



Handbook of Cleaning for Semiconductor Manufacturing

Fundamentals and Applications

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Foreword

Semiconductor electronic properties are extremely sensitive to the presence of trace amounts of foreign substances. This fundamental property of doped semiconductors is the basis for the fabrication of electronic devices. From the dawn of semiconductor based electronic devices, it has been clear that undesired impurities must be kept at very low levels and material purification methods were essential to the successful operation of such devices.

In the 1950's and 1960's, the solid state device of choice was the bipolar junction transistor (BJT), which required a sufficiently long free-carrier recombination lifetime and thus, a low metallic impurity concentration. To achieve this, semiconductor surfaces were cleaned at critical steps in the manufacturing process. In the early 1970's, the first systematic cleaning studies were carried out and resulted in the "RCA cleaning" process. The aqueous oxidizing mixtures (SC-1 and SC-2) were found to be very efficient at removing a broad range of contaminants such as organics and metals. SC-1, in particular, very effectively removes particles. These mixtures were highly selective towards silicon because of the stability of the passivating SiO_x on the silicon surface.

Although the metal-insulator-semiconductor lateral-field effect transistor had been invented in the 1920's, it was not until the late 1970's that the metal-oxide-semiconductor field-effect transistor (MOSFET) became a useful electronic device. It was only at that point that surface cleaning reached the capability needed to fabricate high-quality gate oxides with low levels of Na and K contamination essential for making MOSFET devices with stable threshold voltages. This delayed introduction also reflects the thermodynamic propensity of surfaces and interfaces to be the preferred sites for impurities. Within a decade, MOSFET technology replaced the BJT in large scale integrated circuits.

The field of cleaning is complicated by the fact that contamination is often near the edge of detectable limits; consequently, the progress of cleaning science has been tightly linked to advancements in metrology. For a long time, bulk semiconductor electronic properties, such as free carrier lifetime, were the primary measurement technique for contamination. Because MOSFET performance is in large part driven by the quality of its interfaces, more attention has been directed to surface quality and contamination. New metrology techniques such as high resolution electron energy loss spectroscopy (HR-EELS), high resolution X-ray photoelectron spectroscopy (HR-XPS), and Fourier transform infrared spectroscopy (FTIR) helped reveal a great deal about the nature of the chemical structure of a silicon surface and its relation to the aqueous chemical treatments. Surface inspection for particle contamination began in the 1980's with visual observation under collimated light

and has evolved to scanning laser light scattering measurement tools capable of detecting particles only a few tens of nanometers in diameter. Total X-ray fluorescence (TXRF) was developed in the 1990's and evolved from a research method to a monitoring technique for fast inspection for low-levels of metal contaminants. Time-of-flight SIMS made it possible to detect trace amounts of organic and airborne molecular surface contamination. The availability of these surface measurement techniques made contamination a measurable quantity transforming contamination control and cleaning from an experience-driven field into a science embraced by academic institutes and R&D centers.

The functionality of circuits has increased while feature size has shrunk at an astonishingly high and steady pace. From the early 1990's, the major quest for yield improvements on megabit-level memory chips has significantly boosted the development of improved cleaning processes and cleaner chemicals. During this wave of substantial investigation, concerns were raised that wet cleaning would quickly run out of steam; consequently, various types of dry cleaning were investigated. Wet cleaning, however, has remained the method of choice because of a number of reasons including: excellent particle removal due to a reduction of van der Waals attractions; highly selective chemical reactions; and good dissolution and transport properties.

The RCA clean has been the backbone in semiconductor cleaning because of its abovementioned properties. Current requirements for cleaning have become more constrained than at the time the RCA clean was introduced. Reduction in surface etching amounts and other issues require that the SC-1 mixtures be very dilute and at reduced temperatures. In many cases, the SC-2 step can be replaced by dilute HCl. These approaches have resulted in longer bath lifetimes, reduced chemical costs, and lower waste burdens. An acidified rinse has been used to further suppress contamination. Alternative simple cleaning recipes have been introduced, such as self-saturating chemical oxide growth using sulfuric acid spiked with ozone, followed by an HF-based mixture.

Cleaning tools have evolved to keep up with ever-changing processes. Wet benches consisting of immersion tanks are now equipped with recirculation and filtration units, automated filling *in situ* concentration monitoring, and automatic spiking systems. Simplified recipes have resulted in wet benches with fewer tanks. Single tank tools have been introduced for use with very dilute chemicals. The biggest change has occurred since 2000; single wafer cleaning gradually replacing batch tools for critical applications. Single wafer tools made it possible to treat both sides of a wafer differently and thus, provide isolation of the front and back surfaces allowing for high performance cleaning. For single wafer cleaning, process time limitations favor the use of more concentrated chemicals.

Currently wet cleaning has become more diverse and gained a very high level of sophistication. Cleaning is applied throughout the entire manufacturing process of integrated circuits from incoming wafers to sawing and packaging or 3D-integration. As technology progresses, cleaning requirements become more stringent with smaller margins. Often selectivity is a major challenge as the contaminants to be removed resemble more closely that of the layers to be cleaned. This has led to a variety of tailored cleaning processes for: incoming wafers, pre-gate dielectrics, after-gate stack etch, pre-selective epitaxy, several photoresist

removal steps and post-strip cleans, pre-metal deposition for silicide formation, post-silicide metal removal, post-CMP clean, and post-etch residue removal and cleaning. Specialized cleaning solutions have been introduced consisting of rather complex mixtures of acids, bases, solvents, surfactants, and chelating agents.

In recent years, high- κ metal gate stacks and alternative semiconductor materials such as SiGe, Ge, and even III-V compound semiconductors have been introduced or considered for future generation devices. Unlike Si, many of these materials tend to be attacked by “RCA”-like aqueous oxidizing cleaning mixtures. Therefore, alternatives must be developed such as solvent-based cleaning.

As part of the large effort spent over the last decades in this field, major international forums and symposia have been set up for the large “cleaning R&D” community to enhance and share their collective knowledge base. Many of these findings are published in numerous articles and conference proceedings. Particularly in this highly dynamic environment, it is very important to keep track of this acquired knowledge. The collective wisdom of this field is mostly in the minds of the participating researchers. The mission of this book is to extend this knowledge – capturing and synthesizing the major results and state-of-the-art knowledge of individual researchers and experts in the field of cleaning, surface conditioning, and contamination control.

This volume should become an essential part of a thorough training regimen on cleaning and surface preparation. It is a useful reference work for people active in the field and an absolute must for young engineers and researchers entering the dynamic and exciting discipline of cleaning and surface preparation. This handbook will help the industry avoid the unproductive and feared scenario of “re-inventions” and provide a solid platform to build the new science and technology of cleaning and surface preparation for future applications far beyond the current scope of cleaning science.

Paul W. Mertens
Leuven, Belgium

October 24, 2010

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Introduction

Semiconductor manufacturing continuously faces the most demanding technical challenges of any industry. As features have scaled, one of the most problematic areas of fabrication has been cleaning. Over the last few decades, the art of cleaning has turned into the science of surface preparation, critical cleaning, post-etch residue removal, and particle removal. Years ago the integrated circuit industry “borrowed” techniques from other industries – now the microelectronic engineers and scientists are the technology drivers. They work with the most advanced technology in the world making affordable microprocessors, controllers, and memory devices, so everyone can afford the newest electronic gadgets. These engineers work on devices that have minute features, rare materials, intricate equipment, and specialized processes. They help develop high-yielding, easily manufactured processes for the most sophisticated devices at the minimal cost and with the lowest environmental impact. This handbook celebrates these individuals – those who develop processes that are not physically present on a finished device. The chemicals used are all washed away, along with the contaminating metals, organics, and particles, yielding a pristine surface.

We have assembled authors with specific expertise to provide a thorough and thoughtful look at key range of cleaning topics in this field. The work is divided into three sections. The first six chapters address fundamental processes in chemical cleaning. Chapter 1 examines surface and colloid chemistry in cleaning, and Chapters 2 and 3 describe the chemistries of cleaning and etching processes. Chapter 4 details the surface phenomenon of cleaning. While chapters 5 and 6 discuss the design, delivery, and recycling of chemical formulations used in cleans. The second section (Chapters 7–14) covers a range of cleaning applications. Chapters 7, 8, 9, and 10 discuss cleaning and stripping of front end and back end of the line structures, Chapters 11 and 12 examine passivation and corrosion of copper and passivation of silicon and germanium. Wafer reclamation and wafer bonding preparation processes are discussed in Chapters 13 and 14. The last section of the book offers insight into the trends in cleans technologies. Chapter 15 details novel methods for evaluating the surface cleanliness and condition. The strip and cleans methods needed for the newest photolithography applications are discussed in Chapter 16.

Our book is dedicated to all the engineers past, present, and future that have and still toil feverishly and relentlessly to develop and utilize proven cleaning processes, and invent new ways to solve these crucial issues.

Karen A. Reinhardt
San Jose, California

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Denton, Texas
November 2010.

PART 1

FUNDAMENTALS

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Surface and Colloidal Chemical Aspects of Wet Cleaning

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Abstract

Surface and colloidal chemicals aspects relevant to wet chemical cleaning and drying of semiconductor surfaces are reviewed. Specific areas discussed in this chapter include surface charging of metal oxide and nitride films, development of an electrical double layer, zeta potential of electrified interfaces and its effect on particulate contamination, adsorption of surfactants and metal ions on insulating surfaces, principles of surface tension gradient drying, and wetting and penetration of high aspect ratio features.

Key words: interfacial phenomena, wet cleaning, surface charging of metal oxide and nitride, electrical double layer, metal adsorption, high aspect ratio cleaning, surface tension gradient drying

1.1 Introduction to Surface Chemical Aspects of Cleaning

The fabrication of integrated circuits requires a myriad of liquid-based etching and cleaning processes that are followed by rinsing and drying steps. Interfacial phenomena such as wetting, spreading, adsorption, adhesion, and surface charge play a critical role in determining the feasibility and efficiency of a liquid-based process step. The objective of this chapter is to discuss the fundamental science of the key interfacial phenomena relevant to wafer etching, cleaning, and drying. Specific areas discussed in this chapter include:

1. Surface charging of materials in aqueous cleaning and rinsing solutions – understanding of the physical phenomena related to the adhesion and removal of particulate contaminants and metal ions.
2. High aspect ratio cleaning – understanding the physical limitations induced by surface wetting and capillary forces for processes that require liquid penetration into narrow features.

3. Drying methods – understanding the physics of creating a surface tension gradient at the water/vapor interface through interfacial adsorption.

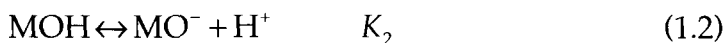
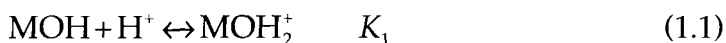
The aforementioned concepts should be considered in unison to understand and explain cleaning processes and to control contamination. For example, to remove metallic and particulate contamination, the cleaning chemical must wet the surface, desorb, and preferably complex the metal ion and create a surface which bears a charge of the same sign as that on the contaminant particles to prevent re-deposition.

1.2 Chemistry of Solid-Water Interface

Successful removal of colloidal particles from surfaces requires an understanding of the repulsive and attractive forces between the particle and the surface. The repulsive forces arise mainly from the interaction of charged double layer at the particle/solution and the wafer/solution interface. The degree of surface hydroxylation and acid-base characteristics of these hydroxyl groups impact the charging of a surface. Sections 1.2.1 and 1.2.2 describe the surface charging of silicon dioxide and silicon nitride in aqueous media.

1.2.1 Surface Charging of Oxide Films in Aqueous Solutions

The surface of a semi-metal oxide film is terminated with hydroxyl (–OH) groups. A comprehensive discussion of hydroxylation of an oxide surface is provided by Yopps *et al.* [1]. The density of these hydroxyl groups is roughly two to three per square nm [2]. When this oxide surface is immersed in an aqueous solution, the hydroxyl groups react with H^+ and OH^- ions. These interactions are represented using the following equilibrium equations [3]:



where M is a metal atom or an element such as Si.

Using the equilibrium constants (K_1 and K_2) for the reactions of the protonation (Eq. 1.1) and deprotonation (Eq. 1.2) of SiOH sites, the fraction of sites with positive, negative and zero charge, viz, θ_+ , θ_- and θ_0 on SiO_2 can be calculated as a function of solution pH. The result of such a calculation is shown in Figure 1.1 for SiO_2 using K_1 and K_2 values of $10^{0.7}$ and $10^{-3.9}$ respectively [4]. The surface charge density (coulombs per square meter), σ_{surf} at any particular pH is given by the expression:

$$\sigma_{surf} = N_s q (\theta_+ - \theta_-) \quad (1.3)$$

where N_s represents the total number of surface sites per square meter, and q is the fundamental electronic charge (coulombs).

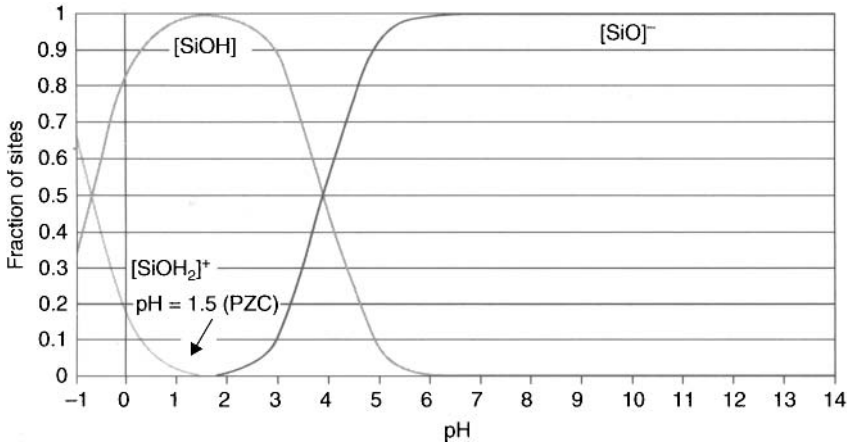


Figure 1.1. Fraction of positive, negative, and neutral sites on a SiO_2 surface immersed in water at various pH values calculated using $K_1 = 10^{0.7}$ and $K_2 = 10^{-3.9}$. Used with permission of the authors.

Figure 1.1 shows that the surface of SiO_2 is positively charged at low pH and negatively charged at high pH. At a pH of ~ 1.5 , the fraction of positive sites is equal to the fraction of negative sites. This pH is called the point of zero charge (PZC) [5]. It is worth noting that at the PZC while the fractions of positively charged and negatively charged sites may be equal, each fraction may not be 0.5. The PZC value is roughly equal to the average of $\text{p}K_1$ and $\text{p}K_2$. Reference [6] outlines surface charging theory with respect to wafer cleaning.

Oxides may be classified as acidic, basic, or amphoteric [7]. Acidic oxides are generally oxides of non-metals (*e.g.* SiO_2 , As_2O_3) that are dissolved by bases. By contrast, basic oxides (*e.g.* alkaline earth oxides such as MgO , FeO) are oxides of metals that are dissolved by acids. Oxides that show both acidic and basic properties are referred to as amphoteric oxides (*e.g.* Al_2O_3 , SnO). Acidic oxides exhibit a low PZC while basic oxides exhibit higher PZC. For example, SiO_2 , an acidic material, exhibits a PZC close to a pH of 2 while Al_2O_3 , a basic material, exhibits a PZC close to a pH of 9. Table 1.1 lists PZC of materials of interest to semiconductor processing.

An acid-base mass titration technique is typically used to determine the PZC of materials. In this technique demonstrated by Schwarz, a suspension of oxide particles in an electrolyte is titrated with a standard acid/base solution [14]. The protonation/deprotonation of the oxide surface causes the solution pH to increase/decrease from the original pH value. A mass balance from the added H^+ / OH^- ions is then made to obtain the extent of adsorption of H^+ and OH^- . The surface charge density, σ_{surf} is given by:

$$\sigma_{\text{surf}} = F \times (\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}) \quad (1.4)$$

where Γ_{H^+} and Γ_{OH^-} are adsorption densities (moles per square meter) of H^+ and OH^- , respectively, and F is the Faraday constant (96500 coulombs/gram equivalent).

The use of this technique is described in many papers [15–18] and only works well for samples with large surface areas such as particles. For materials with low surface areas such as oxide films, the pH change due to adsorption/desorption is too small to be accurately measured causing large errors in mass balance [19].

Table 1.1. Point of zero charge of materials of interest to wafer cleaning

| Material | PZC at pH of | Type | Reference |
|--------------------------------|---|---|-----------|
| SiO ₂ | 2–4 | Acidic | [8] [9] |
| Si ₃ N ₄ | 3–5.5 | Depends on relative proportion of NH ₂ and OH groups | [8] [9] |
| TiO ₂ | 5–6 | Weakly acidic | [10] |
| Al ₂ O ₃ | 8–9 | Amphoteric/mildly basic | [11] [12] |
| Si | 3–4 | Acidic | [8] |
| PSL | No PZC (negative charge at all pH values) | Not applicable (organic) | [13] |

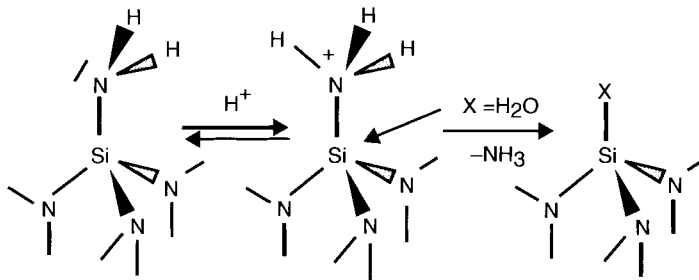


Figure 1.2. Charging of silicon nitride films in water; protonation of amine terminated surface sites leading to formation of positively charged sites that may react with water to form silanol groups [20]. Used with permission from Martin Knotter, NXP.

1.2.2 Surface Charging of Silicon Nitride Films in Aqueous Solutions

Silicon nitride films are most commonly deposited using a chemical vapor deposition (CVD) technique in which silane (SiH₄) reacts with ammonia (NH₃). Plasma-enhanced CVD (PECVD) forms SiN_x and low pressure CVD (LPCVD) forms Si₃N₄. Consequently, silicon nitride films may contain up to 5–6 atomic % hydrogen, especially those formed with PECVD. As shown in Figure 1.2, these films typically have amine (–NH₂) surface groups, which depending on their pK_a value can be protonated leading to the formation of positively charged sites [20]. The negative sites on the surface of nitride films have been postulated [21, 22] to be created by the reaction of surface amine groups with water forming silanol (Si–OH) followed by deprotonation to form negatively charged SiO[–] sites. The isoelectric point (defined in Section 1.2.3) of nitride films can vary widely depending on the hydrolytic strength of –NH₂ groups, which in turn will depend on the solution pH, ionic strength, and temperature.

1.2.3 Electrified Interfaces: The Double Layer and Zeta Potential

A solid immersed in an aqueous solution produces a region of electrical inhomogeneity at the solid-solution interface. An excess charge at the solid-solution