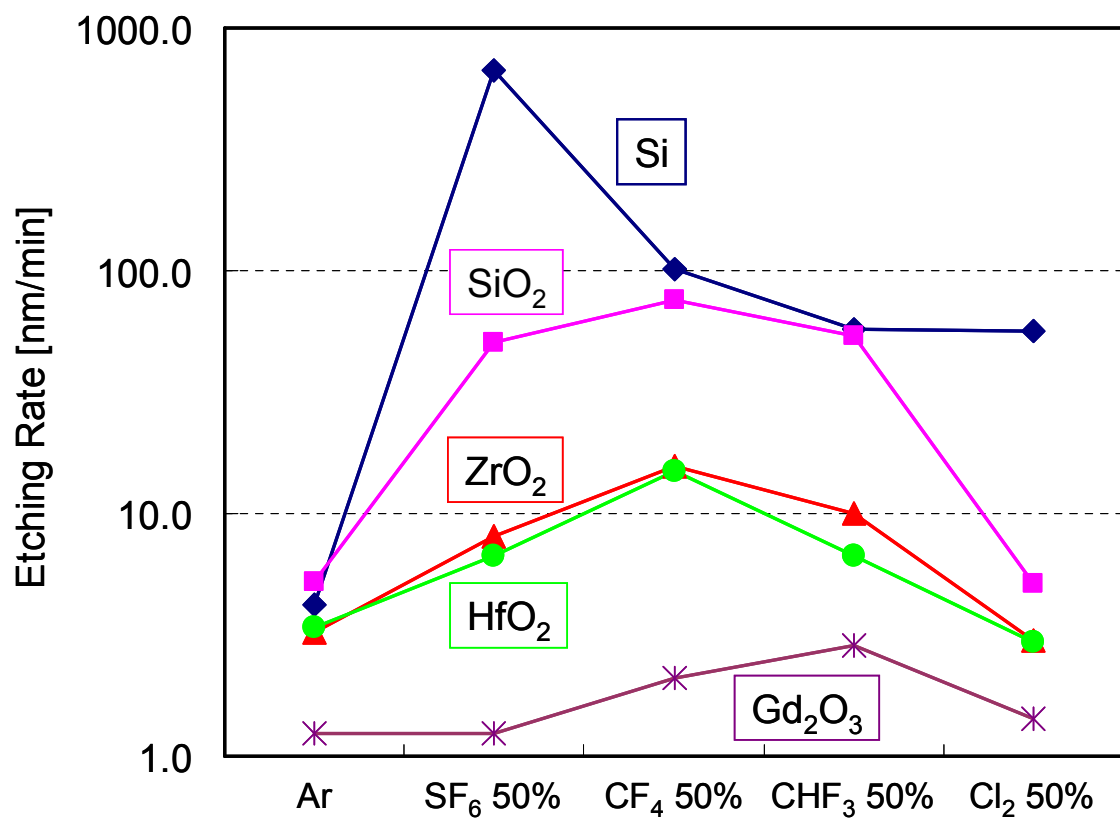


Fig. 4.13. Etching rates of ZrO₂, HfO₂, Gd₂O₃, SiO₂ and Si for different RIE gas chemistries.

Zr 3d

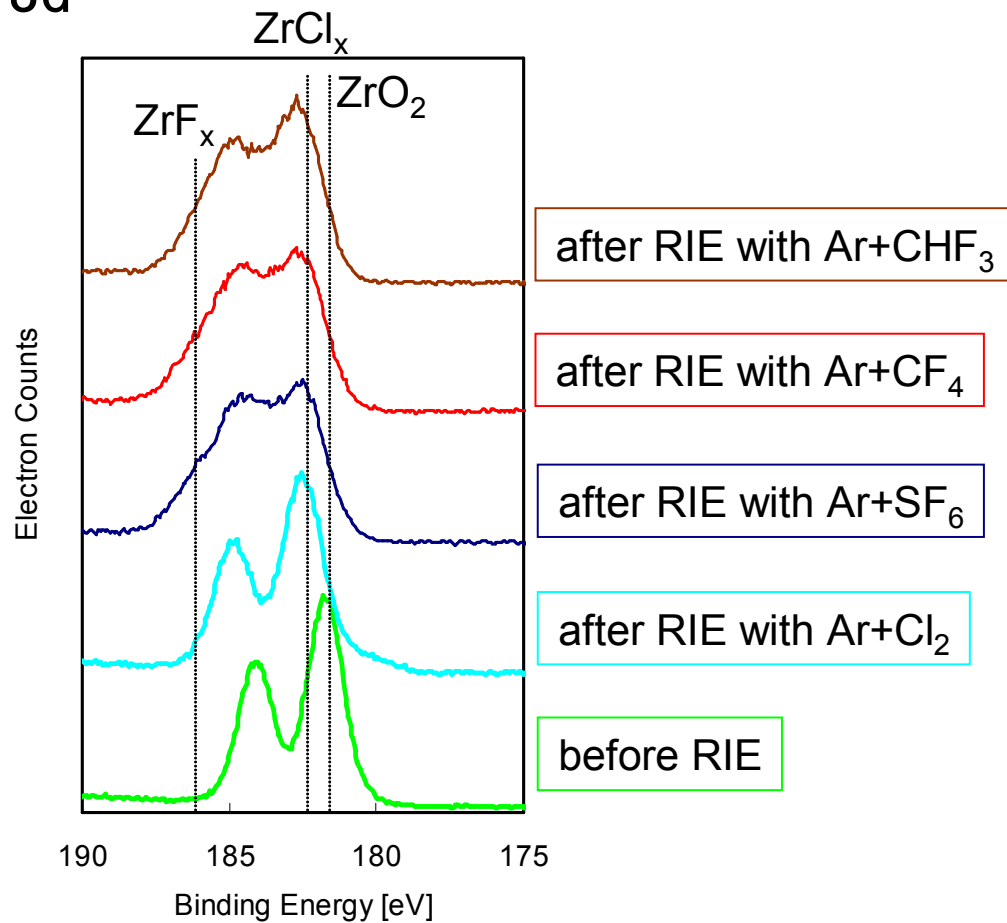


Fig. 4.14. XPS spectra of Zr 3d for ZrO_2 surface after half-etching with different gas chemistries.

Gd 4d

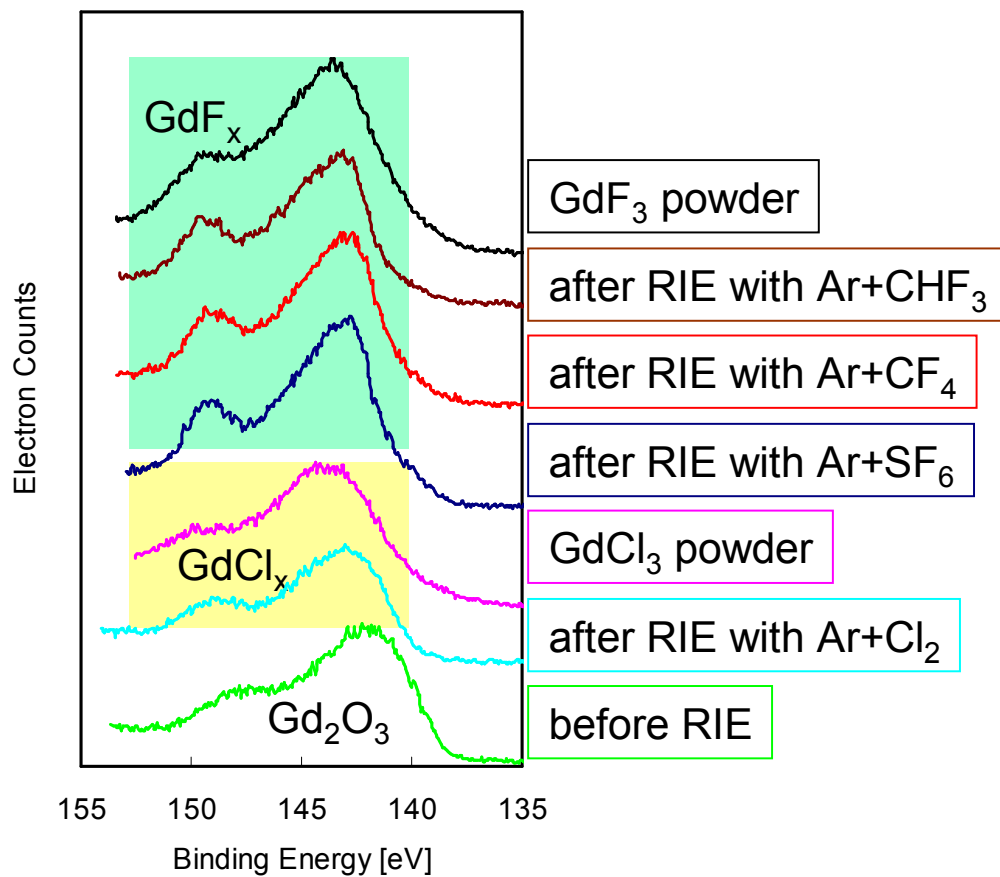
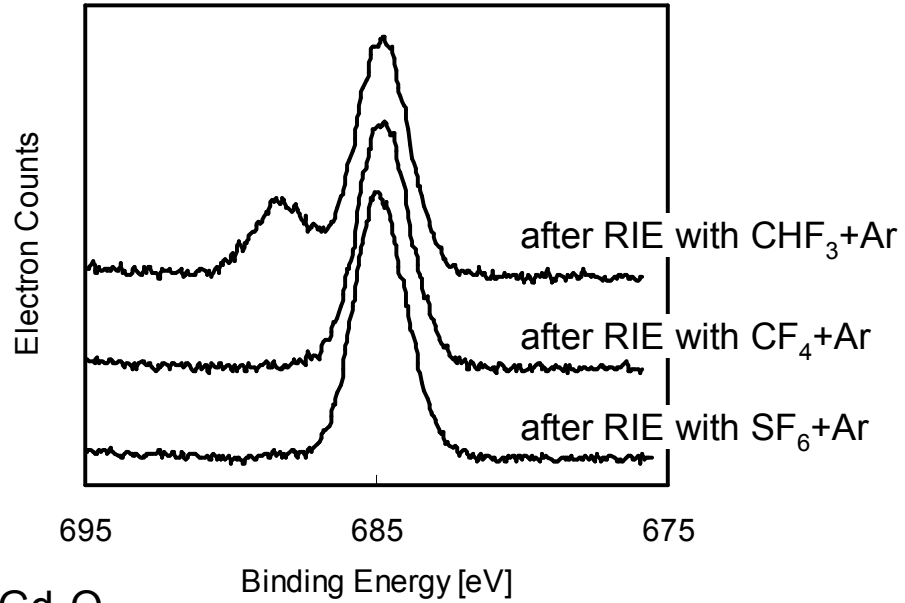


Fig. 4.15. XPS spectra of Gd 4d for Gd₂O₃ surface after half-etching with different gas chemistries.

(a) F 1s of ZrO_2



(b) F 1s of Gd_2O_3

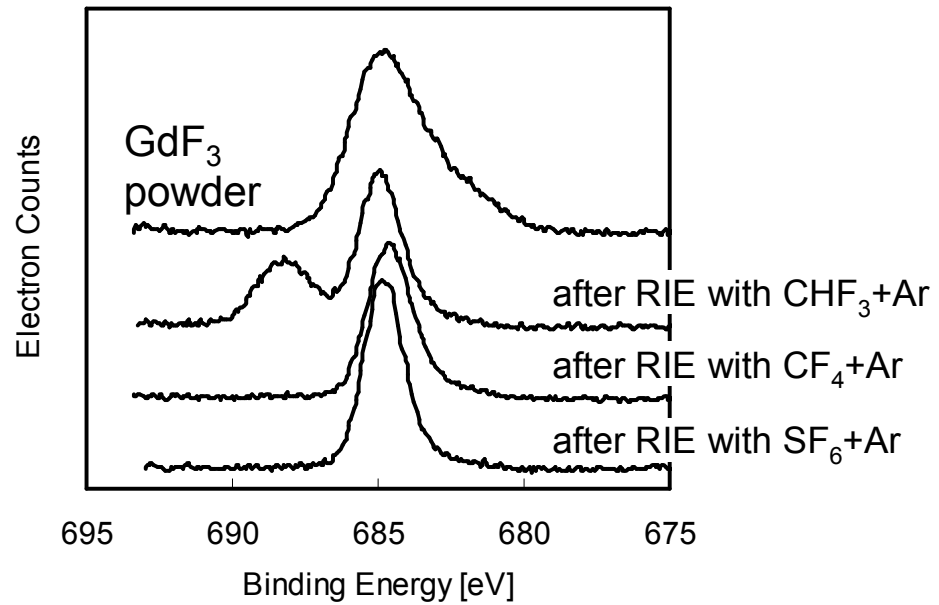
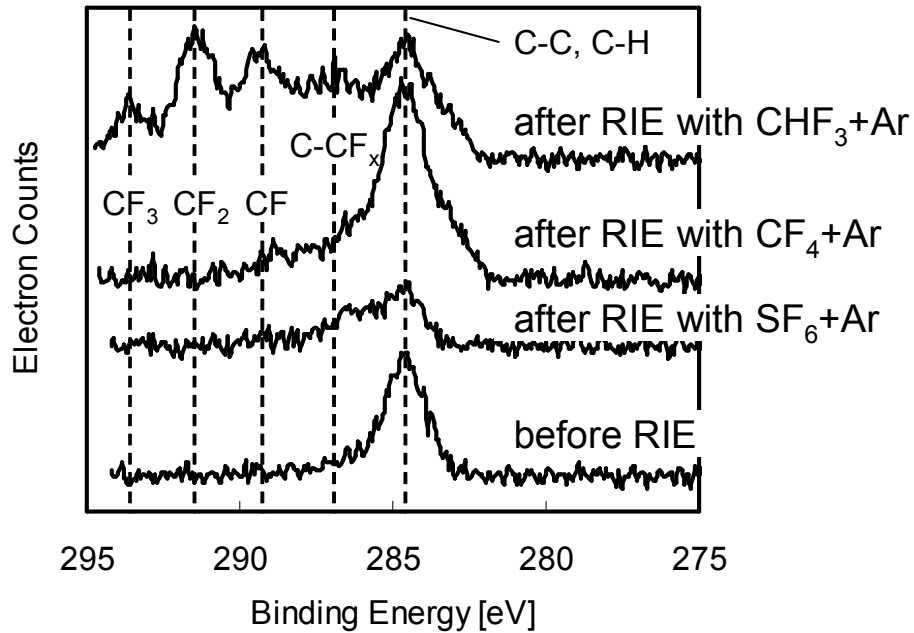


Fig. 4.16. XPS narrow-scan spectra of F 1s for (a) ZrO_2 surface and (b) Gd_2O_3 surface after half-etching with different gas chemistries.

From Zr 3d spectra shown in Fig. 4.14, ZrO₂ surfaces are found to be fluorinated after the half etchings under the conditions of SF₆, CF₄, and CHF₃ additions to Ar. These fluorinations are also confirmed by F 1s spectra shown in Fig. 4.16 (a) because the main peaks at around 685 eV indicate the existence of F-metal bonds. From Gd 4d and F 1s spectra shown in Figs. 4.15 and 4.16 (b), respectively, it is also found that Gd₂O₃ surfaces are fluorinated by the half etchings under the conditions of SF₆, CF₄, and CHF₃ additions to Ar.

It should be noted that the depositions of CF_x film occur on ZrO₂ and Gd₂O₃ surfaces under the CHF₃+Ar condition as was indicated by sub-peaks at around 688 eV in F 1s spectra as shown in Figs. 4.16 (a) and (b). It is considered that fragments such as CF₂ generated by the dissociations of CHF₃ cause those CF_x depositions. Figures 4.17 (a) and (b) show the XPS results of Si surfaces after the half-etchings in F-containing gas conditions. A significant CF_x deposition occurs on the Si surface after the half-etching under the CHF₃+Ar condition. The CF_x deposition is considered to account for the decreases in the etching rates of Si, SiO₂, and ZrO₂ as was shown in Fig. 4.13. However, other phenomenon than the CF_x deposition is considered dominant for the increase in etching rate of Gd₂O₃ under the CHF₃+Ar condition.

(a) C 1s



(b) F 1s

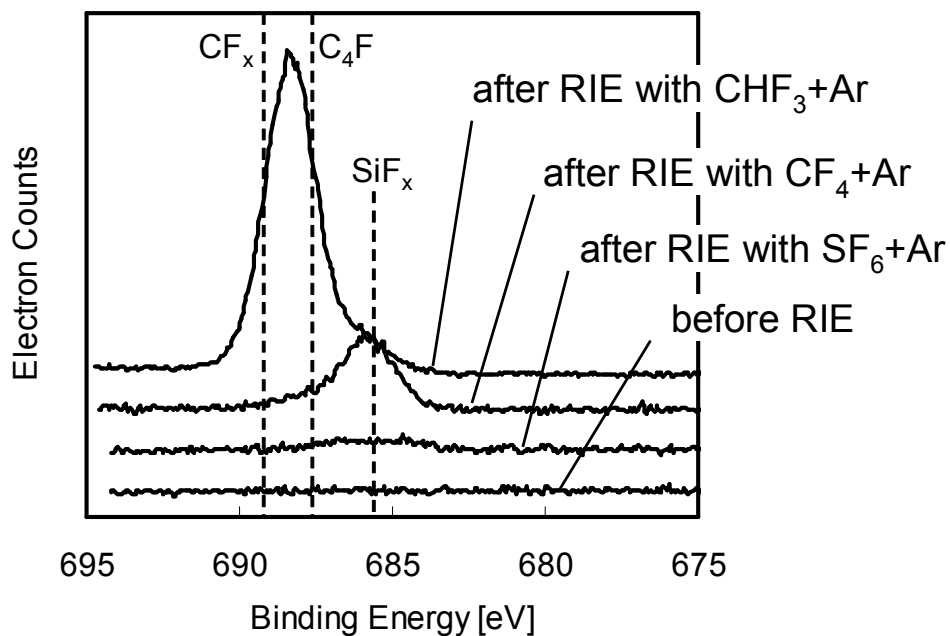


Fig. 4.17. XPS spectra of (a) C 1s and (b) F 1s for Si surface after half etching with F-containing gas chemistries.

Generally, fluorides and chlorides of Zr and Gd are considered non-volatile compounds, as considered by their boiling points shown in Table 4.5. Since fluorides and chlorides of Si are much more volatile than that of Zr and Gd, removing the high-k films without the etching of Si substrate seems to be difficult.

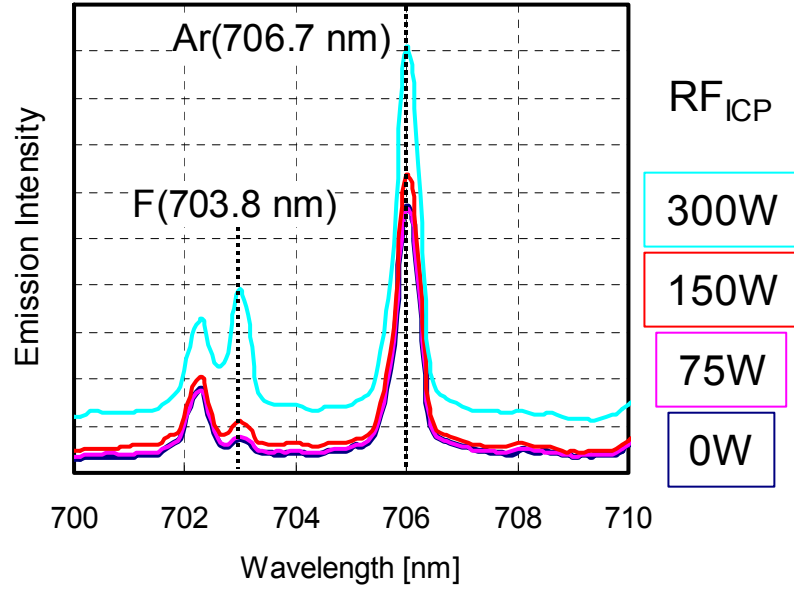
Table 4.5 Melting points and boiling points of fluorides and chlorides of Zr, Gd and Si.

	ZrCl ₄	ZrF ₄	GdCl ₃	GdF ₃	SiCl ₄	SiF ₄
Melting point [°C]	437	640	602	1235	-70	-90.2
Boiling point [°C]	* 331	905	1576	2427	57.6	-86

* Sublimation temperature

In order to enable the selective removals of ZrO₂ and Gd₂O₃ against Si, the tuning of the etching condition was carried out to make more CF_x deposition on Si and less fluorination of Zr and Gd. This is because the use of some etch-inhibiting layer is considered effective to realize the selective etching. For the purpose, the author chose CHF₃ gas chemistry judging from the CF_x deposition result shown in Fig. 4.17 (a) and measured optical emission spectra for CHF₃+Ar gas mixture plasma. Figures 4.18 (a) and (b) show the spectral result for the condition; CHF₃+Ar = 90+10 sccm, the pressure = 4.0 Pa and the power for the electrode = 100 W. The power for the coil was varied in this experiment.

(a) 700-710 nm



(b) 265-275nm

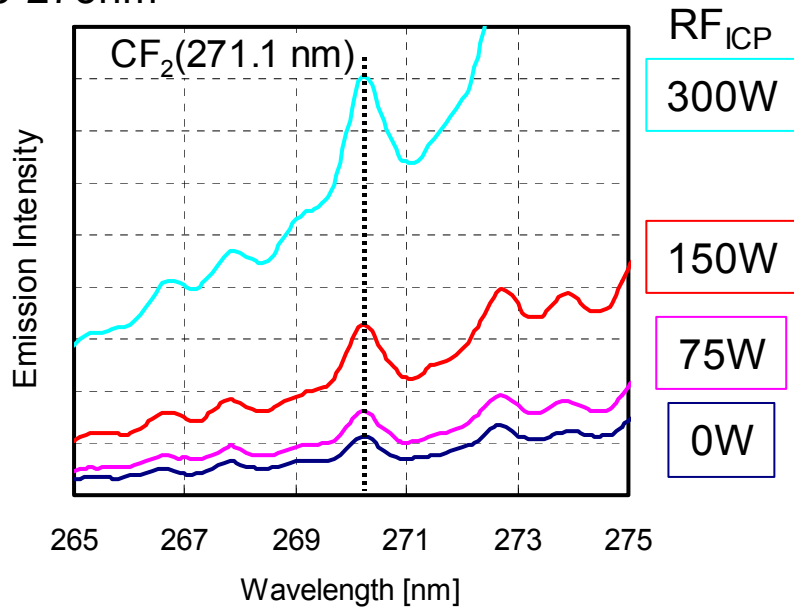


Fig. 4.18. Plasma optical emission spectra for the wavelength ranging (a) 700-710 nm and (b) 265-275 nm under the condition of $\text{CHF}_3 + \text{Ar} = 90 + 10$ sccm, pressure = 4.0 Pa, power of electrode = 100 W.

From Fig. 4.18, the emission intensities of F (703.8 nm) and CF_2 (271.1 nm) are divided by that of Ar (706.7 nm). Figure 4.19 shows the dependence of these ratios on the power for the coil. Obviously, the ratio of the intensities CF_2/F increases with decreasing the power for the coil, which can be explained by the suppression of further dissociations of fragments generated from CHF_3 under the small coil power condition.

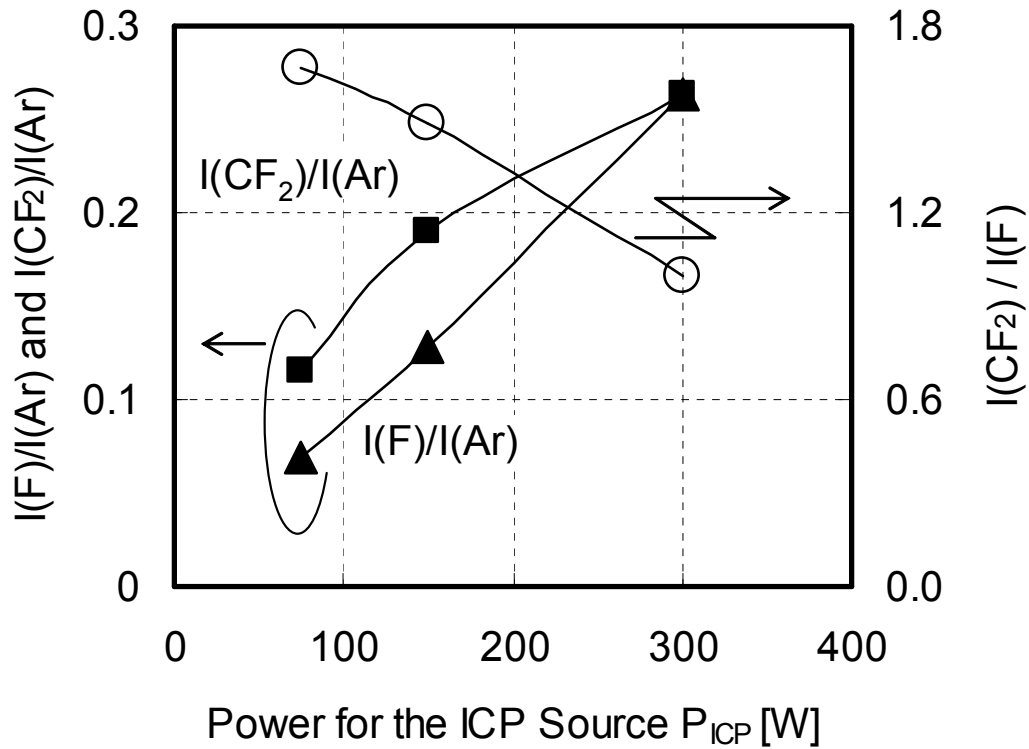


Fig. 4.19. Ratios of emission intensities between CF_2 , F and Ar for the plasma: $\text{CHF}_3 + \text{Ar} = 90 + 10$ sccm, pressure = 4.0 Pa, power of electrode = 100 W.

Then ZrO_2 , Gd_2O_3 , and Si were etched under the following etching condition; the flow rate of $\text{CHF}_3 + \text{Ar} = 90 + 10$ sccm, the pressure = 4.0 Pa, the power for the coil was varied and the power of the electrode = 100 W, respectively. The result is shown in Fig. 4.20. Low etching rate for ZrO_2 3.7 nm/min and almost 0 for both Gd_2O_3 and Si are obtained under the condition of zero-power for the ICP coil. Thus, removing the high-k film against Si is considered possible for ZrO_2 in principle. However, it is difficult to etch Gd_2O_3 film faster than Si substrate. This difficulty of the selective removal of Gd_2O_3 is due to the low vapor pressure of GdF_x as is supposed by Table 4.5.

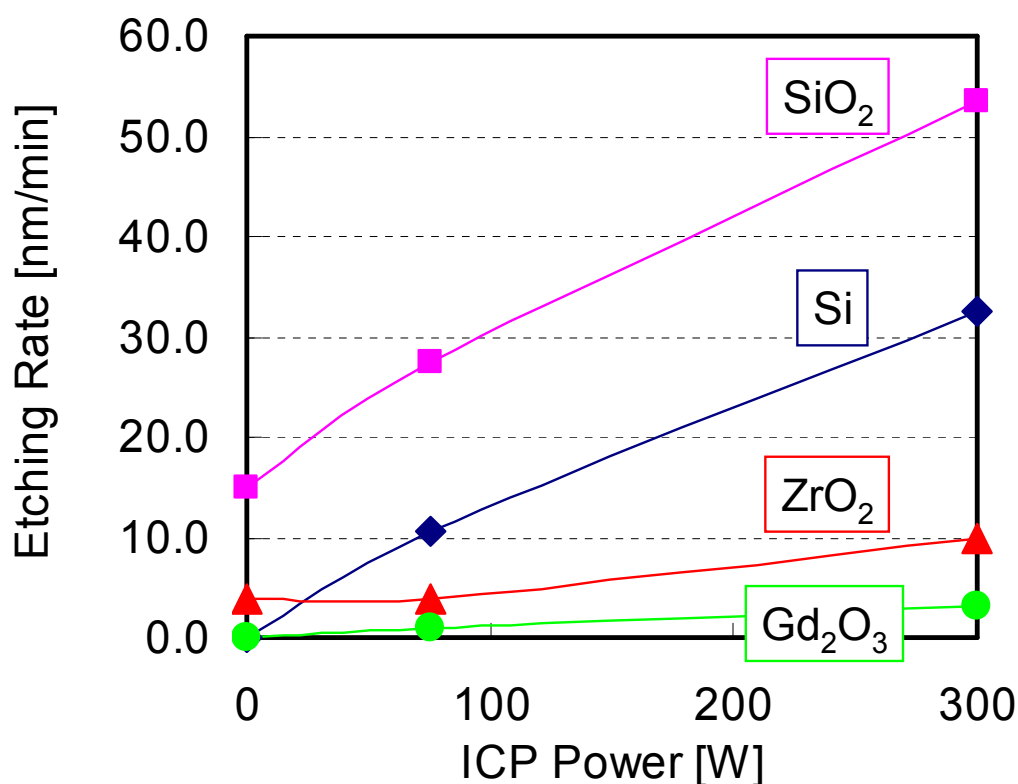


Fig. 4.20. The dependence of etching rates of ZrO_2 , Gd_2O_3 , SiO_2 and Si on the power for ICP coil.

Finally, the etching of the stacked ZrO_2 (100 nm)/Si samples were carried out under the above condition with different etching times to confirm the possibility of the selective removal of ZrO_2 against Si. The result of the etched depth vs. the etching time is shown in Fig. 4.21. From the ratio of the two slopes corresponding to the etching rates of ZrO_2 and Si, ZrO_2 is found to be etched 1.5 times faster than Si. Thus, the selective removal of ZrO_2 against Si has been achieved with the selectivity 1.5. Although the value of the selectivity is insufficient for the device manufacturing, the author considers that it can be improved by tuning the etching condition.

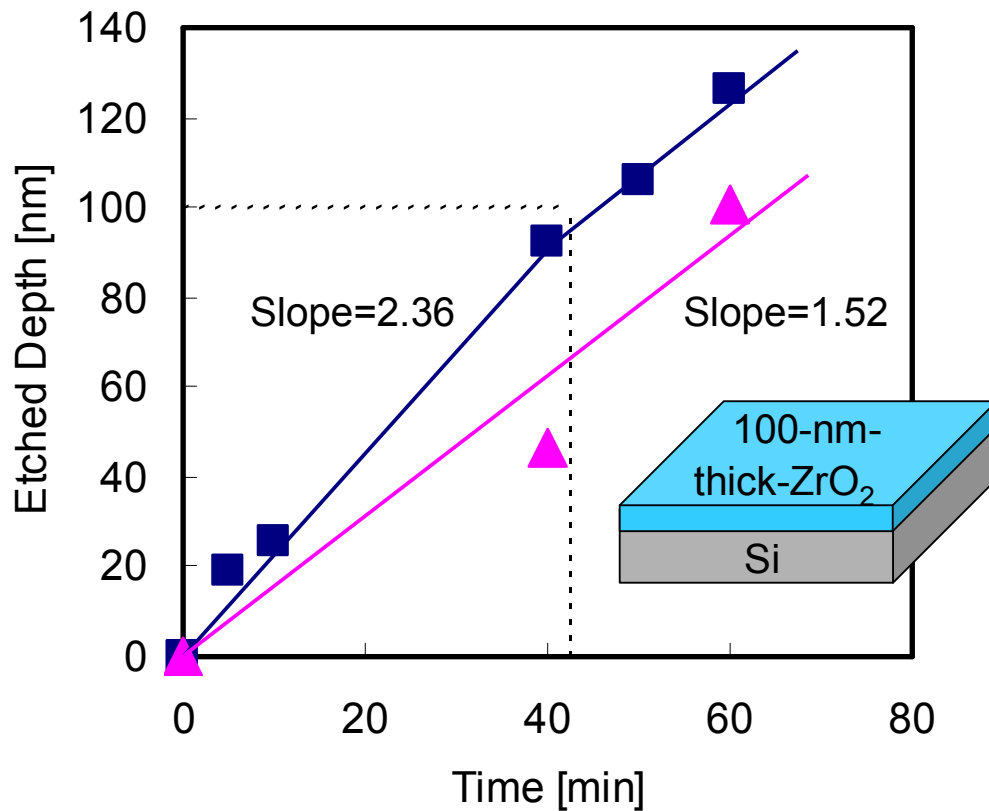


Fig. 4.21. Etched depth vs. etching time for ZrO_2 (100 nm)/Si and Si under the following etching condition; $\text{CHF}_3 + \text{Ar} = 90 + 10$ sccm, pressure = 4.0 Pa, power of electrode = 100 W.

Figure 4.22 shows the XPS narrow-scan spectra of C 1s for surfaces of ZrO_2 and Si after the half etching under the condition used in Fig. 4.20. It is clearly found that no CF_x deposition occurs on ZrO_2 surface while Si surface is covered by a certain amount of CF_x deposition. This indicates that the above selective etching is due to the almost same mechanism as the well-known SiO_2/Si selective RIE.

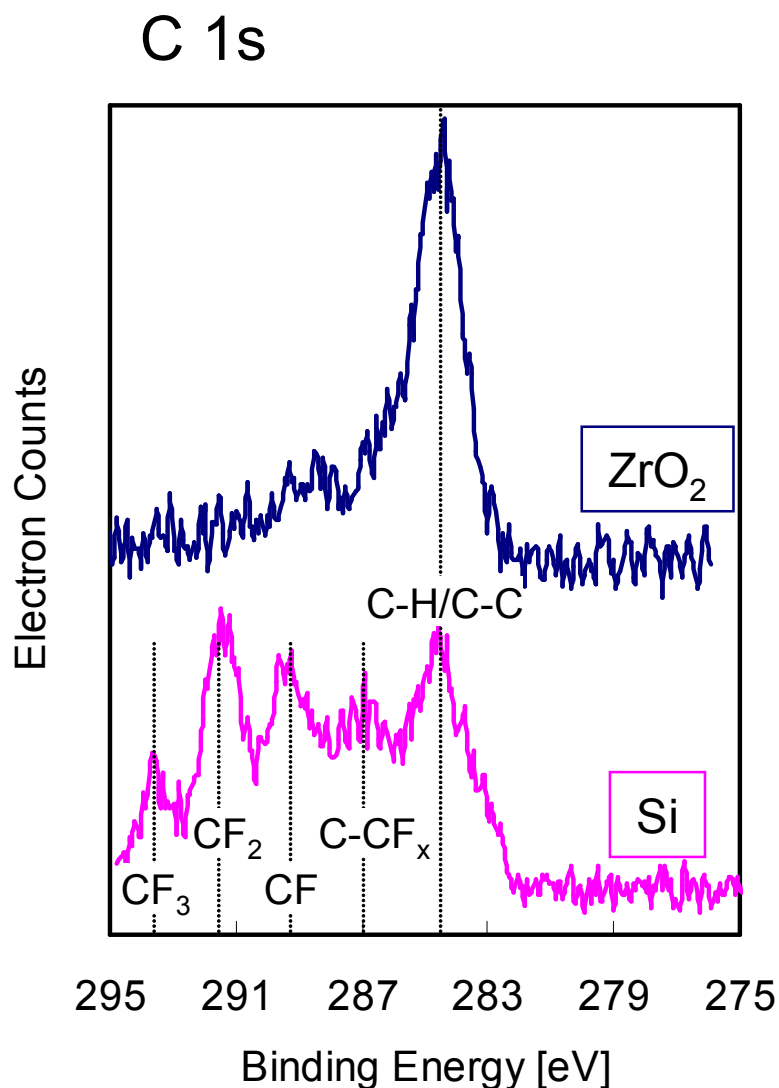


Fig. 4.22. XPS narrow-scan spectra of C 1s for surfaces of ZrO_2 and Si after the half-etching.

4.3.3 Process Flow Consideration

On the basis of obtained results thus far, one can consider the process flow when TaN and ZrO_2 or Gd_2O_3 , are used in a MOSFET as a metal gate electrode and a high-k gate insulator, respectively. In the case of the conventional process flow shown in Fig. 4.23, two kinds of selective etchings should be established. One is TaN or spacer SiN selective etching against the underlayer high-k film. This is considered relatively easy because the etching rate of the high-k film such as ZrO_2 , HfO_2 and Gd_2O_3 is slower than SiO_2 . The other is the high-k selective etching against Si substrate and is difficult because Si can be etched much faster than those high-k films. Basically, ZrO_2/Si selective etching is found possible by using almost the same mechanism as the well-established SiO_2/Si selective etching. However, for Gd_2O_3 film and perhaps rare-earth metal oxides expected as a candidate of post-next MOSFET, however, the selective etching is very difficult because of low volatility of their halogen compounds. In the case of failing to achieve the selective dry etching against Si substrate, another process flow should be integrated instead of the conventional process flow. Otherwise precisely controlled wet etching should be developed. From the view point, the damascene gate process [4.14], for example, may be promising not only because it can avoid thermal degradations of the device but also because it does not need the selective high-k etching against Si substrate.

Conventional process from gate electrode patterning to gate spacer formation

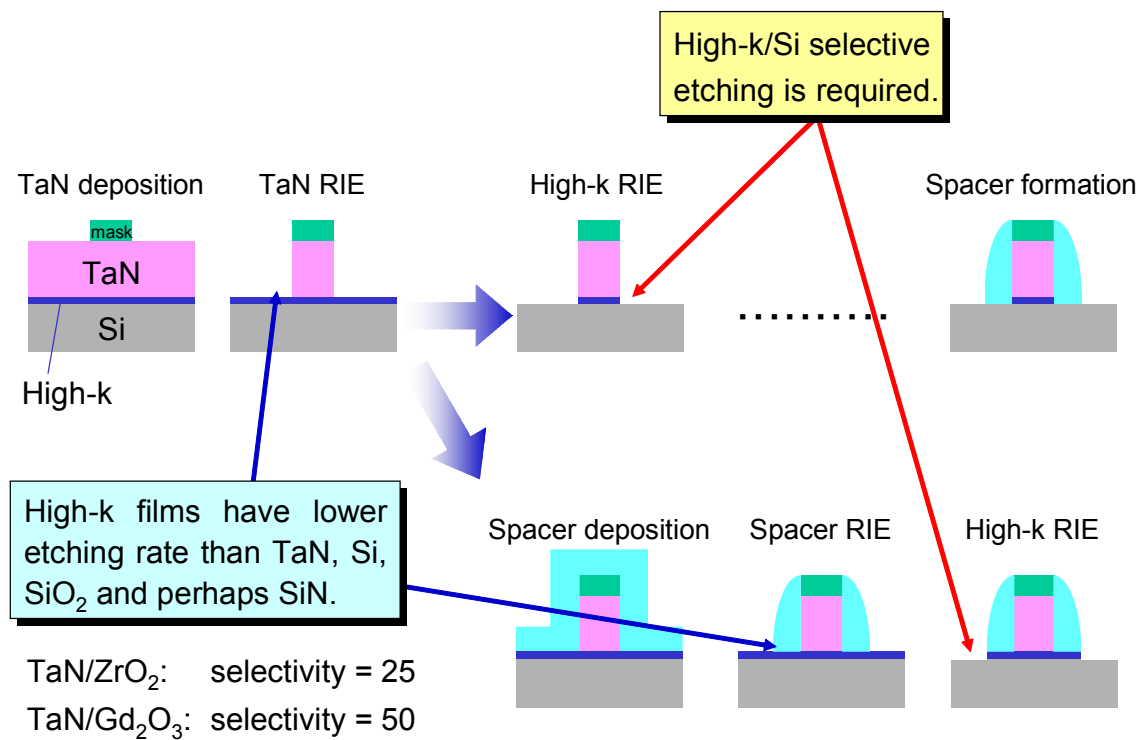


Fig. 4.23. Schematic view of conventional process flow related to MOSFET gate structure formation.

4.4 Summary and Conclusions

On the basis of the approach used in the previous chapters, the dry etching of new materials currently studied for the future CMOS devices has been studied. TaN metal gate electrode and high-k gate insulators such as ZrO_2 and Gd_2O_3 were focused on. In the TaN RIE, the native oxide layer of the TaN surface should be initially removed by the etching using BCl_3 -based gas chemistry. It is considered that B generated from BCl_3 dissociations contributes to extract oxygen reductively from the native oxide of TaN. After the removal, chlorine-based chemistry is suitable for the gate electrode patterning in the respect of the high etching rate compared to fluorine-based chemistry. As far as the TaN etching profile is concerned, it is turned out that TaN tends to be tapered because of the low volatility of Ta-chlorides. Moreover, when the etching gas chemistry contains BCl_3 , the etching profile becomes much more tapered because compounds containing boron nitrides are deposited on the sidewall. In addition, carbon fragments stemmed from the resist etching make deposition on the sidewall and hence contribute to the tapering. In order to obtain the vertical profile of TaN for the gate electrode use, some improvement will be necessary such as high temperature process, much lower pressure condition, inorganic mask without an organic resist, etc.

For ZrO_2 , HfO_2 and Gd_2O_3 films, it is found that the etching rate of Gd_2O_3 is the lowest and that the etching rates of ZrO_2 and HfO_2 are higher than that of Gd_2O_3 but lower than that of SiO_2 for usual fluorine-based and chlorine-based gas chemistries. This indicates that a high etching selectivity to the underlayer can be obtained for the gate electrode etching. As far as the selective removal of the high-k film against Si substrate is concerned, ZrO_2/Si selective etching is found possible by using the

selective deposition of CF_x on Si surface. However, the difficulty of $\text{Gd}_2\text{O}_3/\text{Si}$ selective etching has been suggested at the same time. As a conclusion, MOSFET consisting of a TaN gate electrode and a ZrO_2 insulator can be fabricated by using dry etching in principle. However, in the case of rare-earth metal oxide such as Gd_2O_3 , the selective dry etching against Si-underlayer seems to be difficult because of low volatility of their compounds.

Process flow consideration was carried out on the basis of the obtained dry etching characteristics of TaN, ZrO_2 and Gd_2O_3 . In the case of the conventional process flow related to the MOSFET gate structure formation, two kinds of selective etchings should be established. One is the TaN or spacer SiN selective etching against the high-k film as the underlayer. The other is the high-k selective etching against Si substrate. It is considered that the former is easily realized while the latter is difficult especially for rare-earth metal oxide. If the latter selective etching will not be achieved in both dry and wet process, another process flow should be integrated instead of the conventional process flow. From the point of view, damascene gate process can be advantageous not only because it can avoid thermal degradations of the device but also because it does not need the difficult selective etching process.

4.5 References

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5. Summary and Conclusions

This thesis describes the study on dry etching profile and selectivity in the manufacturing of recent ULSI devices of mainly 180 nm technology node and below. In particular, the behavior of the etching reaction products has been investigated by experiments and chemical analyses. In order to analyze the reaction products in detail, new method 'imitation sidewall method' has been introduced. For various films used in ULSI devices such as Al, TiN, Cr₂O₃/Cr, Al₂O₃, TaN, ZrO₂ and Gd₂O₃, the behaviors of the etching reaction products and the mechanisms determining the etching profile and selectivity have been clarified. On the basis of the etching mechanisms obtained in this study, it has been possible to optimize the dry etching processes and equipments. In fact, the etching profile of the stacked TiN/Ti/Al/TiN/Ti-wiring has been fine-tuned for advanced CMOS devices. The photomask ashing process with high selectivity against Cr₂O₃/Cr film has been introduced to practical use in manufacturing the photomasks for ULSI devices of 180 nm technology node and below. Thus, the study described in this thesis has contributed to productivity improvements of the advanced ULSI devices. In addition, an investigation on dry etching characteristics of materials for the future devices such as TaN, ZrO₂ and Gd₂O₃ suggests the process capability and problems. Finally, a perspective on dry etching technology is described; for the patterning of new materials with more precise etching profile and less electrical damage, it will be increasingly important to develop the dry etching process on the basis of the etching mechanism.

5.1 Summary and Conclusions

Through this thesis, study on dry etching profile and selectivity in ULSI manufacturing has been described. The etching reaction on the etched film surface has been especially focused on. Detailed analyses of the etching reaction products have clarified their behavior determining the etching profile and selectivity. The following is description of the summary and conclusions of each chapter.

In chapter 2, the control of dry etching profile in Al-wiring fabrication has been described. For the Al-wiring dry etching using BCl_3+Cl_2 -based gas chemistries, the author investigated the analyzing method of a sidewall deposit on the Al-wiring pattern. On the basis of the ‘imitation sidewall method’ named in this study, the mechanism of the sidewall protection was clarified for N_2 and CH_2F_2 gas addition cases. As a result, it was found that a N_2 gas addition to a BCl_3+Cl_2 gas mixture made a thick sidewall deposit which contains ammonium salts of Al (NH_4Cl) and Al-chloride (NH_4AlCl_4) in addition to carbon-based compounds. It was also clarified that the CH_2F_2 gas addition caused a sidewall deposit containing AlF_x among carbon-based compounds. Comparison of the two additional gases was made to consider which process is superior. The N_2 addition needs the resist mask etching to form the sidewall protection including ammonium compounds. Thus, the N_2 addition method has a trade-off relation between the sidewall protection the resist selectivity in principle. On the other hand, the CF_x -containing gas addition, which is a generalized case from the CH_2F_2 gas addition, does not need H from the etched resist to form the enough sidewall protection to avoid a side-etch. This mechanism is suitable especially for the thin resist mask case.

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It has been also investigated on the dry etching characteristics of TiN which is usually used for sandwiching the Al-wiring. Experimental results have shown that a vertical etching profile of TiN is obtained by the RIE using Cl radicals and that the involvement of BCl₃ in the etching gas generates the sidewall deposit containing BN-containing compounds. This result indicates that the TiN taper profile control is possible by the amount of the BCl₃ addition to Cl₂. It has also been suggested that the endpoint detection is possible for the TiN RIE by monitoring the emission intensity of Ti atoms/ions in the plasma. Since many Ti spectral line emissions exist, Ti emission can be monitored by the spectral line at 396.2 nm which is usually used for the endpoint detection of Al RIE. By switching the etching condition from the TiN/Ti to Al layer according to the endpoint detection, a smooth patterning of TiN/Ti/Al/TiN/Ti-wiring is found possible without irregularities due to the film thickness and RIE apparatus fluctuations.

Due to the results obtained in the chapter 2, Al RIE processes have been improved. In particular, it has been possible to find the proper process condition at the early stage of the next generation device development. In the fine Al patterning required in advanced CMOS device manufacturing, a CF_x-containing gas addition to a BCl₃+Cl₂ gas mixture was chosen and tuned to adjust the profile of Al-wirings. In fact, the fine-tuned process has been put to practical use in the manufacturing of CMOS devices (180 nm technology node and below, the Emotion Engine™ for PlayStation® 2, for example). In addition, in order to prevent the AlF_x-included film deposited on the etching chamber wall from peeling off, the material, roughness and temperature of the etching chamber wall should be properly chosen for example. Furthermore, the endpoint detection of

the TiN/Ti layer has been adopted in the trial production of 130 nm CMOS devices.

In chapter 3, two kinds of selective etching processes have been studied. One is the process related to a resist ashing using oxygen plasma after a dry etching of the $\text{Cr}_2\text{O}_3/\text{Cr}$ stacked film used as a light blocking film in photomasks. Unexpectedly, it was newly found that the $\text{Cr}_2\text{O}_3/\text{Cr}$ film was etched during the ashing. In order to clarify the mechanism underlying the phenomenon, the author has investigated the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by oxygen plasma. As a result, it was found that the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching occurred when the film temperature was higher than 200 °C due to CrO_x ($2 \leq x \leq 3$) generation and evaporation. The $\text{Cr}_2\text{O}_3/\text{Cr}$ was also etched with oxygen atoms and molecules without ion bombardments above 200 °C. From the results of analyses of the etched $\text{Cr}_2\text{O}_3/\text{Cr}$ film surface and the etching reaction products, it has been concluded that $\text{Cr}_2\text{O}_3/\text{Cr}$ etching can be suppressed by keeping the film temperature below 200 °C to prevent CrO_x ($2 \leq x \leq 3$) from evaporating.

Another selective etching is that of AlO_x against Al. Since AlO_x is more stable thermally and chemically than Al in general, the author attempted the selective deposition of an etch-inhibiting layer on Al surface. This idea came from the mechanism of well-established SiO_2/Si selective RIE. As a result, it was found that $\text{BCl}_3 + \text{CH}_3\text{OH}$ or $\text{BCl}_3 + \text{CH}_2\text{Cl}_2$ gas chemistry generates carbon-rich film deposition much more on Al surface than AlO_x surface. The deposition film is consisting of carbon-rich compounds in which C-C and C=C bonds are dominant. By using the selectively deposited film as the etch-inhibiting layer, the AlO_x/Al selective dry etching has been realized with the selectivity more than 5. It has also been examined that the deposited carbon-rich film can be removed by

oxygen plasma ashing and a wet alkali treatment following the selective etching.

On the basis of the mechanism of the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by oxygen plasma, the guide of the proper resist ashing process and apparatus has been clarified for the photomask manufacturing. That is, both the ashing process and apparatus have been optimized to suppress the $\text{Cr}_2\text{O}_3/\text{Cr}$ etching by keeping the film at low temperature. As a result, the improved ashing process has been put to practical use in manufacturing the photomasks for ULSI (180 nm technology node and below). Since the pattern size of $\text{Cr}_2\text{O}_3/\text{Cr}$ is below 1 μm for those design rules, $\text{Cr}_2\text{O}_3/\text{Cr}$ RIE is indispensable, which makes the resist mask removal difficult due to the resist material change by RIE exposure. Thus, the oxygen plasma ashing has been very important to manufacture the high quality photomasks.

Although the $\text{Al}_2\text{O}_3/\text{Al}$ selective etching has been realized in principle, it has not been used because of the changes in product plans. The author expects that the concept and mechanism of the $\text{Al}_2\text{O}_3/\text{Al}$ selective etching will contribute to the future device manufacturing.

In chapter 4, dry etchings of materials for the future CMOS devices have been investigated on the basis of the techniques developed in the previous chapters. TaN as a metal gate electrode and ZrO_2 and Gd_2O_3 as high-k gate insulators are focused on. In the TaN RIE, a native oxide layer of TaN surface should be initially removed by the etching using BCl_3 -based gas chemistry. After the removal of the native oxide layer, chlorine-based gas chemistries were found suitable for the TaN gate electrode patterning in the respect of the higher etching rate than fluorine-based gas chemistries. It has been turned out that the etching profile of TaN tends to tapered because of the low volatility of the etching

reaction products such as TaCl_x , BN-containing compounds, carbon-based compounds stemmed from the resist etching. The BN-containing compounds result from BCl_3 involvement in the etching gas. In order to obtain the vertical profile of TaN for the gate electrode use, some improvement will be necessary such as high temperature process, much lower pressure condition, inorganic mask without an organic resist, etc.

In the etching of ZrO_2 , HfO_2 and Gd_2O_3 films with usual fluorine-based and chlorine-based gas chemistries, it was found that the etching rate of Gd_2O_3 was the lowest and that the etching rates of ZrO_2 and HfO_2 were higher than that of Gd_2O_3 but lower than that of SiO_2 . This is due to low volatilities of halogen compounds of Zr, Hf and Gd. The etching rate result indicates that in the RIE of a gate electrode, a high etching selectivity to the underlayer can be obtained. On the other hand, the selective etching of those high-k films against Si substrate seems difficult. In fact, the $\text{Gd}_2\text{O}_3/\text{Si}$ selective etching was not realized within this study because of extremely low volatility of their compounds with halogens. The ZrO_2/Si selective etching was found possible by using the selective deposition of the CF_x film on the Si surface. However, the selectivity was 1.5, which is insufficient to put it to practical use.

On the basis of the dry etching characteristics for TaN, ZrO_2 and Gd_2O_3 , the author considered the process flow related to gate structure formation. In the case of the conventional process flow which consists mainly of gate insulator deposition, gate electrode patterning and gate spacer formation, two kinds of selective etchings should be established. One is the TaN or spacer SiN selective etching against the underlayer high-k film. The other is the high-k selective etching against Si substrate. It is considered that the former is easy while the latter is difficult especially

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for rare-earth metal oxide. If the latter selective etching will not be achieved in both dry and wet process, another process flow should be integrated instead of the conventional process flow. From this point of view, the damascene gate process can be advantageous not only because it can avoid thermal degradations of the device but also because it does not need the difficult selective etching process.

5.2 Perspective

According to the 2003 ITRS (International Technology Roadmap for Semiconductors), downscaling of the ULSI devices will continue with the rate $0.7 \times$ per every two-three years [5.1]. The 2003 ITRS defines the many difficult challenges to achieve further scaling and continuing growth of the LSI industry. The author excerpts the challenges related to the fine patterning technology as shown in Table 5.1.

Table 5.1 Difficult challenges related to the fine patterning technology excerpted from 2003 ITRS.

Category	Challenges
Front End Process	New Gate stack processes and materials
	Critical dimension and effective channel length control
	Introduction and CMOS integration of new memory materials and processes
	Surfaces and interfaces – structure, composition, and contamination control
Lithography	Optical masks with features for resolution enhancement and Post-optical mask fabrication
Interconnect	Engineering manufacturable interconnect structures compatible with new materials and processes
	Three dimensional control of interconnect features
	Manufacturability and defect management that meet overall cost/performance requirements
	Mitigate impact of size effects in interconnect structures
	Patterning, cleaning, and filling at nano dimensions
Factory Integration	Emerging factory paradigm and new wafer size change
Environment	Climate change mitigation
Yield Enhancement	High-Aspect-Ratio inspection
Modeling and Simulation	Modeling of equipment influences on features generated in deposition and etching processes
	Modeling of processing and electrical properties of new materials

It is considered that the challenges listed in Table 5.1 are originated from the introduction of new materials, the patterning requirements of small geometry structure in a large wafer size, and environmental requirements on global warming.

As briefly described in chapter 4, new materials such as high-k gate insulators and metal gate electrode materials will be required for a gate stack of future MOSFETs. In interconnect structures, the combination of low-k (low dielectric constant) material and low-resistivity metal has been used for minimizing the interconnect delay. In the future, low-k materials having much lower electric permittivity will be needed. New memory materials have been and will be introduced for high-k DRAM (Dynamic Random Access Memory), FeRAM (Ferroelectric Random Access Memory), MRAM and so forth. In fabricating phase-shift photomasks, materials to be dry-etched have started to change to quartz, SiON/TaHf [5.2], etc. In addition, the etching mask for critical etch processes has become complicated stack with 2-3 layers consisting of organic and inorganic materials. Thus, many new materials have been introduced and their patterning by RIE is required with the etching profile and selectivity well-controlled. Since each material has own etching capability by an RIE condition, it would become difficult to carry out the etching of a new material itself and/or the selective etching of the new material. Thus, new etching process on the basis of novel etching mechanism would be necessary to realize the dry etching of new and unetchable materials. For example, in the case of the etching of a metal whose halogen compounds are non-volatile, it might become an important technique to produce metal carbonyl complexes which evaporate easily. If the new material is still difficult to be dry-etched, alternative process should be investigated; the combination of dry etching and other treatments such as light irradiation, wet etching and so forth, selective growth of the new material, and different process integration to avoid the patterning of the new material. Thus, it will become increasingly important to totally optimize the patterning

process flow to meet the wide variety of patterning requirements.

The downscaling of the ULSI and hence the smaller geometries of the patterning dimension cause many difficulties and challenges to overcome as can be seen in Table 5.1. For example, the physical gate length of a MOSFET is predicted 18 nm in 2010 according to the 2003 ITRS. In such a small geometry, the effect of surface roughness of the patterned sidewall will become significant in addition to that of the etching profile. The roughness is called LER (Line Edge Roughness). If the line-edge of the resist mask is rough, the sidewall of etched pattern becomes rough. Thus, first of all, the line-edge of the resist should be straight and smooth after the photolithography. During the dry etching, the line-edge of the resist also should remain smooth. For this purpose, it will be important to optimize ion energy bombarding to the resist, the etching gas chemistry, and the amount of the deposition of reaction products on the resist sidewall. Thus, all the resist material, the photolithography and the etching condition should be optimized. In addition, the line-edge of the film to be patterned should be kept smooth during the dry etching because the LER becomes worse due to the inhomogeneous etching of the sidewall surface of the etched pattern. In order to avoid the inhomogeneous etching, both the film homogeneity and suppression of the lateral etching of the film are required. The film is homogeneous if it is single-crystalline or amorphous. In practice, however, the etched film is often poly-crystalline which is not homogeneous due to the existence of crystal grains and the grain boundaries. In order to minimize the LER for the poly-crystalline film etching, the etching rates should be equal between the grain and the grain boundary. Therefore, the author considers it increasingly important to control the etching rate of the grain boundary by, for example, precipitation

of some material at grain boundaries.

The downscaling of ULSI generates high A/R (Aspect Ratio; the ratio of depth to width) features. In particular in the interconnects, higher A/R trench and hole patternings are required in advanced ULSI. When the A/R becomes higher, the suppression of electrical damage induced by charged particles in the plasma becomes more significant as well as the etching profile and selectivity control. It has been well known that the gate insulator of MOSFETs under the denser pattern (equivalent to higher A/R) tends to suffer more dielectric breakdowns due to electron shading effect [5.3]. In a high A/R feature, electrons are easily screened by the sidewall and are accumulated on the resist mask. In contrast, ions which have a large vertical velocity component can reach the bottom of the high A/R feature. In the typical ILD RIE with the organic resist mask, the bottom of the trench or hole is charged positively and the mask is charged negatively. In the case where the positively charged bottom is connected to the gate electrode, an electric field is applied to the gate insulator resulting in its deterioration due to carrier injections during the RIE. Since the future device has higher A/R feature and thinner gate insulator, the device will tend to suffer more damage due to the charge accumulation effect. In order to avoid the electric damage, combinations and further optimizations of the currently used methods are considered useful; decreasing electron temperature, decreasing plasma density, neutralizing the positive charging with negative ions generated by time modulation of plasma discharge, increasing the electrical conductivity of the sidewall polymer by tuning the etching condition and so forth. At the same time, the author considers it important to have an overall understanding of the charge carrier behavior between the plasma, the high A/R feature and the

MOSFET. Furthermore, the model of the charge carrier behavior is desired to be taken into TCAD (Technology Computer-Aided Design) simulations, which will enable us to predict the damage to devices due to the charge accumulation. Ultimately, neutral beam etching without charged particles is expected to be put to practical use in the dry etching of the high A/R patterning.

The downscaling of ULSI devices leads to the vertical downsizing as well as horizontal one in general. This requires the precise control of etching time and/or sufficient etching selectivity against the underlayer, that is, the etching must be stopped immediately after the film to be patterned is etched off. In the first place, a good uniformity of film thickness and etching rate across the whole wafer should be realized. Furthermore, it is required that the etching is uniform between the dense patterns and the coarse ones. The former global uniformity depends strongly on the etching apparatus, and the latter local uniformity is affected by the pattern layout design and the etching conditions. Even if the local and global uniformity of the etching are realized, the precise control of the endpoint of the etching is needed. If the much sufficient etching selectivity to the underlayer is realized, the precise endpoint detection is not always necessary because one can carry out a certain amount of the overetching. In order to have the sufficient etching selectivity, it is considered that the use of etch-inhibiting layer becomes more important. In the case where the etch-inhibiting layer cannot be used, the etching endpoint detection must be carried out with much higher precision than currently possible. For example, in-situ film thickness monitoring, plasma impedance monitoring, in-situ plasma density monitoring, high sensitive plasma emission monitoring, and so forth.

Recently, it has been required to reduce GHG (Greenhouse Gases) emissions in order to mitigate global warming. Although the major GHG are CO₂, CH₄ and N₂O, current dry etching processes require the use of high GWP (Global Warming Potential) fluorinated compounds including CF₄, C₂F₆, C₃F₈, c-C₄F₈, CHF₃, NF₃, and SF₆, collectively termed PFCs (Perfluorocompounds). The emissions of PFCs are small relative to major GHG emissions, accounting for less than 2% of the total GHG emissions. However, PFCs have strong infrared absorption in the atmosphere and long atmospheric lifetimes, and thus have high GWPs as shown in Table 5.2, which presents those PFCs and their environmental impact if released to the atmosphere [5.4]. Although PFC gases listed in Table 5.2 are unsurpassed for SiO₂ RIE processes, the PFC emissions must be reduced to 10% below the 1995 baseline level by year-end 2010. For this purpose, the following three technologies have been investigated: destruction and capture, beneficial reuse, and alternative chemicals. Considering that the global warming is an important issue to our existence on the planet, the reduction of PFC emissions should and will become the first priority of the development of the dry etching processes that require the usage of PFCs. Therefore, it will be increasingly important to promote research and development leading to the reduction of PFC emissions. In order to contribute the reduction of PFC emissions by dry etching process improvements, the author considers that replacing PFCs with alternative chemicals should be accelerated by cooperation among semiconductor manufacturers, suppliers of equipment, and gas suppliers.

Table 5.2 PFCs and their climate impacts.

Compound	Atmospheric Lifetime (years)	Global Warming Potential (100 year)
CO ₂	variable	1
C ₂ F ₆	10,000	9,200
CF ₄	50,000	6,500
SF ₆	3,200	23,900
NF ₃	740	10,800
CHF ₃	264	11,700
C ₃ F ₈	2,600	7,000
c-C ₄ F ₈	3,200	8,700

In addition, the development time and cost should be reduced year by year. It is effective to anticipate the etching behavior on the basis of the etching model and/or simulations in order to carry out the etching process development effectively and economically. Naturally enough, in order to predict the etching performance, the accurate modeling is indispensable. As far as the prediction of the etching profile and selectivity is concerned, the model should take into account fragments in the plasma, their transfer process to the etching surface, etching reactions, and behaviors of etching reaction products. In addition, the loading effect (pattern density) and the aspect ratio dependent etching should be also considered. Recently, topography simulations have been developed and become to a practical use [5.5]. However, the detailed behavior of the etching reaction products has hardly been taken into the calculation model. This is because its behavior

5. Summary and Conclusions

has not been clarified well even at a qualitative level although the reaction products play important roles in the control of the etching profile and selectivity as described in this thesis. Therefore, the behavior of the reaction products has to be modeled in quantitatively though it seems a challenging work. In order to accomplish the quantitative modeling of the etching reaction products, ‘quantum chemical molecular dynamics simulation [5.6]’ based on the first principle model is expected useful in addition to the traditional analysis described in this thesis. Thus, in the future, the following integrated simulation model is expected; the coupling plasma simulation including transport process with quantum chemical molecular dynamics simulation including the reaction products behavior. After taking the plasma charging effects causing electrical damage to the device, such an integrated topography simulation is then coupled to the TCAD simulation. The TCAD simulation with the well-established topography simulation will drastically reduce the number of experiments and cost of new generation device development.

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Related Papers in Refereed Journals and Presentations at International Conferences

Chapter 2

Paper

- 1) S. Saito, K. Sugita, J. Tonotani and M. Yamage, “Formation of Ammonium Salts and Their Effects on Controlling Pattern Geometry in the Reactive Ion Etching Process for Fabricating Al Wiring and Polysilicon Gate”, Jpn. J. Appl. Phys. 1, vol. 41, no. 4A, p.p. 2220-4, April, 2002
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Chapter 4

Presentation

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