NIPPON STEEL TECHNICAL REPORT No. 83 JANUARY 2001

UDC 669 . 782 : 621 . 382 : 66 . 069 .1

Cleaning Technology of Silicon Wafers

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Abstract

High quality wafers are in demand, as increasingly high integration of VLSIs became a commercial practice. This is especially true with highly clean wafers with little metallic impurities and particulate and organic matters on the surface. For producing the highly clean wafers, it is necessary to establish wafer surface cleaning technologies through experimental and theoretical analysis of the behavior of the surface impurities. This paper explains adhesion mechanisms of metallic and particulate impurities to silicon wafer surfaces and proposes some cleaning methods.

1. Introduction

Increasing integration density of LSIs (large scale integration circuits) call for higher quality silicon wafers. Higher-quality wafers mean the superior quality in crystal precision, shaping quality, and surface quality. Problems concerning chip size increase and manufacturing cost increase must be considered. Practical application of 300-mm wafers has been discussed in recent years. Extremely high surface cleanliness is required of the 300-mm wafers[1)] (refer to **Fig. 1**). Specifications for organic impurities have begun to be prescribed as well as traditional impurities such as metals and particles. These impurities are generated from wafer manufacturing equipment, chemicals, human bodies, clean room materials, dust-free garments and reaction products, and are often deposited on the wafer surfaces[2)]. They cause interconnect failures and crystal defects, then degrade the device performance. For this reason, the surface cleanliness of silicon wafers is continuously improved.

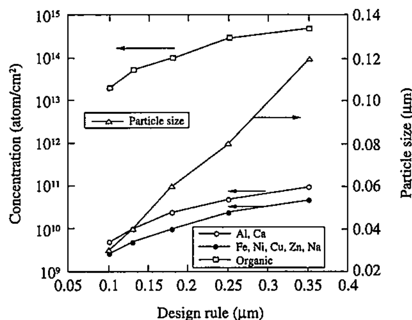

Fig. 1 Relationship between device design rule and required wafer surface cleanliness[1)]

To meet these requirements, it is important to theoretically analyze the phenomena that are taking place on the silicon wafer surface and to perform the process design on the basis of the results of the theoretical analyses. This report especially deals with the adhesion mechanisms of metals and particles to the wafer surface, and introduces new cleaning methods based on our theoretical examination.

2. Adsorption mechanism of Metals to Silicon Wafer Surface

Since iron on silicon wafer surface causes crystal defects and degrades device performance, as much of it should be removed as is possible. Henley et al.[3)] indicated that an iron contamination level of 10^{10} cm^{-3} is required for a gate oxide thickness of 8 nm. Like iron, other metals (e.g., nickel, chromium, copper, zinc, and sodium) degrade the device performance (or change the transistor threshold values, induce crystal defects to degrade the p-n junction leakage and gate oxide integrity, or accelerate oxidation). They must be reduced to meet shrinking device sizes. To remove these metals or to control their adsorption in the cleaning solution, it is necessary to understand their behavior in the cleaning solution.

Two major mechanisms are present for metal adsorption in the cleaning solution. One is chemical absorption, as is represented by the adsorption of metals to native oxide (SiO_2) in an alkaline solution. The other is electrochemical adsorption to bare Si in an acidic solution. To understand these mechanisms, we conducted ionic equi-

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librium analysis and electrochemical analysis. The results of these studies are discussed below.

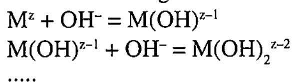
2.1 Ionic equilibrium analysis

An $NH_4OH+H_2O_2+H_2O$ mixture (APM), also called "Standard Cleaning solution 1 (SC-1)" which is a representative alkaline cleaning solution, has such an extremely excellent particle removal capability that it is widely used[4]. However, if metal ions exist in the cleaning solution, they adsorb on the wafer surface[5]. Especially, iron, when present even in a trace amount less than parts per billion (ppb), degrades the electrical performance such as recombination lifetime, τ_r. It poses a serious problem when it is carried over from the previous process or when low-purity chemicals are used.

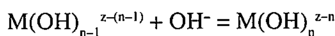
Metal adsorption in the SC-1 cleaning solution was traditionally explained using metal oxide formation enthalpy or a complex ion model[6], but was rarely discussed quantitatively. An analysis of the issue was tried according to the chemical equilibrium theory[7].

In the SC-1 cleaning solution, formation of native oxide (SiO_2) by hydrogen peroxide and etching of SiO_2 by alkalis proceed at the same time. For this reason, the overall wafer thickness is slowly reduced, but a certain thickness of SiO_2 exists on the wafer surface, irrespective of the time[8]. In this case, if the etching rate is slow enough and the metal adsorption and desorption reactions are fast enough, a certain metal ion adsorption equilibrium holds between SiO_2 and the solution. Actually, since the etching rate of SiO_2 by the SC-1 cleaning solution is a few mono-layers per minute[9] while the adsorbed amount of metals reaches a constant value within one second after wafer immersion, this equilibrium may be considered to hold. The relationship between the metal ion concentration in the solution and the adsorbed amount at a given temperature is called "adsorption isotherm". **Fig. 2** shows adsorption isotherms for a 1:1:5 mixture of 29% ammonium hydroxide, 31% hydrogen peroxide, and de-ionized water, and the temperature of 80°C[10].

Here, the ionic equilibrium in the solution is focused on. For a metal ion denoted by M^z, the following chemical equilibrium holds in the SC-1 cleaning solution:



$$M^z + OH^- = M(OH)^{z-1}$$
$$M(OH)^{z-1} + OH^- = M(OH)_2^{z-2}$$
.....



$$M(OH)_{n-1}^{z-(n-1)} + OH^- = M(OH)_n^{z-n}$$

The existing proportion of metal hydroxide complexes denoted by M^z to $M(OH)_n^{z-n}$ is a function of pH and can be theoretically calculated if each equilibrium constant is given[11].

The results of calculation for Fe in a concentration of 1×10^{-8} mol/L (about 0.5 ppb) are shown in **Fig. 3**(a). Since the pH of the SC-1 cleaning solution is about pH 10.6 (for 1:1:5 proportion), the existing proportion of hydroxide complexes is $Fe(OH)_3 > Fe(OH)_4^- > Fe(OH)_2^+ > Fe(OH)^{2+} > Fe^{3+}$ in decreasing order. From this result, however, it cannot be directly concluded that the adsorbed species in the SC-1 cleaning solution is $Fe(OH)_3$. If the reaction is in chemical equilibrium, the adsorbed amount depends on the product of the concentration and adsorption equilibrium constant of each complex (if a complex exists in a small amount but is fully large in equilibrium constant, it can become a main adsorbed species). A further study was made to identify the adsorbed species.

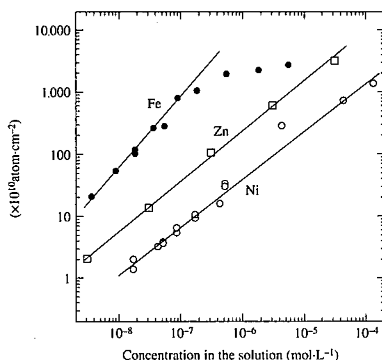


Fig. 2 Adsorption isotherms of Fe^{3+}, Ni^{2+}, and Zn^{2+} in SC-1 solution (1:1:5, 80°C)

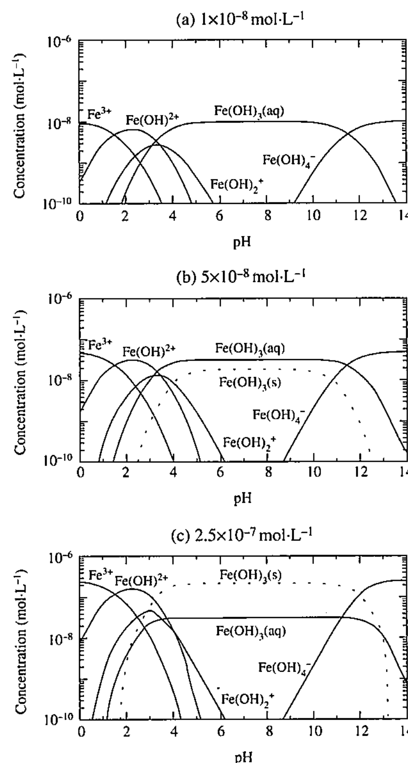


Fig. 3 pH dependence of Fe^{3+} hydroxide complexes

$Fe(OH)_3$, a hydroxide complex of Fe without charges, can dissolve in an aqueous solution to a certain concentration, but becomes solid and precipitates when it exceeds the critical concentration determined by the solubility product. The dissolved species and solid species are denoted by $Fe(OH)_3$ (aq) and $Fe(OH)_3$ (s), respectively (aq and s stand for aqueous and solid, respectively). The results of the calculation including the formation of the solid species are shown in Figs. 3(b) and (c). When the Fe concentration reaches about 5×10^{-8} mol/L, $Fe(OH)_3$ (s) starts to form. When Fe is added to a higher concentration, the concentration of the other dissolved hydroxide complexes saturates in the pH range of 4 to 11.

The calculated concentration of $Fe(OH)_3$(aq) at pH = 10.6, (corresponding to the pH of the SC-1 cleaning solution), is shown in **Fig. 4**(a). The measured adsorption isotherm of Fe is shown in Fig. 4(b). The start of formation of $Fe(OH)_3$(s) almost coincides with the start of saturation of the adsorbed amount of Fe. This means that the adsorbed species is one of the dissolved hydroxide species $Fe(OH)_x$(aq) other than the solid species $Fe(OH)_3$ (s). The finding that the solid species is not the adsorbed species is supported by the measurement by total-reflection x-ray fluorescence spectroscopy (TXRF).

Fig. 5 shows the TXRF angle-scan measurement results for a wafer produced in the region where the solid species $Fe(OH)_3$(s) is

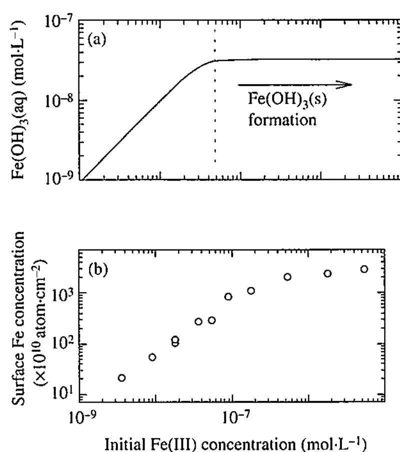


Fig. 4 Comparison of calculated values of $Fe(OH)_3$ (aq) concentration (a) and measured values of Fe adsorbed amount (b) at the pH of 10.6

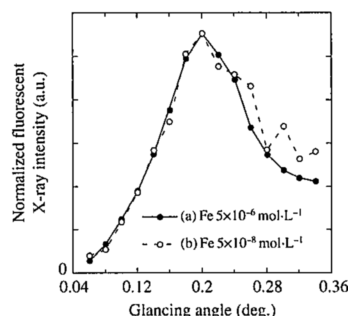


Fig. 5 Comparison of TXRF angle-scan measurement results of wafers with Fe adsorption in $Fe(OH)_3$ (s) formation region and non-$Fe(OH)_3$ (s) formation region

formed and for a wafer produced in the region where the $Fe(OH)_3$(s) is not formed. The vertical axis indicates normalized maximum values. The TXRF angle-scan profile depends on the depth distribution of analyte elements. The dissolved species and solid species are considered to adsorb in the bulk of SiO_2 in film form and on the surface of SiO_2 in particle form, respectively. If the solid species adsorbs, the angle-scan profile should be different from that obtained when the dissolved species adsorbs. In actual data (Fig. 5), both profiles almost agree with each other. This may be taken to mean that the solid species does not adsorb.

The above-mentioned experiments show that the adsorbed species is one of the dissolved hydroxides. When Fig. 3 is looked at here again, the pH dependence of the existing proportion of the hydroxide complexes varies with each other. If the pH dependence of the adsorbed amount is measured and compared with the calculated values, the adsorbed species can be identified. By adding tetramethylammonium hydroxide ($N(CH_3)_4^+OH^-$, TMAH) to the SC-1 cleaning solution, the pH was changed in the range of 10.5 to 12, and the pH dependence of Fe adsorption was investigated. The results are shown in **Fig. 6**.

The slope in this pH range was −0.56 in linear approximation. The slopes expected from the chemical equilibrium calculation are given for each dissolved species in **Table 1**. When x = 3, the calculated value agreed best with the measured value. This means that the main adsorbed species is the neutral hydroxide complex $Fe(OH)_3$(aq) dissolved in the SC-1 cleaning solution. The greatest likelihood of neutral hydroxide complexes to adsorb is supported by the theoretical calculation proposed by R.O. James et al.[12] for metal adsorption.

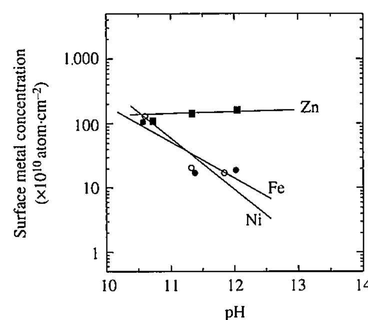


Fig. 6 pH dependence of adsorbed amount of Fe, Ni, and Zn

Table 1 Comparison of pH dependence for adsorbed amount and for hydroxide complex concentration

Measured value		Calculated value with respect to $M(OH)_x$(aq)				
(Slope at pH = 10.5 - 12)		x = 0	x = 1	x = 2	x = 3	x = 4
Fe	−0.56	−3.38	−2.38	−1.38	−0.38	+0.62
Ni	−0.81	−2.78	−1.78	−0.78	+0.22	+1.22
Zn	+0.13	−2.63	−1.63	−0.63	+0.37	+1.37

Ni and Zn were also studied. These metal ions are known to react with ammonia to form extremely stable ammine complexes. The existing proportions of various complex species calculated by considering the formation of the ammine complexes are shown in **Figs. 7 and 8**. From these diagrams, it can be seen that most of Ni and Zn exist as ammine complexes in the SC-1 cleaning solution (pH = 10.6). **Table 2** shows the critical concentration, calculated from the solubility product of $Ni(OH)_2$(s) and $Zn(OH)_2$(s), at which these species start to precipitate. It is evident that the Ni and Zn contaminant concentrations never reach the critical concentration for the formation

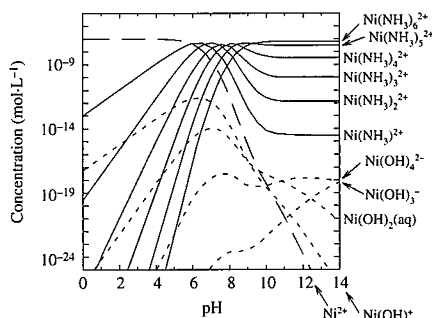


Fig. 7 pH dependence of Ni^{2+} hydroxide and ammine complex concentrations

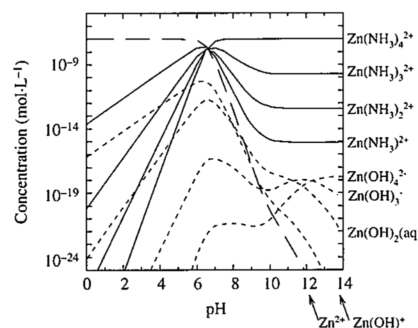


Fig. 8 pH dependence of Zn^{2+} hydroxide and ammine complex concentrations

Table 2 Ammine and hydroxide complex concentrations in ammoniacal solution

	Critical concentration for the formation of hydroxide precipitates as expressed by $\Sigma M(OH)_x(aq)$		
	$\Sigma M(NH_3)_x(aq)$ (mol L^{-1})	$\Sigma M(OH)_x(aq)$ (mol L^{-1})	$\Sigma M(OH)_x(s)$ (mol L^{-1})
Ni^{2+}	1×10^{-4}	7×10^{-16}	$\approx10^{-5}$
Zn^{2+}	1×10^{-4}	4×10^{-18}	$\approx10^{-5}$

of the respective solid species in usual. This is the reason why the adsorption isotherms of Ni and Zn do not level off as Fe does in Fig. 2.

By measuring the pH dependence of the adsorbed amount for Ni and Zn in the same manner as Fe, it may be possible to identify the adsorbed species. The measured values are shown in Fig. 6, and the calculated values are given together with those for Fe in Table 1. For Ni, the calculated values agreed best with the measured values when n = 2. This suggests that the adsorbed species is the neutral hydroxide complex $Ni(OH)_2$ (aq) dissolved in the SC-1 cleaning solution as noted for Fe. Zn does not show any match between calculated and measured values. This may be explained by formation of the polynuclear complex $Zn_2(OH)_6^{2-}$, inhibitor effect of TMAH, or saturation of the adsorbed amount, but is identified yet.

According to the above results, it is believed that the adsorbed species are not ammine complexes but hydroxide complexes also for Ni and Zn. To substantiate it, the adsorption behavior of Ni in a solution, which does not contain ammonia, was investigated. The pH of the system was adjusted with potassium hydroxide (KOH) in place of ammonia, and the pH dependence of the adsorbed amount was measured. The results are also shown in Fig. 6. The adsorbed amount was larger by more than one order of magnitude than when ammonia was contained. This is probably because a large amount of hydroxide complex, which is considered to be the adsorption species, was formed. The adsorbed amount, however, increases only by one or two orders of magnitude (against six to nine orders of magnitude expected from Fig. 7) and exhibits no pH dependence. This may be because the adsorption sites are saturated.

From the above discussion, it was found that the adsorbed species in SC-1 solution is a neutral hydroxide complex dissolved in the solution. This finding can be put to use in developing methods for reducing metal adsorption in the SC-1 cleaning solution. For example, lowering the pH to reduce the existing proportion of $Fe(OH)_3$ (aq) may prevent the Fe adsorption. Or adding a chelating agent that forms a stable complex with $Fe(OH)_3$ (aq) can also be effective[13].

2.2 Metal adhesion mechanism in acid solution

Acid cleaning solutions are excellent in metal removal characteristics, but the adhesion of Cu and Au is considered problematic in solutions, such as a solution of diluted hydrofluoric acid[14-17]. These adhesion behavior are explained by using the ionization tendency. Given the conduction type, resistivity and anion effect, however, it is difficult to explain them simply by the ionization behavior alone. To support this thinking, the adhesion behavior of metals in acidic solutions by electrochemical technique was analyzed[18]. The results are introduced here. First, the relationship between the pH of the solution and the metal adhesion amount is described. In this case, the recombination lifetime was examined by the μ-PCD method to determine the metal adhesion amount. A longer recombination lifetime indicates a smaller metal adhesion amount, and a shorter recombination lifetime indicates a larger metal adhesion amount. As shown in **Fig. 9**, the metal adhesion amount decreases with decreasing pH in the solution.

There are solutions, such as a solution of hydrochloric acid, that are short in the recombination lifetime despite their low pH. The relationship between the silicon rest potential generated in the solution and the recombination lifetime was subsequently investigated. The rest potential depends on the oxidizing and reducing species in the solution, and is called the oxidation-reduction potential in an ideal equilibrium condition. The rest potential changes with the ion species and pH of the cleaning solution. As can be seen from **Fig. 10**, the more noble the silicon rest potential, the greater the degree to which the metal adhesion is inhibited.

Next, the energy band diagram of silicon in the solution was investigated.

Generally, when a substance is immersed in a solution, it forms an electrochemical double layer on its surface. In the double layer, there are specific adsorption ions and adsorption molecules. Hydrated ions and coordinated water molecules, among other things, exist on the solution side of the outermost layer. This also applies when silicon is immersed in the cleaning solution. Since silicon is a semiconductor, a space charge layer is formed in the bulk near the surface. The size of the space charge layer is known to depend on the oxidation-reduction potential of the cleaning solution[19]. This can be measured to compare the potentials of the silicon surface, metals, and ions in the cleaning solution. It is necessary to decide the size of the space charge layer by electrochemical impedance analysis.

Fig. 11 shows an electrically equivalent circuit consisting of silicon space charge layer capacitance, electrochemical double layer capacitance, cleaning solution resistance, and polarization resistance. The Cole-Cole plot of the equivalent circuit is given in **Fig. 12**. The capacitance C is the capacitance obtained by connecting the space charge layer capacitance and the electrochemical double layer ca-

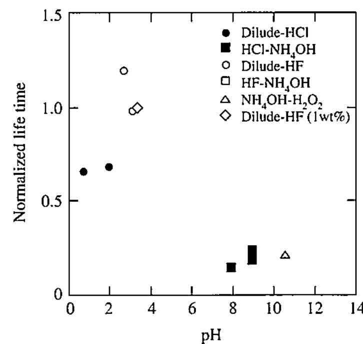


Fig. 9 Relationship between solution pH and recombination lifetime

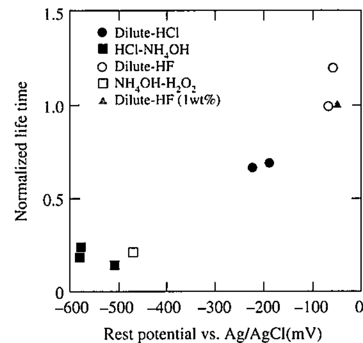


Fig. 10 Relationship between solution rest potential and recombination lifetime

pacitance in series. The electrochemical double layer capacitance is usually so large that the capacitance C can be handled as the space charge layer capacitance and determined from the Cole-Cole plot. The capacitance C is measured with respect to the potential in the solution, and the flat band potential is obtained from the Mott-Schottky plot.

As an example, the results of this analysis conducted on n-type silicon wafers (10 Ω·cm) in an aqueous solution of 1% hydrofluoric acid (HF) are shown in **Figs. 13 and 14**. The flat band potential is obtained as 0.071 V vs. Ag/AgCl from the Mott-Schottky plot, and the energy band diagram at the flat band conditions in the solution can be drawn as shown in **Fig. 15**. Since the resistance of the wafers is 10 Ω·cm, the conduction band is located at 0.28 V on the cathode side of the Fermi level, and the valence band is located at 0.82 V on the anode side of the Fermi level. When the silicon wafer is immersed in the diluted HF aqueous solution, resultant bend bending is

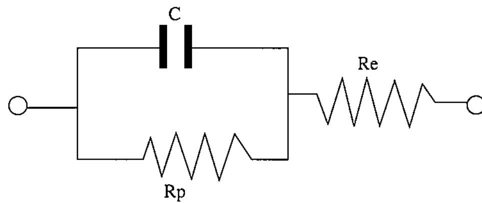


Fig. 11 Equivalent circuit of electrochemical double layer

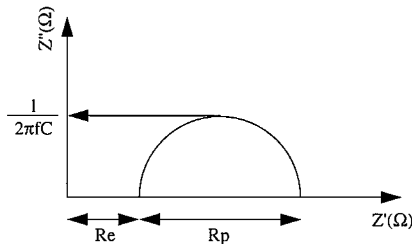


Fig. 12 Cole-Cole plot of equivalent circuit

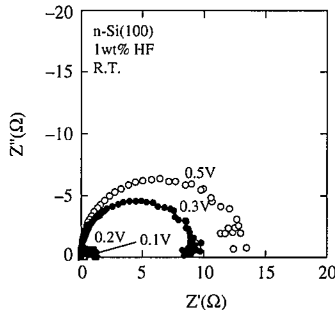


Fig. 13 Cole-Cole plot of equivalent circuit

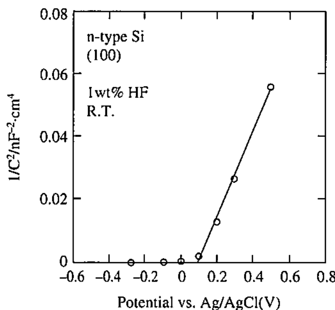


Fig. 14 Mott-Schottky plot

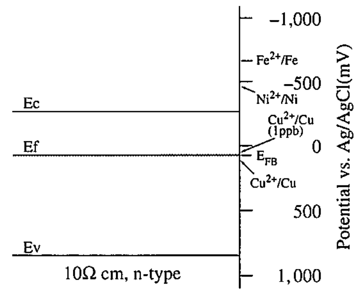


Fig. 15 Energy band diagram of Flat band conditions

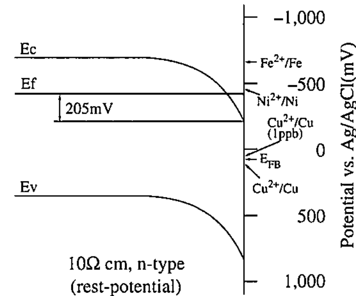


Fig. 16 Energy band diagram of in 1wt% HF solution

derived as shown in **Fig. 16**. The band ends are fixed on the solution side with respect to the reference electrode, and the Fermi level shifts by 0.485 V to the cathode side. This causes the conduction band end crosses the Fermi level, the surface to degenerate, and electrons to accumulate.

When the equilibrium potentials of metals and ions existing in the solution are calculated, they become as shown at the right side of Fig. 16. The phenomena of metal removal and adhesion in the solution can be discussed by comparing the equilibrium potentials with the Fermi level of silicon. Since potentials of Fe and Ni are positioned at the cathode side of the Fermi level, they receive no electrons from silicon and exist as ions in the solution (or Fe and Ni are dissolved in the solution). In contrast, the potential of Cu is positioned at the anode side of the Fermi level, receives electrons from the degenerated silicon surface, and is likely to electrically deposit as metal. This shows that to prevent the adhesion of Cu, it is necessary to use such an oxidizer that positions silicon on the anode side of the Fermi level. When the energy band diagram structure of the silicon in an aqueous solution is clearly understood in this technique, the difference in adhesion behavior with the conduction type, difference in adhesion behavior with the resistivity, and the effect of anions on adhesion behavior can also be explained[20,21].

3. Particle Adhesion Mechanism

The phenomenon of particles adhering to the silicon wafer surface can be replaced by the phenomenon of particles adhering to a huge flat electrode, and can be considered as hetero-coagulation in colloid chemistry[22,23]. The energy that acts between the silicon wafer surface and the particles is analyzed by the DLVO theory, a hetero-coagulation theory.

Fig. 17 shows the calculated values of interaction energy acting between the silicon wafer and the particles of polystyrene latex (PSL). The potential energy can be calculated from the repulsive force due to the electrochemical double layer and the attractive force due to the van der Waals force. The electrochemical double layer depends

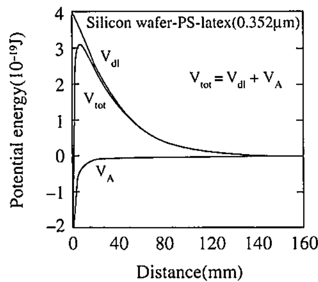


Fig. 17 Interaction energy acting between silicon wafer surface and polystyrene latex (PSL)

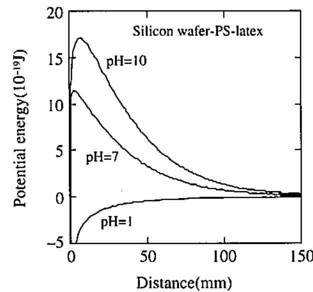


Fig. 18 Solution pH, and interaction energy acting between silicon wafer and polystyrene latex (PSL)

on the surface potential (eg., zeta potential) and the concentration, type and pH of the solution, among other factors. The van der Waals force depends on the size of particles, among other factors. It is possible to analyze the particle adhesion behavior in detail by this interaction energy. Usually, the particle adhesion characteristics are often explained by the polarity of the zeta potential alone. It is difficult to explain the particle adhesion behavior due to the difference in surface state and the difference in the conduction type of the silicon substrate. Various phenomena can be explained by this calculation of the energy acting between the silicon wafer and particles.

Fig. 18 shows the calculated values of interaction energy when the pH of the aqueous solution is changed. It is evident that when the aqueous solution is low in pH, it exhibits a negative potential energy and causes the attractive force to act between the silicon wafer and the particles. When the aqueous solution increases in pH and becomes alkaline, the repulsive force acts between the silicon wafer surface and the particles to inhibit the adhesion of particles. To explain the phenomenon of particle removal, it is necessary to understand the phenomena taking place near the silicon wafer surface. When the aqueous solution is alkaline, it is suggested in view of the aforementioned potential energy that a very strong attractive force acts near the silicon wafer surface. Particles present near the silicon wafer surface are considered to adhere to the silicon wafer surface with a strong adsorption force. However, the ammonium hydroxide-hydrogen peroxide-de-ionized water mixture (APM), a popular semiconductor cleaning solution, has an excellent capacity to prevent the adhesion of particles to the semiconductor surface and to remove the particles from the semiconductor surface. The APM has such an etching capability that it etches and lifts off the particles adhering to the silicon wafer surface. This makes the APM a cleaning solution with excellent particle adhesion prevention and particle removal performance. As far as the particle adhesion is concerned, it is necessary to design the cleaning solution to suit the silicon surface condition and the actual condition of particles.

The size dependence of particle adhesion was investigated. The model particles used in our experiment are the particles of polystyrene latex (PSL). The size dependence of PSL particles adhering to the silicon wafer surface was investigated. The results are shown in **Fig. 19**. As can be seen from Fig. 19, the smaller the size, the more likely the PSL particles are to adhere to the silicon wafer surface. The results of analysis conducted according to the DLVO theory to understand this behavior are shown in **Fig. 20**. This theoretical calculation can explain the finding that the smaller the size of the PSL particles, the less the energy barrier the PSL particles encounter and the more likely the PSL particles are to adhere to the wafer surface. These calculation results enable us to infer the difficulty of the technical challenge of ever toughening particle requirements we will face in the era of the 0.10 μm design rule.

The surface condition dependence of particle adhesion were investigated to find that that particles are more likely to adhere to a hydrophobic surface than to a hydrophilic surface as shown in **Figs. 21 and 22**. In addition, the conduction type was investigated to find that particles are less likely to adhere to a p-type than to an n-type as shown in **Figs. 23 to 25**. In this way, the electrochemical analysis of particle adhesion behavior made it possible to explain particle size

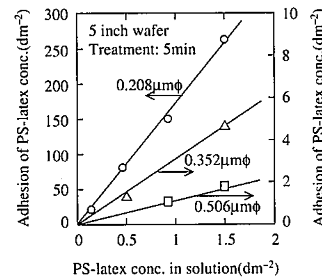


Fig. 19 Size dependence of particles adhering to silicon wafer surface

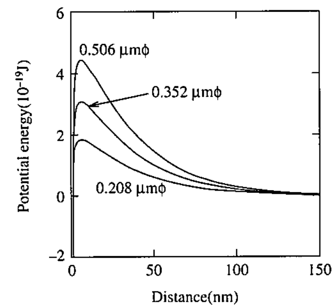


Fig. 20 Size dependence of particles adhering to silicon wafer surface as calculated according to DLVO theory

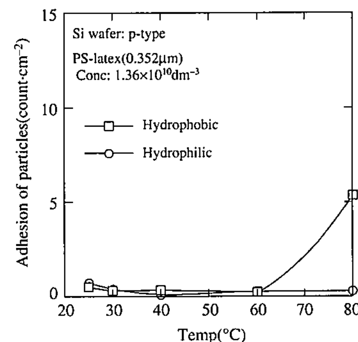


Fig. 21 Wafer surface condition and number of particles adhering to silicon wafer

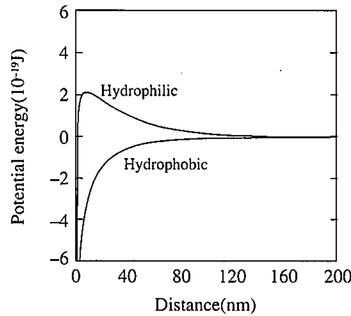


Fig. 22 Results of calculation according to DLVO theory

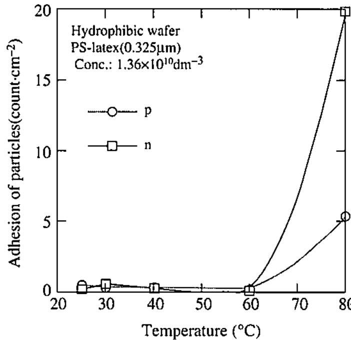


Fig. 23 Adhesion behavior of particles to hydrophobic surface

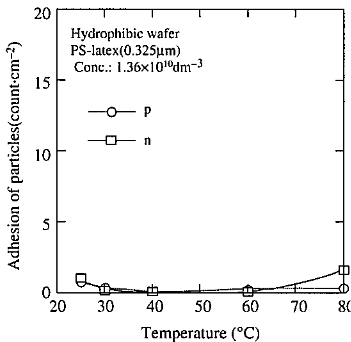


Fig. 24 Adhesion behavior of particles to hydrophilic surface

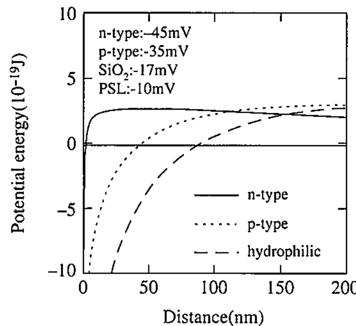


Fig. 25 Interaction energy (conduction type dependence)

dependence, surface condition dependence, conduction type dependence, and other aspects of particle adhesion. Such theoretical analysis will increase in effectiveness with decreasing size and number of particles to be addressed.

4. New Cleaning Processes

Various cleaning methods have been proposed in recent years. They can be divided into two main groups. One group is designed to improve the solution system, and the other utilizes external forces. The former group includes cleaning with ozone[24], electrolyzed water[25-29], surfactant[30], and cleaning with chelating agent[31-35]. The latter includes cleaning with ultrasonic waves[36]. These new cleaning processes are used in combination in many applications. Many of the new cleaning practices have been developed after understanding of the adhesion behavior of metals and particles. Given ever increasing severity of silicon wafer surface cleanliness requirements, it will become necessary to clarify the atomic-level phenomena taking place on the silicon wafer surface and find out next-generation silicon wafer cleaning methods.

The new cleaning processes are described below.

4.1 Functional water

Functional water is the ultra pure water that has gas components (e.g., ozone, oxygen, chlorine and hydrogen) dissolved and is provided with oxidizing or reducing capability. As compared with conventional cleaning process, the use of functional water makes possible sharp reduction of the consumption of chemical solutions and ultra pure water for rinses. Utilization of functional water is attracting attention in wet cleaning processes in the electronics field in response to toughening environmental regulations and necessity for cleaning cost reduction in recent years. Functional water is increasing in practical usage with development of semiconductor-grade functional water production systems. Functional water can be classified by its production method into gas-dissolved water and electrolyzed water. Ozonated water, hydrogenated water, and electrolyzed water in the former category are described below.

4.1.1 Ozonated water

Ozone is a powerful oxidizer. Ozonated water is an ultra-pure water in which ozone gas is dissolved, and can oxidize and remove organic matter and impurity metals adhering to wafers. The sulfuric acid-hydrogen peroxide-deionized water mixture (SPM) and ammonium hydroxide-hydrogen peroxide-deionized water mixture (APM) have been traditionally used for organic removal. Ozonated water can be used to remove organic contaminants at room temperature without using conventional concentrated chemical solutions.

Since its oxidation-reduction potential is more noble as shown in **Fig. 26**, ozonated water has a high metal-removal ability. Since noble metals like Cu can stably exist as ions in ozonated water, they can be prevented by ozonated water from re-adhering to the wafer surface. Ozonated water shows a more powerful metal removal ability if its pH is shifted toward the acid side of the pH range by adding hydrochloric acid, for example. Ozonated water was formerly used in amounts of a few parts per million (ppm) to about 20 ppm in many

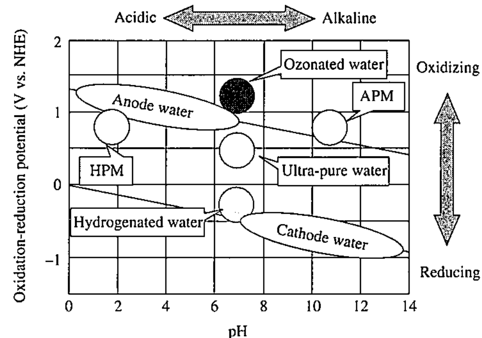


Fig. 26 Properties of functional water

cases. Recent development of ozonated water systems has made it possible to produce ozonated water with a supersaturated concentration of as high as 50 to 100 ppm. Ozonated water is expected to be used in many more applications.

4.1.2 Hydrogenated water

Hydrogenated water has a reducing capability as opposed to the oxidizing capability of ozonated water. It displays a particle removal ability when imparted with a physical force like a megasonic force. When this capability was found, hydrogenated water started to attract attention. The mechanism involved may be considered as follows. Particles are liberated into hydrogenated water by the physical force like mega-sonics and are negatively charged by the reducing capability of hydrogenated water. The negatively charged particles repel the silicon wafer surface of the same charge, do not re-adhere, and are removed from the surface. As compared with alkaline cleaning solutions like the APM as the most popular particle removal solution, hydrogenated water etches the wafers little and it is favored for wafers whose roughness must not be degraded and for surface-decorated wafers.

Rinsing with ultra pure water is not required after cleaning with hydrogenated water. Use of hydrogenated water in the rinse bath can prevent the particle adhesion in the rinse step. It is difficult to uniformly apply megasonics in conventional batch cleaning tanks. If there is metal ion contamination, the metal ions may adhere to the wafer surface. Given these problems, hydrogenated water is often used for spin cleaning wafers one at a time.

4.1.3 Electrolyzed water

Electrolyzed water is made from ultra pure water or an electrolyte solution, and electrolyzed water on the anode side and electrolyzed water on the cathode side are both used. Ozonated water and hydrogenated water can also be made from the anode and cathode sides, respectively, when ultra pure water is electrolyzed. When a solution containing chloride ions like hydrochloric acid or ammonium chloride is electrolyzed, an acid solution containing hypochlorous acid and having a strong oxidizing capability is produced on the anode side. This anodic solution has a strong oxidizing ability like ozonated water, and features excellent capabilities to remove metals and prevent the re-adhesion of metal contaminants.

As the wafer diameter increases with the resultant necessity of single wafer cleaning process, the consumption of chemical solutions is on the rise. Conversely, the mounting awareness of environmental protection is increasing the severity of requirements for reducing the manufacturing cost and eliminating some of the manufacturing steps. Functional water is low in manufacturing cost. The gas components of gas-dissolved water are spontaneously discharged out of the system after use. Electrolyzed water returns to the original raw solution condition if the anode water and cathode water are mixed after use, and is thus low in environmental load. Functional water has an excellent cleaning capability and is certain to find increasing applications as cleaning water capable of meeting ever severe environmental and cost requirements.

4.2 Cleaning with addition of chelating agent

Many complexes such as neutral hydroxides, solid hydroxides exist in SC-1 solution on the basis of ionic equilibrium, and neutral hydroxides adsorb on the wafer surface. Addition of a chelating agent to the SC-1 solution is proposed as one of the methods to reduce the adsorption of metal contaminants. Chelating agents react with metal ions to form stable complexes. A cleaning process which utilizes such chelating agents are already proposed.

5. Conclusions

The metal adsorption and particle adhesion mechanisms have been discussed above. Analysis of these adhesion behaviors is helpful in the development of technology for achieving higher cleanliness as required by relentlessly increasing integration density of VLSIs. The RCA cleaning process proposed in the 1970s has supported the present semiconductor industry. The advent of 300-mm wafers is about to change the cleaning methods for improving wafer surface cleanliness. To meet this change, it is necessary to analyze and control the reactions taking place on the silicon wafer surface at the atomic level. Such efforts will lead to the discovery of technology breakthroughs and the further advancement of the semiconductor industry.

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