

A REVIEW OF ADVANCED WET CLEANING

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Abstract: In order to manufacture ultralarge scale integrated devices with high performances and reliability in large volume the wafer surface must be kept ultraclean all the time. At present the only suitable method is wet cleaning. Advanced wet cleaning methods were developed from standard RCA cleaning based on hydrogen peroxide mixtures. New efforts were concentrated to prevent silicon surface etching during RCA cleaning, and to prevent hydrophobic Si surface contamination in diluted HF or buffered HF solutions and/or during subsequent DI water rinsing. In this article a review of the latest results in improved wet chemical cleaning is presented.

Pregled sodobnih postopkov mokrega čiščenja silicijevih rezin

Ključne besede: polprevodniki, vezja integrirana, proizvodnja množična, zagotavljanje kakovosti, stopnja integracije ultravisoka, rezine silicijeve, površine rezine, mikrohrapavost površine, kontaminacija s kovinami, kontaminacija z delci, ultra čistost površine, čiščenje mokro, RCA metoda čiščenja, pregled literature

Povzetek: Za masovno izdelavo kvalitetnih in zanesljivih integriranih vezij z ultravisoko stopnjo integracije je potrebno doseči dobro kontrolirano proizvodnjo. Zato je ključnega pomena skrajna čistost površine rezine. Trenutno je edina primerna metoda, ki omogoča ustrezno čiščenje, mokro kemijsko čiščenje. Izpopolnjene metode temelje na standardni metodi RCA, ki imajo za osnovo kisle in bazične raztopine vodikovega peroksida. V zadnjem času so naporji usmerjeni proti preprečitvi jedkanja površine v peroksidni raztopini amonijevega hidroksida in preprečitvi kontaminacije hidrofbne površine Si rezine med jedkanjem v razredčenem HF, oz. pufrskem jedkalu, in med poznejšim izpiranjem v vodi. Članek podaja pregled najnovejših dosežkov na področju izpopolnjenega čiščenja silicijevih rezin.

Introduction

The importance of clean Si substrate surface in the fabrication of semiconductor devices has been recognized since the early days of semiconductor manufacturing in the 1950s. As the requirements for improved device performances and reliability in the era of VLSI and ULSI technologies have become more and more stringent, methods to avoid contamination and processes to generate ultraclean surfaces have become critically important. Now it is generally accepted that over 50% of yield losses in modern IC fabrication is due to the microcontamination. Especially detrimental effect have metal impurities if present on the wafer surface; during high temperature processing they might diffuse into the wafer interior. Another problem are the organic contaminants and native oxide that can prevent selective epitaxy. Therefore, microcontamination must be minimized before every high temperature step (oxidation, diffusion, epitaxy). Similarly, contaminants (especially particles) must be removed from the surface before and/or after low temperature steps (CVD, dopant implantation, plasma processes). Last but not least, wafers must be postcleaned after photoresist stripping at every mask level.

Throughout the history of the semiconductor manufacturing many wafer cleaning techniques have been developed and been used. But the wet process is still

employed to clean the Si wafer due to its remarkable characteristics: it causes no damages on the wafer and it is effective at low temperature. Foundations of the modern wet cleaning were established by W. Kern et al. in 1965 in RCA and published in 1970, Ref. /1/. The original two step cleaning process did remain basically unchanged for more than 25 years.

The state of the Si surface in modern technologies with critical dimensions reduced to the submicron and even sub-half micron level is becoming far more important than in the 1970s. With the introduction of Total Reflection X-Ray Fluorescence Spectroscopy (TRXRF) for the surface contamination analysis, Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) for the surface microroughness determination, new standards for the state of the silicon surface have been established. Besides cleanliness of the surface, microroughness becomes increasingly important factor in the 1990s.

Wet cleaning procedure

During the early stage of semiconductor manufacturing (until the 1970s), the Si wafer cleaning was based on the organic solvent extraction, boiling nitric acid, aqua regia, concentrated hydrofluoric acid and mixtures of sulfuric-chromic acid. All of the methods mentioned had

some problems, such as contamination with chromium or waste disposal in the case of the sulfuric-chromic acid mixture. Generally speaking the chemicals had high level of impurities and particles and so tended to contaminate the surface of the wafer. Particles from the wafer surface were removed by ultrasonic treatment in detergent solution or by brush scrubbing. Malfunction of these methods can cause serious problems.

Successful immersion wet cleaning of the wafer surface consists of three basic steps:

- removal of organic contaminants
- oxide removal
- removal of alkaline and metal contaminants.

Two different approaches have been adopted:

a) RCA process mentioned in the introduction with so called oxide terminated silicon surface,

b) dilute HF cleaning process with hydrogen terminated silicon surface.

Both approaches have pros and cons. RCA cleaning is relatively complicated (3 different solutions, instability of the solution due to decomposition of H_2O_2 at elevated temperatures, problems of cross contamination, Si surface etching, Ref. /2/) but yields the Si surface passivated with 1.5 nm of relatively clean native oxide. On the other hand, the dilute HF cleaning is relatively simple and generates chemically cleaner bare silicon surface. Unfortunately this clean hydrophobic surface can be easily contaminated with particles and organic material from rinsing DI water /3,4/. It was reported in Ref. /6/ that the organic contamination can carbonize at high temperatures in nonoxidizing atmosphere and form β -SiC that can start polycrystalline growth during epitaxial deposition. Even contamination with phosphorous from DI water with about 100 ppb of TOC were reported, Ref. /4,5/.

RCA cleaning

Original RCA process for bare and oxidized silicon wafers was based on a two step oxidizing and complexing treatment in hydrogen peroxide solutions:

The first process step was designed to remove organic surface film by oxidative breakdown and dissolution in hot mixture of water diluted ammonium hydroxide and peroxide (10 min, 5:1:1 $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$, 75-80°C, known as SC-1 or APM). During this step, group IB and IIB metals as well as heavy metals Au, Ag, Cu, Ni, Cd, Zn, Co and Cr are dissolved and removed by complexing by ammonium hydroxide; so called amino complexes are formed ($\text{Cu}(\text{NH}_3)_4^{+2}$ in case of copper).

In the second step the rinsed wafers are exposed to a mixture of hot water diluted hydrogen peroxide and

hydrochloric acid (10 min, 6:1:1 $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$, 75-80°C, known as SC-2 or HPM). During this step the alkali ions and cations such as Al^{3+} , Fe^{+3} and Mg^{+2} that in NH_4OH form insoluble hydroxides are removed. The second step is also designed to eliminate all metallic contaminants that were not entirely removed during the first alkaline cleaning step.

After the introduction in the 1970s the original scheme have been modified. Optional sulfuric-hydrogen peroxide (10 min, 2:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$, 100-130°C known as SPM) mixture as a first step to remove gross organic contaminants was introduced. The contaminated hydrous oxide formed during APM cleaning can be removed during another optional step by etching off in diluted or buffered HF (DHF, BHF) before HPM treatment. However, unless ultra pure and particles free point-of-use ultrafiltrated HF is used, more harm than good can be done. Highly reactive HF treated Si surface can be easily contaminated with organic contaminants and particles from HF solution, DI water and air. Contrary to the APM solution, HPM does not eliminate these contaminants. If the preclean is used, than DHF step can not be harmful, since APM removes all the contaminants. On the other hand, the level of contamination in APM can be significantly reduced using ultra pure peroxide with low Al and stabilizer content. Bare silicon wafers after HPM treatment should not be exposed to DHF, since the clean passivated surface would be destroyed, and could easily be recontaminated.

Original immersion technique using fused silica beakers and overflowing quenching with DI water to terminate the reaction have been changed during the years to more refined automated wet bench immersion systems (for instance Ref. /7/). There are also tendencies to change the original immersion technique to centrifugal spray cleaning /8/, megasonic cleaning /9,10/, closed system chemical cleaning /11/, and dry (vapor) wafer cleaning /12/.

Literature survey

From the 1972, when Henderson /6/ published that HF cleaning after HPM can produce roughening and carbon contamination of the surface during vacuum heating, up to now many independent articles verifying the effectiveness of RCA cleaning have been published. For instance Meek et al. /13/ showed that APM/HPM cleaning is much more effective removing Cu and Ca as HF-HNO_3 . Gluck /14/ reported in 1978 that desorption efficiency of APM for gold is better than efficiency of HPM, but the sequential treatment APM+HPM is the most effective method to remove gold in high (10^{14} at/cm³) concentration. In 1983 Phillips et al. /15/ compared the efficiency of various aggressive reagents including aqua regia, hot fuming HNO_3 , $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$, APM and HPM. The most effective procedure to clean with inorganic materials purposely contaminated wafers was SPM followed by APM/DHF/HPM sequence. Their results were confirmed

in 1986 by Becker et al in Ref. /16/. It was also shown that the reversed sequence DHF/APM/HPM is far more effective for particle removal but slightly less for metal ion removal as the original one.

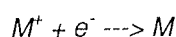
RCA cleaning generates very clean surfaces as long as very clean chemicals are used. It was reported /17,18/ that high Al contamination found on the wafer surfaces after APM and five times less after HPM clean, originated from even sub ppm contaminated hydrogen peroxide. In 1989 Morota et al. /19,20/ postulated the most appropriate model for contamination of the silicon surface during cleaning in APM, HPM and DHF solutions. The absence or presence of the SiO₂ film on the surface affects adsorption of metals. Desorption of Al and Fe was most effective with DHF, and desorption of Cu and Cr with HPM. Metals with high enthalpy of oxide formation adsorb on oxidized Si surface by oxide formation (Al, Cr, Fe), whereas metals with high electronegativity (Au, Pt, Ag) deposit electrochemically onto the bare Si surface. Tables I and II represent tendencies of metals to precipitate directly onto the silicon (I) and to form oxide (II).

Particle removal efficiency was studied by many authors. They all agree that reversed sequence HF/APM/HPM generate the cleanest surface, Ref. /3,4,16,21/. Later Ohmi et al. /22/ showed that 1:1:5 APM efficiently removes particles larger than 0.5 µm, but increases the number of smaller ones, measured as a haze, and latter recognized as surface etching. APM solution with lower NH₄OH concentration effectively removes all particles, Ref. /22/.

Negative aspects of RCA cleaning are etching of the silicon surface in alkaline solution APM. Up to the end of 1980s measurements did not reveal any attacking of the

Table I

Electronegativity of metals according to Ref. /30/.

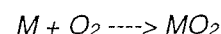


Element	Electron Negativity (Pauling)	Half-Cell Reduction Potential V	-
Au	2.4	1.68	↑↑
Pt	2.2	1.19	
Ag	1.9	0.80	
Hg	1.9	0.79	
Cu	1.9	0.34	
Si	1.8	0.10	Tendency to be precipitated on bare Si
Pb	1.8	-0.13	
Sn	1.8	-0.14	
Ni	1.8	-0.23	
Fe	1.8	-0.41	
Zn	1.6	-0.76	

Al	1.5	-1.66	
Mg	1.2	-2.34	
Ca	1.0	-2.87	
Na	0.9	-2.71	
K	0.8	-2.92	

Table II

Enthalpy of oxide formation according to Ref. /30/.



ΔH < 0, (Heat Releasing Process)

Oxide	ΔH ₂₅ ²⁹³ /kJ/mol/	-
Al ₂ O ₃	-1675	↑↑
Cr ₂ O ₃	-1130	
CrO ₂	-583	
CrO ₃	-580	
Fe ₃ O ₄	-1118	
Fe ₂ O ₃	-822	Tendency to be included into oxide film
SiO ₂	-909	
NiO	-241	
CuO	-155	

silicon surface as long as the hydrogen peroxide concentration was not depleted to less than 75% of the original recommended concentration, Ref. /4/. However, severe silicon surface roughening was reported in Ref. /24/ for cleaning in water diluted NH₄OH, less severe for BHF and none for APM. On the other hand, it was reported that APM (80°C, 5:1:1) solution slightly etch the SiO₂ and Si₃N₄ films. Measured etch rates were from 0.13 /4/ to 0.4 nm/min /25/ for thermal SiO₂ film, and 0.09 /4/ to 0.2 nm/min /25/ for CVD deposited Si₃N₄ film.

Extensive work of Grundner et al. /26,27/ showed that the hydrophobic silicon surface state after the DHF dip is due to Si-H, some Si-CH_x and Si-F groups, while hydrophilicity is caused by Si-OH groups. It was also shown that the contact angle of a water droplet is in good correlation with the silicon surface status. Typically, for the hydrophobic surface the angle is higher than 80, whereas for the hydrophilic one is less than 20. Generally, the higher is the contact angle after cleaning, the better is quality of the thermally grown oxide.

Present understanding of Si surface cleaning

Any effective cleaning must leave undamaged, smooth, ultraclean Si surface completely free from particles, organic materials, metallic impurities, adsorbed molecule impurities and native oxide. The very first step of any wafer cleaning must be the removal of organic

surface contamination preventing full exposure of the surface to the action of subsequent cleaning. This is mostly done by SPM and partially by APM cleaning. Control of the first technique is quite poor due to high temperature of the mixture and its composition instability. In beginning of the 1990s the new, low temperature Ozone-Injected Ultrapure Water techniques have been developed, Ref. /36/.

It is expected that it will replace the old SPM solutions due to high organic impurity removal efficiency, better controllability of the process and less chemical waste.

Removal of metallic impurities

Metallic impurities on the wafer surface can cause irreversible damage on semiconductor devices such as increase of p/n junction leakage current, poor dielectric breakdown voltage, and a decrease of carrier lifetime. Results from Figs. 1 a and b show that for the modern sub and sub-half micron ULSI devices the contamination of the silicon surface should be kept below 10^{11} at/cm². Def. Density and Life Time vs. Surf. Contamination

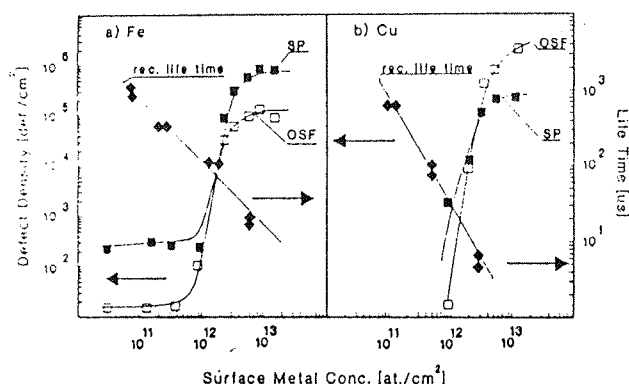


Figure 1: Dependence of the surface defects (saucer pits: SP, oxidation stacking faults: OSF), and the recombination carrier lifetime on the surface metal concentration after the two step annealing ($1150^{\circ}\text{C}/1\text{h N}_2 + 1000^{\circ}\text{C}/16\text{h O}_2$); (a)-Cu and (b)-Fe, Ref. /28/.

in order to prevent these damages, Ref. /28/. Such a low surface concentration can be assured only with ultra clean chemicals (contamination below 10 ppb), as shows Fig.2. This limit is significantly lower than it was obtained at the end of 1980s. Concentration of typical unwanted metals (most frequent are Fe, Al and Ca) in native oxide for the commercially available wafers was measured in the range between 10^{11} to 10^{13} at/cm², Ref. /29/. In the same range was the contamination measured after plasma etching and ion implantation /37/. APM step of the conventional RCA cleaning can hardly reduce the contamination to the values below 10^{11} at/cm². The reason for this is the tendency of Al, Cr and Fe to form oxides (Table II) on the silicon surface during APM cleaning. The tendency for contamination is directly related to the cleanliness of the APM (especially hydrogen peroxide) chemicals. As shows Fig.3, Ref. /31/, subsequent HPM treatment reduces the unaccept-

Surface Metal Conc. vs. Ion Conc.

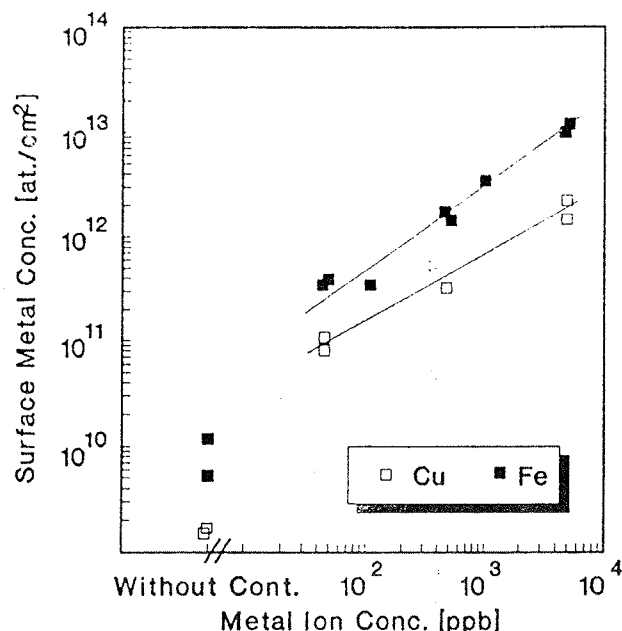


Figure 2: Relationship between the surface metal concentration measured by ASS and metal concentration in the contaminated solution. Ref. /28/.

able high iron level to below XRTRF detection limit 3×10^{10} at/cm². Anyway, the most effective way to keep the contamination as low as possible is to use ultra pure chemicals and/or to remove the contaminated thin oxide by the controversial etching in water diluted HF.

Highly electronegative metal ions (Cu...) are directly adsorbed onto the Si surface (Table II). They can be only partially removed by HPM step of RCA cleaning which

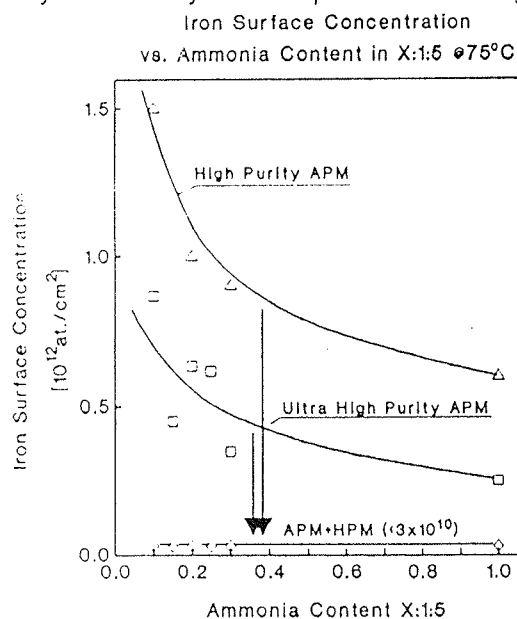


Figure 3: Iron surface concentration measured after APM cleaning step with chemicals of different purity levels. Iron contamination is significant even after ultra high pure APM clean. Final HPM cleaning is essential to get very clean surface with iron contamination below detection limit 3×10^{10} at/cm², Ref. /31/.

leaves sometimes unwanted passivated surface. In a case where the hydrogen terminated surface is needed the last step must be DHF cleaning. Unfortunately it is ineffective to remove directly adsorbed ions like Cu. Even more, the surface can easily be contaminated with these metals (as well as with particles and organic contaminants) in contaminated conventional DHF (Fig. 2) and/or during final DI water rinse.

Cross contamination can be prevented and metallic impurities removal can be enhanced by addition of H_2O_2 to the DHF. Fig. 4 shows that improved DHF (0.5%HF + 10% H_2O_2) almost completely prevents cross contamination of p and n silicon surface in up to 1 ppm contaminated solution, but not of the doped n^+ and p^+ surfaces. It is also important to prevent contamination during BHF etching of thick oxide layers. The addition of fluorocarbonated (FC) surfactants to improve wettability of the Si surface also reduces the cross contamination of p, n and p^+ surfaces to below 10^{11} at/cm² as shows Fig 5. Only contamination on n^+ surfaces can not be prevented in BHF63 (6%HF+30% NH_4OH) contaminated with 10 ppb of Cu.

Once the surface is contaminated it is very important to clean it. Besides the mentioned RCA cleaning very good results on n and p type wafers can be obtained with improved DHF, while BHF solutions even with added surfactants are not effective. Fig. 6, Ref. /30/, shows the ability of different solutions to clean copper contaminated n and p wafers (10 min dip in 1ppm contaminated water increase surface concentration to 10^{13} - 10^{14}

Cu Segregation at Si Surface

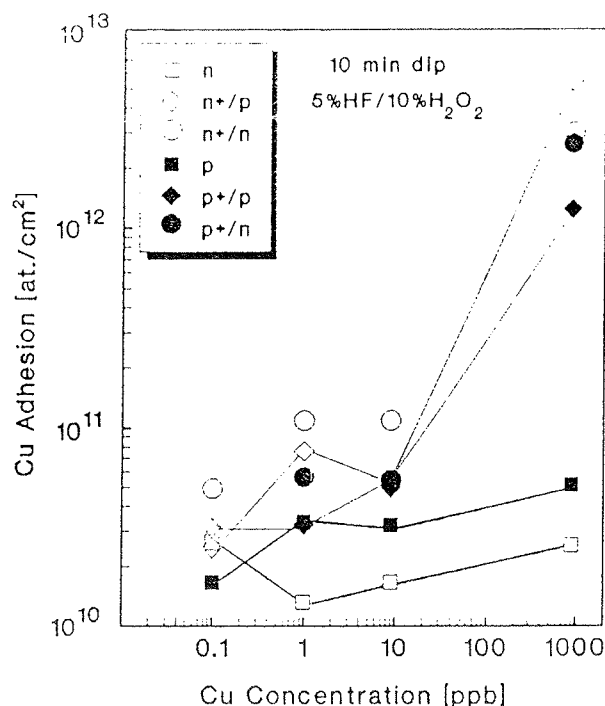
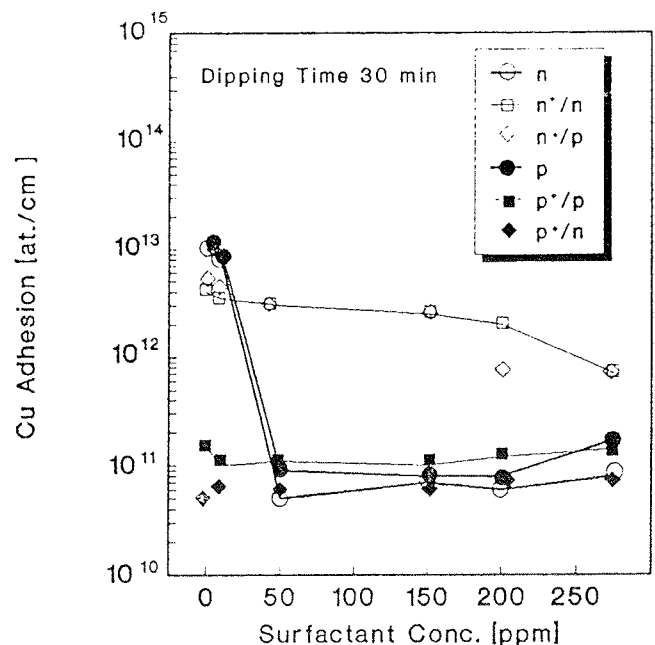


Figure 4: Copper segregation at six different Si surfaces in contaminated 0.5% HF+10% H_2O_2 solution at room temperature, Ref. /37/. (a) n, n^+ on n, n^+ on p, (b) p, p^+ on p, p^+ on n Si wafers.

BHF63

Cu 10 ppb



Hydrocarbon Surfactant, Illuminated

Figure 5: Cu segregation at six different Si surfaces in contaminated (10 ppb Cu) BHF63 with hydrocarbon surfactant dependent on surfactant concentration, Ref. /37/.

at/cm²). Obviously, DHF (0.5% HF), as well as BHF (A is the conventional solution with the NH_4F concentration of 35-38%, and B is advanced solution: 17% of NH_4F , 0.17%HF and 400 ppm of a surfactant) do not remove copper from the surface. APM and HPM solutions lower the Cu surface concentration to the 10^{11} level. The most effective is cleaning in water diluted solution of 0.5%HF+10% H_2O_2 for more than 1 min at room temperature. In this way high Cu concentration can be

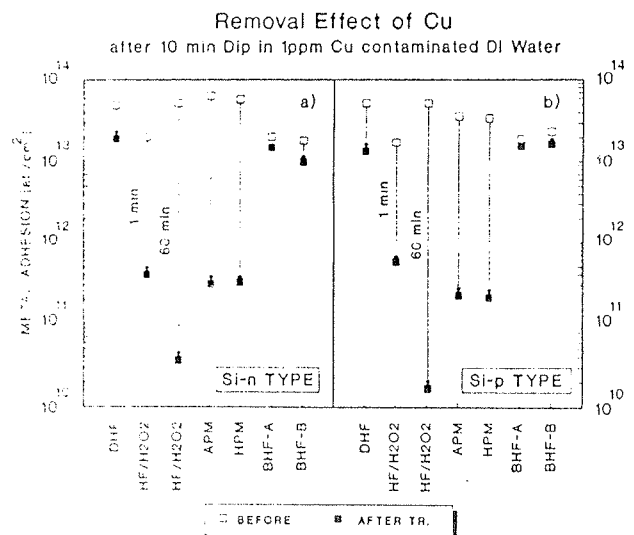


Figure 6: Copper surface contamination removal efficiency for several cleaning methods: (a) n-type, (b) p-type (100) Si surface, Ref. /30/.

reduced to the acceptable level below 10^{11} at/cm² in a relatively short time, Ref. /37/.

Unfortunately advanced DHF solution with hydrogen peroxide does not remove the copper-like metals from n⁺ and p⁺ surfaces. At present, there is no other choice but to use the APM+HPM cleaning.

Particle adhesion and removal

Efficiency of APM and other alkaline solutions to remove particles from the wafer surface has been known for almost 10 years. The most comprehensive explanation of the particle removal mechanisms have been postulated by Itano et al. /32/. According to their results the particle deposition (or removal) depends on the pH value of the solution. With increased pH value, silicon etch rate increases, whereas deposition rate decreases. For pH values higher than 10, the haze count increases very abruptly due to irregular surface etching.

Figure 7 shows particle removal efficiency for APM solutions with different NH₄OH concentrations (X:1:5) at 80°C, Ref. /32,33/. The highest efficiency for 10 min cleaning is obtained in 0.05:1:5 solution. For concentrations higher than 0.1:1:5, efficiency drops due to the extensive etching.

Particle removal efficiency depends on etching of the silicon surface. Fig. 8 shows etch rates as measured by

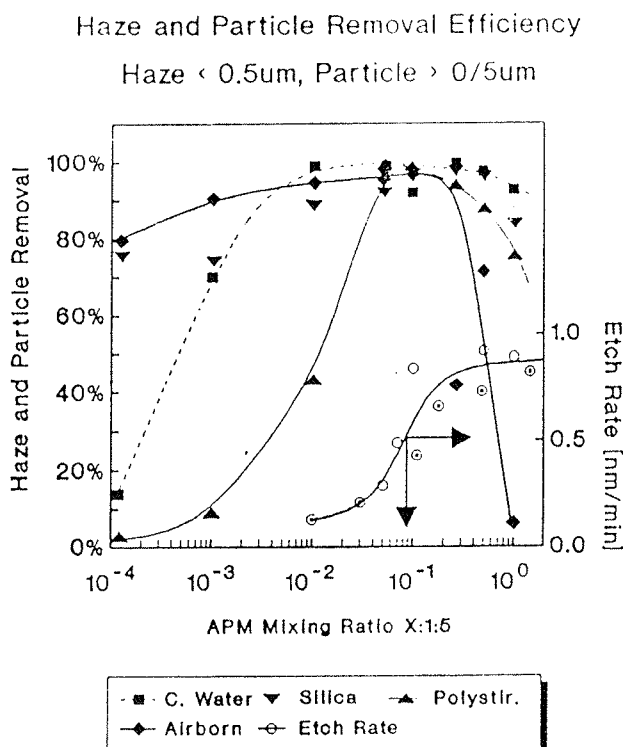


Figure 7: Haze and particle removal efficiency in APM with different NH₄OH concentrations at 80°C. The optimum solution is 0.05:1:5 with etch rate 0.25 nm/min. Solutions with etch rate higher than 0.6 nm/min (1:1:5) may cause surface etching, Ref. /32,33/.

Etch Rate in APM (X:1:5)

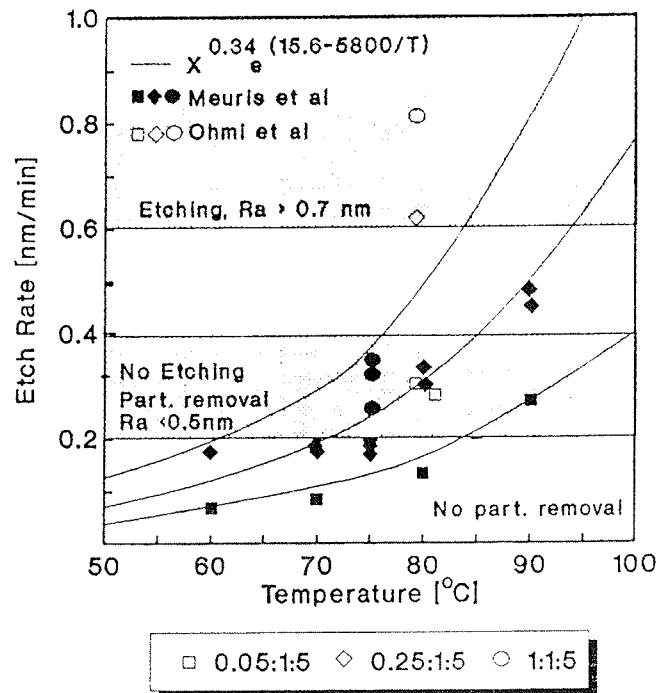


Figure 8: Silicon etch rate in APM as measured by Meuris et al, Ref. /31/ and Ohmi et al, Ref. /33/. In Ref. /31/ the cold water is used for rinsing after APM cleaning, while in Ref. /33/ hot water is used. The most efficient particle removal is obtained with solutions having etch rate 0.2 - 0.4 nm/min. For the etch rate higher than 0.6 nm/min the silicon surface is roughened with average microroughness $R_a < 0.7$ nm. Si surface microroughness

Meuris et al. /31/, and Ohmi et al., /33/. A large discrepancy in etch rates is due to the difference in wafer rinsing. In Ref. /31/ wafers were rinsed in cold DI water, while in Ref. /33/ wafers were rinsed in hot DI after APM cleaning. It is also shown in Ref. /33/ that the surface roughness is almost 2 times higher for the hot water rinse than for the cold water rinse. In Fig. 8 one can see two main regions regarding particle removal efficiency. Safe and efficient particle removal is guaranteed for solutions with etch rate 0.2-0.4 nm/min. Average surface roughening in this region is below 0.5 nm. Solutions with etch rate over 0.6 nm/min cause extensive surface roughening with average $R_a > 0.7$ nm. Solutions with etch rate from 0.4 to 0.6 nm/min should also be avoided due to unreliable control of the etch rate. Solutions with the highest efficiency and low etching rate (0.25 nm/min) are 1:1:5 solution at 65°C, 0.25:1:5 at 75°C with cold water rinse and 0.05:1:5 at 80°C and hot water rinse.

Si surface microroughness

Dielectrics in modern ICs are very thin. Oxide thicknesses are sometimes even less than 10 nm. For such thin layers, the average surface microroughness R_a should be close to the atomic dimensions ($R_a \approx 0.2$ nm).

Fig. 9 shows microroughness measured by STM after cleaning in different solutions for 10 min, Ref./33/. One can see that HPM and SPM cleaning do not damage the surface (small increase of R_a for SPM is due to 4 times repeated cleaning). On the other hand, frequently used conventional BHF with NH_4F concentration of 35-38% drastically increases microroughness. Advanced BHF (17% of NH_4F , 0.17% of HF, 400 ppm of surfactant) does not attack the surface. Surprisingly, even 0.5% DHF significantly deteriorate the surface. Triplett et al. even show in Ref. /34/ that surface microroughness after DHF etching depends on the rinsing time in water. APM cleaning increases microroughness as one can see in Fig. 9. Microroughness depends on the silicon material ($R_a^{\text{epi}} < R_a^{\text{FZ}} < R_a^{\text{CZ}}$), surface point defect concentra-

Surface Microroughness vs. Cleaning

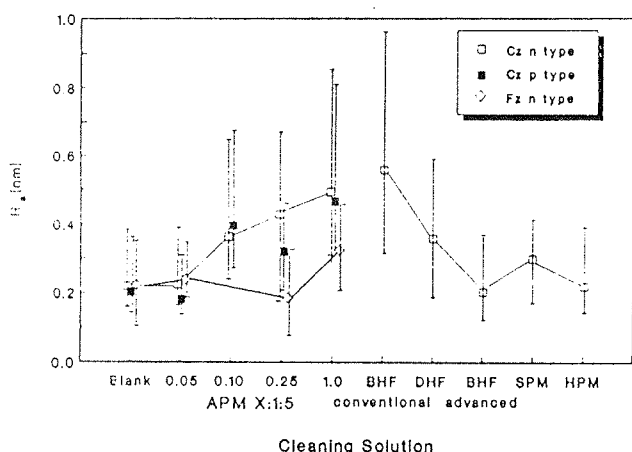


Figure 9: Average surface microroughness R_a of n-type Cz wafer after cleaning in different solutions under the following conditions: etch time 10 min, APM and HPM temperature 80°C , 4 times repeated SPM cleaning and cold DI water rinse after APM, Ref. /33/.

Surface Microroughness after RCA Clean

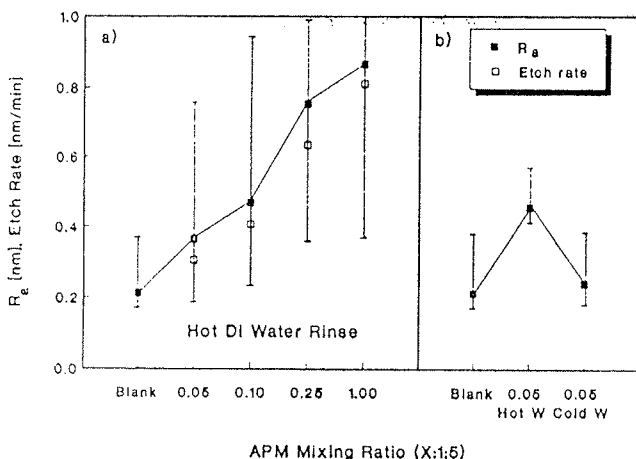


Figure 10: (a) Average surface microroughness R_a of wafers treated in an entire RCA cleaning process with different APM solutions and using hot water rinse after APM. (b) Surface microroughness after APM cleaning in 0.05:1:5 solution and hot and cold (room temperature, RT) DI water rinse, Ref. /33/.

tion (after 4h wet oxidation at 1000°C $R_a^{\text{epi}} \cong R_a^{\text{FZ}} \cong R_a^{\text{CZ}}$), and APM etch rate.

Fig. 10.a illustrates the relationship between microroughness after RCA clean, etch rate, and APM concentration, Ref. /33/. Average microroughness after 10 min etching in APM at 80°C with hot water rinse equals about 10% of the removed silicon thickness. As shows Fig. 10.b surface roughening can be halved by using cold instead of hot water rinse after APM step.

A parameter directly related to the long term quality of the oxide is its charge to breakdown (Q_{bd}). Results show that it decreases with average surface microroughness. The dependence is shown in Fig.11 for measurements with a constant electric field 9.5 MV/cm, Ref /33/. Obviously the surface microroughness must be kept below 0.4 nm to assure the highest possible oxide quality ($Q_{\text{bd}} > 30 \text{ C/cm}^2$).

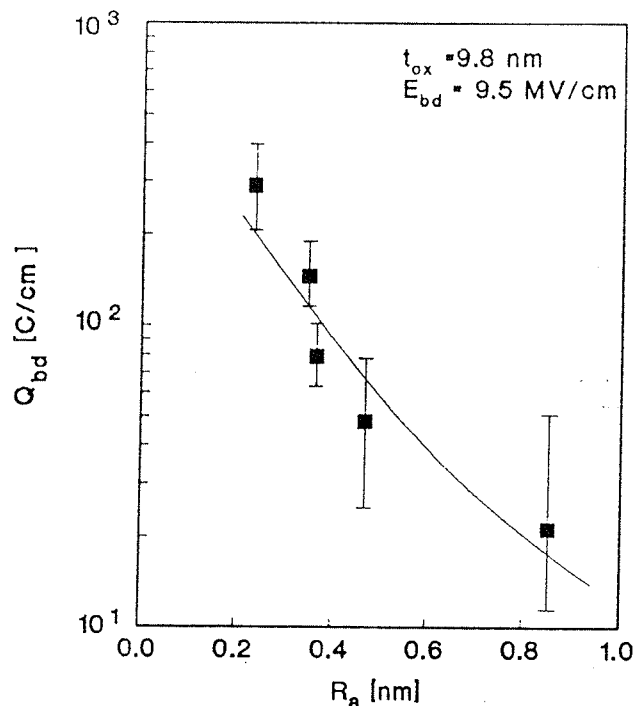
 Q_{bd} vs. Surface Microroughness

Figure 11: Surface microroughness dependence of Q_{bd} under a constant field of 9.5 MV/cm for p-type CZ wafer, Ref /33/.

Hydrogen terminated surface

The thickness of thermal grown thin oxides in modern ULSI IC technologies approach the thickness range of the native oxide grown on the Si surface exposed to air and to the thin oxide grown during cleaning in the APM and HPM solutions. Such an oxide can not be tolerated; so the last cleaning step must be etching of the contaminated native oxide in the DHF. After the DHF cleaning the Si surface is hydrophobic. In Ref. /35/ was shown that the contact angle of a water droplet is a very good measure of the surface status and oxide quality. When

the contact angle exceeds 60° the surface is covered with less than 1% of oxygen monolayer. Typically contact angle for the DHF cleaned and DI water rinsed surface is about 70° .

As it was shown the DHF treatment can cause metal and particle contamination. To prevent particle adhesion and improve cleaning efficiency the effects of the following three possible additives have been studied during the last years:

- hydrogen peroxide, H_2O_2 ,
- isopropanol (IPA),
- FC surfactants

In Fig. 4 it was already shown that the addition of H_2O_2 into the DHF (0.5%) enables Cu removal from contaminated silicon surface and prevent Cu segregation onto p and n silicon surface in contaminated DHF. Fig. 12, Ref./33/, represents Cu removal efficiency from n type Si for H_2O_2 -DHF solution at room temperature as a function of hydrogen peroxide concentration. As one can see almost complete removal of Cu is guaranteed for 60 min cleaning in solution with 5-10% of H_2O_2 in DHF. Even such a prolonged etching in DHF with more than 0.1% of H_2O_2 added does not increase the average surface microroughness from the initial value and does not destroy the hydrophobic nature of the Si surface. The contact angle measured after cleaning in 3% H_2O_2 - 0.5%DHF exceeds 60, Ref. /35/, whereas for the 0.5% DHF exceeds 70. Unfortunately addition of hydrogen peroxide to the DHF does not solve the problem of particles contamination in DHF solutions. Only minor improvements (times 2) in particle contamination was reported in Ref. /38/.

Very significant reduction of the particle deposition was reported for DHF mixtures with minute amounts of IPA, Ref. /38/. Addition of 200-1000 ppm of IPA to 0.5%DHF almost does not change the state of the surface. The contact angle after 60 s dip in solution with 200 ppm IPA is identical to what is obtained when no IPA is added and it is no longer changed by subsequent DI- water rinse. When 1000 ppm of IPA is added to the 0.5%DHF

solution the particle density after rinsing is comparable to what is obtained after standard RCA clean. As a result, almost 50% increase in yield on gate oxide capacitors was reported.

Effect of addition of surfactants to the DHF solution is still under study. But it is already known that the contact angle after treatment nearly equals that one measured after treatment with 0.1%IPA + 0.5%DHF, Ref. /35/.

Conclusions

An ultraclean Si wafer surface is essential for achieving the advanced ultra large scale integrated production which incorporates low-temperature and high selectivity processes. Such a surface is completely free of particles, organic impurities, metallic impurities, native oxide, surface microroughness and adsorbed impurities. Since metallic impurities can cause fatal damage to device characteristics the contamination level must be suppressed to below 10^{11} atom/cm². The only method to remove trace impurities from the surface at the present is wet cleaning.

An advanced improved wet cleaning process proposed in Ref. /36/ consists of the following steps:

- removal of organic contaminants in $\text{H}_2\text{O} + \text{O}_3$ at room temperature. This is highly effective replacement for classical SPM cleaning at 130°C . Total removal of organic contaminants is essential for effectiveness of subsequent cleaning steps.
- removal of particles, organic and metal impurities in APM. Advanced 0.05:1:5 solution is highly effective to remove surface particles and partially effective to remove Cu like metals precipitated onto the surface, and does not deteriorate the surface smoothness.
- removal of native oxide and metals in DHF + H_2O_2 generate native oxide free surface clean of metals which tends to incorporate into the native oxide (Fe, Al, Ca...) as well as Cu-like metals. This solution is very appropriate to clean n and p type surfaces with the highest demands for cleanliness and smoothness, such as the wafer surface before gate oxidation. Since this solution attacks the n^+ and p^+ surfaces, the only method to remove metal contaminants from them is still APM + HPM cleaning.

Further improvements in cleaning could be obtained using DHF solution heated to 70°C , cleaning in an inert ambient, or even in using dry wafer (vapor) cleaning in an enclosed system, as it is for instance Advance 600/2 Vertical Reactor Cluster Tool for polysilicon gate application /35,39/. In such a system, the wafer surface is never exposed to air, neither before oxidation, nor before polysilicon deposition. The result is a significant improvement of the oxide quality.

In order to decrease the metal concentration on the Si wafer surface to less than 10^{10} atoms/cm², the concentration of metals with electronegativity higher than Si (for example Cu) in chemicals and water should be de-

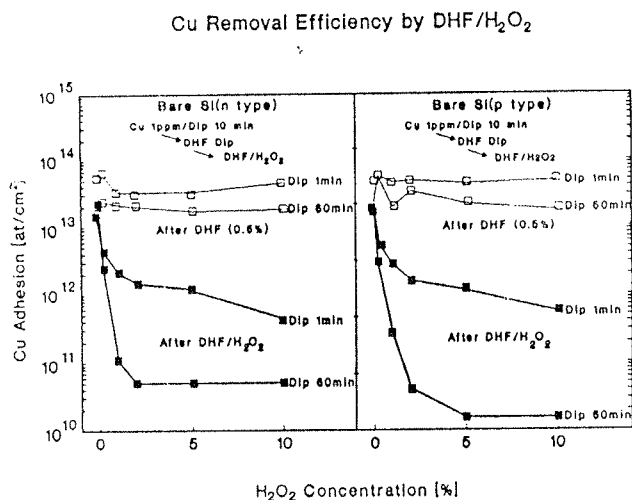


Figure 12: Copper removal efficiency by DHF- H_2O_2 with H_2O_2 concentration ranging from 0-10% for 10 and 60 min dipping time, Ref. /33/.

creased to less than 10 ppt which is hard to reach even with present ultraclean chemicals. A very promising way to delivered such clean chemicals is point of use chemical generation which is useful for preparation of HF, HCl, NH₄OH and ozonated ultra pure water.

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