Surface Active Buffered Hydrogen Fluoride Having Excellent Wettability for ULSI Processing

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Abstract—Buffered hydrogen fluoride is an essential chemical for wet processing of ultra large scale integration (ULSI) device manufacturing. However, buffered hydrogen fluoride has been demonstrated experimentally to exhibit poor quality in wet cleaning of the silicon wafers or etching of high-aspect ratio contact holes and via holes due to its poor wettability of the silicon wafer surface. A surface active buffered hydrogen fluoride has been developed through the addition of surfactants. It has been confirmed as exhibiting excellent wettability, resulting in improved wet cleaning and etching without causing any roughness of the silicon wafer surface. Wettability control of buffered hydrogen fluoride through the addition of surfactants is discussed based on requirements for ULSI wet chemical processing.

I. INTRODUCTION

THE VALUE of total clean technology in the manufacture of devices of ever decreasing geometries has been well documented [1]–[8]. Environmental clean technology is one of the important elements in ultra clean technology for achieving ultra clean wafer surfaces. Contamination control of wafer surfaces is a key technology for the progress of wet chemical processing in ultra large scale integration (ULSI) manufacturing [9]. In conjunction with the advances in microfabrication technologies, the minimum dimensions of ULSI devices have been reduced to the submicron range. As a result, the difficulties in wet chemical processing for such devices, because of their highly varying topographical surfaces, have increased. If the wettability of the solution on a wafer surface is not improved it is almost impossible to perform complete wet cleaning or wet etching of high aspect ratio contact holes and via holes, having typical dimensions of about 1 to 2 μm deep and a lower submicron opening, such as 0.25 μm. For example, with buffered hydrogen fluoride (BHF), it is practically impossible to penetrate uniformly into such deep holes because of its poor wettability on the wafer surfaces. Therefore, it is considered critically important to control the wettability of the solution in order to perform complete cleaning and surface

etching of such high aspect ratio contacts and via holes [10], [11].

Buffered hydrogen fluoride is a well-known, excellent wet-etching reagent for silicon oxides. But, for the etching of submicron and high aspect ratio via holes, special attention must be given to BHF's physicochemical properties, such as wettability and surface tension. So far, it has been considered that the wettability can be improved by the reduction of surface tension with the addition of surfactants in BHF. Generally, fluorocarbon surfactants have been used in order to reduce the surface tension, but they do not improve wettability because of their inability to reduce the contact angle. There have been no in-depth scientific studies performed on the characteristics and performance of surfactants on the wet chemical processing of wafer surfaces.

We have studied 350 surfactants including various fluorocarbon and hydrocarbon surfactants such as anionic, cationic and nonionic surfactants for submicron processing applications. As a result, we discovered that the optimum surfactants for submicron processing must satisfy the following requirements:
1) same etch rate as that of conventional BHF;
2) low contact angle;
3) non-segregation;
4) non-foaming;
5) low in particulate;
6) low in impurities (possibility of purification);
7) low particulate adhesion on the wafer surface;
8) no surface residues;
9) excellent surface smoothness;
10) high SiO_2/Si etching selectivity.

In order to satisfy these requirements, surfactants must satisfy the following characteristics:
- good solubility in BHF;
- hydrophilic at the wafer surface;
- non-decomposition in BHF;
- non-reaction with BHF;
- sufficient lowering of contact angle at the critical micelle concentration (CMC).

Fluorocarbon surfactants have been confirmed not to satisfy these requirements, particularly (2), (3), and (8), because of their hydrophobic chemical structure. We have

discovered only a single hydrocarbon surfactant of aliphatic amine that satisfies these requirements.

II. ESSENTIAL PREREQUISITES OF SURFACE ACTIVE BUFFERED HYDROGEN FLUORIDE

Buffered hydrogen fluoride (BHF) is produced by mixing 50 wt% hydrofluoric acid and 40 wt% ammonium fluoride in varying proportions. The composition of BHF used in these experiments is shown in Table I. BHF exhibits high 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 [12], [13]. BHF has poor wettability on bare silicon and resist coated surfaces. Several attempts have been made to improve the wettability of BHF by adding fluorocarbon surfactants, but the wettability on the silicon surface could not be improved. Fig. 1 shows relationship of contact angle to free energy for a three phase, air-liquid-solid, system. Wettability of BHF must be evaluated by the contact angle which relates the free-energy of the solid-liquid interface, because the contact angle (θ) is related to the free surface energies through the Young equation.

$$\gamma_s = \gamma_l \cos \theta + \gamma_i \tag{1}$$

where, γ_s, γ_l and γ_i are free energy of solid surface, liquid surface and solid-liquid interface, respectively. In order to improve the wettability of BHF on the wafer surface, it is necessary to reduce the free-energy of the solid-liquid interface, resulting in a reduction of contact angle. It is not always appropriate to evaluate the wettability by the surface tension related to the free-energy of liquid-gas interface. In Figs. 2 and 3, there are some surfactants having high contact angle in spite of low surface tension.

For an understanding of the relationship of the contact angle to wettability, a very simple procedure has been developed, which is the visual inspection of the wafer surface after the silicon wafer is immersed into BHF and pulled out vertically. The relationship of contact angle to wettability is shown in Fig. 4, where the contact angle is controlled by the addition of a surfactant (an aliphatic amine) to BHF 63. It can be seen that lowering the contact angle of BHF 63 on the silicon wafer surface to 30 degrees resulted in excellent wettability. Good solubility of surfactants in BHF is an essential prerequisite in order to maintain the surfactant concentration in BHF at the same level after the filtration procedure.

At first, the effects of surfactants addition to BHF have been evaluated to observe the relationship of the contact angle to the surface tension before and after filtration. The concentration of surfactants is set at a constant 1000 ppm. Effects of fluorocarbon surfactants and hydrocarbon surfactants are shown in Figs. 2 and 3, respectively, where the results of cationic and amphoteric surfactants are illustrated. Other nonionic and anionic surfactants exhibit very similar tendencies to those shown in Figs. 2 and 3.

Comparing the values in Table I to those in Fig. 2, it can be seen that the fluorocarbon surfactants lower the

TABLE I
COMPOSITION AND INTERFACIAL TENSION OF BHF USED IN THE EXPERIMENTS

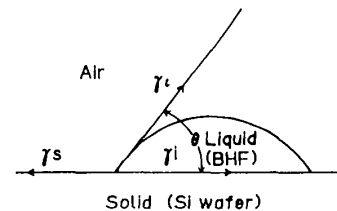| BHF	Composition (%)		Surface Tension (dyne/cm)	Contact Angle (on Si wafer) (deg)
	NH$_4$F	HF		
201	38.1	2.4	90.1	73
63	30.0	6.0	86.9	73

Fig. 1. Contact angle at liquid-solid-vapor boundary line. γ_s: Free energy of solid surface. γ_l: Free energy of liquid surface. γ_i: Free energy of solid-liquid interface. θ: Contact angle. $\gamma_s = \gamma_i + \gamma_l \cos \theta$.
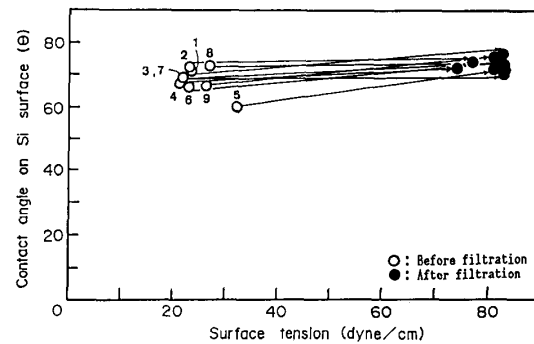

Fig. 2. Contact angle and surface tension before and after filtration of fluorocarbon surfactants (cationic and amphoteric) in BHF 63. 1) Perfluoro Alkyl Trimethyl Ammonium Salt. 2) Perfluoro Alkyl Trimethyl Ammonium Iodide. 3) Perfluoro Alkyl Trimethyl Ammonium Salt. 4) RfC$_2$H$_4$SC$_2$H$_4$N(CH$_3$)$_3$CH$_3$SO$_4$. 5) RfSO$_2$NRC$_2$H$_4$N$^+$(CH$_3$)$_3$I$^-$. (6)-(9) Perfluoro Alkyl Betain.

surface tension but do not lower the contact angle. Almost all kinds fluorocarbon surfactants are segregated from BHF solution by filtration, after which the surface tension regains its original high value. These characteristics come from the intrinsic hydrophobic chemical structure and the poor solubility in BHF of fluorocarbon surfactants.

Fig. 3 shows the relationship of the contact angle to the surface tension of BHF containing various hydrocarbon surfactants. Most hydrocarbon surfactants increase the surface tension of BHF after filtration. This fact indicates that surfactants must remain dissolved in BHF in order to decrease the contact angle and the surface tension. Of all the samples, only surfactants 6, 7, and 8 exhibit drastic decreases in contact angle and surface tension of BHF. These surfactants are aliphatic amines having carbon number of 8, 9, and 10. Aliphatic amines having carbon number less than 8, (surfactants of Nos. 1-4, and 5) are
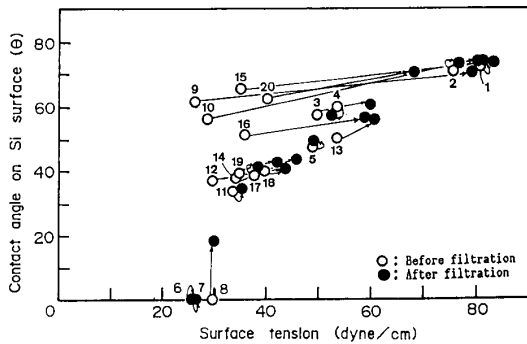
Fig. 3. Contact angle and surface tension before and after filtration of hydrocarbon surfactants (cationic and amphoteric) in BHF 63. 1) Propylamine. 2) Butylamine. 3) Amylamine. 4) Hexylamine. 5) Heptylamine. 6) Octylamine. 7) Nonylamine. 8) Decylamine. 9) Laurylamine. 10) Tetradecylamine. 11) Octadecylamine Acetate. 12) Coconutamine Acetate. 13) Trioctylamine. 14) Stearylamine Acetate. 15) Dodecyl Trimethyl Ammonium Chloride. 16) Lauryl Trimethyl Ammonium Chloride. 17) Alkyl Benzyl Dimethyl Ammonium chloride. 18) Dimethyl Alkyl Betaine. 19) 2-Alkyl-N-Carboxy Alkyl-N-Carboxy Ethyl Imidazolinium Betaine. 20) Coconut Alkyl Dimethyl Benzyl Ammonium Chloride.

BHF	Contact angle	Wetting area of BHF on silicon wafer surface	Wettability
Conventional	73°		No wetting zone
	52°		A little wetting zone
	37°		A little wetting zone
surface active	30°		The whole wetting surface

Fig. 4. Relationship of contact angle to wettability of BHF on silicon wafer surface.

very soluble in BHF, so that 1000 ppm addition to BHF is not enough to decrease the contact angle and the surface tension. On the other hand, aliphatic amines having carbon number greater than 10, (surfactants of Nos. 9 and 10) are not soluble and are segregated from BHF 63 through filtration. Other hydrocarbon surfactants do not exhibit enough reduction in the contact angle of BHF.

It has been concluded from Figs. 2 and 3 that only aliphatic amines having adequate carbon number among all surfactants exhibit a drastic decrease in contact angle of BHF resulting in excellent wettability on the silicon wafer surface. Moreover, aliphatic amines are easily purified to achieve cleanliness of semiconductor grade by a distillation procedure.
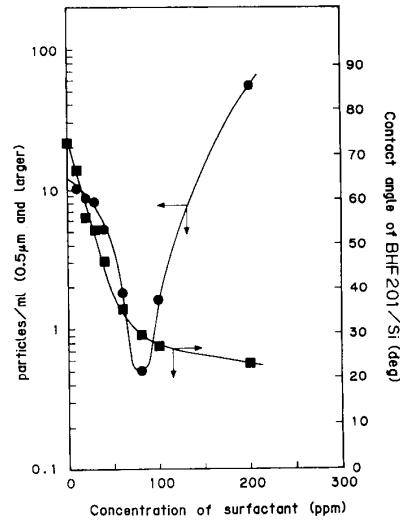

Fig. 5. Number of particles and contact angle after recirculating-filtration versus concentration of aliphatic amine in BHF 201. Particle counter; HIAC/ROYCO 4100-346CLS.

The concept of CMC of surfactants in solution is important for the regulation of surface active properties. It is recognized that surface tension and contact angle decrease with an increase of surfactant concentration and reach constant values at the CMC. Further increase in surfactant concentration, greater than this CMC, causes generation of excess micells of surfactant molecules in the solution, resulting in the generation of particles in semiconductor wet chemical processing. In general, various physical properties of solution vary in the neighborhood of the CMC, such as contact angle, surface tension, osmotic pressure, etc. [14].

It has been demonstrated that the number of particles in BHF increase in proportion to the concentration of surfactants and cannot be reduced sufficiently even though recirculating-filtration. However, our experiments indicate that the number of particles in BHF after recirculating-filtration is significantly reduced at around the CMC region for aliphatic amines having adequate carbon number, as shown in Figs. 5 and 6. The number of particles after recirculating-filtration is plotted as a function of the concentration of aliphatic amine in BHF 201 and BHF 63. Also the variation of the contact angle is simultaneously illustrated. The number of particles in BHF 201 and BHF 63 have minimum values at the surfactant concentration of 80 ppm and 140 ppm of aliphatic amines, respectively. When surface active BHF goes through recirculating-filtration, it has been shown experimentally that the pressure loss due to filtration will be decreased at a flow rate of 4.27 l/min compared to conventional BHF at 3.8 l/min. It is proposed that the lowering of the filter resistance is due to the improvement in wettability of the filter matrix.

The number of particles in BHF are reduced to the minimum value of 0.5/ml from 12/ml by the addition of aliphatic amine at a concentration of 80 ppm in BHF 201
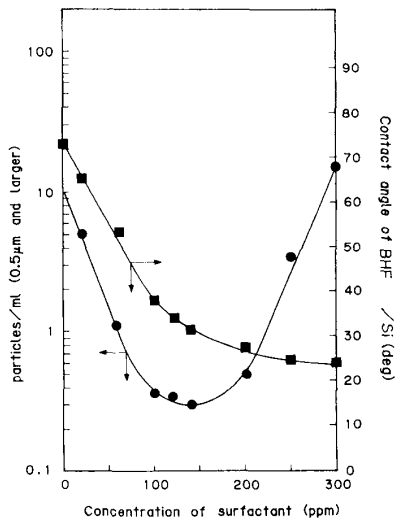
Fig. 6. Number of particles and contact angle after recirculating-filtration versus the concentration of aliphatic amine in BHF 63.
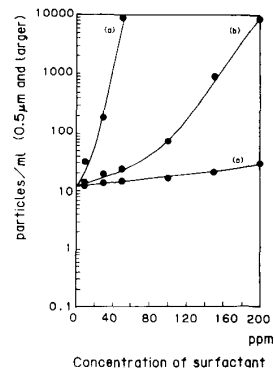

Fig. 7. Relationship of particle counts and concentration of some surfactants in BHF 63. (a) Polyoxyethylene polypropylene glycol ether. (b) Ammonium dialkylsulfosuccinate. (c) Ammonium alkylbenzensulfonate.
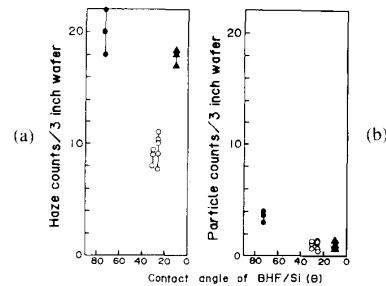

Fig. 8. Counts of hazes and particles adhered on 3-in silicon wafer treated with BHF versus contact angle of BHF/Si. ▲: adequate concentration of surfactant. ●: base level (diluted HF having 0.5%). □: excess concentration of selected surfactant.

and to 0.3/ml at a concentration of 140 ppm in BHF 63 by recirculating-filtration. Further increase of surfactant concentration over this optimum concentration is accompanied by an increase of particles, which mainly come from micelle of the surfactant. The optimum concentration values coincide with the CMC. Other surfactants increase the particle count in proportion to the concentration of surfactants as shown in Fig. 7.

Fig. 8 shows the relationship of contact angle versus number of particles (0.5 μm and larger) and that of haze (less than 0.5 μm) adhered to a 3-in water surface treated with BHF. The base line for this experiment have been established at about 20 hazes and four particles on a 3-in wafer surface treated with diluted hydrofluoric (HF) acid having 0.5% solution. With conventional BHF the number of hazes and particles on the wafer surface after treatment were almost the same as that of the base line. However, in the case of surface active BHF the number of hazes and particles are reduced to less than half of the level achieved by using conventional BHF. It is important to note that adding too much surfactant to the BHF, over the CMC, increases haze count due to micelle adhesion. Low particulate adhesion is considered to be the result of the lower contact angle on the silicon surface and its improved wettability by the addition of aliphatic amine to BHF.

Figs. 9 and 10 show micrographs of silicon dioxide etched with BHF 201 and BHF 63 respectively, where silicon dioxide shown on the right hand side is etched with BHF to a thickness of 0.5 μm. Surfactant concentrations are increased from (a) to (d). It is seen in Fig. 9 that non-uniform etching (non-uniformity of interference color) appears with the surfactant concentration higher than 120 ppm. When silicon dioxide is etched by BHF 201 having surfactant concentration in CMC, (a) indicates the uniform etching. But (b), (c), and (d) indicate non-uniform
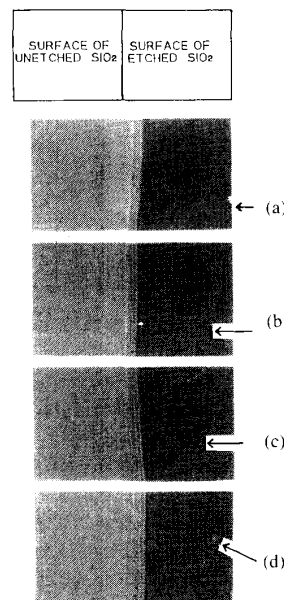

Fig. 9. Micrographs of SiO₂ etched surface by BHF 201 having various concentration of surfactants (aliphatic acid). (a) Uniform etching. (b) Non-uniform etching. (c) Non-uniform etching. (d) Non-uniform etching. (a) 60 ppm. (b) 120 ppm. (c) 150 ppm. (d) 200 ppm.
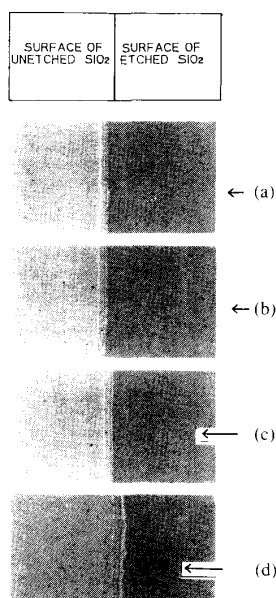
Fig. 10. Micrographs of SiO₂ etched surface by BHF 63 having various concentration of surfactants (aliphatic amine). (a) Uniform etching. (b) Uniform etching. (c) Non-uniform etching. (d) Non-uniform etching. (a) 100 ppm. (b) 200 ppm. (c) 300 ppm. (d) 400 ppm.

TABLE II
EFFECT OF BINARY SURFACTANTS IN 201BHF

Mixed concentration (ppm)		Binary effect	
Aliphatic Amine	Aliphatic Acid	Contact angle (θ)	Defoaming time (s)
120	0	32	no defoaming
90	30	31	10
60	60	38	45
30	90	52	no foaming
0	120	64	no foaming

etching due to the surfactant concentration of BHF higher than CMC. This etching non-uniformity is enhanced with an increase of surfactant concentrations in the region higher than the CMC.

The CMC of the binary surfactant system in BHF 63 is 200 ppm. Non-uniform etching is not observed in Fig. 10, even when the surfactant concentration is increased up to 200 ppm. The reason for this is that micelle generation is not as rapid in BHF 63 as in BHF 201, even when the surfactant concentration becomes greater than the CMC.

The excellent surface active properties of aliphatic amine is limited by the time required for defoaming. Huge amounts of foam appear in practical procedures such as filtration and bottling. This foam comes from the entrainment of air into BHF when bottling. Foaming causes various problems in micro-processing, which are described next.

1) Foam covers the surface of the liquid and overflows from the processing vessel during handling of BHF with added surfactant.

2) Etch defects occur by adhesion of the foam to the surface being etched, or by covering trenches or holes with foam.

3) When pulling out the wafer from the processing vessel, foam causes stains on the surface of wafer.

4) Foam causes problems in waste treatment.

Accordingly, it is important to select the surfactants having characteristics of non-foaming or defoaming in a short time. The character of foaming can be changed by mixing different kinds of surfactants. Thus, developing a recipe for defoaming is very important.

Foams disappear when a binary functional surfactant system is used; that is, a combination of aliphatic amine and aliphatic acid or aliphatic alcohol. The combination of aliphatic amine and aliphatic acid or aliphatic alcohol is called a binary surfactant system. Aliphatic acids and aliphatic alcohols are surfactants with good solubility properties and have a defoaming effect on aliphatic amine solutions, although they do not have excellent wettability. Defoaming effects achieve by the binary surfactant system are shown in Table II. The Ross–Miles test [15] is a well-known measure of the degree of foam formation; that is, the thickness of layer of foams in BHF. We measure the degree using a simple technique as follows: 10-ml BHF is poured into a 25-ml sample bottle; then, the bottle is shaken for ten seconds. The time required for defoaming is measured except for the foam adhering on the inside wall. Defoaming time is defined as the time taken to defoam when layers of foams are made after 10 s of shaking. Aliphatic amines at 120 ppm in BHF give a low contact angle value of 32 degrees but defoaming time is over 180 s. In the binary system described above the composition ratio of aliphatic amine and aliphatic acid is changed at a fixed total concentration of surfactants. The defoaming effect decreases with an increase of aliphatic acid concentration; while the contact angle gradually increases. In this binary surfactant system, it is apparent that adding of aliphatic amine mainly results in low contact angles and that aliphatic acid has a defoaming effect in BHF 201. In a wet process, there is no problem if the defoaming time is within 45 s.

In summary, aliphatic amine satisfies the requirements for submicron processing. However, in practice aliphatic amine has the problem of foam generation resulting from the entrainment of air into BHF. With a binary surfactant system, this problem can be overcome. The binary surfactant system dramatically reduces foam generation without changing the wettability, contact angle and surface tension.

Under present wet etching processes, the life span of BHF solutions is determined by the increase in particles formed. However, by using surface active BHF, particle counts can be reduced through recirculating-filtration. In other words, the life span of liquid chemicals in the vessel is extended up to the life time determined by an increase of reaction products.

III. WETTABILITY EFFECT ON SUBMICRON PATTERN ETCHING

The wettability effect of surface active BHF has been evaluated using patterned wafers. Fig. 11 shows the residues after etching with BHF. The patterned wafers were etched with conventional BHF and surface active BHF, and rinsed with DI (deionized) water for 10 s. The wafer surfaces were observed under microscope. Silicon wafers having a resist thickness of 1.3 μm (OFPR-800) and of 1.0-μm silicon dioxide were etched with BHF 63 to a thickness of 0.5 μm SiO$_2$. No residue is observed around the patterned edge treated with surface active BHF, compared with high levels of residues observed on wafers treated with conventional BHF. It is suspected that when a patterned wafer is etched with surface active BHF, DI water rinsing time can be made shorter compared with conventional BHF. The surface active BHF is displaced by DI water without difficulty, because the hydrocarbon surfactants in surface active BHF have a hydrophilic property.

We have investigated the wettability effect on submicron pattern etching by comparing the imperfection ratio of submicron pattern after etching with BHF. Line patterns having 0.75 μm width are etched with conventional and surface active BHF 63, and then imperfections are observed using a microscope. The number of checked patterns are 225 lines and the results are shown in Table III. Where, imperfection patterns are defined as not perfect etching of patterns, such as non etched or partially etched. There is no imperfection with the surface active BHF 63, against the conventional BHF 63 having 17 imperfections. Thus, it is clear that surface active BHF can contribute to the yield performance of submicron devices.

10-μm square holes patterned on a wafer were etched with conventional BHF 63 and surface active BHF 63. Heterogeneous etching is observed by the interference colors on the etched surface through a microscope. Results are shown in Fig. 12. The surface active BHF etched all holes perfectly, while the conventional BHF showed non-uniformity of color, indicating incomplete etching. The cause of incomplete etching is that the contact angle of conventional BHF is more than 70 degrees on a silicon surface, which means it does not have wettability. From these results, it is clearly recognized that the improvement of wettability, i.e., reduction of contact angle is necessary.

Many defects have been caused by the stain residues on the wafer surface after etching in conventional BHF 63 for 5 min, rinsing with DI water for 10 min (flow rate 4.2 l/min), removing the resist with H$_2$SO$_4$ − H$_2$O$_2$ and rinsing with DI water for 10 min (flow rate 4.2 l/min), as shown in the SEM photographs of Fig. 13. A great deal of residue is observed after etching in conventional BHF, but none are observed after etching the surface active BHF.

Roughness of the silicon wafer surface causes difficulties in succeeding processes. Fig. 14 shows the microphotographs of silicon surface smoothness after immer-
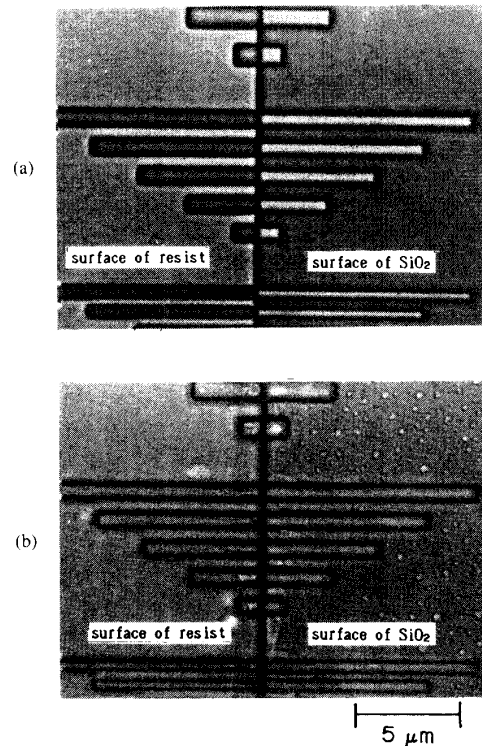

Fig. 11. Residue around patterned edge after etching with BHF and rinsing with DI water. (a) Surface active BHF. (b) Conventional BHF.

TABLE III
THE IMPERFECTION RATIO OF 0.75-μm-LINE PATTERNED BY BHF

BHF	Number of Imperfection (x)	Ratio of Imperfection (%) (y)
Conventional	17	6.7
Surface active	2	0

The imperfection number of line pattern before etching are 2, so ratio of imperfection is derived from

$$y = \frac{x - 2}{225*} \times 100.$$

*225: checked number of line patterns.

sion in surface active BHF 63 and conventional BHF. The wafer surfaces are quite different after immersion in BHF for 92 h at room temperature. The silicon is etched smoothly in surface active BHF, while it is etched nonuniformly in conventional BHF. It is suspected that hydrogen bubbles generated by the reaction of Si and HF adhere on the surface. This produces a non-uniform etch and creates terraces on the surface. These terraces have height differences of several micrometers. It is recognized that these terraces have negative effects on succeeding processes, such as film deposition. In surface active BHF, the hydrogen bubbles are allowed to escape by the surface activity and the silicon is etched smoothly.

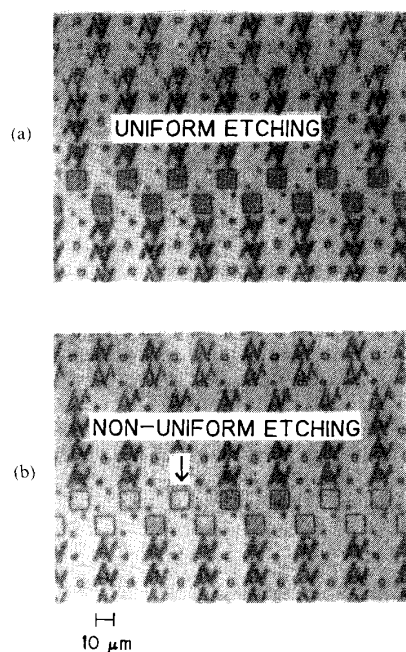Smoothness of a silicon surface drastically degrades

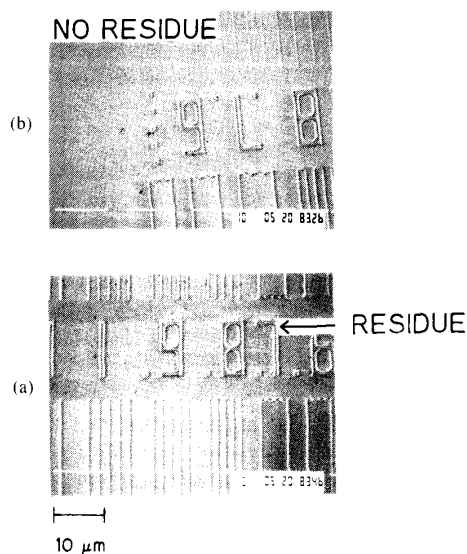Fig. 12. Etching uniformity of 10-μm square holes with BHF 63. (a) Surface active BHF. (b) Conventional BHF.

Fig. 13. Residue on wafer treated with surface active and conventional BHF. (a) Surface active BHF. (b) Conventional BHF.

after etching of SiO_2 in conventional BHF, but complete smoothness of surface is achieved by using surface active BHF.

IV. ETCHING CHARACTERISTICS OF SURFACE ACTIVE BHF

The influence of surfactants on etch rate has been investigated. Fig. 15 shows etch rate dependence on surfactant concentration. It can be seen that the curve shows
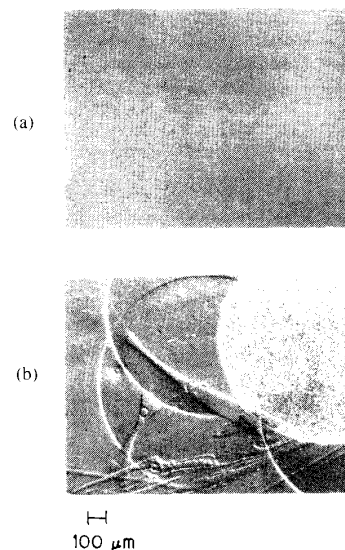

Fig. 14. Microphotographs of silicon wafer surfaces after immersion in surface active BHF and conventional BHF for 92 h. (a) Surface active BHF. (b) Conventional BHF.
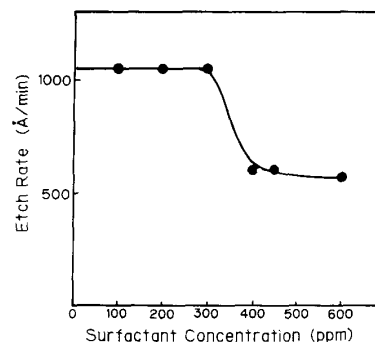

Fig. 15. Etch rate dependence on surfactant concentration (aliphatic amine in BHF 63).

normal etch rates up to 300 ppm; however, it drops drastically at 300 ppm and above. The decrease of etch rate occurs due to covering of the SiO_2 surface with surfactant micells. The surface active BHF exhibits the same etch rate as conventional BHF. It is generally desirable that surfactants do not change the etch rate of BHF. Accordingly, the surfactants in surface active BHF are selected such that the same etch rate as conventional BHF is obtained. At the same time the etch rate of silicon is reduced to one-fourth of that of conventional BHF. Thus etching selectivity of SiO_2 to Si is improved by about 3.6 times, as shown in Table IV.

The etched profiles with conventional BHF and surface active BHF are observed by the following method: a 1.0-μm thick SiO_2 layer is thermally grown and coated with 1.0-μm resist. The patterned resist is baked at 110°C for 10 min. After that, the wafers are etched in conventional BHF 63 and in surface active BHF 63 at 25°C for 3, 6, and 9 min, respectively, rinsed in DI water for 10

TABLE IV
EFFECT OF BHF ADDED SURFACTANTS ON ETCHING SELECTIVITY RATIO

BHF	Etch Rate (A/min)		Selectivity Ratio*
	SiO₂	Si	
Conventional	852	1.14	748
Surface active	862	0.32	2695

$$*\text{Selectivity ratio} = \frac{\text{SiO}_2 \text{ etch rate}}{\text{Si etch rate}}.$$
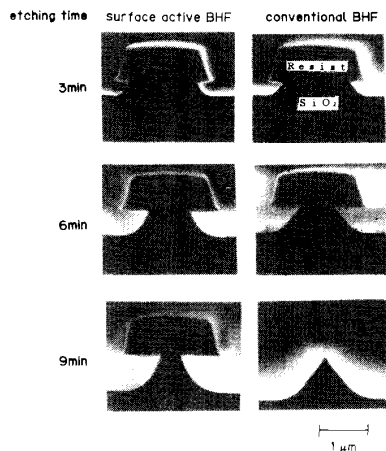
BHF: BHF 63.
Etching temperature: 23°C.

Fig. 16. Etch profiles resulting from etching in conventional and surface active BHF (BHF 63).

min (flow rate 4.2 1/min) and dried with N₂. Fig. 16 shows the cross-sectional view of the etch profiles. Etching in surface active BHF results in isotropic etching much improved over those etched in conventional BHF. Furthermore, it appears that the conventional etch process has two different etch rates. From these results it can be concluded that surface active BHF affords a more controllable etch process.

It is well-known that small amounts of contaminants and etching residue existing in the wafer surface are incorporated into the oxide during conventional high-temperature oxidation and that these contaminants seriously affect the electrical characteristics of the oxide.

We have examined the silicon to SiO₂ interface of thermal oxides grown at the wafer surface after etching native oxide using surface active BHF and diluted HF solution, respectively. The wafer surface without native oxides are oxidized at 1000°C to 500-Å thickness.

The Si to SiO₂ interface is investigated by high-frequency C-V (capacitance voltage) method. The gate area is 4.0×10^{-2} cm² and measurement frequency is 1 MHz.

Fig. 17 shows run to run fluctuations of fixed charge densities for oxide films formed on n-type substrate after diluted HF and surface active BHF etching. It is seen from Fig. 17 that fixed charge densities at each run have been
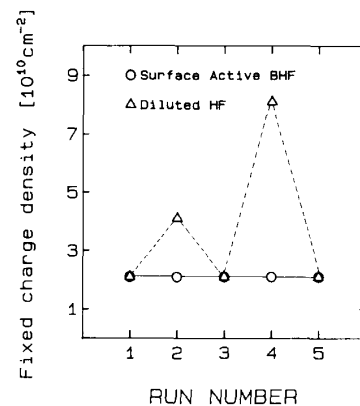

Fig. 17. Run to run fluctuations of fixed charge densities for oxide films formed on n-type substrate after diluted HF and surface active BHF etching.

confirmed to be maintained at 2.0×10^{10} cm⁻² for surface active BHF etching while they have exhibited fluctuations for run to run ranging from 2.0×10^{10} cm⁻² to 8.0×10^{10} cm⁻² for diluted HF etching. This result clearly indicates that there does not remain residue of surfactants such as aliphatic amine, acid and alcohol on the wafer surface. An optimized addition of surfactants to BHF has been demonstrated to improve the MOS (metal oxide semiconductor) capacitor characteristics due to its excellent etching performance such as good surface smoothness.

V. CONCLUSION

By the incorporation of selected hydrocarbon surfactants, a surface active BHF has been tailored to achieve the following requirements: 1) same etch rate as that of conventional BHF; 2) low contact angle; 3) non-segregation; 4) non-foaming; 5) low particulate count; 6) low in impurities (possibility of purification); 7) low particulate adhesion on the wafer surface; 8) no surface residues; 9) excellent surface smoothness; 10) high SiO₂/Si etching selectivity.

In order to satisfy these requirements, surfactants must satisfy following characteristics: 1) good solubility in BHF, 2) hydrophilic property at the wafer surface, 3) non-decomposition in BHF, 4) non-reaction with BHF, 5) sufficient lowering of contact angle at the critical micelle concentration (CMC). Aliphatic amines satisfy these requirements but have foaming problems. Using a binary surfactant system, consisting of a combination of aliphatic amine and aliphatic alcohol or aliphatic acid, the requirements have been achieved.

However, excellent results can be obtained only with careful control of the surfactant concentration. For example, excess surfactant concentration, greater than the CMC, gives high particulate adhesion and stains on the silicon surface.

It is necessary that the surfactants dissolve in BHF at the CMC, in order to realize their maximum effective-

ness. Because of its excellent wettability on the silicon wafer, surface active BHF improves etching of high-aspect ratio contact via holes. Moreover, it has been demonstrated that low particulate adhesion on the wafer surface, high etching selectivity and high surface smoothness of the silicon surface after etching can be achieved with these surfactants. Moreover, it has been demonstrated that the surface active BHF contributes to a decrease of run to run fluctuations of the fixed charge density.

The surface active BHF is also effective in the removal of particles from liquid chemicals during recirculating-filtration. Thus, the life span of liquid chemicals is extended up to the life time determined by an increase of reaction products.

ACKNOWLEDGMENT

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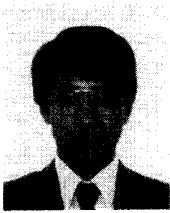
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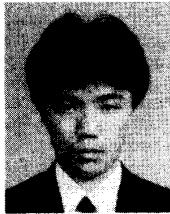
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