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Principles of Wet Chemical Processing in ULSI Microfabrication

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***Abstract*—Fine patterning technology for integrated device manufacturing requires properties such as surface cleanliness, surface smoothness, complete uniformity and complete etching linearity in wet chemical processing. In our work an improved chemical composition for buffered hydrogen fluoride (BHF: NH_4F + HF + H_2O) is determined based on fundamental research into the chemical reaction mechanism of BHF and SiO_2. Advanced wet chemical processing based on investigation of chemical reaction mechanisms and properties of liquid chemicals, concentrating on the SiO_2 patterning process by BHF is described. The principles of wet chemical processing in silicon technology is based on the following four items: the determination of the dominant reaction (etching) species, the influence of the solubility of the etching products in BHF on etching uniformity and linearity, stability of chemical composition without solid phase segregation, and an improvement of the wettability of liquid chemicals on wafer surface by the addition of a surfactant are proposed.**

I. INTRODUCTION

IMPROVEMENT of surface chemical technology in wet chemistry is an essential requirement for progressive ULSI processing. Especially, since improvements in device integration usually require fine patterning of high aspect ratio contact and via holes, surface chemical technology must achieve perfect smoothness of the wafer surface. Acidic ammonium fluoride solution, called buffered hydrogen fluoride (BHF), is an important chemical because of its reactivity to silicon compounds. It is widely used as a surface treatment agent for processes such as etching, patterning and cleaning of silicon wafer surfaces. The chemical composition of BHF is usually a mixture of 40% NH_4F and 49% or 50% HF, ranging in weight ratios of NH_4F : HF from 5 : 1 to 30 : 1. High concentrations of NH_4F are considered to buffer the reaction rate of SiO_2 and to prevent the attack of HF on the photoresist. Although work has been done on effects of varying concentration of NH_4F in BHF [1]-[4], additional attention to the problems caused by high concentration of NH_4F is required. The chemical activity and the functional properties of BHF must be enhanced in order to improve wet etching technology. In this work, theoretical consideration is directed to the chemical composition of BHF based on the spectroscopic study of the dissociation of the NH_4F-HF-H_2O system.

The high concentration of NH_4F has been confirmed to reduce the solubility of the reaction product ($(NH_4)_2SiF_6$) and to result in insufficient etching of SiO_2 because of the precipitation of ($(NH_4)_2SiF_6$) on the wafer surface. Furthermore, high NH_4F concentrations in BHF has been demonstrated to cause the segregation of crystalline (NH_4HF_2), due to the reduced solubility of (NH_4HF_2) in BHF [5].

Perfect surface smoothness is a key technology for manufacturing of ULSI devices having very thin gate and storage capacitor oxides and having very shallow junctions. It will be shown in this study that the smoothness of silicon wafer surface required by such constraints cannot be obtained through wet chemical etching without the improvement of the wettability of BHF.

Wettability control of BHF through the addition of surfactants has previously been discussed, based on ten requirements for advanced wet processing: comparable etching rates as traditional BHF, low contact angle, non-segregation, non-foaming, low particle, low impurities, low particulate adhesion on wafer surface, no surface residuals, excellent surface smoothness, and high etching selectivity [6]-[9].

This paper is going to propose an advanced surface-active BHF having an optimal chemical composition and good wettability, based on ultra clean grade liquid chemicals, in which impurity levels are suppressed to less than 0.1 ppb [10]. Further, we describe the four principles studied in wet chemical processing of silicon: determination of dominant reaction (etching) species, stability of the chemical composition of the etching solution, solubility of reaction product, and wettability of the wafer surface.

II. FUNDAMENTALS OF WET CHEMICAL PROCESSING IN SILICON TECHNOLOGY

1. Dominant Reaction (Etching) Species

Etching rates of thermal silicon oxide films having a thickness of 1 μm are observed in various compositions of BHF at 25°C and are plotted in Fig. 1. The vertical axis is NH_4F weight concentration and the horizontal axis is HF weight concentration. Solid lines depict constant etching rates of 200 Å/min, 500 Å/min, 1000 Å/min, and 1200 Å/min as a function of NH_4F weight concentration and HF weight concentration. The two dashed lines correspond to conventional BHF compositions and equivalent mole ratios. The conventional BHF composition line indicates the direct mixing of 40% NH_4F solution and 50% HF solution. The equivalent mole ratio line is determined from the fact that the molecular weight of NH_4F is 37 and that the HF is 20.

It is seen from Fig. 1 that the etching rate of SiO_2 increases with an increase of HF concentration but it is almost independent of NH_4F concentration above the equivalent mole ratio line. On the other hand, it has been found [2] that SiO_2 films are not

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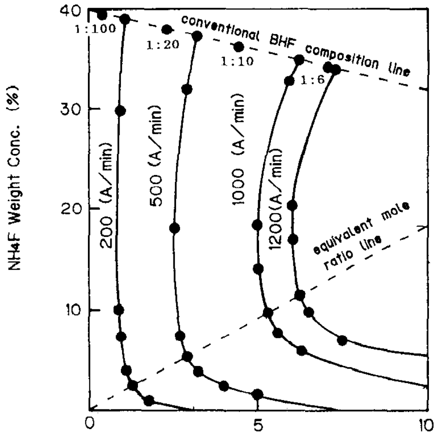


Fig. 1. Relationship of components and etching rate of thermal oxide in NH_4F-HF-H_2O system.

etched by NH_4F solution, which is a strong electrolyte, i.e., there exist large number of F^- ions in solution. These two results seem to indicate that the dominant etching species of SiO_2 is HF_2^-, not the F^- ion [11].

The reaction of BHF and SiO_2 is described by

$$SiO_2 + 4HF + 2NH_4F \rightarrow (NH_4)_2SiF_6 + 2H_2O. \quad (1)$$

Details of the etching step are

$$SiO_2 + 3HF_2^- + H^+ \rightarrow SiF_6^{--} + 2H_2O \quad (2)$$

$$2NH_4^+ + SiF_6^{--} \rightarrow (NH_4)_2SiF_6. \quad (3)$$

In the HF-H_2O system, the ionization process has been represented by two steps which generate the bifluoride ion HF_2^- [8]:

$$HF \rightleftarrows H^+ + F^- \quad (4)$$

$$HF + F^- \rightleftarrows HF_2^-. \quad (5)$$

The first step, with an equilibrium constant ranging from 2.4×10^{-4} to 1.3×10^{-3} (25°C) [12], implies a dissociation of HF into H^+ and F^- ions at a rate of only a few percent. So, dilute hydrofluoric acid behaves as a surprisingly weak acid, in marked contrast with other hydrohalic acids. The F^- ion generated from the equilibrium equation (4) produces the bifluoride ion HF_2^- following (5), but the concentration of F^- ions is very small due to the small equilibrium constant, thus, only small numbers of bifluoride ions HF_2^- are generated by hydrofluoric acid. Because NH_4F is a strong electrolyte, a large amount of F^- ion is generated by the NH_4F-HF-H_2O system according to the following:

$$NH_4F \rightarrow NH_4^+ + F^-. \quad (6)$$

A large amount of F^- facilitates the generation of a generates a large amount of bifluoride ions, HF_2^-, following (5).

The conductivity of NH_4F solution is shown in Fig. 2. We have measured the conductivity using parallel electrodes made of platinum. The cell constant is 1.025 and carried out at 3000 Hz. With the increase of NH_4F concentration the conductivity increases; it reaches a maximum value at the concentration of 7 mol/l and then decrease. The ratio of effective ion concentration decreases with the increase of NH_4F, owing to ion interaction. This indicates that NH_4F does not dissociate completely. In the equilibrium state of the NH_4F-HF-H_2O system, the concentrations of significant species are expressed by the following:

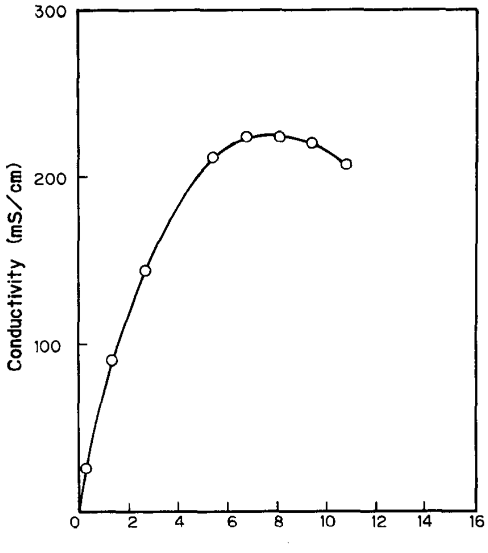


Fig. 2. Relationship of conductivity and NH_4F concentration in NH_4F-H_2O system.

$$\frac{[H^+][F^-]}{[HF]} = K_1 \quad (7)$$

$$\frac{[HF][F^-]}{[HF_2^-]} = K_2 \quad (8)$$

$$m = [HF] + [H^+] + [HF_2^-], \quad (9)$$

$$m + n\alpha = [HF] + [F^-] + 2[HF_2^-]. \quad (10)$$

Where m is the mole concentration of HF, n is the mole concentration of NH_4F and α is the dissociation ratio of NH_4F. Using the values $K_1 = 1.3 \times 10^{-3}$ (at 25°C), $K_2 = 0.104$ (at 25°C) [2] and the concentration of $[H^+]$ measured with pH paper [13], these equations are solved for the various mixtures of NH_4F-HF-H_2O solutions (see Appendix). The concentration of $[H^+]$ is measured with pH paper and plotted as a function of NH_4F concentration for three typical HF concentrations, such as 1 mol/l, 1.5 mol/l and 2.5 mol/l, in Fig. 3, where H^+ ion concentration is confirmed to decrease drastically with an increase of NH_4F concentration. The concentrations of significant species such as $[HF_2^-]$, $[H^+]$, $[HF]$, and $[F^{-1}]$ are tabulated for three representative HF concentrations in the NH_4F-HF-H_2O system in Table I, where the degree of NH_4F dissociation α, is expressed as a function of NH_4F concentration.

FT-IR spectra of the NH_4F-HF-H_2O system are measured by a cell consisting of a CaF_2 or BaF_2 window with a 25-μm cell length [14]. The results are shown in Fig. 4, where FT-IR spectra are illustrated for three different NH_4F concentrations at HF concentration of 2.5 mol/l. The spectrum of HF_2^- ion appears at 1210 cm^{-1} and its absorption intensity increases with an in-

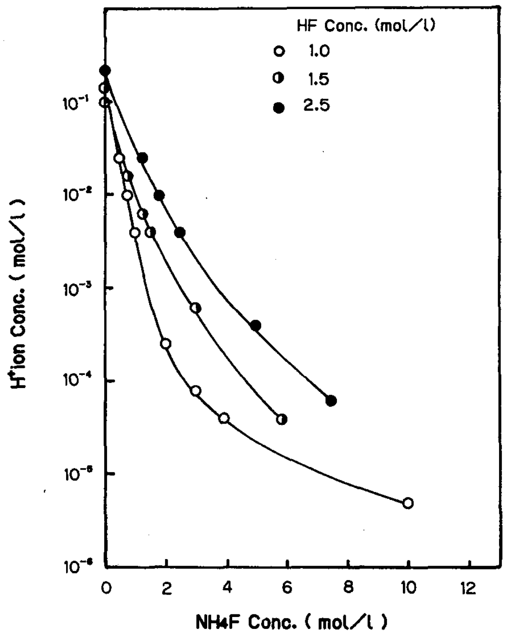


Fig. 3. Relationship of H^+ ion concentration and NH_4F concentration.

TABLE I
Composition and Calculated Concentrations in the NH_4F-HF-H_2O System

Composition			Calculated concentrations (at 25°C)			
HF mol/ℓ	NH_4F mol/ℓ	$[H^+]$ 1) mol/ℓ	α 2)	$[HF_2^-]$ mol/ℓ	[HF] mol/ℓ	$[F^-]$ mol/ℓ
1.0	0.000	9.8×10^{-2}	—	8.7×10^{-2}	0.82	6.0×10^{-3}
1.0	0.270	2.5×10^{-2}	0.96	0.26	0.72	3.0×10^{-2}
1.0	0.500	2.5×10^{-2}	0.54	0.26	0.72	3.5×10^{-2}
1.0	0.540	7.9×10^{-3}	0.98	0.45	0.54	9.0×10^{-2}
1.0	0.750	1.0×10^{-2}	0.65	0.42	0.57	7.0×10^{-2}
1.0	1.000	4.0×10^{-3}	0.70	0.57	0.43	0.13
1.0	2.000	2.5×10^{-4}	0.77	0.86	0.14	0.68
1.0	3.000	8.0×10^{-5}	0.72	0.92	8.0×10^{-2}	1.24
1.0	3.890	6.3×10^{-5}	0.60	0.93	7.0×10^{-2}	1.39
1.0	6.000	4.0×10^{-5}	0.45	0.94	6.0×10^{-2}	1.77
1.0	10.000	5.0×10^{-6}	0.61	0.98	2.0×10^{-2}	5.09
1.5	0.000	0.14	—	0.13	1.23	1.0×10^{-2}
1.5	0.270	5.0×10^{-2}	1.00	0.29	1.16	3.0×10^{-2}
1.5	0.750	1.6×10^{-2}	0.88	0.61	0.87	7.0×10^{-2}
1.5	0.811	1.3×10^{-2}	0.90	0.66	0.83	8.0×10^{-2}
1.5	1.125	6.3×10^{-3}	0.86	0.84	0.65	0.14
1.5	1.500	4.0×10^{-3}	0.75	0.95	0.55	0.18
1.5	3.000	6.3×10^{-4}	0.59	1.25	0.25	0.51
1.5	4.500	1.0×10^{-4}	0.61	1.39	0.11	1.36
1.5	5.840	4.0×10^{-5}	0.62	1.43	7.0×10^{-2}	2.19
2.5	0.000	0.23	—	0.22	2.05	1.0×10^{-2}
2.5	0.270	0.12	1.00	0.37	2.01	2.0×10^{-2}
2.5	1.250	2.5×10^{-2}	0.86	1.03	1.45	7.5×10^{-2}
2.5	1.350	1.6×10^{-2}	0.98	1.23	1.25	0.11
2.5	1.875	1.0×10^{-2}	0.83	1.42	1.07	0.14
2.5	2.500	4.0×10^{-3}	0.80	1.75	0.75	0.24
2.5	5.000	4.0×10^{-4}	0.62	2.23	0.28	0.86
2.5	7.500	6.3×10^{-5}	0.62	2.39	0.11	2.24
2.5	9.730	1.6×10^{-5}	0.72	2.45	5.0×10^{-2}	4.51
1.2	10.300	4.0×10^{-6}	0.72	1.18	2.0×10^{-2}	6.27
2.7	4.595	1.6×10^{-4}	0.87	2.55	0.17	1.46

1) $[H^+]$ is calculated from pH value which is measured with pH paper
$pH = -\log[H^+]$
2) α : degree of NH_4F dissociation

crease of NH_4F concentration. The dependence of the intensity of HF_2^- spectrum on NH_4F concentration is shown in Table II, where etching rates of SiO_2 films are simultaneously tabulated. A plot of the calculated value of $[HF_2^-]$ concentration against absorption intensity of $[HF_2^-]$ is found to be linear, as shown in Fig. 5. The empirical equation can be expressed as

$$[HF_2^-]_{cal} = 8.518[HF_2^-]_{abs} + 0.014. \tag{11}$$

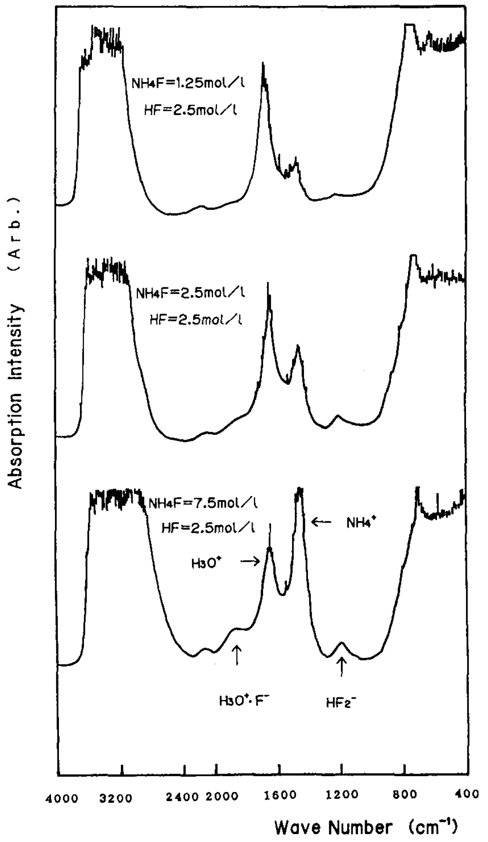


Fig. 4. FT-IR absorption spectra of NH_4F-HF-H_2O system.

TABLE II
SPECTROSCOPIC EXAMINATION AND EVALUATION OF HF_2^- ION CONCENTRATION AS RELATING TO THE COMPOSITION OF NH_4F-HF-H_2O SYSTEM

Composition HF mol/ℓ	Composition NH_4F mol/ℓ	HF_2^- conc. mol/ℓ	HF_2^- Absorption intensity at ca. 1210cm^{-1}	Etching rate (A/min)
1.0	0.000	8.7×10^{-2}	ND	117
1.0	0.270	0.26	0.026	207
1.0	0.500	0.26	0.046	259
1.0	0.540	0.45	0.043	593
1.0	0.750	0.42	0.061	300
1.0	1.000	0.57	0.073	333
1.0	2.000	0.86	0.093	385
1.0	3.000	0.92	0.104	405
1.0	3.890	0.93	0.111	405
1.0	6.000	0.94	0.124	417
1.5	0.000	0.13	ND	179
1.5	0.270	0.29	0.028	280
1.5	0.750	0.61	0.071	415
1.5	0.811	0.66	0.069	343
1.5	1.125	0.84	0.085	493
1.5	1.500	0.95	0.120	527
1.5	3.000	1.25	0.158	591
1.5	4.500	1.39	0.159	602
1.5	5.840	1.43	0.161	594
2.5	0.000	0.22	ND	300
2.5	0.270	0.37	0.033	415
2.5	1.250	1.03	0.130	772
2.5	1.350	1.23	0.129	795
2.5	1.875	1.42	0.173	900
2.5	2.500	1.75	0.218	968
2.5	5.000	2.23	0.274	987
2.5	7.500	2.39	0.276	902
2.5	9.730	2.45	0.275	822
1.2	10.300	1.18	0.114	336
2.7	4.595	2.55	0.281	1019

This result seems to support above described method for calculating HF_2^- ion concentration. HF_2^- ion concentrations in the NH_4F-HF-H_2O system from Table II are plotted as a function of NH_4F concentration for the three HF concentrations, in Fig. 6, where theoretical values are also shown by dashed lines. It is seen from Fig. 6 that the HF_2^- ion concentration tends to saturate in NH_4F concentrations greater than an equivalent mole ratio of HF and NH_4F. Theoretical results coincide well with experimental values. In Fig. 7, etching rate of thermal silicon dioxide films is plotted as a function of NH_4F concentration for the three HF concentrations. It is worthwhile to note in Figs. 6 and 7, that the dependence of the etching rate on NH_4F concentration is well described by the HF_2^- ion concentration dependence on NH_4F concentration except for NH_4F concentrations higher than several mole concentrations. In spite of the constant HF_2^- ion concentration, the etching rate of SiO_2 starts to decrease with an increase of NH_4F concentration greater than the above mentioned several mole concentrations. This phenomenon is attributed to the decrease of H^+ ion concentration with an increase of NH_4F concentration (as shown in Fig. 3) combined with the fact that the surface reaction of SiO_2 with HF_2^- ions requires the existence of H^+ ions (as described in (2)).

Fig. 8 shows the ratio of etching rate to HF_2^- concentration as a function of the $[H^+]/[HF_2^-]$ ratio. It can be seen that the etching rate of SiO_2 gradually decreases with decreasing in H^+ concentration even if the HF_2^- concentration remains constant. Fig. 8 indicates the existence of two different SiO_2 etching mechanisms for different ranges of H^+ ion concentrations, as shown next:

$$E_1 = 1282.8[HF_2^-] + 388.8[HF_2^-]\log[H^+]/[HF_2^-] \quad (12)$$

when

$$([H^+]/[HF_2^-] \geqq 2 \times 10^{-2})$$

$$E_2 = 757.9[HF_2^-] + 79.0[HF_2^-]\log[H^+]/[HF_2^-] \quad (13)$$

when

$$([H^+]/[HF_2^-] < 2 \times 10^{-2}).$$

Here, E_1 and E_2 are etching rates of thermal silicon oxide (Å/min) and $[HF_2^-]$, and $[H^+]$ is the HF_2^- ion concentration (mol/l) and the H^+ ion concentration (mol/l), respectively. As can be seen from (12) and (13), etching rate depends mainly on the $[HF_2^-]$ concentration. The functionality of $[H^+]$ is small, because it changes logarithmically. The mechanism of why the H^+ ion concentration influence SiO_2 etching is changed at the $[H^+]/[HF_2^-]$ ratio of 2×10^{-2} is now under investigation.

2. Solubility of the Reaction (Etching) Product in the Etching Solution

Ammonium hexafluorosilicate ($(NH_4)_2SiF_6$) is produced by the reaction of SiO_2 and BHF. Its solubility (except for that in NH_4F [15]) in BHF has never been reported. We have measured the solubilities of ($(NH_4)_2SiF_6$) in several BHF compositions, by filtration and collection of the undissolved portions, and have plotted them as a function of NH_4F concentration in Fig. 9. The solubility of ($(NH_4)_2SiF_6$) in BHF has been demonstrated to increase with a decrease of NH_4F concentration

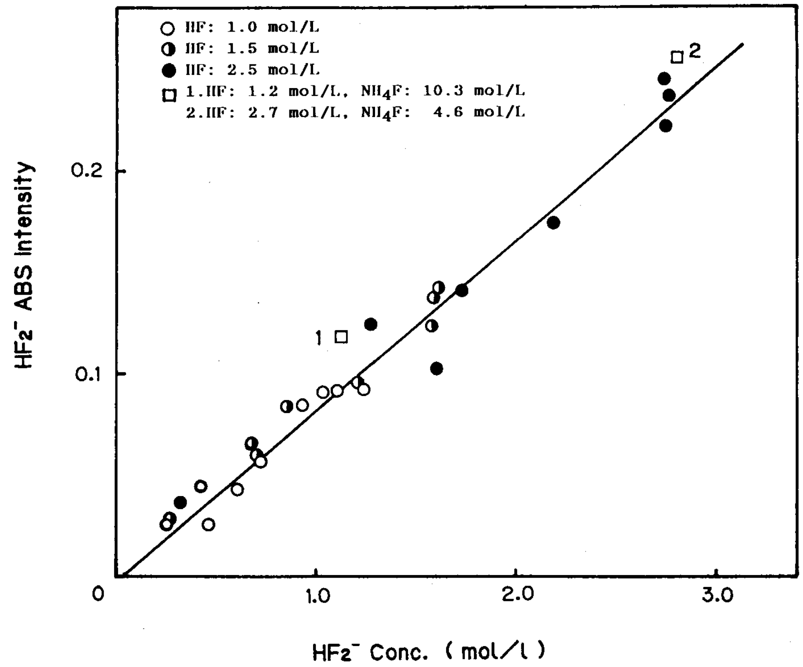


Fig. 5. Relationship of HF_2^- absorption intensity in FT-IR spectrum and theoretically calculated HF_2^- concentration. ○: HF = 1.0 mol/l. ◑: HF = 1.5 mol/l. ●: HF = 2.5 mol/l. □: 1) HF = 1.2 mol/l; NH_4F = 10.3 mol/l; 2) HF = 2.7 mol/l; NH_4F = 4.6 mol/l.

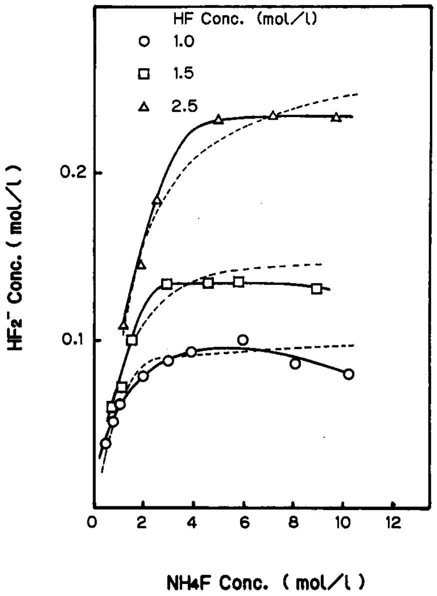


Fig. 6. Relationship of HF_2^- concentration and NH_4F concentration.

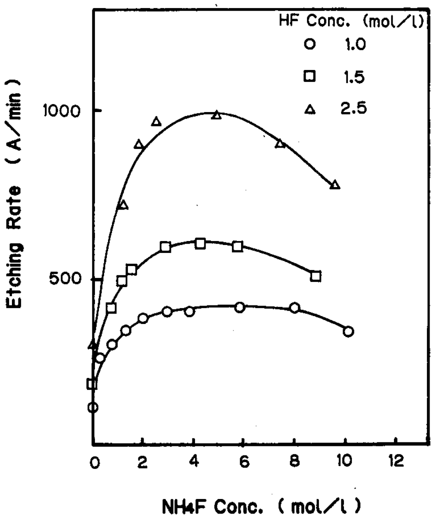


Fig. 7. Relationship of etching rate of SiO_2 and NH_4F concentration.

while the HF concentration maintains constant. With the NH_4F concentration held constant, the solubility of $((NH_4)_2SiF_6)$ decreases with increasing HF concentration. In the vicinity of 20% NH_4F concentration, the solubility of $((NH_4)_2SiF_6)$ shows a localized increase in concentration. It has been reported that solid phase changes from $(NH_4F \cdot (NH_4)_2SiF_6)$ to $((NH_4)_2SiF_6)$ between 19.04 and 21.42 wt. % NH_4F, and within this concentration region two solid phases coexist in solution [15].

The relationships between etching depth and time for 10 μm × 10 μm holes with improved (1.7% HF: 15% NH_4F) and conventional (2.4% HF: 38.1% NH_4F) BHF are shown in Fig. 10. The etching rate for both BHF is 370 Å/min at 25°C. 10-μm^2 contact holes with a resist (OFPR-800) thickness of 1.3 μm are patterned on 1.0-μm thick silicon dioxide and the holes

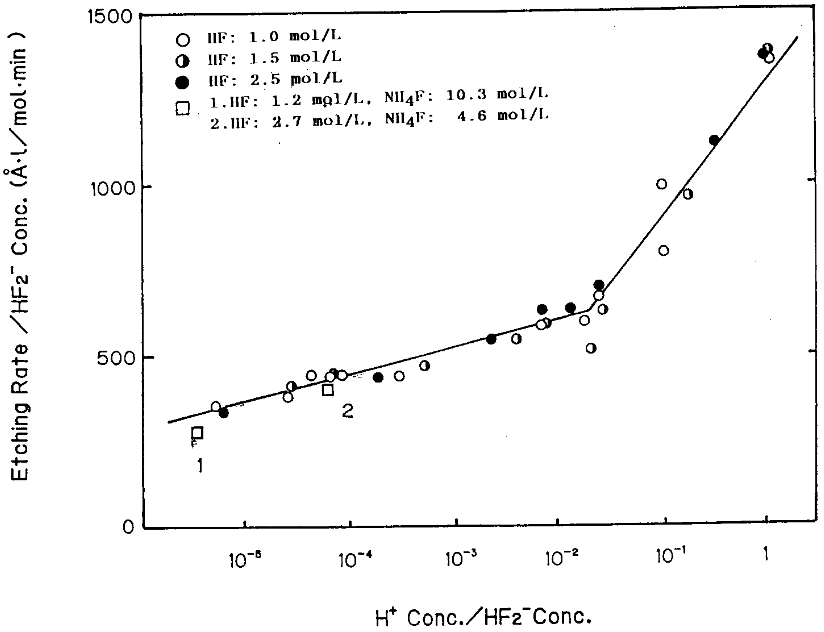


Fig. 8. Etching rate of SiO_2 normalized by HF_2^- concentration versus H^+ concentration normalized by HF_2^- concentration. ○: HF = 1.0 mol/l. ◑: HF = 1.5 mol/l. ●: HF = 2.5 mol/l. □: 1) HF = 1.2 mol/l; NH_4F = 10.3 mol/l; 2) HF = 2.7 mol/l; NH_4F = 4.6 mol/l.

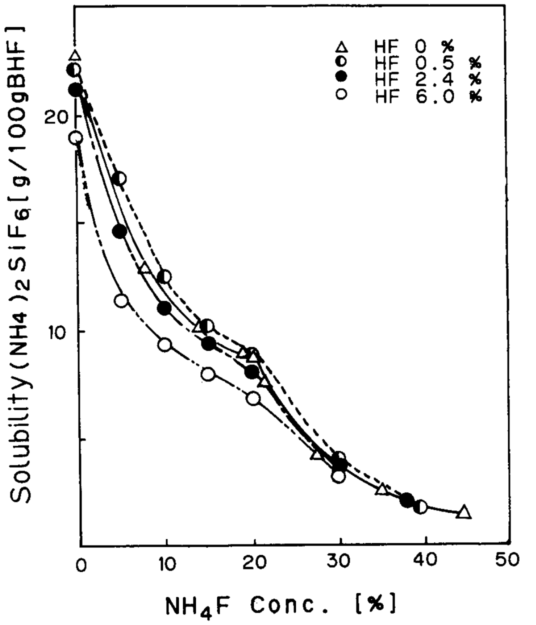


Fig. 9. Solubility of ammonium hexafluorosilicate $(NH_4)_2SiF_6$ in NH_4F-HF-H_2) solution versus NH_4F concentration at 25°C.

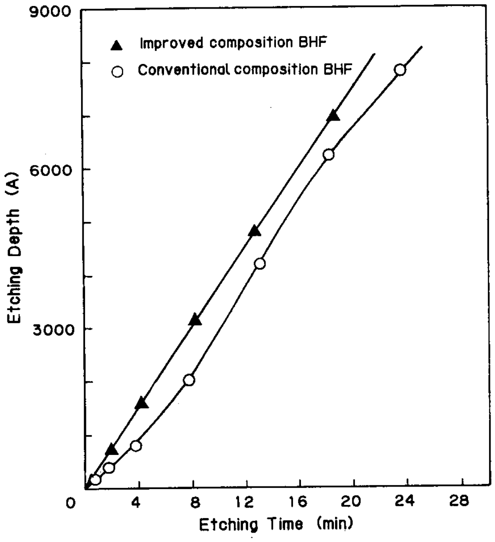


Fig. 10. Relationship of etching depth of SiO_2 feature having size of 10 × 10 μm^2, and etching time.

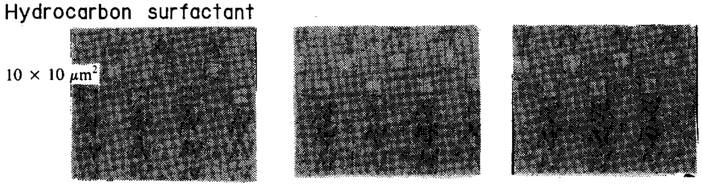
are etched with improved and conventional BHF. The etched thickness is measured by a surface profilometer. Complete etching linearity of improved BHF has been confirmed up to 1 μm thickness in SiO_2. While the etching rate of conventional BHF is lower than improved BHF at the start of etching to 8 min, it is approximately the same as improved BHF from 8 min to 20 min, and is slower again after 20 min.

As can be seen from the above mentioned results, etching linearity is enhanced with improved BHF. This is attributed to the increased solubility of the reaction products. The control of etching process is difficult in conventional BHF because the etching rate of SiO_2 does not increase linearly with the etching time. Contact holes of various sizes from 0.7 μm to 10.0 μm are etched with conventional BHF, improved BHF and ad-

TABLE III
IMPERFECTION RATIO OF CONTENT HOLE ETCHING

	Imperfection ratio (%)								
	Conventional BHF			Improved BHF			Advanced BHF		
NH_4F (%)	39.6	38.1	30.0	15.0	15.0	15.0	15.0	15.0	15.0
HF (%)	0.5	2.4	6.0	0.5	2.4	6.0	0.5	2.4	6.0
Surfactant[1] (ppm)	0	0	0	0	0	0	100	100	100
Contact hole size									
10.0μm	99.6	99.5	96.9	0	0	0	0	0	0
1.0μm	91.5	74.2	71.1	0	0	0	0	0	0
0.9μm	91.0	61.0	59.8	0	0	0	0	0	0
0.8μm	86.6	43.8	45.3	0	0	0	0	0	0
0.7μm	68.9	38.9	40.1	0	0	0	0	0	0

1) Surfactant : Hydrocarbon surfactant



vanced surface active BHF (advanced BHF), i.e., containing a selected surfactant in improved BHF. The heterogeneous etching is easily observed by the interference color of etched surface with a microscope. If any irregularity in interference is noted, it is counted as an imperfection. One thousand contact holes for each size are etched by using their BHF solution; imperfection ratios are shown in Table III. The conventional BHF gives higher imperfection ratio while the improved BHF and the surface active BHF exhibit complete etching uniformity for all sizes of contact holes. In the case of conventional BHF, the imperfection ratio increases with increasing NH_4F concentration and contact hole size.

The concentration of $((NH_4)_2SiF_6)$ at the liquid-solid interface, where the etching takes place is directly proportional to the size (surface area) of the contact hole. Consequently, the local saturation of the reaction product $((NH_4)_2SiF_6)$ causes suppression of the etching rate.

Improved BHF and advanced BHF do not show this saturation effect because of the higher solubility of $((NH_4)_2SiF_6)$ in these solutions. Thus, it can be concluded that the composition of the etching solution must be designed to maximize the solubility of the etching reaction products.

3. *Stability of Chemical Composition*

Solid phase segregation from a liquid a chemical occurs at temperatures less than a critical value, the solid phase segregation temperature.

Conventional BHF is plagued by solid phase segregation of NH_4HF_2 during transportation and storage, particularly in winter. In conventional BHF with HF concentrations of 6-8%, solid phase segregation occurs at temperatures from 9-17°C.

The relation between solid phase segregation temperature and NH_4F concentration has been measured and is shown in Fig. 11. Two relationships, the freezing depression curve and the solubility curve, are observed to have a point of intersection. This represents the minimum solid phase segregation temperature.

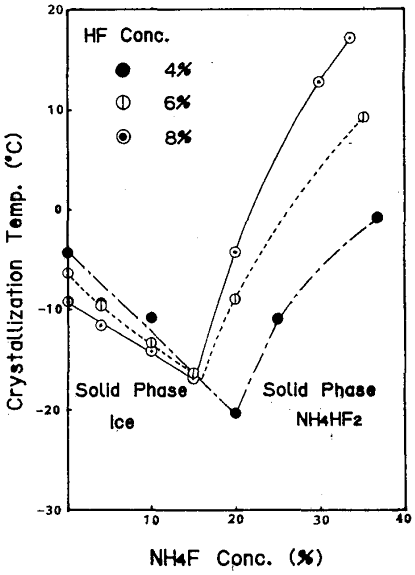


Fig. 11. Solid phase segregation temperature of NH_4F-HF-H_2O solution versus NH_4F concentration.

In the region of NH_4F concentrations below the point of intersection, the freezing temperature decreases with increasing NH_4F concentration, and the equilibrium solid phase is ice. In the region above the intersection, the segregation temperature increases with increasing NH_4F concentration. This is due to the decreasing solubility of the solid phase species (NH_4HF_2) in solutions of increasing NH_4F concentration. Conventional BHF is likely apt to exhibit segregation of NH_4HF_2 crystals due to the reduction of NH_4HF_2 solubility. Segregated solid phase chemicals have been confirmed to be difficult to redissolve, even if the ambient temperature returns to a temperature higher than the solid phase segregation temperature. This results in a variation of the composition of the liquid chemicals, and consequently, in a variation of the etching rate. Solid phase segregation temperature of BHF can be lowered by decreasing NH_4F concentration. It is desirable to formulate liquid chemicals such that the solid segregation temperature is as low as possible. For example, BHF having NH_4F concentration of 15% has a usefully lowered segregation temperature of −18°C.

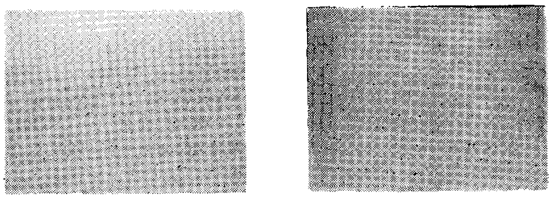
4. *Wettability of the Wafer Surface*

It is critically important to improve the wetting characteristics of liquid chemicals in order to achieve complete cleaning of the wafer surface. However, BHF have large surface tension values ranging from 84 dyne/cm to 93 dyne/cm and high contact angles ranging from 69 degrees to 73 degrees on bare silicon surfaces [9], [16]. BHF generally has poor wettability on bare silicon and resist-coated surfaces, resulting in rough silicon surfaces after SiO_2 etching. In order to improve the wettability of BHF on a wafer surface, it is necessary to add selected hydrocarbon surfactants such as aliphatic amines, acids and alcohols. This surface active BHF has been reported in a previous paper [6]–[9], in which it has been shown that the following 10 characteristics are essentially required of surfactants: 1) same etching rate as BHF; 2) low contact angle; 3) non-segregation; 4) non-foaming; 5) low particulates; 6) low impurities (possibility of purification); 7) low particulate adhesion on wafer surface; 8) no surface residuals; 9) excellent surface smoothness; and 10) high etching selectivity.

Rough silicon wafer surfaces cause problems in succeeding process steps, particularly for shallow junction devices. Uniformity of SiO_2 etching by BHF has been demonstrated to be significantly improved by decreasing NH_4F concentration down to 15 weight percent. Less smoothness of the silicon surface is obtained after etching with both conventional BHF and improved BHF, as shown in Fig. 12, where the etching time is increased to 1 h in order to show the surface roughness. Complete smoothness of silicon surface after the SiO_2 etching is achieved by the advanced BHF including surfactants such as aliphatic amine and aliphatic alcohol. Even after immersing the wafer in the advanced BHF for 48 h after the SiO_2 etching, complete smoothness of the silicon surface is guaranteed as shown in Fig. 12. Smoothness of the etched silicon surface is affected by the manufacturing conditions of silicon wafer, i.e., FZ method and CZ method, the conductivity type and the crystal orientation of the wafer. Silicon wafers, especially those having (111) crystal orientation produce severe surface roughness when they are immersed in conventional BHF and improved BHF for 48 h. *N*-type silicon wafers exhibit better etching smoothness than p-type silicon wafers. The results are summarized in Table IV.

Liquid chemicals have been demonstrated in a previous work [4] to exhibit excellent wettability on wafer surfaces for high quality wet chemical processing. Excellent surface smoothness on the silicon surface after the SiO_2 etching is essential to give high yield and reliability required by ULSI devices having shallow junctions.

Furthermore, advanced BHF extends bath life as it is amenable to recirculation filtration, where the lifetime is limited by the etching product level instead of the particle concentration level. The life-time of conventional BHF is determined by the density of particle contamination. Recirculation filtration does not work well because of the poor wettability of conventional BHF.

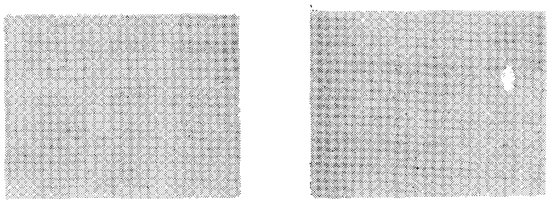


1 Hr 1 Hr

Conventional composition BHF Improved composition BHF

NH_4F 38.1% HF 2.4% NH_4F 15.0% HF 2.4%

(a) (b)



1 Hr 48 Hr

NH_4F 15.0% HF 2.4% Hydrocarbon Surfactant 200ppm

(c) (d)

Fig. 12. SEM photographs of etched silicon wafer surface. Silicon wafer: CZ p (100) 6–8. (a) By conventional BHF for 1 h. (b) By improved BHF for 1 h. (c) By advanced BHF for 1 h. (d) By advanced BHF for 48 h.

TABLE IV
SMOOTHNESS ON SILICON SURFACE ETCHED BY BHF

	Conventional Composition		Improved Composition		Advanced Surface Active	
Silicon Wafer	1 h	48 h	1 h	48 h	1 h	48 h
FZ n (100) 3–5 (Ω)	R	R	R	VR	VS	—
CZ p (100) 6–8 (Ω)	R	R	R	VR	S	S
FZ n (111) 100 (Ω)	S	VR	R	VR	VS	S
CZ p (100) 20 (Ω)	R	R	S	VR	S	S
CZ n (100) 20 (Ω)	R	R	S	VR	VS	R

Note VS: Very-smooth S: Smooth
VR: Very-rough R: Rough
Conventional composition BHF: NH_4F 38.1%, HF 2.4%
Improved composition BHF: NH_4F 15%, HF 2.4%
Advanced surface active BHF: NH_4F 15.0%, HF 2.4%, Hydrocarbon surfactant 200 ppm.

III. CONCLUSION

Improvement of the chemical composition of BHF has been examined from a theoretical viewpoint, based on ionization mechanisms of liquid chemicals and surface chemical reactions. The dissociation mechanism of BHF has been examined theoretically and experimentally, concluding that HF_2^- is the dominant reactive ion species in SiO_2 etching. The relationship of etching rate of silicon oxide films and HF_2^- and H^+ ion concentrations has been determined. Etching rate of SiO_2 films in the NH_4F-HF-H_2O system has been confirmed to increase linearly with the HF_2^- ion concentration, while it decreases logarithmically with a decrease of the H^+ ion concentration, even if the HF_2^- ion concentration is kept constant. We conclude that the composition of liquid chemicals for etching solution must be selected to have the most appropriate concentration of HF_2^- ion species for the etching rate. The composition and properties of liquid chemicals should be designed by considering the following characteristics: sufficient solubility of etching product in the etching solution; sufficiently segregation temperatures for the solid phase; and excellent wettability.

1) Ordinary compositions of BHF having excess NH_4F concentration cause several serious problems excess NH_4F does not contribute to the ionic reaction with silicon oxide and seriously degrades the etching uniformity and linearity due to the lack of solubility of etching product in BHF.

2) We have found that the solubility of the etching product of SiO_2 increases in BHF with a decrease of NH_4F concentration.

3) Another practical hindrance is the solid phase segregation of NH_4HF_2, crystals formation in a low temperature environment. This solid phase segregation creates particles and results in compositional variation of the liquid chemical. Considering the transportation and the stocking of liquid chemicals, particularly in winter, the solid phase segregation temperature must be made as low as possible. The improved composition of BHF, having an NH_4F concentration of about 15%, is confirmed to resolve these problems and perform etching with complete linearity and uniformity.

4) Through appropriate surfactants addition, liquid chemicals exhibit excellent wettability on wafer surfaces and allow high quality wet chemical processing. Complete smoothness of the wafer surface after the SiO_2 etching has been achieved by an introduction of advanced surface active BHF having an NH_4F concentration of 15% and selected hydrocarbon surfactants such as aliphatic amine and aliphatic alcohol.

APPENDIX

By combining (4)–(10) in Section II, we obtain the expression

$$[HF_2^-] = \frac{2[H^+](\alpha n + [H^+]) + K_1K_2 - \sqrt{K_1K_2\{K_1K_2 + 4[H^+](\alpha n + [H^+])\}}}{2[H^+]} \tag{14}$$

$$[F^-] = K_2 \frac{[HF_2^-]}{[HF]} \tag{15}$$

$$[HF] = \frac{1}{K_1}[H^+][F^-]. \tag{16}$$

The concentrations of respective species are obtained by using the values from [7] $K_1 = 1.3 \times 10^{-3}$, $K_2 = 0.104$, $[H^+]$ is measured with pH paper, results are tabulated in Table I.

ACKNOWLEDGMENT

This research has been mainly carried out in the Super Clean Room in the Laboratory for Microelectronics, Research Institute of Electrical Communication, Tohoku University. If it is noted that proceeding work of importance related to this article is not cited as a reference, it is due to our incomplete survey of references. It would be greatly appreciated if such information of comments are provided to the authors.

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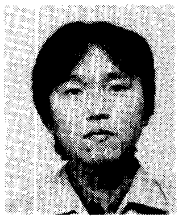

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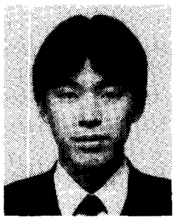

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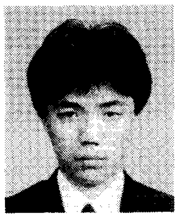

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His research activities include 260 original papers and 190 patent applications. He received the Ichimura Award in 1979, the Teshima Award in 1987, and the Inoue Harushige Award in 1989. He serves as a General Chairman of the International Symposium on Power Semiconductor Devices and of the Institute of Basic Semiconductor Technology Development (Ultra Clean Society).

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