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Scanning Tunneling Microscopy (STM)/Atomic Force Microscopy (AFM) Studies of Silicon Surfaces Treated in Alkaline Solutions of Interest to Semiconductor Processing

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ABSTRACT

Alkaline solutions such as NH_4OH, choline and TMAH ($(CH_3)_4NOH$) have been introduced in semiconductor wet processing of silicon wafers to control ionic and particulate impurities following etching in acidic solutions. These chemicals usually mixed with hydrogen peroxide and/or surfactants to control the etch rate of silicon. The highest etch rate was observed in NH_4OH solutions at a pH in alkaline solutions. It indicates that the etch rate depends on the content of OH^- as well as cations of alkaline solutions. STM/AFM techniques were used to characterize the effect of alkaline solutions on silicon surface roughness. In SC1 (mixture of $NH_4OH : H_2O_2 : H_2O$) solutions, the reduction of the ammonium hydroxide proportion from 1 to 0.1 decreased the surface roughness (R_{rms}) from 6.4 to 0.8Å. The addition of H_2O_2 and surfactants to choline and TMAH reduced the values of R_{p-v} and R_{rms} significantly. H_2O_2 and surfactants added in alkaline solutions passivate bare silicon surfaces by the oxidation and adsorption, respectively. The passivation of surfaces in alkaline solutions resulted in lower etch rate of silicon thereby provided smoother surfaces.

1. Introduction

Wet chemical cleaning of silicon wafers is widely practiced in the semiconductor industry to remove particulate, metallic and organic contaminants. The commonly used RCA standard cleaning processes are based on acidic or alkaline hydrogen peroxide solutions[1]. The alkaline RCA cleaning solution, referred to SC1, is based on ammonium hydroxide, hydrogen peroxide and water at a ratio of 1 : 1 : 5. It is primarily designed to remove organic contaminants from the wafer surface. The SC1 solution, due to the presence of NH_4OH, is capable of etching silicon at a rate of 0.11μm/min at 85～92℃[2]. The hydrogen peroxide helps to passivate the silicon surface. Mishima et al.,[3] working with polystyrene and silica particles, reported that an $NH_4OH-H_2O_2$ solution of the standard ratio (1:1:5, $NH_4OH : H_2O_2 : H_2O$) increased the haze formation on the wafers and decreased the particle removal efficiency as compared to solutions of lower NH_4OH content such as 0.1 : 1 : 5. There is an increasing trend towards the use of solu-

tions containing significantly smaller quantities of NH_4OH.

Quaternary ammonium hydroxides (QAH) such as choline ($[(CH_3)_3N^+CH_2CH_2OH]OH^-$) and tetramethyl ammonium hydroxide (TMAH) have been tried in place of SC1 for wafer cleaning. Choline ($pK_b=0.1$, where $pK_b=-\log K_b$, and K_b is the dissociation constant of a base) and TMAH ($pK_b \approx 0$) are much stronger bases than NH_4OH ($pK_b=4.7$). They are also typically free from alkali metals. Cleaning sequences involving choline have shown better removal of particles[4] and heavy metals, and result in lower number of oxidation induced stacking faults (OISF) after HF treatment[5]. Even though choline etches silicon, the etch rate can be controlled by adding nonionic surfactants. The addition of hydrogen peroxide can be used to minimize the etch rate.

Electronic grade TMAH was introduced[6-7] in the 80's to clean silicon wafers and develop resist films in the process for manufacturing semiconductor devices. Dilute aqueous TMAH solutions, with and without selected surfactants, can be used for removing organics, heavy metals and particles from silicon wafers. At a temperature of near 70℃, TMAH shows better cleaning capability and etches silicon at rates ranging from 180Å/min at 0.077%. TMAH can also be added to a SC1 mixture (1 : 1 : 3 : 20 TMAH : NH_4OH : H_2O_2 : H_2O) for particle and metal ion removal.

STM (scanning tunneling microscopy)/AFM (atomic force microscopy) techniques have been widely applied to semiconductor processing to observe the change of surfaces to the atomic level. As the integration of the device increases, the careful control of microroughness of silicon surfaces after the pre-gate oxide cleanup becomes critical owing to the integrity of the oxide. Even though there are studies on the effect of SC1 solutions on silicon surface roughness, there is no study of choline and TMAH. In this study, STM/AFM techniques were used to investigate and compare the effect of alkaline solutions on silicon surface roughness.

2. Experimental Materials and Procedures

2. 1. Materials

P-type silicon wafers (150mm in diameter) with the resistivities of 10 to 80 MΩ·cm were used for the experiments. Choline was purchased from Sigma Chemical Co. as a 50% solution. Aliquots of this solution were appropriately diluted with 18 MΩ·cm DI (deionized) water to prepare choline solutions for experiments. Reagent grade TMAH was purchased from Aldrich Chemical Co. as a 10% solution. Aliquots of this solution were diluted with DI water to prepare TMAH solutions. Electronic grade NH_4OH (28% as NH_3) and H_2O_2 (30%) reagents were used to make appropriate compositions of SC1 solutions. Semiconductor grade H_2SO_4 (98%) and 5 : 1 BOE (buffered oxide etch, etch rate : 1000Å/min) were also used in the experiments. High purity non-ionic surfactant (NCW 601A, polyoxyalkylene alkylphenyl ether) was provided by WAKO Chemical Co. as a 30% solution.

2. 2. Experimental Procedures

Wafers were cut with a diamond saw into 13 mm×19mm size samples in a class 100 cleanroom. Immediately after cutting, samples were spin-rinse cleaned with DI water to remove silicon

particles produced during cutting. Samples were transferred to a class 10 cleanroom for further chemical cleaning. Piranha (8 : 2 ratio of H_2SO_4 : H_2O_2) etch was performed for 10min followed by a DI water rinse for 5min. Wafers were cleaned by etching in 5 : 1 BOE for 30 sec and then rinsing in DI water for 30 sec. The samples were subsequently dried using dry nitrogen gas.

The etch rate of silicon in various alkaline solutions was measured by analyzing the silicon concentrations in alkaline solutions using a Jarrell-Ash 800 Inductively Coupled Plasma Spectrometer (ICP). P-type (100) wafers were immersed in 20 ml of ammonium hydroxide, choline and TMAH solutions for 3 hrs. The concentration of silicon in solutions was measured in ppm. The concentration of silicon was converted into total dissolved weight of silicon, and then density of silicon was used to calculate the etched thickness of silicon using following equations assuming $\rho_{solution}$ is 1 :

$$\text{m, grams} = (\text{C, ppm}/10^6) \times \text{V, ml} \quad \text{------} \ (1)$$

$$\text{and t, cm} = \text{m}/(\rho_{si} \times \text{A}) \quad \text{--------------------} \ (2)$$

where, m is the amount dissolved in solutions in grams, C is the silicon concentration measured in ppm, V is the volume of solution, ρ_{si} is the density of silicon (2.33 g/cm^3), A is the total area of silicon sample (5.2642cm^2), and t is the thickness of silicon etched in solutions.

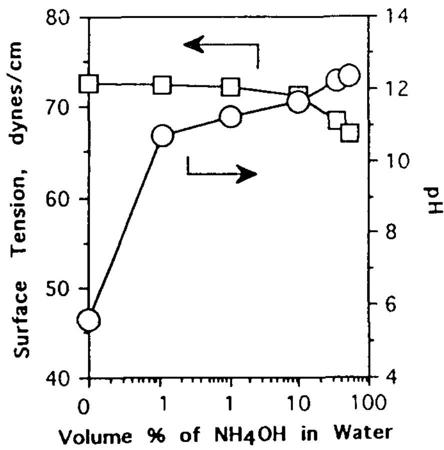
The roughness of silicon surfaces was observed and measured with a Digital Nanoscope II. Approximately 1cm^2 pieces were cleaved from the center of each of the samples and degreased in acetone and methanol followed by nitrogen blow-dry. For obtaining STM images, the native oxide on the samples surface was removed either by dipping samples in 49% HF for 10 sec or by leaving samples under 0.05 wt% HF solution during imaging. AFM images were obtained by scanning the surface with a Si_3N_4 tip without removing the native oxide. The root-mean-square surface roughness (R_{rms}) and peak-valley roughness (R_{p-v}) of samples were measured within the regions investigated. The surface tensions of alkaline solutions were measured using Cahn DCA312 dynamic contact angle analyzer.

3. Results and Discussion

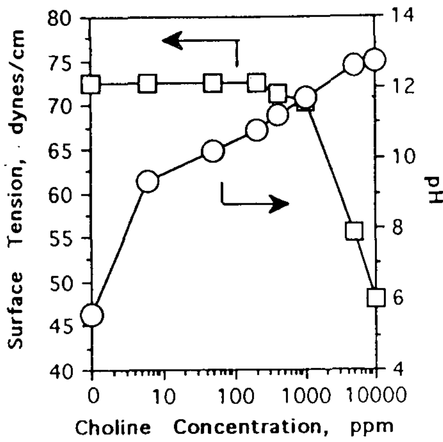
3.1. Characterization of Chemicals

The pH and surface tensions of choline, TMAH and ammonium hydroxide solutions were measured as a function of the solution concentration at 25℃ as shown in Figure 1. The rapid change in pH was observed even in small addition of alkaline chemicals to DI water. After the rapid increase, pH continued to increase but less rapidly due to the gradual saturation of OH^- in DI water. The surface tension of choline showed somewhat different changes when compared with other chemicals. It became surface active at a concentration of 400 ppm and reached 47.6 dynes/cm at 10000 ppm (1 wt%). Other chemicals showed the slight changes of the surface tension over the concentration ranges investigated.

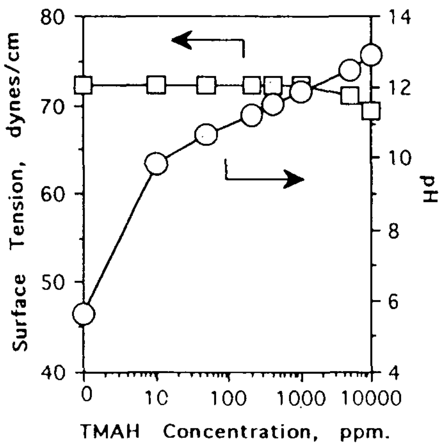
The alkaline solutions used in this study are capable of etching silicon. In order to characterize the etching capability of these solutions, the etch rate of p(100) samples was calculated by measuring the amount of dissolved silicon in solutions using ICP atomic emission spectroscopy. Figure 2 (a) and (b) show the etch rate of p (100) bare silicon in alkaline solutions at room



(a)

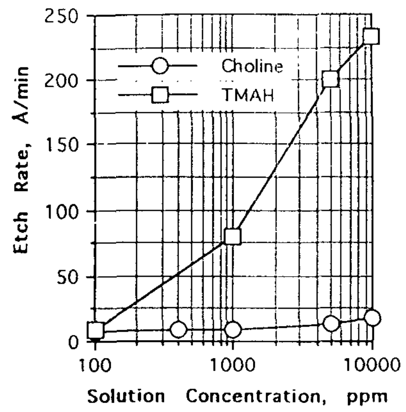


(b)

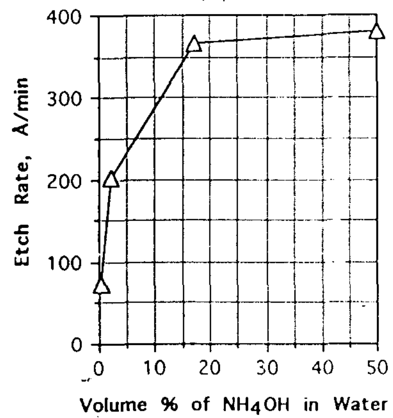


(c)

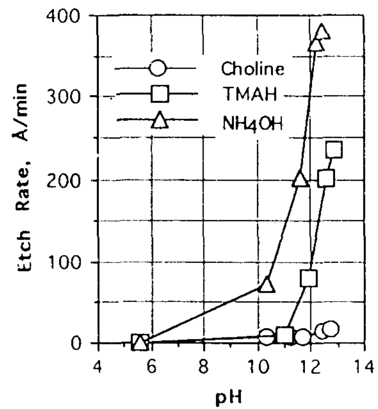
Fig. 1. pH and surface tensions of (a) ammonia, (b) choline, and (c) TMAH solutions as a function of concentrations.



(a)



(b)



(c)

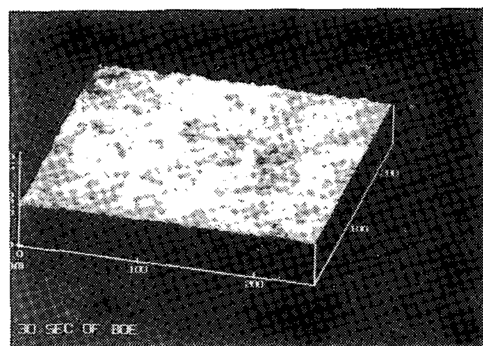
Fig. 2. Etch rates of p (100) silicon wafer in alkaline solutions at 25℃, (a) choline and TMAH and (b) 1 : 5 NH_4OH : H_2O solutions as a function of their concentrations. (c) Etch rates of p (100) silicon wafer in choline, TMAH, and 1 : 5 NH_4OH : H_2O solutions as a function of pH at 25℃.

temperature. The etch rate of silicon was measured to be 18 Å/min and 234 Å/min in 10000 ppm choline and TMAH solution, respectively. The etch rate of silicon in TMAH solutions depended strongly on the concentration of TMAH. When the concentration of TMAH was decreased to 100 ppm, an etch rate of 8.8 Å/min was measured. A 1 : 5 $NH_4OH : H_2O$ (17 vol.%) solution was found to etch silicon at a rate of 367 Å/min. When the ammonia volume ratio was decreased to 0.01 in water, the etch rate was still high (73 Å/min). The etch rate of the SiO_2 coated wafer was measured to be <0.1 Å/min in these alkaline solutions.

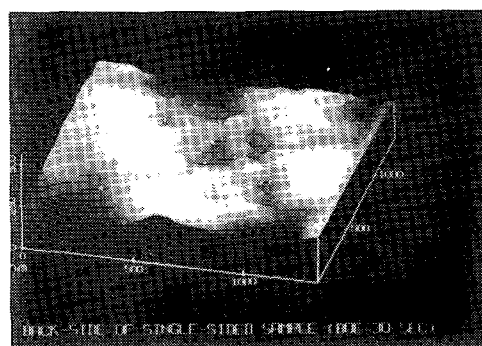
Considering pK_b values of alkaline chemicals, it was expected that TMAH ($pK_b \approx 0$) and choline ($pK_b = 0.1$) would have higher etch rates than ammonia solutions ($pK_b = 4.7$). However, as shown in Figure 2(c), the highest etch rate was measured in ammonia solutions at a given pH. This shows that OH^- actually is not the only factor controlling the etch rate[8], but perhaps the cations of the different alkalis play an important role in etching. The cation of the surface active choline, which has the longest chain length among alkaline solutions investigated, may be adsorbed on the silicon surface, thereby reduces the etch rate significantly. Also the oxidation of silicon in choline solutions[9] might reduce the etch rate.

3. 2. STM/AFM Studies

STM/AFM techniques were used to observe the effect of alkaline solutions on surface roughness. Figure 3(a) and (b) show STM and AFM micrographs of polished and unpolished surfaces of p(100) wafers after a 30 sec BOE etch. The



(a)



(b)

Fig. 3. (a) STM micrograph on polished and (b) AFM micrograph on unpolished p (100) wafer after 30 sec BOE etch.

unpolished surface is 500∼600 times as rough as the polished side (1250 Å peak-valley). The R_{p-v} and R_{rms} values for the surface roughness present on the polished surface were 2.0 and 0.2 Å, respectively.

Due to the high etch rate of NH_4OH solutions at the concentrations used in semiconductor processes, SC1 solution, i.e. NH_4OH mixed with H_2O_2 was used for the STM/AFM studies. Figure 4(a) and (b) show STM micrographs of surfaces treated with 0.1 : 1 : 5 and 1 : 1 : 5 SC1 solutions for 10 min. These samples were HF (49 %) etched for 10 sec prior to measurement to make the surface conductive. Within the area

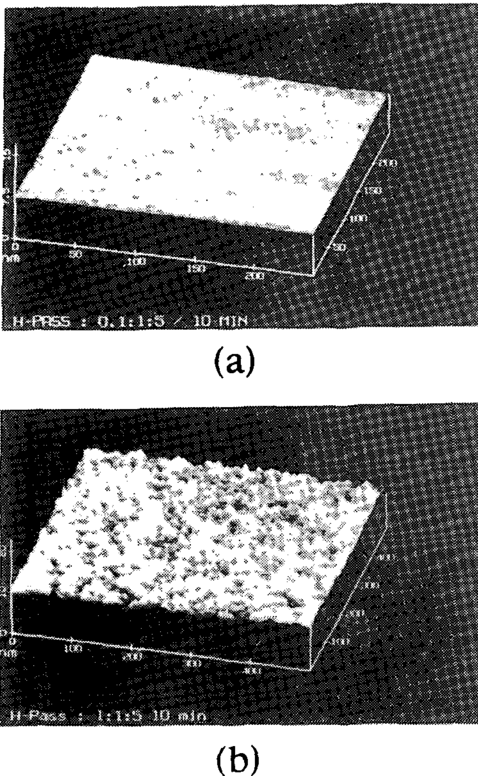


Fig. 4. The STM micrographs of (a) 0.1 : 1 : 5 and (b) 1 : 1 : 5 SC1 treated samples (500× 500nm scanning area).

investigated, R_{rms} increased with NH_4OH concentration for the two SC1-treated-samples. In SC1 solutions, the reduction of the ammonium hydroxide proportion from 1 to 0.1 decreased the surface roughness (R_{rms}) from 6.4 to 0.8Å. A flat and featureless surface was observed for the 0.1 : 1 : 5 sample. The roughness changes at different ratios of NH_4OH indicate that a lower proportion of ammonia in SC1 is favorable for a smoother surface. Table 1 shows a summary of the roughnesses measured by STM /AFM.

Hydrogen peroxide and a non-ionic surfactant (NCW 601A) were added to 5000 ppm choline solutions to observe the effect of these

Table 1. The roughness of silicon surfaces treated with various alkaline solutions by STM/AFM

p(100)Silicon Wafers	R_{p-v}(Å)	R_{rms}(Å)
BOE etched for 30 sec, polished side	2.0	0.2
BOE etched for 30 sec, back side(unpolished)	1250	–
SC1 0.1 : 1 : 5, NH_4OH : H_2O_2 : H_2O	7.9	0.8
SC1 1 : 1 : 5, NH_4OH : H_2O_2 : H_2O	52.3	6.4

chemicals on surface roughness. Figure 5 shows samples treated with 5000 ppm choline with and without addition of H_2O_2 and surfactant. In plain choline solutions, the silicon surface was rendered rough with R_{p-v} and R_{rms} values of 180.9Å and 22.4Å, respectively.

The addition of 200 ppm H_2O_2 to choline reduced the values of R_{p-v} and R_{rms} to 48.6 and 6.4 Å, respectively. Increasing the H_2O_2 addition to 1 wt% reduced the surface roughness further. Also, when 200 ppm of the non-ionic surfactant (the critical micelle concentration, the threshold concentration at which micellization begins, was measured to be 100 ppm) was added to the choline solution, the surface roughness was similar to that of a sample treated with a 200 ppm H_2O_2 solution. Table 2 summarizes the roughnesses of these samples.

The etch rate of TMAH solutions is much greater than that of choline at equivalent concentrations. Even in the 600 ppm TMAH solution, the R_{p-v} and R_{rms} values were measured to be 832.2 and 123.3Å, respectively, which were much higher than values measured in the 1 wt % (10000 ppm) choline solution. Adding H_2O_2 to TMAH significantly decreased the surface roughness. The addition of 200 ppm H_2O_2 to

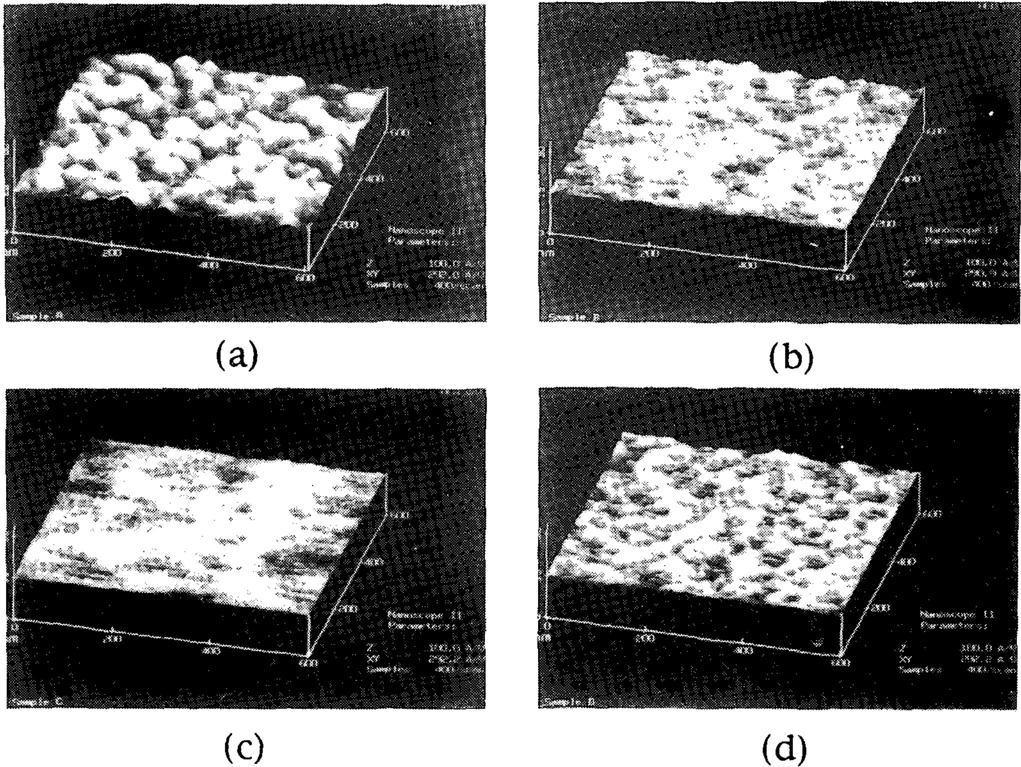


Fig. 5. AFM micrographs of 5000 ppm choline treated silicon samples for 10 min. (a) without the addition of H_2O_2 and surfactants, (b) with the addition of 200ppm H_2O, (c) with the addition of 1wt% (10000ppm) H_2O_2, and (d) with the addition of 200 ppm non-ionic surfactant.

Table 2. The roughness of samples treated in 5000 ppm choline for 10 min with and without the addition of H_2O_2 and non-ionic surfactant

Samples treated in	R_{p-v}(Å)	R_{rms}(Å)
5000 ppm choline	180.9	22.4
5000 ppm choline with 200 ppm H_2O_2	48.6	6.4
5000 pm choline with 1 wt% (1000 ppm) H_2O_2	32.8	4.2
5000 ppm choline with 200 ppm non-ionic surfactant	40.1	5.6

TMAH provided a smoother surface than the addition of 200 ppm non-ionic surfactant. Figure 6 shows samples treated with 600 ppm TMAH solutions with and without the addition of H_2O_2 and surfactant. Table 3 summarizes the roughness of these TMAH-treated samples.

The addition of even 200 ppm H_2O_2 and surfactants to alkaline solutions decreased the etch rate significantly[2,4]. Hydrogen peroxide which is a strong oxidizer, passivates the hydrophobic silicon surface into the hydrophilic surface by growing a very thin chemical oxide (~10Å). The passivated surface prevents the silicon from being etched by alkaline ions. In contrast, surfactants have longer nonpolar organic tails than 10 carbon layers[10]. They tend to adsorb on the silicon surface at the air-liquid interface. The hydrophilic carbon tails not only passivate the surface but also disturb the etching actions

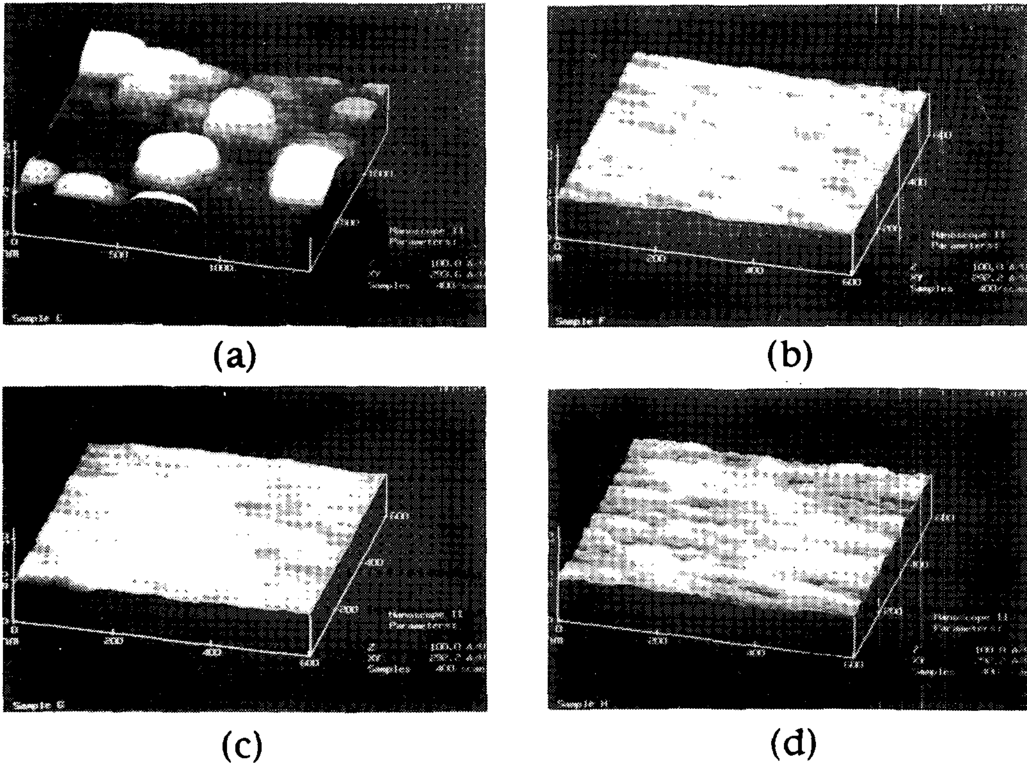


Fig. 6. AFM micrographs of 600 ppm TMAH treated silicon samples for 10 min. (a) without the addition of H_2O_2 and surfactants, (b) with the addition of 200ppm H_2O_2, (c) with the addition of 1wt% (10000 ppm) H_2O_2, and (d) with the addition of 200 ppm nonionic surfactant.

Table 3. The roughness of samples treated in 600 ppm TMAH for 10 min with and without the addition of H_2O_2 and non-ionic surfactant

Samples treated in	R_{p-v}(Å)	R_{rms}(Å)
600 ppm TMAH	832.2	123.3
600 ppm TMAH with 200 ppm H_2O_2	14.3	1.8
600 ppm TMAH with 1 wt% (1000 ppm) H_2O_2	13.5	1.8
600 ppm TMAH with 200 ppm non-ionic surfactant	20.1	2.8

by alkaline ions. As noticed in etch rate measurements of choline solutions, choline acts like a surfactant at a concentrations higher than 400 ppm. Without the addition of H_2O_2 or surfactants a very smooth surface (R_{rms}=22.4 Å) was obtained when etched in 5000 ppm choline for 10 min.

4. Summary and Conclusions

1) Choline appears to become surface active at the liquid-air interface at a solution concentration of approximately 400 ppm. The addition of 10000 ppm choline decreased the surface tension of water to 47.6 dynes/cm. In contrast, the surface tensions of ammonia and TMAH solutions decreased only slightly as the concentration of solutions was increased. Rapid increases of pH were observed in a small addition of all

alkaline chemicals in DI water.

2) The highest etch rate was observed in ammonia solutions at a given pH value. This indicates that the etch rate depends not only the content of OH^- ions but also the cations of alkaline solutions.

3) Without the addition of H_2O_2 and surfactant, silicon etched in choline solutions resulted in the smoothest surface. This might be related to the surface modification by choline cations such as oxidation and adsorption.

4) The even small addition of H_2O_2 and surfactant to alkaline solutions decreased the etch rate significantly and provided much smoother surfaces when silicon was treated in solutions. This was attributed to the passivation of surfaces by H_2O_2 and surfactant.

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