The Journal of Korea Vacuum Science & Technology
Vol. 3, No. 1, April 1999, pp. 24~29

Anisotropic etching of polysilicon in a $Cl_2/CH_3Br/O_2$ Plasma

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(Received February 2, 1999)

Abstract – The characteristic behaviors of CH_3Br were examined first for the dry etching of polysilicon in a $Cl_2/CH_3Br/O_2$ plasma. CH_3Br is revealed one of the excellent additive gases to control anisotropy of etching profile and to give no undercutting for various types of polysilicons. CH_3Br acts as a passivation precursor on the side wall in etch cavity by forming polymer-like films such as CH_x-Br_y(x+y=1, 2). The decrease of etch selectivity due to the reaction of the C-containing species from CH_3Br with the surface O atoms of SiO_2 was overcome by the addition of O_2 into plasma, resulting that the selectivity increased by 2~3 times. According to the results of optical emission signals, CH_3Br should be dissociated into several fragments to give more hydrogen atoms than bromine atoms in our helical resonator system.

I. Introduction

Current plasma etch processes now commonly used to etch materials for semiconductor device fabrication consist of an electrical discharge of halogen bearing gases. Halogen typically encountered in these processes are fluorine, chlorine, and bromine. The process begins with application of a masking material, such as photoresist, to protect the desired geometries of the device from the etch process. The device in progress is then placed in a plasma reactor and etched. The subsquent steps are determined by the type of the device being fabricated. This process is essentially valuable for the definition of small geometries of the order of few hundred nanometers. For the definition of geometries of less than one micron, it is essential that the etching proceeds only in the vertical direction. The fragile nature of the small geometry structures cannot have reasonable degree of reliability if any significant undercutting takes place during the process.

Plasma etching techniques may be classified according to etch rate, selectivity, anisotropy, the degree of loading effect, and texture. Selectivity refers to the ratio of etch rates between two different materials immersed in the same plasma; for an example Si and SiO_2. Anisotropy is affected by the preferential etching in a direction normal to the surface of a wafer. "Loading" is a term used to describe a measurable depletion of active etchants from gas phase, brought about by the consumption of this reactant in the etching process.

A very common silicon etch process is based on fluorine. When a discharge of CF_4 is created, it is not the CF_4 molecules themselves that participate in the etching reaction. Instead, the etching is accomplished by the radical species which are created by the dissociation of CF_4 molecules; namely fluorine atoms. A mechanism for the F-atom reaction with a Si film leading to gasification products, SiF_4 and SiF_2, has been proposed by Flamm and Donnelly [1]. The steady-state surface seems to be a stable "SiF_2-like" that must be penetrated by impinging F atoms in order for the SiF_4 to be formed. The etch rate of silicon in pure CF_4, however, is relatively low due to the low concentrations of F atoms. If small amounts of O_2 are added to the CF_4 feed gas, the etch rate of Si is observed to increase dramatically [2]. The addition of the O_2 is accompanied by an increase in the density of F-atoms in the discharge due to the reactions between the oxygen atoms and CF_x species.

As described above, when fluorine-containing species such as CF_4 or SF_6 [3] are dissociated in an electrical discharge, fluorine atoms are liberated, and volatilize the silicon as SiF_4. Such processes mostly show isotropic behavior because of neutral F radicals generated from CF_4 or SF_6. Chemistries based

Table 1. Br-containing species and their melting and boiling points (obtained from the merck index twelfth edition 1996).

	BBr_3	CH_3Br	CH_2Br_2	$CHBr_3$	C_2H_5Br
m.p.(°C)	−46.0	−93.7	−52.7	7.5	−119
b.p.(°C)	90.0	3.6	97.0	150	38.2

on chlorine are now considered to be necessary for vertical etching of silicon [4] and discharge of pure Cl_2 have been found useful for this purpose since Cl_2 generates both radicals and positive ions (Cl and Cl_2^+). However, some silicon materials such as highly doped polysilicon, may still experience some undercutting if etch conditions are not closely controlled [5]. Thus it is an object of this paper to provide an anisotropic etch solution which is applicable to any material containing a large fraction of silicon.

The role of additive gases such as O_2, N_2, HBr in Cl_2 plasma [6-9] is to passivate the side walls of the etched silicon from reactive etchant containing Cl species. Those gases control the degree of anisotropy of etching profile by the formation of polymer-like film with the silicon surface. In case of HBr, anisotropic etching is very well performed by the formation of a Si-Br compound on the side walls of the etched cavity, while the ion bombardment on the flat surface inhibits the formation of the compound in that area. The silicon is known to be etched as Si-Cl-Br compound [10]. However, HBr gives more serious corrosion problem compared with other gases such as Cl_2, HCl, O_2, and N_2 when it is exposed to air, especially in semiconductor mass production line. HBr is more corrosive than other halogen-containing gases [11], especially when a gas supplying line has cracks. The generally accepted reason is that HBr adsorbs on metal surface for a long period and combines with water molecules, if there exists a crack on the line, to corrode metals through the electrochemical reaction between aqueous HBr and metal surface.

In the dry etching of polysilicon with Cl_2 plasma, it is very important to select proper additive gas (es) to control the anisotropy of etching profile. For example, one of the candidates containing bromine species is Br_2. However it is not so good material to use in a semiconductor line since it has only 150 Torr of vapor pressure at room temperature, resulting that Br_2 tends to condensate easily on chamber walls and gas supplying lines. Some of the other chemicals containing Br species are listed at Table 1. Only CH_3Br among them has lower boiling point than room temperature (20°C), in other words, only CH_3Br exists as a gas at that temperature. As the total number of atoms increases in a molecule, the boiling temperature shifts to higher value since the molecular weight becomes heavier, unless specific chemical bonds are formed between molecules.

In this paper we introduce the results of dry etching of polysilicon with $Cl_2/CH_3Br/O_2$ plasma in a helical resonator system. The results are mostly focused on etch rate, vertical profile, and each selectivity over substrate. OES (Optical Emission Spectrometer) measurements are also performed to analyze the characteristics of CH_3Br.

II. Experimental

The plasma reactor and its components for experiments are described in ref. 12, and brief descriptions are as follows; The plasma reactor is connected to an ultrahigh vacuum (UHV) chamber, and consists of a 279 mm height and 508 mm diameter stainless-steel cube, forming a "downstream" region. The etchant gas is connected to the top of the cube and spreads by several holes before going into the plasma generating region. A quarter wave helical coil having 9.5 mm dia. surrounds the inner quartz tube and electrostatic ground shield, which is used to improve the inductive coupling [13, 14]. The location of test wafer for etching is at the bottom of the quartz tube, and a wafer can be moved vertically by 9.5-cm. The plasma reactor and the sample holder are cooled with cooling fluid and backside He, respectively, to prevent temperature rise during process. The discharge is operated at a pressure of 2~15 mTorr, which is measured with convectron gauges in pumping line between the chamber and a dry pump, and with baratron gauges to measure etchant gases and backside He pressure. The helical resonator plasma source was operated at a radio frequency (rf) of 13.56 MHz and its power is varied from 500 to 3000 W. The substrate stage is biased with a second rf power (13.56 MHz), varing from 0 to 150 W.

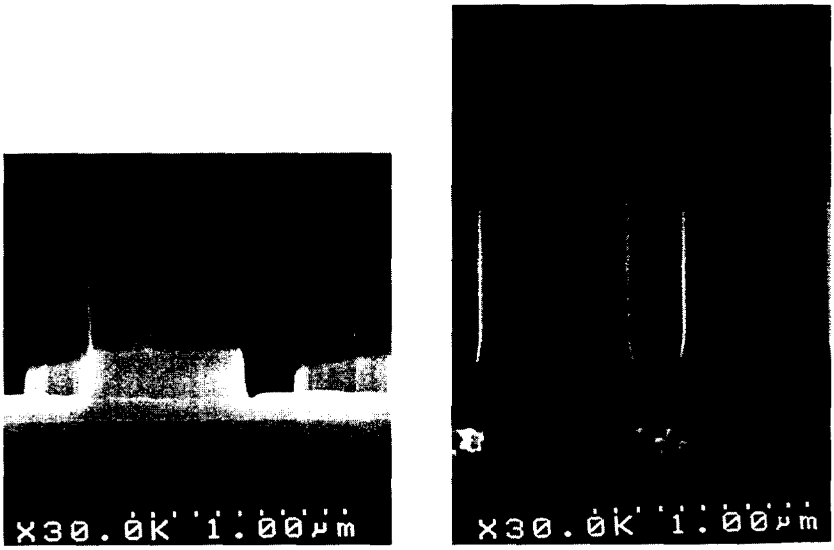
The substrate for this experiment is n-type Si (100). Photomask patterned 2000 Å (Gate-polysilicon) or 7000 Å (Storage-polysilicon) thick polycrystalline Si films deposited on 1000 Å of SiO_2 on Si(100) are used to get high selectivity over substrate and proper etching profile, respectively.

A Sofie instrument's SEM/VU20 model is used for optical emission measurements. The detector of spectrophotometer is located at the outside of a view port of the etching chamber with focusing lenses, which means emission signal recorded at some instance is the summation over emissions from the plasma area which is normal to the face of lenses. After passing through a monochrometer, emission light is amplified electrically and then sent to personal computer for analysis with the wavelength resolution of 0.1 nm.

III. Results and Discussion

3.1. Dry Etching of Gate(G-) and Storage(S-) Polysilicon

Figures 1(a) and 1(b) represent the SEM profiles of etched polysilicon(G- and S-poly, respectively) with $Cl_2/CH_3Br/O_2$ plasma. It was obvious from our repeated experimental results that CH_3Br has great advantages over other additive gases such as O_2, N_2, HBr to provide etching anisotropy. In other words the additive CH_3Br determined the shape of etching profile, i.e. vertical or sloped one, and gave no undercutting under the normal etch condition. As mentioned previously, HBr is a well-known gas to control etching anisotropy of polysilicon by the formation of Si-Br on the sidewalls of cavity. In order to get proper etching profile and anisotropy, the ratio of flow rate of HBr to Cl_2 is known to be in the range of 5~200% which means that the reguired amounts of HBr have different values for different types of polysilicon etching. In other words, in case that the concentration of impurities (phosphorous or boron) or the area of polysilicon to be etched is changed, the amount of adding HBr is changed, thus proper amount of HBr should be determined again to optimize the process condition. According to our experimental results, the ratio of flow rate of CH_3Br to Cl_2, 5~30% can control the etching profile for various polysilicons. The vertical profile is obtained at 5~20% ratio and the sloped profile starts from 20% ratio, and the degree of sloped profile increases continuously as increasing the ratio of CH_3Br to Cl_2 with minor differences for different types of polysil-



(a) **(b)**

Fig. 1. Vertical SEM profile of Gate(a)- and Storage(b)- polysilicon etching.

icons.

The role of CH_3Br has not been fully understood yet. CH_3Br would be dissociated in a plasma, giving several fragments like CH_3, CH_2Br, CH_2, CHBr, CBr, C, Br, H, etc. The sidewall passivation film of the etched cavity would be composed of the above fragments. Among the fragments, CH_xBr_y (x+y=2) has the similar orbital shape with carbene (CH_2) or fluorocarbene (CF_2) which is recognized as a precursor of passivation film in silicon oxide etching of CF_4/CHF_3 plasma. Those kinds of carbene shaped species have one pair of nonbonding electron and two bonding arms, therefore they can combine together easily, thus make single and double bond conjugation to form polymer-like film on the sidewall surface. TOF SIMS (time-of-flight secondary Ion Mass Spectrometry) analysis after treatment with CH_3Br revealed that the major species covered on silicon surface mostly consist of CH_2, CHBr, CH, etc, in turn.

The etch selectivity over substrate SiO_2, after addition of CH_3Br, becomes lower than that of HBr. This seems to be due to the carbon-containing species from CH_3Br which can react with surface oxygen of SiO_2, finally to form CO or CO_2 and to be easily removed from the surface. Therefore, in order to increase the selectivity, we added small amount of O_2 into plasma whose role is to react with carbon-containing species before their arriving to the surface of SiO_2. In other words O radicals from O_2 plasma react with C-containing species from CH_3Br plasma, thus substrate SiO_2 is prohibited from reacting with C-containing species during etching. The small addition of O_2 increased the selectivity dramatically by 2~3 times.

The optimum process conditions for G- and S-polysilicon etching are listed in Table 2, respectively. In case of G-polysilicon etching, we used two steps, namely main etch and over etch. With only main etch step, it was difficult to get high etch selectivity, therefore, we changed our process condition to acquire high selectivity at over etch step even though there is some loss in etch rate. For S-polysilicon, one step process was good enough for proper etching profile and selectivity to be used at mass production line. The easy control of etching profile and selectivity over substrate were the common features of G- and S-polysilicon etching after addition of CH_3Br into plasma.

3.2. The Characteristic Behavior of CH_3Br as an Additive Gas

Figures 2(a) and 2(b) show the polysilicon etch rate and selectivity over substrate silicon oxide, respectively, both in Cl_2/O_2 and $Cl_2/O_2/CH_3Br$ plasmas. As shown in Fig. 2(a), when CH_3Br is added to Cl_2/O_2, the silicon etch rates decrease in the whole experimental range of source power. As mentioned in section 3.1, CH_3Br itself played an important role for the control of anisotropy in silicon etching and the TOF SIMS analysis of samples after treatment with CH_3Br revealed the abundance of CH_2, CHBr and, CH on the surface. Above results and Fig. 2(a) strongly confirm that CH_3Br acts as a passivation gas on the side walls in etch cavity by forming polymer-like films such as CH_xBr_y (x + y = 1, 2). The etch selectivity over silicon oxide also decreased after addition of CH_3Br to Cl_2/O_2 plasma (Fig. 2(b)) since the reaction of C-containing species from CH_3Br with surface oxygen atom of substrate SiO_2.

The effects of additive O_2 can be deduced from the analysis of Fig. 3. Figure 3 represents the polysilicon etch rate and selectivity over substrate SiO_2 with respect to the change of O_2/Cl_2 ratio. The etch rate decreases and selectivity increases with increasing the O_2 amounts. It was already reported that [9], as oxygen is added to chlorine, the silicon etch rate

Table 2. The optimum conditions for Gate- and Storage-polysilicon etching step.

	Step	Pressure (mT)	Source Pwr(W)	Bias Pwr(W)	Flow Rate (sccm)	Etch Rate (Å/min)	Sel over SiO_2
Gate Polysilicon	Main Etch	27	1200	85	$50Cl_2/10O_2/6CH_3Br$	3048	21
	Over Etch	27	2100	85	$50Cl_2/10O_2/6CH_3Br$	2448	87
Storage Polysilicon	1 Step	10	1500	85	$90Cl_2/5O_2/25CH_3Br$	3109	5.2

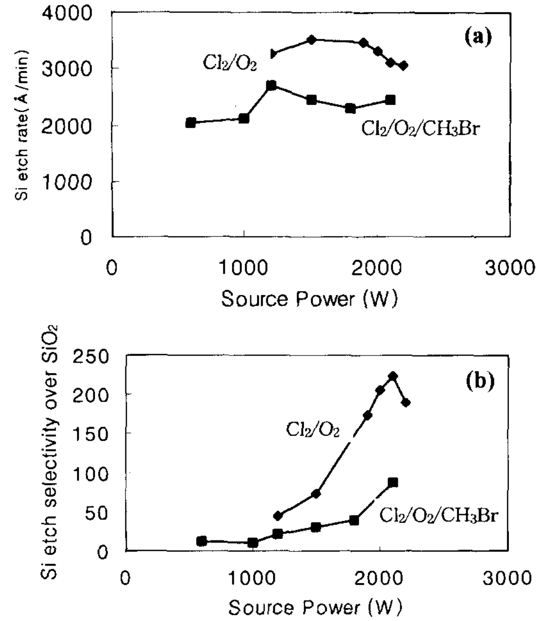


Fig. 2. Polysilicon etch rate(a) and selectivity over substrate silicon oxide(b) both in Cl_2/O_2 and $Cl_2/O_2/CH_3Br$ plasmas (2.7 mT/ Bias Power 85W/ 50sccm Cl_2/ 6sccm CH_3Br/ 10sccm O_2).

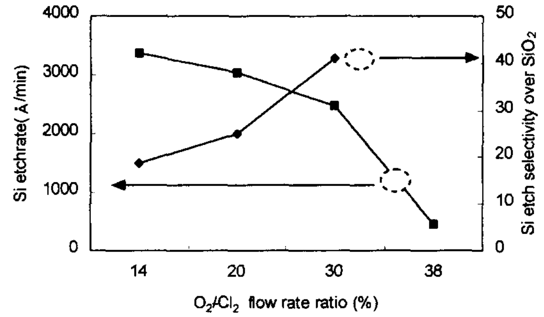


Fig. 3. Polysilicon etch rate and selectivity over substrate SiO_2 with respect to the change of O_2/Cl_2 flow rate ratio (2.7 mT/ Source Power 1200W/ Bias Power 85W/ 6sccm CH_3Br).

decreases due to the reduction of chlorine ions and radicals available for silicon etching. It is not surprising that etch selectivity over substrate SiO_2 increases to a certain point as increasing O_2/Cl_2 ratio. As explained, the O atoms generated from O_2 plasma react with C-containing species before their arrivals to the surface of SiO_2. Etch selectivity is the ratio between etch rate of polysilicon and silicon oxide at a given condition. The increase of selectivity in Fig. 3 is mainly attributed to the faster reduction of silicon oxide etch rate than the polysilicon etch rate. The measured etch rate of silicon oxide are 180, 120, and 60 Å/min at ratios of 14, 20, 30% of O_2/Cl_2, respectively. Polysilicon was unetched at whole ranges of O_2/Cl_2 ratios greater than ~35%. Those phenomena were observed repeatedly at flow rates of Cl_2 at 50, 70, and 80 sccm. The silicon surface seemed to be converted into silicon oxide when it was exposed to a plasma containing large amounts of oxygen.

Figure 4 shows the emission intensity changes of H and Br atoms from CH_3Br plasma as increasing the source power up to 3000W. H and Br emissions were obtained at the wavelength of 486 (H_β) and 470 nm, respectively. To ensure whether the emissions in a given wavelength are actually attributed to CH_3Br itself or not, optical signals were checked with and without gas flow of CH_3Br. The dissociation of CH_3Br in a helical resonator plasma would generate a lot of species composed of radicals and ions. The compositions of each species are usually affected by both the characteristics of molecule itself such as bonding energy, ionization potential, etc, and environmental conditions such as pressure, flow rate, and type of plasma generator. The possible fragments generated by plasma dissociation of CH_3Br are C, H, Br, CH, CBr, CH_2, CHBr, CH_2Br, CH_3Br^+, CH_2^+, CBr^+, etc. Among those processes generating above fragments, the dissociation processes giving only H and Br atoms would be listed as followings;

$$\begin{array}{llr}
CH_3Br \rightarrow & CH_3 + Br & \\
 & CH_2Br + H & (1) \\
\rightarrow & CH_2 + H + Br & \\
 & CHBr + H + H & (2) \\
\rightarrow & CH + H + H + Br & \\
 & CBr + H + H + H & (3) \\
\rightarrow & C + H + H + H + Br & (4)
\end{array}$$

Assuming that the process (1) would dominate among (1)-(4), the H and Br curves in Fig. 4 should have the similar range of slope, however the increasing rate of of H curve looks faster than that of Br. Above observation strongly suggests that the dissociation process of CH_3Br proceeds toward (2),

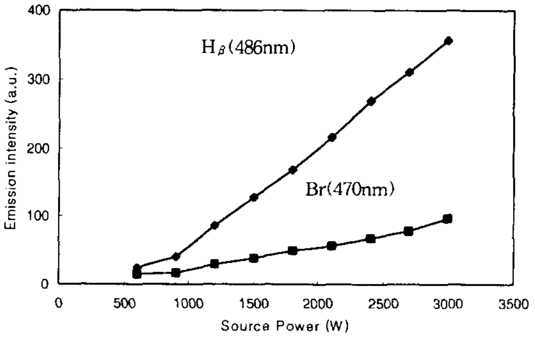


Fig. 4. Optical emission intensity changes of H and Br atoms from CH_3Br plasma at the range of 600~3000 W (2.7 mT/ Bias Power 85W/ 50sccm Cl_2/ 30sccm CH_3Br/ 10sccm O_2).

(3), and (4), in turn, as increasing the source power of plasma reactor. It is one of the well-known features for high density plasma (like our helical resonator plasma) to dissociate molecule into small fragments more efficiently compared with conventional capacitively-coupled plasma. The bond dissociation energy of C-Br and C-H of CH_3Br were known as 2.97 and 4.13 eV, respectively [15-17].

IV. Conclusions

In the dry etching of polysilicon with Cl_2 plasma, the additive gas CH_3Br has great advantages in anisotropy control over other gases such as O_2, N_2, HBr. CH_3Br acts as a passivation gas on the side wall in etch cavity by forming polymer-like films such as CH_xBr_y ($x + y = 1, 2$). The decrease of etch selectivity due to the reaction of the C-containing species from CH_3Br with the surface O atoms of SiO_2 was overcomed by the addition of O_2 into plasma. The characterisic behaviors of CH_3Br, i.e. etch rate, selectivity, and the amount of H and Br atoms in plasma, were examined by changing the source power of helical resonator plasma system.

References

[1] Daniel L. Flamm and Vincent M. Donnelly, *Plasma Chem. Plasma Process* **1**, 317 (1981).
[2] Daniel L. Flamm, *Solid State Technology* **22**, 109 (1979).
[3] C. M. Mellinar-Smith and C. J. Mogab, "Plasma Assisted Etching Techniques for Pattern Delineation" , in "*Thin Film Processes*" , J. L. Vossen and W. Kern, eds., Academic Press, N.Y. (1979).
[4] Vincent M. Donnelly and Daniel L. Flamm, *Solid State Technology* **24**, 161 (1981).
[5] G. C. Schwartz and P. M. Schaible, *J. Vac. Sci. Technol.* **16**, 410 (1979).
[6] S. C. McNevin, *J. Vac. Sci. Technol.* **A9**, 816 (1991).
[7] K. V. Guinn, C. C. Cheng, and V. M. Donnelly, *J. Vac. Sci. Technol.* **B13**, 214 (1995).
[8] K. Nishikawa, T. Oomori, K. Ono, and M. Tuda, *Jpn. J. Appl. Phys.* **35**, 2421 (1995).
[9] H. S. Kim, Y. J. Lee, and G. Y. Yeom, *J. Korean Vac. Sci. & Technol.* **2**, 122 (1998).
[10] United State Patent : number 4,490,209.
[11] *Monthly Semiconductor World* (Japan), pp. 60-64, June (1996).
[12] Whikun Yi, *J. Korean Vac. Soc.* **8**, 63 (1999).
[13] J. M. Cook, D. E. Ibbotson, and D. L. Flamm, *J. Vac. Sci. Technol.* **B8**, 1 (1990).
[14] J. M. Cook, D. E. Ibbotson, P. D. Foo, and D. L. Flamm, *J. Vac. Sci. Technol.* **A8**, 1820 (1990).
[15] Hideo Okabe, *Photochemistry of Small Molecules*, Wiley, New York, 1978, p. 300.
[16] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, *Natl. Bur. Stand. (U.S.) Tech. Note* **270-3** (1968).
[17] J. J. Decorpo, D. A. Bafus, and J. L. Franklin, *J. Chem. Thermodyn.* **3**, 125 (1971).