國立交通大學

工學院半導體材料與製程設備學程

碩士論文

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碩士論文

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摘　要

堆疊式電容為動態隨機存取記憶體(DRAM)的關鍵組件。為增加電容值，目前製程大多利用高選擇比之氫氟酸將氮化鈦(TiN)下電極周圍之介電質做濕式等向性回蝕刻(Crown Wet Etching Back Process)，以期達到雙倍表面積的覆蓋率(Surface Area Coverage)之目的。回蝕刻製程後易產生許多副產物與雜質並會重新附著於晶圓表面，進一步影響到製程良率。研究中藉由應用材料公司(Applied Material)所發展之缺陷量測機台做掃描式電子顯微鏡(SEM)外觀分析及X光能量分散光譜（EDS)元素分析後得知副產物成分以碳(Carbon)、矽(Silicon)、鈦(Titanium)及氧(Oxygen)為主。本研究主要目的為找出一個適合高深寬比電容結構的清洗方式，期能去除電容製程後所產生之副產物並避免電容結構倒塌且維持電容間的電子特性。研究方向包含選取適當機台(單片處理機台或批次噴灑式處理機台)及不同種類pH值之混合酸液(EKC6800、REZI38、EKC265、ELM C30、EcoPeeler)。決定出最適當的機台與酸液後，將進一步探討處理時間與旋轉速度對雜質及副產物去除能力之影響。

研究結果顯示之最佳條件為兼具製程容忍度大且雜質去除率最高的條件:酸液 EKC265 搭配批次噴灑式處理機台。含氰胺(HDA)之化學混合溶劑 EKC265,使雜質與基板之間的界面電位(zeta potential)處於同極性而互相排斥,進而提升雜質去除率。氰胺為強氧化還原劑,使金屬氧化物質還原成可溶於異丙酮(IPA)之螯合物。此外選擇應用於 EKC265 處理時間則不宜過久,若處理時間太長 Titanium 將被過度回蝕刻,結構易倒塌;然則太短雜質去除率有限,多種不同處理時間經搭配並選擇適當之旋轉速度後所得最佳化條件,可使雜質去除率達到 80%。旋轉速度低於 650rpm 以下則雜質去除率呈線性,但於 650rpm 以上去除率則下降;主要原因為化學反應效果於 650rpm 以上被限制全由物理力量主導所致。最後的最佳化條件經重複驗證後,被證實可用於 60nm 以下之動態隨機存取記憶體世代且對於產品良率具有顯著改善。

The Study of Cleaning Methods for DRAM Capacitor

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Degree Program of Semiconductor Material and Process Equipment

College of Engineering

National Chiao Tung University

ABSTRACT

In a modern stacked-capacitor DRAM device, the structure of the storage capacitor can be thought of as a vertical cylinder made of titanium nitride (TiN). To maximize the capacitance of the cell in high-performance DRAM devices, the dielectric material surrounding the storage nodes needs to be removed during the fabrication process to increase the surface area. This process is known as the crown capacitor wet etch process. However, the wafer surface is highly contaminated by particle defects during the dielectric material removal process. Using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS), these particulate defects are shown to be mostly silicon-rich, titanium-rich, carbon-rich and oxygen rich. Particulate defects that appeared on top of the capacitor are the major yield killers for the DRAM device. This study will focus on choosing a suitable tool (between the batch type spray tool and the single wafer tool); and chemical (EKC6800, REZI38, EKC265, ELMC30 and EcoPeeler) with a high residue and particles removal ability. The best optimized cleaning recipe, which includes process time and rotation speed, is developed to provide a sufficient process window for this process.

Also, the results of this work are discussed and analyzed. The batch type process spray tool in combination with the hydroxylamine (HDA) based chemical: EKC265 with high pH, is proved to be efficient in removing particles and residues of high aspect ratio capacitor structures in this work. Zeta potential in the alkaline solution (EKC265) is negative, thus it tends to repel the particles on specimen surface which is also negative-charged. In addition, the combination of HDA and an organic amine form a strong reducing complex solution which can reduced insoluble metal oxide into a lower oxidation state and subsequently chelated with the ligand to form a more soluble metal complex.

Particle count reduces proportionally with chemical treatment time. However, there is a risk of pattern collapse with a long treatment time due to the increment of titanium etch amount. Rotation speed also plays an important rule for particle removal. A higher rotation speed implies stronger external momentum to detach particles. But, it will also limit the efficiency of the chemical reaction. Thus, a balance between chemical reaction and physical reaction has to be considered.

The final optimal condition proves to be significant to yield improvement and is demonstrated to be robust and able to be implemented for 60nm generation DRAM.

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This thesis could not be finished without the help and support of many people who are gratefully acknowledged here.

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Lastly, I offer my regards and blessings to my family who supported me in all aspect during the completion of the project.

Ng Wei Yeeng.

Outlines

Figure Captions

Chapter 1 :

Chapter 2 :

Chapter 3 :

Chapter 4 :

Table Captions

Chapter 1 :

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Chapter 4 :

Graph Captions

Chapter 3:

Chapter 4:

Chapter 1: Introduction

1.1 DRAM capacitor

A typical dynamic random access memory (DRAM) cell consists of an access transistor and a storage capacitor (1T/1C). There are two types of storage capacitors, stacked-capacitors and trench capacitors, of which the latter offers highest density, at the expense of process complexity [1]. In 1977, M.Koyanagi fabricated the first DRAM test chip with a stacked capacitor cell using 3 μm NMOS technology [2]. Then, a stacked capacitor cell was employed in a 1Mbit DRAM production for the first time by Fujitsu [3]. Hitachi also employed a stacked capacitor cell in 4Mbit DRAM production [4]. Many other DRAM companies used a trench capacitor cell in the early stage of 4Mbit DRAM production. However, the stacked capacitor cell, which eventually came to occupy a major position in 4Mbit to 4Gbit DRAM's, has evolved by introducing the three-dimensional capacitor structures with a fin-type electrode [5] and a cylindrical electrode . As the design rule of DRAM shrinks down below 100nm, the novel MIM capacitor processes are inevitable [6].

To achieve sufficient memory cell capacitance in a limited area, a crown wet process is designed to gain more effective capacitor area by using etch rate selectivity of wet etchant. (Figure 1.1) A brief fabrication process procedure for a capacitor over bitline (COB) is proposed. After the transfer gate transistor formation, W/WN bit line is defined before storage capacitor formation. Silicon nitride and thick CVD PSG / BPSG are deposited according to the required storage node height. Then, the storage node region which is packed with minimum space is defined by PSG/BPSG etching. Subsequently, TiN film which is used for the storage node is deposited with a CVD tool. The gap of the cup-shaped capacitor is then filled by PSG. Next, CMP polishes the wafer structure until the silicon nitride end point is detected. Then, another patterning process is undergone to etch off the supporting silicon nitride. Finally, the whole wafer will be treated under a 49% HF portion, due to the high etch rate selectivity of SiN to BPSG/PSG and SiN film, all of the BPSG and PSG will be removed completely, while the SiN remains to support the cylinder. Now, a so-called crown shaped stacked capacitor with sufficient cell capacitance is formed. The feature of the crown shaped stacked capacitor structure is that both in- and out-sides of the storage node are used as cell capacitors.

However, after the crown wet capacitor formation, particulate defects which prove to be a yield killer are found all over the process wafer. The cleaning method after the crown shaped stacked capacitor formation will now be discussed.

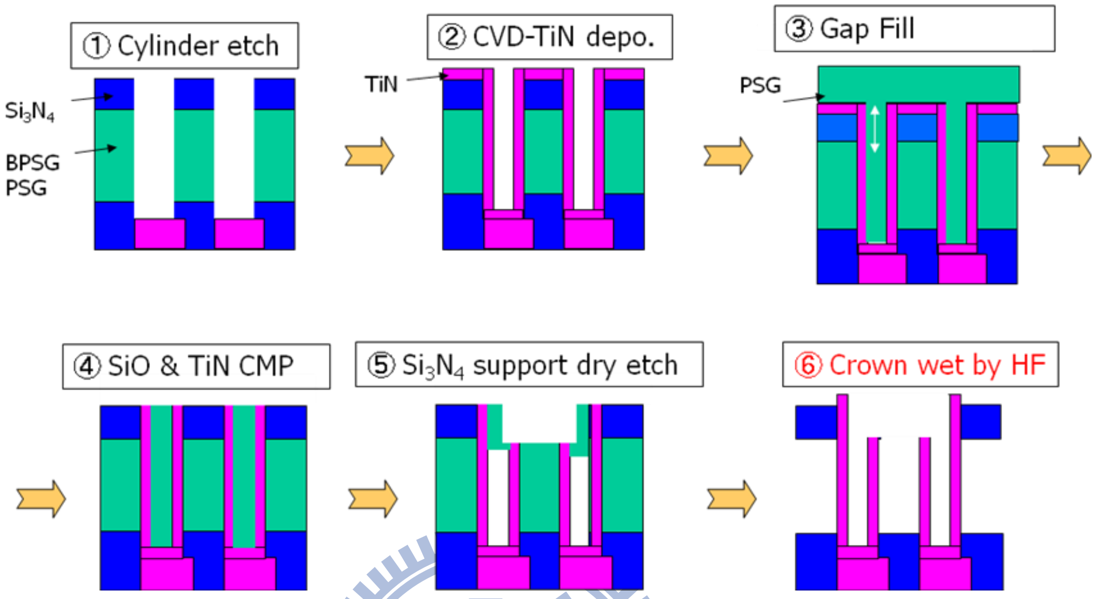

Figure 1.1 Fabrication procedure of crown stacked capacitor.

1.2 Wet cleaning process

In general, compared with other industrial products, the yield of VLSI is conspicuously low. Among the causes of failure in mass-produced devices, random structural defects caused by particle adhesion onto the wafer or reticle occupy an extremely large proportion, and have become the single largest cause of yield reduction [7]. Furthermore, along with the increment of memory integration levels, the failure of pattern defects caused by particles increased most markedly.

Across the range of manufacturing techniques, maintaining wafer cleanliness has become the crucial issue for improving yield and reliability. Every wafer-processing step is a potential source of contamination, not only from particles but also from a variety of other contaminants. In order to remove these contaminants, cleaning steps appear repetitively within the semiconductor process flow, occupying 30~40% of all the process steps. As the advanced semiconductor device technology progresses from the half-micron era to the quarter-micron era and beyond, the severity of demands for cleanliness will continue to increase [7].

Cleaning process is required to achieve (i) ultraclean surface, (ii) without any adverse side effects, (iii) within a short period of time, (iv) with high reproducibility, (v) at low cost. The requirement by the industry is becoming more severe along with further integration of ULSI [8]. Cleaning technology, therefore, must be innovated to meet the ever-increasing requirements.

The high-performance and multi-performance features needed for this generation of cleaning are: controllable selectivity, multi-functionality, adaptability to high aspect ratios and finer structures, efficient cleaning for high density particles and reduction of cleaning costs and of the number of cleaning process steps. A variety of wet cleaning processes are performed to remove metallic ions and particles. The current ULSI wet-cleaning technology is based on the so-called RCA cleaning published by Kern and Puotinen of RCA, Inc. in 1970 [9]. Table 1.1 shows a process flow of a typical current ULSI wet-cleaning based on the RCA cleaning [10]. It also shows characteristics of each cleaning solution.

These cleaning steps use ultrahigh-purity chemicals and ultra pure water in which metallic contaminant is reduced to the ppt order or less. H_2O_2 used in SPM (H_2SO_4 / H_2O_2), HPM (HCl / H_2O_2 / H_2O), and APM (NH_4OH / H_2O_2 / H_2O) is a strong oxidizing agent. H_2O_2 oxidizes and decomposes contaminants to raise the removal efficiency, and oxidizes the top surface of Si substrate to form a passivation (SiO_2) film at thickness around 1 nm. HCl, a typical strong acid, dissolved oxidized metal (oxides, hydroxides, and ions). H_2SO_4 decomposes organic contaminant and HF dissolves SiO_2, whereas these two acids can also dissolve oxidized metals. NH_4OH, the only alkali component, not only dissolves organic contaminants but also removes insoluble particle [10].

However, these chemicals cannot be applied to metal surfaces as it uses H_2O_2, strong acids, and strong alkali which corrode metal materials such as Al, W, Cu and Ti.

Although organic solvent or ultrapure water can be used for post-metallization cleaning, their cleaning performance is not sufficient. Reduction of pattern size which leads to higher aspect ratio is important in DRAM device, in addition, it becomes increasingly important to improve the cleaning performance [11].

Table 1.1 Typical cleaning solutions used in the semiconductor manufacturing process [10].

Cleaning Solution	Composition	Purpose
APM (SC-1)	$NH_4OH/H_2O_2/H_2O$	Removal of organics and particles
HPM (SC-2)	$HCl/H_2O_2/H_2O$	Removal of metallic ions, surface passivation by native oxide formation
SPM	H_2SO_4/H_2O_2	Removal of organic contaminations & metallic ions
DHF	HF/H_2O	Removal of native oxide film and metallic ions

1.3 Objectives

This thesis will focus on the study of metal surface cleaning method for post-crown-wet- stacked capacitor in the $6F^2$ 60 nm DRAM technology. The objective of this work is first to study how to get a defect and particles free wafer after the HF dip crown wet process (as mentioned in section 1.1, procedure 6) , in order to gain more yield for a 60 nm DRAM in 300mm wafer. In other words, this thesis focuses on unraveling the key process of particle generation, and the most efficient way to remove them. Then, a model will be setup which takes into account the physical and chemical wet cleaning mechanism. The principles behind the model will be then discussed. The procedure to derive defects and particles with 300mm defect inspection tool of Applied Material (AMAT) Complus 3T is demonstrated.

1.4 Organization of the thesis and methods

The focal point of this work is to find the ideal way to remove crown capacitor particles after wet etch treatment. All specimen used were 300mm DRAM wafers, with capacitor structures (which also known as storage node) height of 1.7um, critical dimension (CD) 0.091 um, and an aspect ratio of 18.7. In Chapter 2, an overview of wafer contamination, including defect and particles sources analysis will be presented. Then, the process variable of this study which will involve different kind of chemicals and tool will be introduced in Chapter 3. The investigated processing steps include: the removal of BPSG and PSG in HF solution (Crown Capacitor Wet Etch) and the follow up cleaning and polymer residue removal process. They are common processing steps in the DRAM fabrication facility used for this study. In Chapter 4, the experimental design and results will be discussed. To analyze defect sources, measurements before and after the processing step are conducted. The observation of the change in particle and defect counts due to different experimental parameters will be discussed which leads to a better understanding of the impact of each parameter on particle removal. The thesis ends with a general conclusion of the research described together with suggested future study in Chapter 5.

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Chapter 2: Overview of Particulate Contamination Aspects: Defect and Particle Sources Analysis

2.1 Introduction

In the semiconductor process, the word “contamination” has generally implied any items other than intentionally applied matter and morphologies which adhere inadvertently to the wafer and give rise to external disturbances. Silicon is constitutionally very sensitive to these kinds of external disturbance, and this sensitivity has been exacerbated by the development of ultrafine processes [1].

Contaminants are morphologically categorized into four groups: particles, metallic contaminants, organic contaminants, and unintended native oxide. A cleaning process is required to thoroughly remove these contaminants without inducing any adverse side effects such as excessive etching, increase of surface microroughness, and pattern damage [1].

The device characteristic degradation caused by each form of contamination is shown in Table 2.1 [2], and these connections are not independent phenomena, but rather, are interrelated in a complex way, and even hasten the development of each other. The structure of ultrafine devices with high aspect ratios causes a local concentration of stress within the wafer, which influences the distribution of metallic contaminants and other impurities; this seems to accelerate degradation, such as the reduction of the dielectric strength of thin insulating films and the increase of junction leakage current. Because degradation is generated by this kind of reciprocal action between the device structure and contamination, the same contamination level can result in failures in some devices and none in others. Of the various forms of contamination, the one which causes most device failures in mass production is the particle. In fact, more than 70 to 80% of the sources of yield reduction in DRAM devices are due to particles. The rest are due mostly to metallic contamination. Other problems appear during process development and trial operations of new equipment, and in many cases countermeasures can be found before they are implemented in mass production.

Table 2.1 Device characteristic degradation due to contamination.

Contaminant	Degradation of device characteristic
Particle	Pattern defects, oxide dielectric strength failure, ion-implantation failure
Metallic Ion	Junction leakage failures, interface states increase, Vth shift, gate oxide degradation, lifetime reduction
Organics	Abnormal film growth, contact resistivity increase, crystalline defects, gate oxide degradation
Native Oxide Film	Contact resistivity increase, crystalline defects (Epi), selectivity degradation of selective CVD, gate oxide integrity degradation
Surface microroughness	Gate oxide integrity degradation, mobility degradation due to surface scattering

Particle contamination has for the most part entailed measuring the number of particles and their diameters, but in order to determine the origin of contamination and devise an effective countermeasure for its prevention, it is also essential to analyze the particle composition and chemical states.

This chapter will give an overview of analysis for particles adhered to the wafer after crown capacitor wet process, so that we can take a fuller look at the direction of improvements.

2.2 Origins of Defect and Particles Occurrence

In order to clarify the defect source of the crown capacitor process, a step-by-step defect analysis is undergone. The defect inspection is executed after crown wet etch, high-k deposition, CVD TiN deposition, boron poly-silicon deposition, tungsten sputter, PETEOS deposition and tungsten etch respectively. This analysis used 6 wafers in 1 lot to check the defects occurrence and its origin. Defects are categorized into two simple classifications: big particle defects and sheet particle defects. A more detailed defect classification will be used in experimental design.

As shown in Figure 2.1, most of the big particles and sheet particle defects originate from the 3S crown capacitor process. In the crown wet process step, particle generation occupied 50% of all investigated process. Hence, understanding particles generated on crown capacitor wet etch back process is very important to gain a better line yield for 68 nm DRAM.

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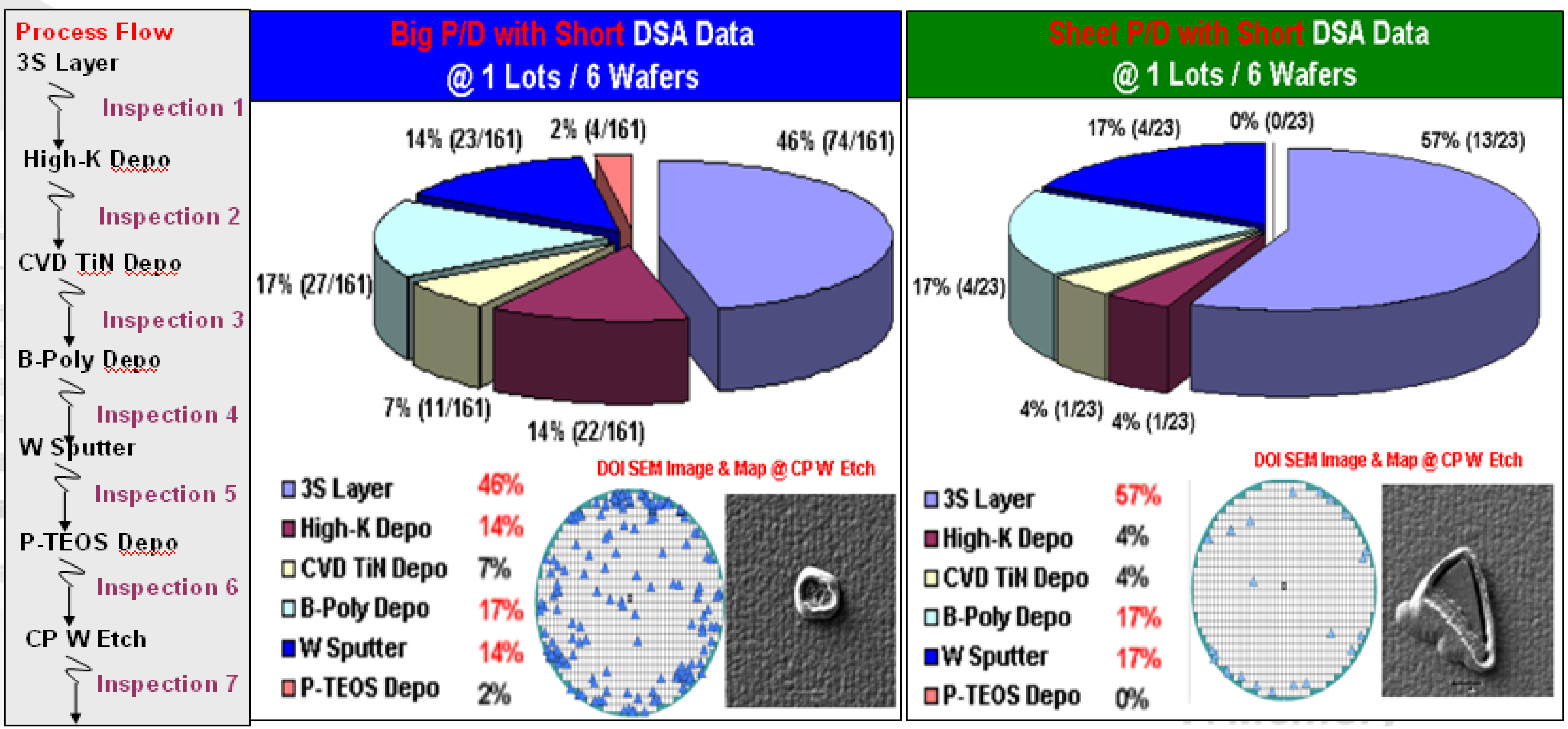


Figure 2.1 Defect source step-by-step inspection.

2.3 Types and Composition Analysis of Particles

In the semiconductor production line, short cycle time and high yield are demanded. In order to ensure high yield in mass production, it is very important to control, reduce, and prevent the particles generated by each process step. Finishing the product requires days or even months, it is often too late to begin detection and analysis at the end of the process; in addition, it becomes increasingly difficult to isolate the deficiencies of a process after several steps. Thus, defects detection at an early stage, after the process step, can help us measure the number of particles and their diameters; as well as determine the origin of contamination and analyze the particle composition of chemical states [2].

Both Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) are applied in this analysis. SEM is used to produce the image for particle morphology; while, EDS can provide elemental analysis.

2.3.1 *Defect Types Categorization*

In this investigation, the 300mm wafer is divided into two zones to clarify the defect sources: zone A, 15mm to the edge; zone B, radius of 135mm from the center (Figure 2.2). Defects are classified according to shape, size, and elemental component. The cover rate of each zone will be analyzed.

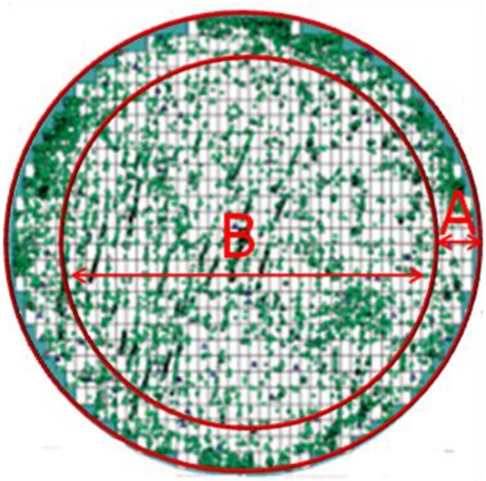


Figure 2.2 Schematic of specimen defect zone. (Zone A: 15mm to wafer edge; Zone B: radius 135mm from wafer center).

2.3.2 Analysis of Composition

Figure 2.3 shows the distribution of defects in zone A. 65% of the particles in zone A are larger than 1µm, these include big sheet particles and big peeling particles; which are mostly titanium (Ti) or titanium nitride (TiN). Another 35% of particles covered on the wafer are smaller than 0.5µm, and they are notable as small particles. These small particles contain both Ti and TiN. The reason Ti and TiN appear on the wafer edge is speculated to be due to the pattern damage from ugly dies during lithography and etching processes. Bottom electrodes that are made of Ti can be weak and easy to collapse.

As for Figure 2.4, defects in zone B are described. Mostly defect particles distributed in the wafer center are organic-like residues. They consist of carbon, oxygen, and some of them are fluoro-like. The reaction of 49% HF and BPSG is believed to form these kinds of carbon rich, silicon rich and fluorine rich residues. These residues are believed to be chemicals bonded with the surface of Ti and form strong van der wall forces.

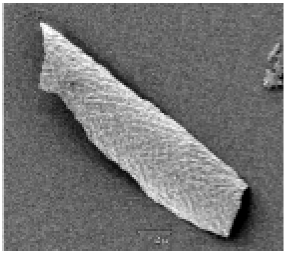
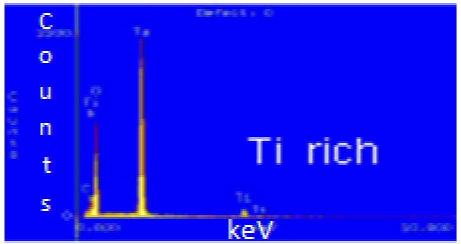
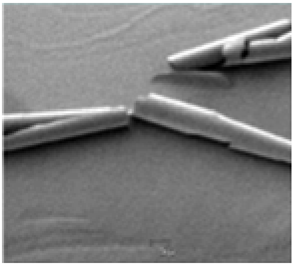
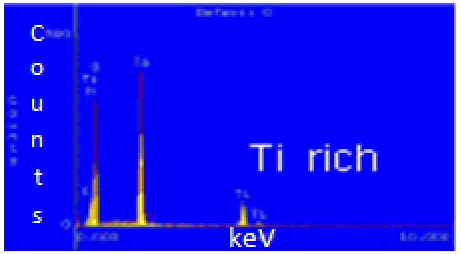
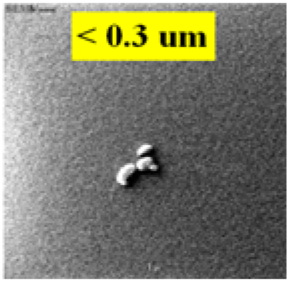
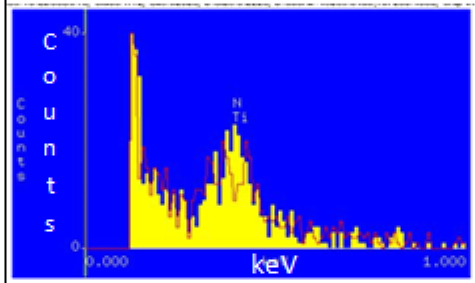
Zone A (15 mm to the edge)				
Image	Item	EDS	Major Component	Cover Rate
	Sheet Particles (SEM magnification: 5K)		Titanium, Titanium Nitride	30%
	Peeling Particles (SEM magnification: 10K)		Titanium, Titanium Nitride	35%
	Random Small Particles (SEM magnification: 10K)		Titanium Nitride	35%

Figure 2.3 Categorization and EDS analysis for defects at zone A.

Zone B (135mm in radius from wafer center)

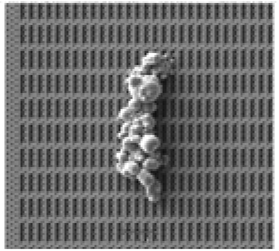
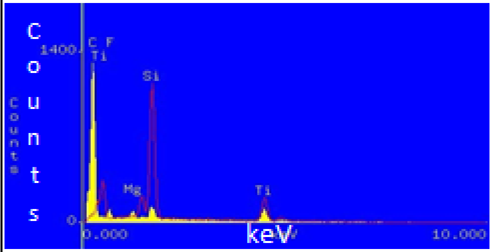
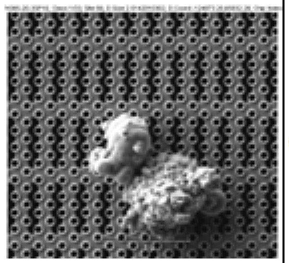
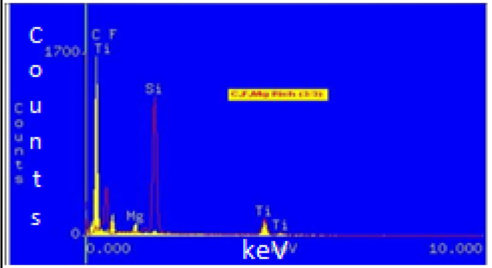
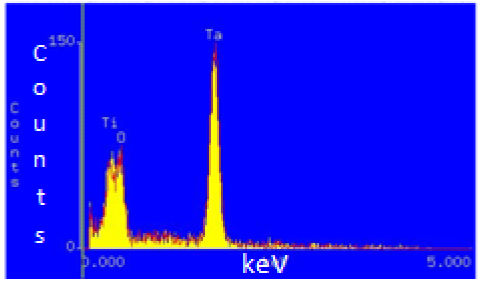
Image	Item	EDS	Major Component	Cover Rate
	Residues (SEM magnification: 10K)		Carbon, Fluoro	57%
	Residues (SEM magnification: 10K)		Carbon, Fluoro, Titanium	
	Small Particles (SEM magnification: 20K)		Titanium, Oxygen	43%

Figure 2.4 Categorization and EDS analysis for defects at zone B (135 mm in radius from wafer center).

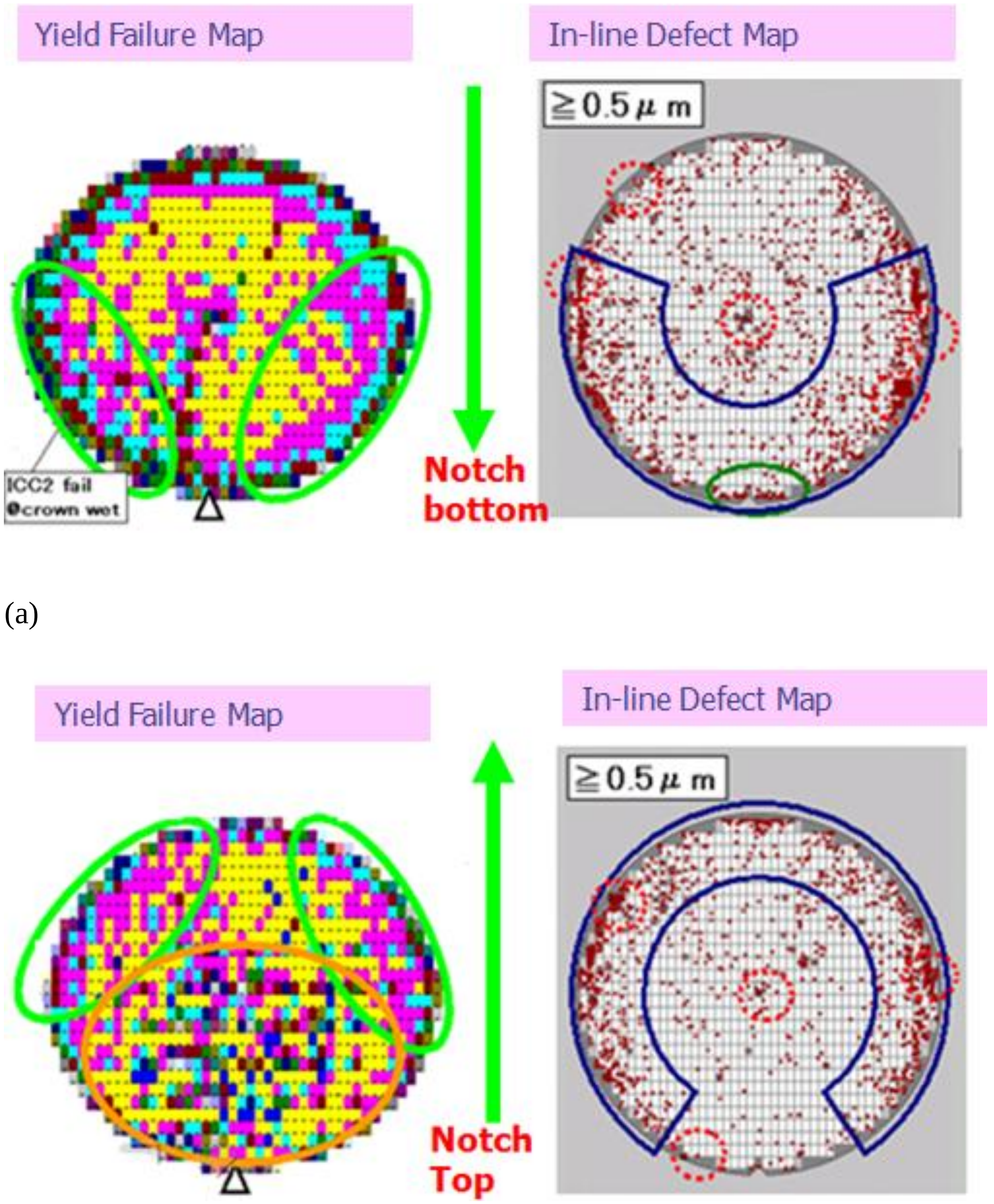
2.4 Effects of Particulate Contaminations on DRAM Device

Device characteristic degradation due to particles include pattern defects, degradation of the insulating film's dielectric strength, and failures due to local masking during ion implantation and etching. Of these, the biggest cause of degradation is the pattern defect. Wafer yield loss is mostly determined by short and open circuits caused by particles generated during metallization [3].

2.4.1 Defect Impact on Wafer Yield Failure

Figure 2.5 (a) and (b) compare the direct impact of defects after the crown wet etch process on the wafer failure map. As in Figure 2.5 (a) the failure of Icc_2 standby current is coloured in pink; the notch orientation of lot A during 49%HF wet process is shown by an arrow pointing at the bottom of the tank (Figure 2.5 a): the wafer failure map shows exactly the same distribution as the defect inspection map. On the other hand, in lot B (Figure 2.5 b) the notch orientation is 180 degrees reversed to the top and both the defects map and wafer failure map rotates. Meanwhile, as observed from both Figure 2.5 (a) and (b), the coverage of defects near the bottom of the tank is proved to be denser compared to the top and wafer center. This is mainly due to the flow field close to the wafer guide and the frictions at the touch point between wafer guide and wafers.

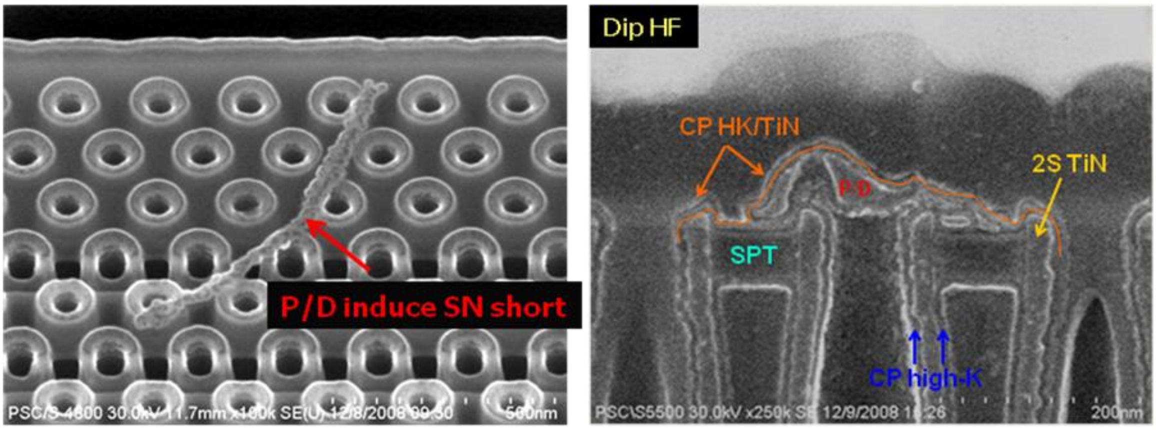
Figure 2.6 is the analysis in wafer failure test. The SEM cross-section indicates that the particle defects appear before High-K dielectric deposition but after bottom TiN electrode formation. Thus, it is proofs that these particle defects comes from crown wet capacitor etch process from wet bench.



(a)

(b)

Figure 2.5 (a) Failure map versus in-line defect map of lot A; wafer notch pointed to bottom of wet bath tank during crown wet etch back process. (b) Failure map versus in-line defect map of lot B; wafer notch pointed to top of wet bath tank during crown wet etch back process.



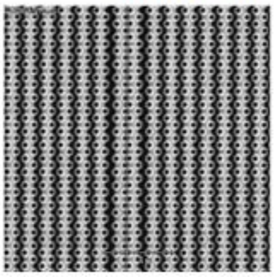
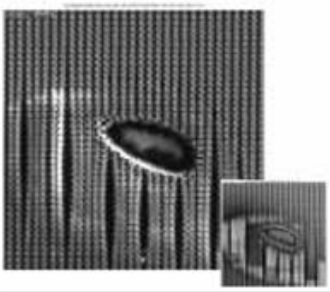
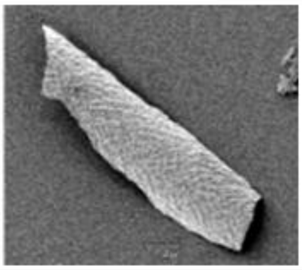
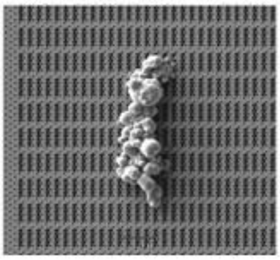
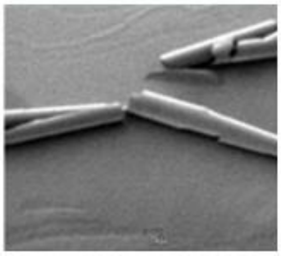
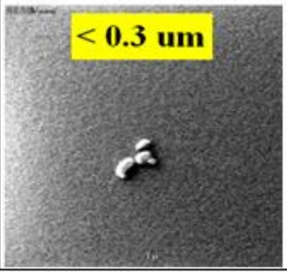
(a) (b)

Figure 2.6 (a) Top view of particle defect induced capacitor short (b) Cross section of particle defects appear before high-K dielectric deposition and after bottom TiN electrode formation.

2.4.2 *Summary of Yield Loss for Each Defect Categorization*

All defects including pattern collapse, particles and residues after the crown wet etch process are taken into account the yield loss. 250 wafers together with defects and wafer yield data are compared and analyzed. The average yield loss is predicted. Table 2.2 summarizes the correlation of each defect type after crown wet etch to the yield loss. However, pattern collapse and penetration which caused 1 percent of yield loss will not be focused on this study. This study will focus generally on the particle removal ability: how to remove big sheet particles, residues, peeling particles and wafer edge cluster, small particles, that totally impact 2.2 percent of wafer yield loss will be evaluated.

Table 2.2 Summary of yield loss for crown wet etch defects.

Defect Type	Defect Map	Yield Loss
Pattern Collapse (SEM magnification: 10K)		0.80%
Penetration (SEM magnification: 10K)		0.20%
Big Sheet Particle (SEM magnification: 5K)		0.30%
Residues (SEM magnification: 10K)		0.60%
Peeling Particles (SEM magnification: 10K)		0.90%
Wafer Edge Cluster Small Particle (SEM magnification: 10K)		0.40%
Total Yield loss		3.20%

2.5 Particle Adhesion in a Liquid Bath

To understand the particle detachment from the wafer surface, it is essential to understand the particle adhesion on the wafer. This section will briefly introduce three key parameters that contribute to the deposition and detachment of particles on the wafer surface. After the treatment of concentrated HF on the crown wet capacitor, hydrophobic surface is considered in the following discussion.

2.5.1 Zeta Potential

Particles dispersed or suspended in a liquid system are called colloids. Colloids typically acquire an electrical charge when immersed in a liquid medium [4]. Charge on a colloid is often measured in terms of a zeta potential, the potential at the shear plane between the colloid and the liquid. A typical charge distribution surrounding a colloid is sketched in Figure 2.7 [5]. Electrical potential at the colloid surface is maximum and decreases through the surrounding layers of excess positive ions until reaching the value of the bulk solution where equilibrium concentrations of positive and negative ions exist.

Relative motion of the colloid with respect to the solution divides the positive ion sheath into two regions: (i) the ion region near the charged colloid that moves with the colloid; and (ii) the diffuse region remote from the colloid which moves with the bulk liquid. The boundary between these two regions is the shear plane, and the potential at this shear plane is called zeta potential.

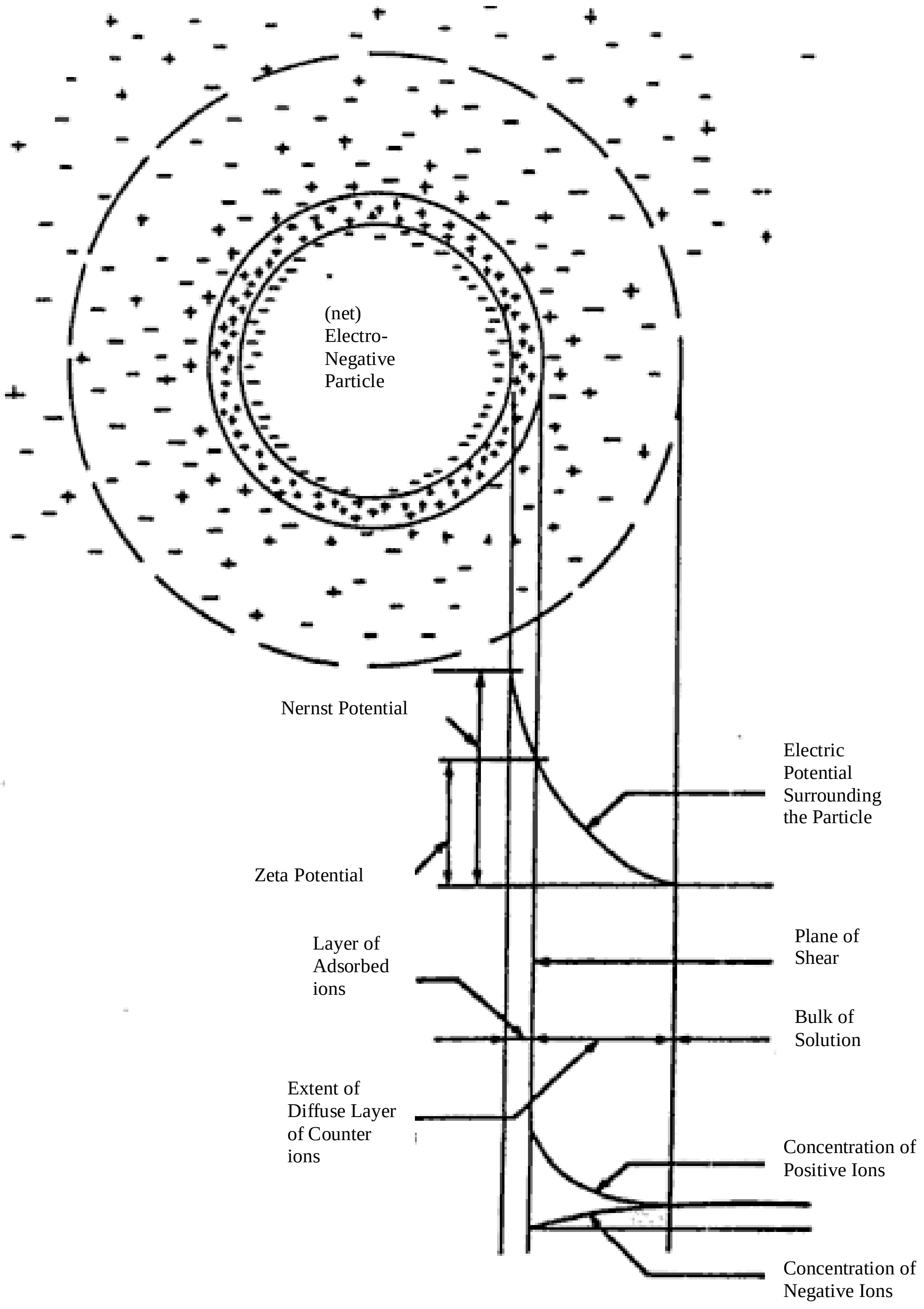


Figure 2.7 Electrostatic double layer around a particle [5].

In liquid, both the wafer surface and the particles acquire surface charge, which is characterized by zeta potential. It is independent of particle size but depends on the electrolyte pH: in acidic conditions (low pH) the zeta potential is positive, and in alkaline solution it tends to be negative, as shown in Figure 2.8. Like charges repel each other and opposite charges attract each other. Acid cleans, such as HF, which result in a positive zeta potential for most particles and a negative zeta potential for silicon surfaces, are therefore prone to particle adhesion [6].

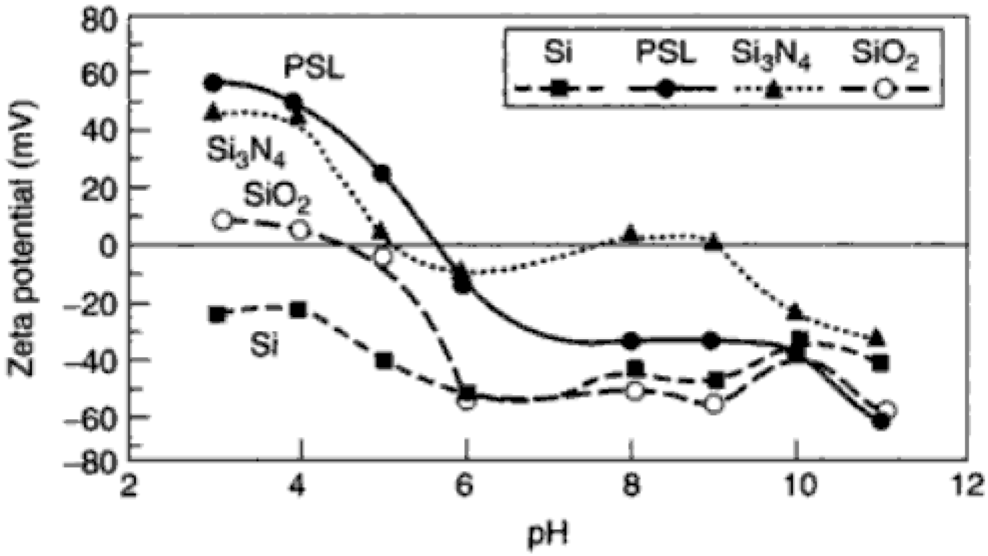


Figure 2.8 Zeta potential: pH influences particle adhesion and removal [7].

2.5.2 Electric Double Layer Repulsion

The fundamental interactions occurring between particles and the wafer surface in solutions are the van der Waals force and the electrostatic force (the reciprocal action of an electrical double layer) [8].

If a negatively charged colloid is repelled from a negatively charged wafer surface, then it is the repulsive forces that dominate the interaction between them, no contact between them will take place and no deposition will occur. This interaction is called electrostatic double layer repulsion (EDR) [7].

The width of the diffuse layer depicted in Figure 2.7 depends on the ionic strength of the liquid surrounding the particle. At high concentration, the range of the region of excess positive charge is short because the particle charge can be balanced by only a small volume of liquid.

2.5.3 Van der Waals Attraction

Van der Waals attraction between molecules arises from an interaction between the electron clouds surrounding each molecule. The displacement in electron distributions induced by the presence of the other molecule introduces a dipolar electric force which is always attractive [9].

The entire reciprocal action between the particle and wafer is shown as the sum of the electrical double layer potential and the van der Waals potential; if it is positive, repulsion acts between the particle and wafer, and if it is negative, attraction. On the other hand, the electrical double layer in the vicinity of the charged suface changes according to the sphere of influence of the ion density in the solution. When the ion density in the solution increases, van der Waals attraction is superior to the electrical double layer repulsion, and particles are deposited.

Figure 2.9 shows the case in which the zeta potentials of the particle and the wafer surface are the same sign. When the signs are different, the electrical double layer force and van der Waals force acts as an attraction, conditions which cause particles to deposit easily.

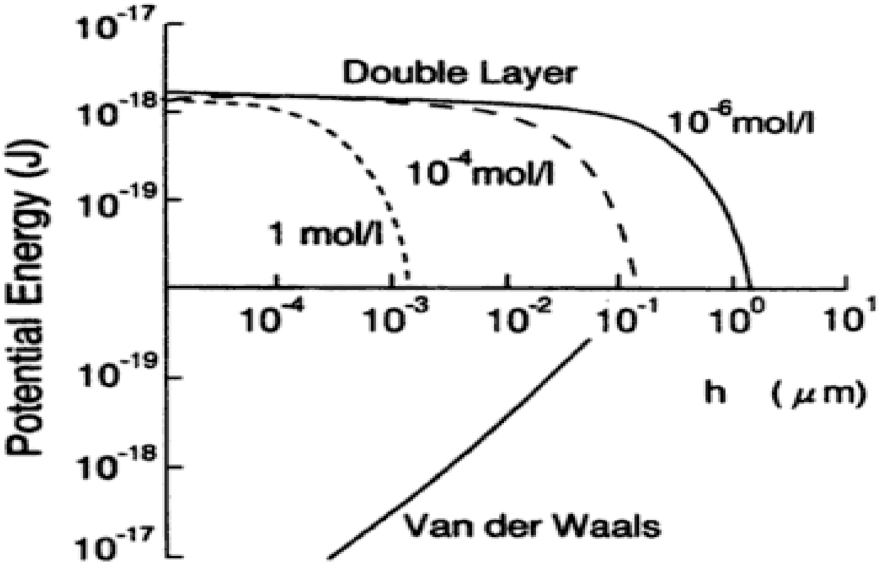


Figure 2.9 An example of a calculation of the reciprocal interaction between a particle and the wafer surface.

2.5.4 DLVO Theory

The interaction energy between two particles can be represented according to the DLVO theory of colloidal stability [10][11]. The DLVO theory of colloidal stability assumes that the coagulation behavior of particles depends mainly on the van der Waals interactions energy and on the double layer interaction energy. DLVO theory suggests that the stability of a particle in solution is dependent upon its total potential energy function V_T. This theory recognizes that V_T is the balance of several competing contributions:

$$V_T = V_A + V_R + V_S \qquad \text{(Equation 2-1)}$$

Where V_S is the potential energy due to the solvent, it usually only makes a marginal contribution to the total potential energy over the last few nanometers of separation. Much more important is the balance between V_A and V_R, these are the attractive and repulsive contributions. They potentially are much larger and operate over a much larger distance.

$$V_A = -\frac{A}{(12\pi D^2)} \qquad \text{(Equation 2.2)}$$

Where A is the Hamaker constant and D is the particle separation. The repulsive potential V_R is a far more complex function.

$$V_R = 2\pi\varepsilon a \xi^2 \exp(-\kappa D) \qquad \text{(Equation 2.3)}$$

where a is the particle radius, π is the solvent permeability, κ is a function of the ionic composition and ξ is the zeta potential.

DLVO theory suggests that the stability of a colloidal system is determined by the sum of these van der Waals attractive (V_A) and electrical double layer repulsive (V_R) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together (Figure 2.10). But if the particles collide with sufficient energy to overcome that barrier, the attractive force will pull them into contact where they adhere strongly and irreversibly together. Therefore, if the particles have a sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. However, if a repulsion mechanism does not exist then flocculation or coagulation will eventually take place.

In certain situations (e.g. in high concentration HF), there is a possibility of a "secondary minimum" where a much weaker and potentially reversible adhesion between particles exists together (Figure 2.11). These weak forces are sufficiently stable, and can't be broken up by Brownian motion, but may dissociate under an externally applied force such as vigorous agitation.

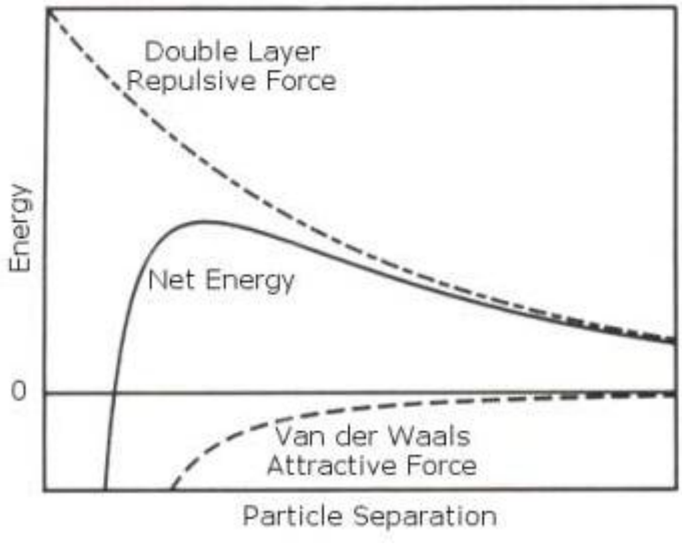


Figure 2.10 Schematic diagram of variation of free energy with particle separation according to DLVO theory. The net energy is given by the sum of the double layer repulsion and the van der Waals attractive forces that the particles experience as they approach one another.

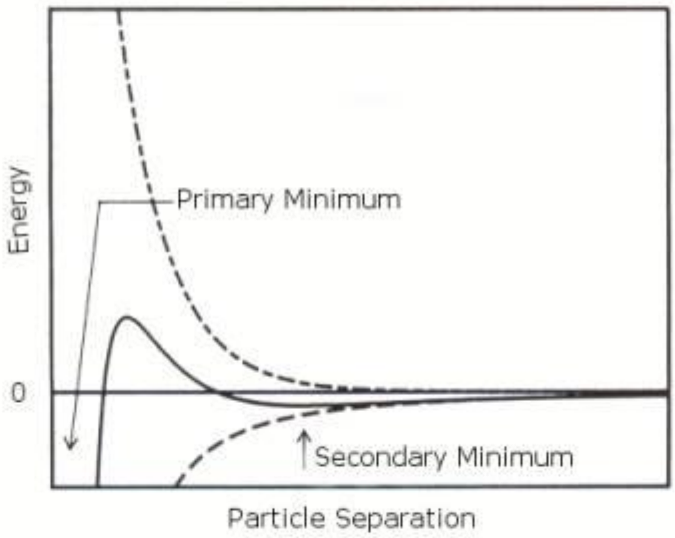


Figure 2.11 Schematic diagram of the variation of free energy with particle separation at higher salt concentrations showing the possibility of a secondary minimum.

2.6 Conclusions

From the defect source analysis result, it is proved that the root cause of most capacitor loop electrical characteristic failure is due to crown wet etch particle defects. And these defects are mainly big sheet particles which are Ti- rich; and polymer residues which are carbon-rich and silicon-rich. Thus, a cleaning process method to remove these particles after the crown wet capacitor process will be investigated, and will be introduced in the next two chapters.

Section 2.5 introduced how these particles are attached in the HF liquid bath. The zeta potential is used to explain the particles adhesion and removal from the wafer surfaces. The DLVO theory, a combination of both van der Waals forces and electric double layer repulsion, guided the experimental methods chosen in the next chapter.

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12. C. Ruggiero, M. Mantelli, A.Curtis, S.Zhang, P. Rolfe, “A computer model of the adhesion behaviour of particles under the influence of DLVO and hydrophobic interactions”, Proceedings of the 20th Annual International Conference of the IEEE Engineering in Medicine and Biology Society, vol 6, pp.2838-2841, 1998.

Chapter 3: Process Parameters and Analysis Methods

As stated in chapter 2, particulate defects with a size bigger than 0.5 µm prove to have a direct yield loss on 68nm generation DRAM device. These kinds of particulate defects are in fact a consequence of a variation in surface properties and a result of a series of process steps. A cleaning process has to be performed in order to remove these particles. How these particles can be removed is a worthwhile study, since the conventional methods of intensive megasonic irradiation for contaminant de-absorption and for etching of the underlying film by as much as several nanometers can be no longer applied. This is because pattern collapses and dimensional fluctuation due to the etching have become critical [1]. Therefore, a series of cleaning experiments which comprise of single wafer equipment and batch type spray process equipment were undergone in order to get a clean surface after the capacitor crown wet process.

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3.1 Processing Tools and Steps

The fabrication of DRAM devices encompassed a number of treatments, such as film deposition, photolithography, cleaning and etching steps. The facility included in this study is a Class-100 clean room (Figure 3.1). A Class-100 clean room maintains less than one hundred particles larger than 0.5 micron meter in each cubic foot of air space. The process step to be investigated will focus on the wet cleaning step after the crown wet capacitor formation. It is essential yet difficult to remove the residues and defects from the bottoms of cylinder holes as well as from the wafer surface. Otherwise, the gap fill of the upper capacitor electrode will be unstable, resulting in both performance and functional yield losses [2,3] . To be compatible with this study, the following processing tools were chosen .

1. Single Wafer Type Tool (SEZ DV38-DS).
2. Batch Type Spray Process Tool (TEL PR300z).

Figure 3.1: Class-100 Clean Room.

3.1.1 Processing Tool: Single Wafer Type Tool

Designed with the 300mm wafer Da Vinci ™ platform, SEZ DV38-DS offers eight double-sided process modules; enabling simultaneous, high-throughput removal of wafer front-side polymers and backside organics or particles (Figure 3.2). The process takes place in a multilevel process chamber. The chemistry is dispensed onto the top wafer surface or simultaneously onto both wafer surfaces at one level. Then, the wafer is moved to another process level where it is rinsed with DI water and dried. This approach isolates the wafer frontside and backside, eliminating cross-contamination between wafer surfaces [3] (Figure 3.3).

Figure 3.2: SEZ DV (Da Vinci) 38-DS series.

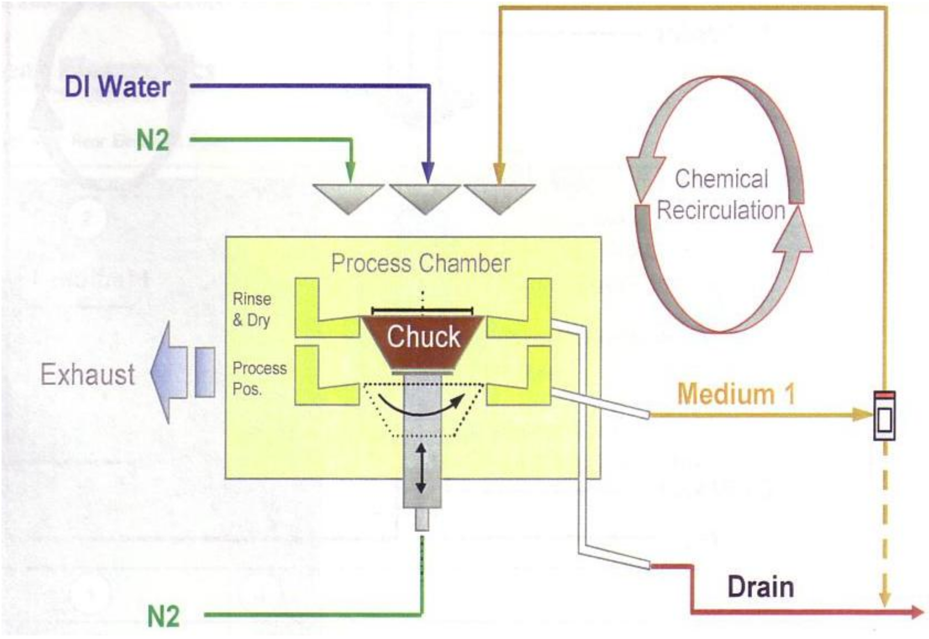


Figure 3.3: Schematic of SEZ DV 38-DS process chamber.

3.1.2 Processing Tool: Batch Type Spray Process Tool

Although batch type spray process tool cleaning has been a mature technology for wafer cleaning for many years, there are still advancements made today, especially targeted for the 60nm and below technology node. According to an article presented by FSI on Semiconductor Manufacturing Magazine [4], centrifugal batch spray systems have successfully demonstrated higher particle removal efficiencies compared to non-megasonic wet benches, due to greater hydrodynamic forces. The other advantages for IC manufacturers, like leverage cost and cycle time reduction, also consolidate its role in semiconductor wet cleaning technology.

The batch type spray process tool, TEL PR300z, from Tokyo Electron Limited, Akasaka, Japan, that is commonly used for stripping photoresist from 12 inch wafers for back end of line (BEOL) processing is used in this work (Figure 3.4). TEL PR300z has one process chamber with a maximum 25 wafers processing.

The TEL PR300z process chamber can be divided into an inner and outer chamber. The inner chamber nozzle is responsible for spraying chemicals, rinsing IsoPropanol (IPA) & gas nitrogen (N_2). Meanwhile, as for the function of the outer chamber nozzle, it uses DI water clean to rinse and Nitrogen gas to dry (Figure 3.5). During the cleaning process, the process rotor will rotate a maximum of 25 wafers. The chamber nozzles will remain static while the wafers are rotating (Figure 3.6 & Figure 3.7).

Figure 3.4 TEL PR300z Cleaning System.

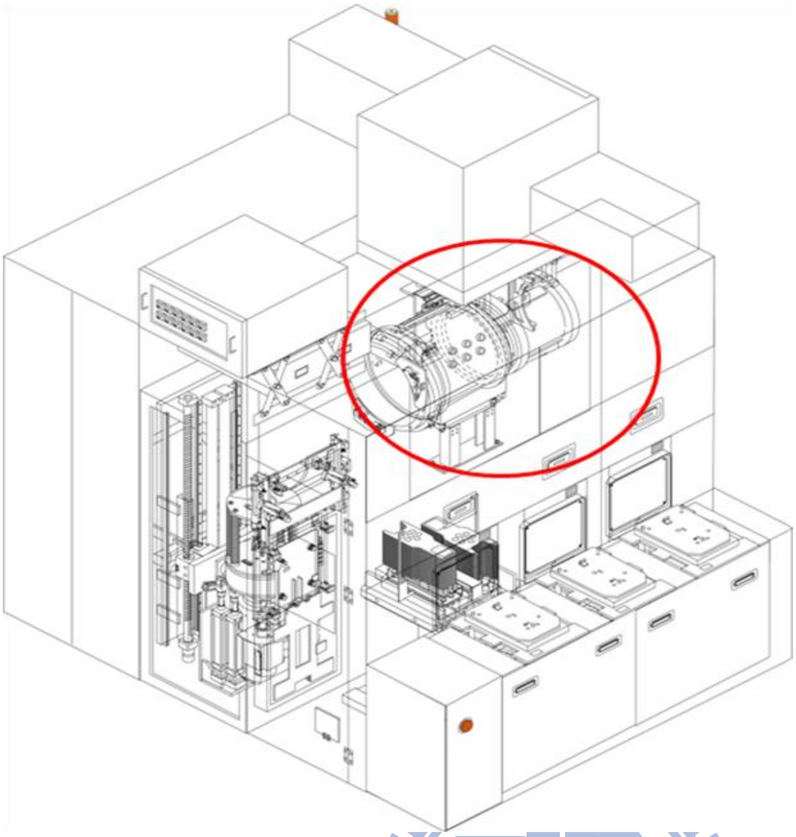


Figure 3.5 Transparent schematic of equipment overview (Process chamber circled in red).

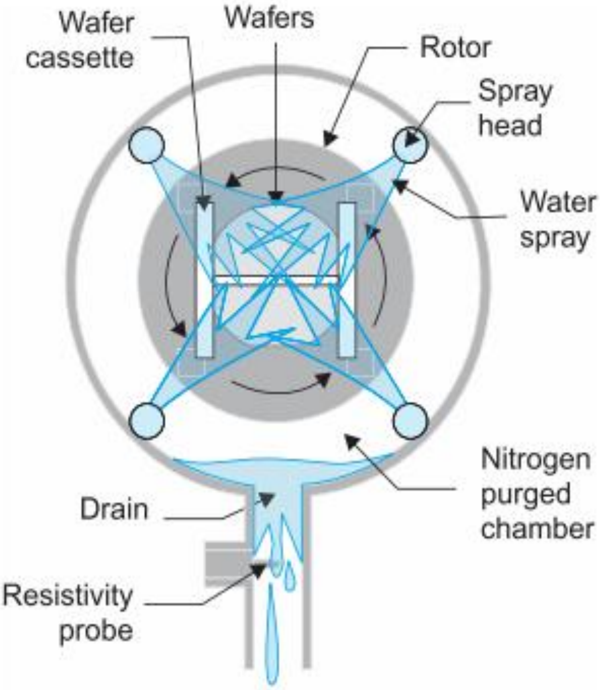


Figure 3.6 Schematic of process chamber function during process.

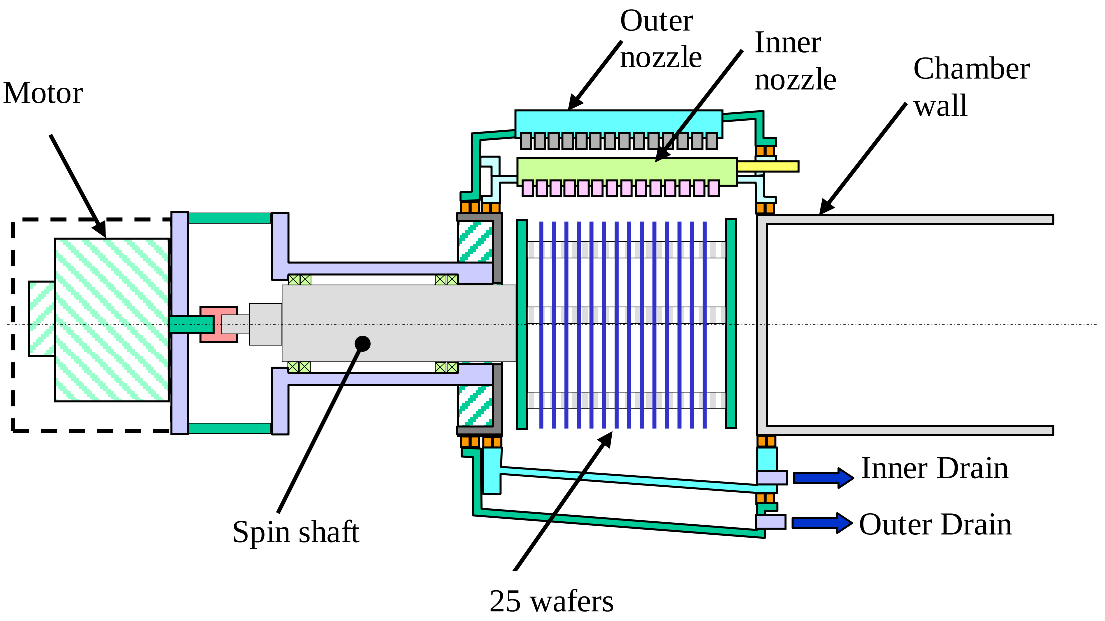


Figure 3.7 Schematic of TEL PR300z process chamber cross-section.

3.1.3 Processing Steps

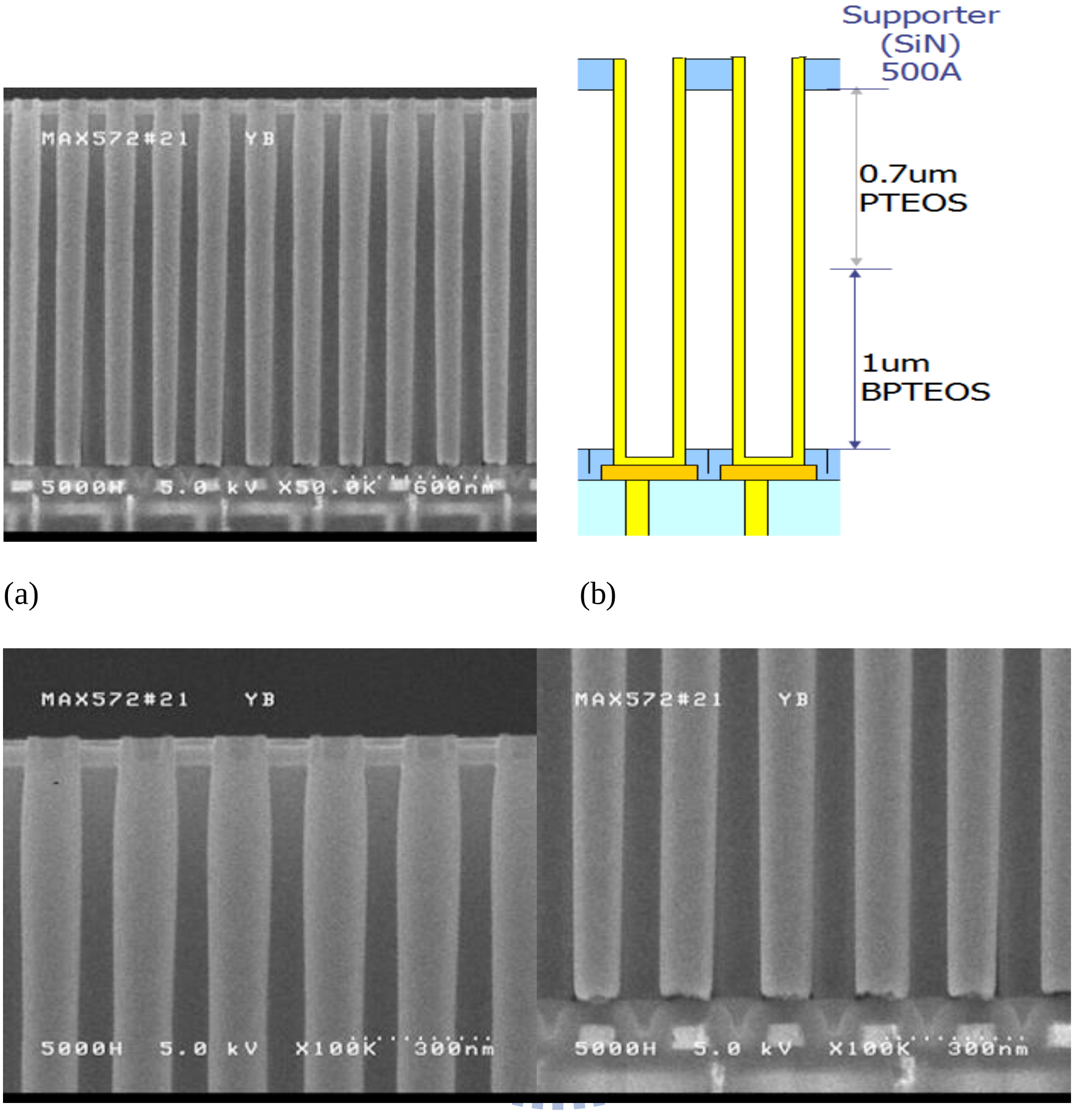
This work emphasizes ways and methods to remove particles and residues generated from the oxide etch crown capacitor process. Thus, the investigative process steps include:

1. Crown capacitor wet etch.
2. Polymer residues and particles removal.

3.2 Sample Preparation

As substrates, one-sided polished silicon wafers are chosen with a thickness of 775µm and a diameter of 300 mm. Transistors are well formed, and bottom Titanium Nitride (TiN) electrodes on crown-shaped capacitors are integrated on top of a contact landing pad. The critical dimension of the capacitor is 0.091µm in diameter and 1.7µm in height, corresponding to the aspect ratio 18.7 as illustrated in Figure 3.8(a). Figure

3.8(b) to Figure 3.8(d) show the exact image of the crown capacitor from a SEM cross-section view. The capacitor cylinders with TiN bottom electrodes exposed, are supported with 50 nm Si_3N_4 film on the top of the cylinders open area. This architecture work of the crown-shaped capacitor stands solidly on a tungsten (W) landing pad which functions as the contact. The relevant process is presented in Chapter 1, Figure 1.1.



(a) (b)

(c) (d)

Figure 3.8

(a) SEM cross-section view of crown-shaped capacitor (50 K magnification).

(b) Schematic of crown-shaped capacitor architecture.

(c) Bottom of crown-shaped capacitor, contact with W landing pad (100 K magnification).

(d) Top-side of crown-shaped capacitor, support-Si_3N_4 structured to prevent capacitor collapse (100 K magnification).

3.2.1 Crown Capacitor Wet Etch Process

A wet bench tool, TEL UW300z (Figure 3.9) was chosen to perform the crown capacitor wet etch process. 49 wt% hydrogen fluoride (HF) with a temperature 20 degrees°C and circulation flow rate of around 23 liters/min is used to etch off ILD (Inter-Layer Dielectric). The main purpose of using 49 wt% HF is due to its high selectivity of various ILD films. The selectivity of Si_3N_4 to PSG is 1 to 65 tested on non-pattern film wafers. As a consequence of using pure HF solution, exposed ILD films are etched off completely; meanwhile partial amount of Si_3N_4 film will remain to support the cylinder capacitor. The remaining Si_3N_4 film is called the supporting-Si_3N_4 structure. The supporting- Si_3N_4 plays the important role of keeping the crown cylinders from collapsing (Figure 3.8 d).

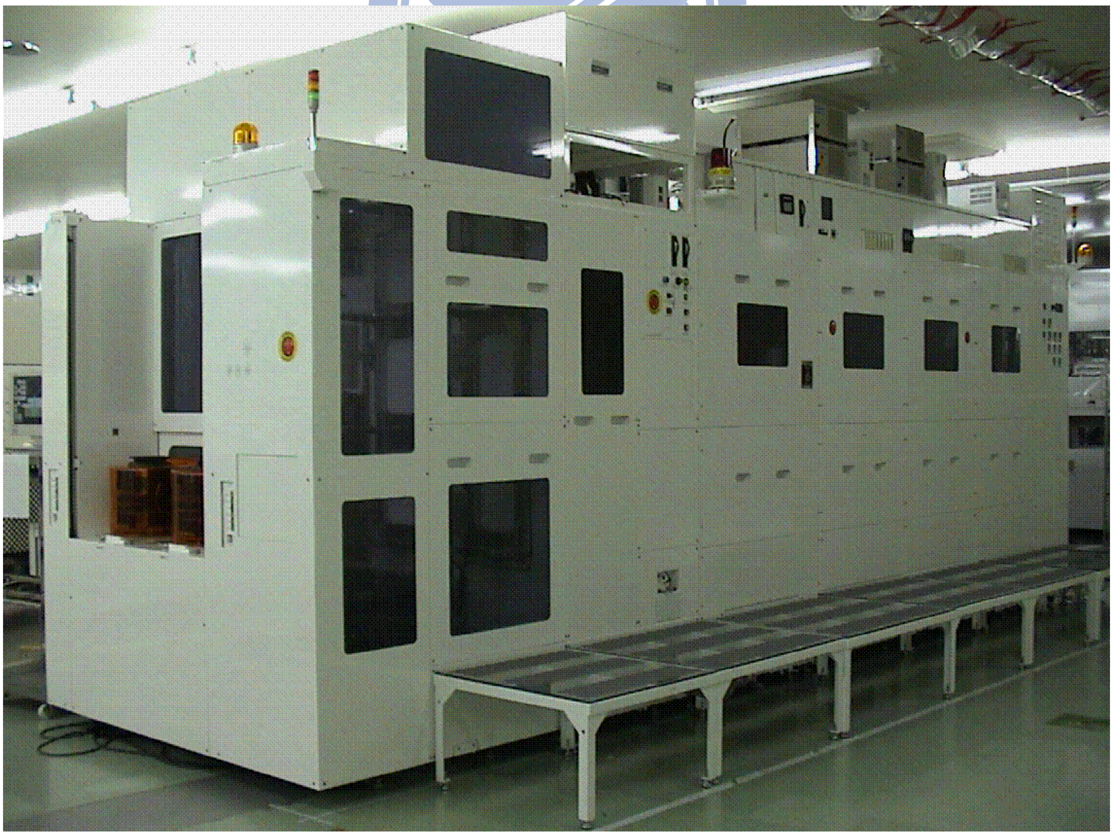


Figure 3.9 Wet bench TEL UW300z.

To be accessible with clean room facilities and equipment tank configuration, two conditions are designed in order to prepare a defect-less sample.

1. 49 wt% hydrogen fluoride (HF), 20 degrees°C, 20 liters/minute , 27 seconds → DI water rinse, 80 liters/minute, 600seconds → IPA 90 seconds + N_2 300 seconds dry (as illustrated in Figure 3.9).
2. 49 wt% HF, 20 degrees°C, 20 liters/minute , 27 seconds → DI water rinse, 80 liters/minute, 600 seconds → 1:200 $NH_4OH:H_2O$, Room Temperature, 600 seconds → IPA 90 seconds + N_2 300 seconds dry (as illustrated in Figure 3.10).

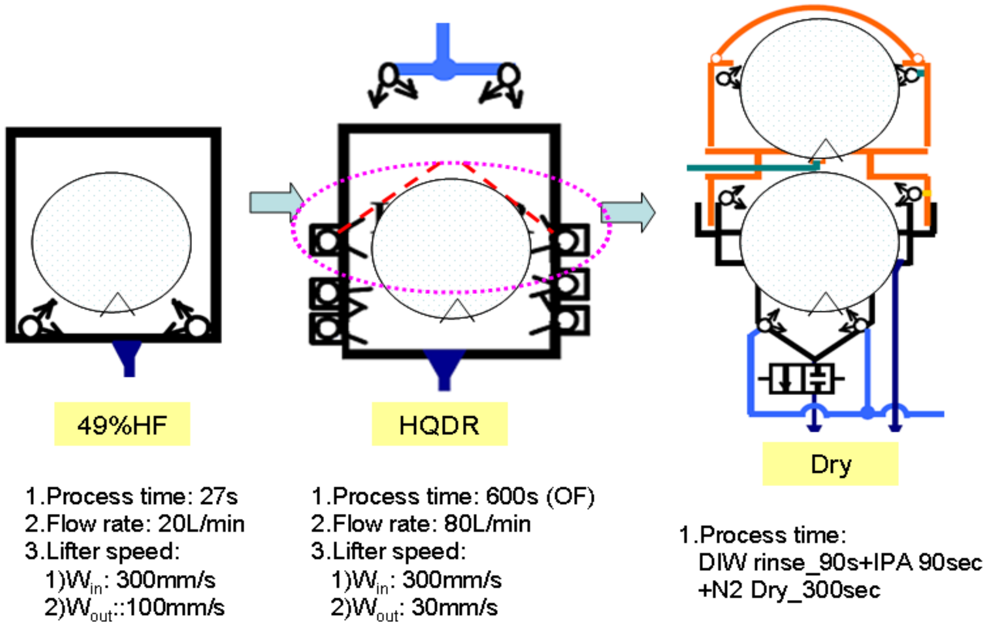


Figure 3.10 Crown Wet Etch Process Condition 1.

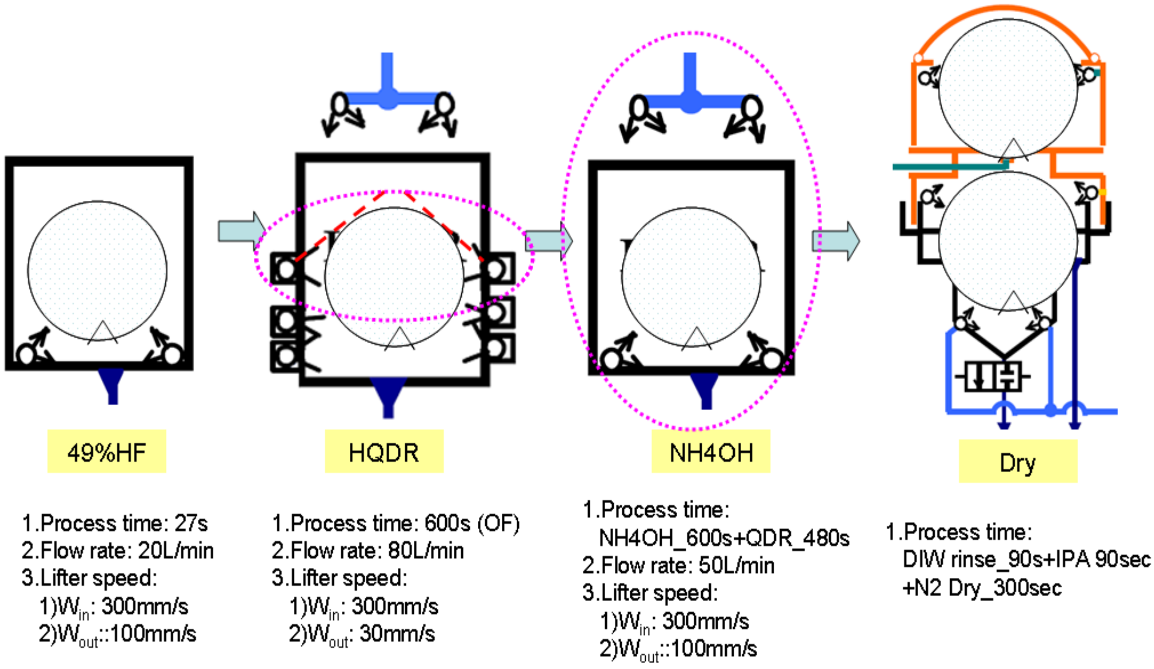


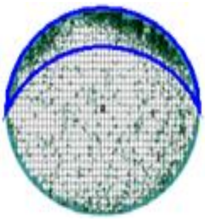
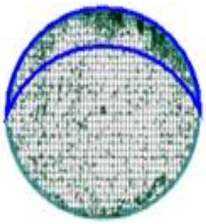
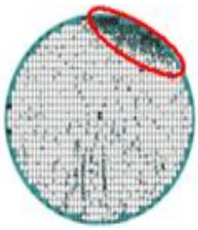
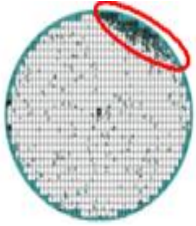
Figure 3.11 Crown Wet Etch Process Condition 2.

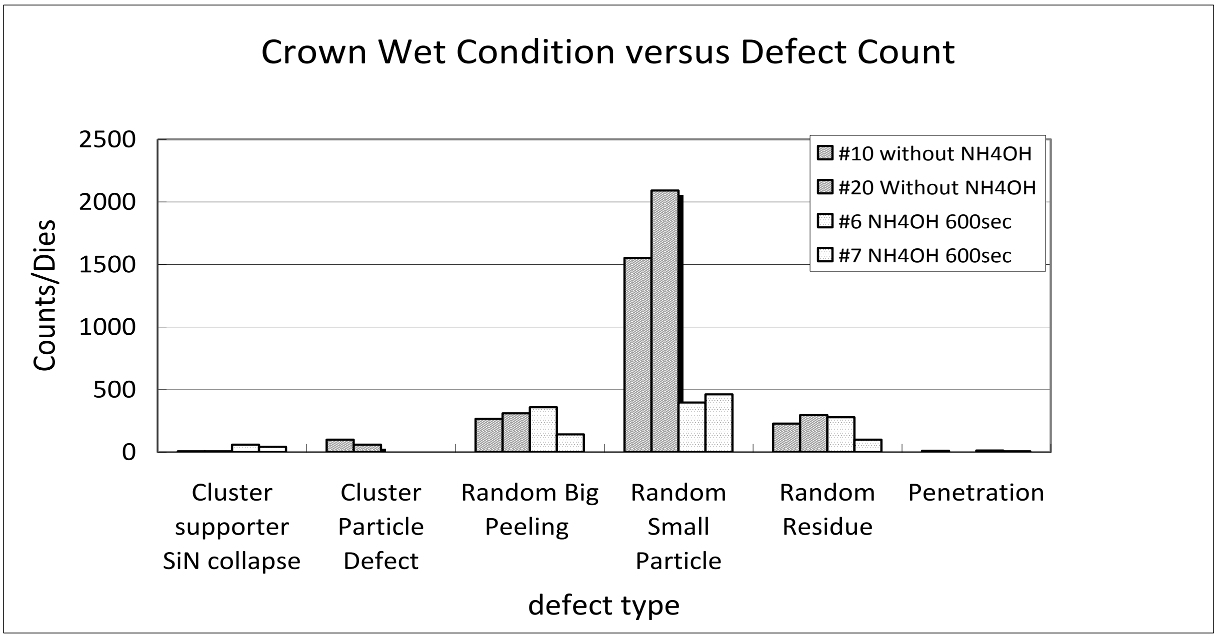
Two experiment wafers, together with an extra twenty three pieces of dummy wafers that are put into the same cassette, are processed for each condition. These wafers are inspected after the crown capacitor wet etch treatment. The defect inspection tool used is the Applied Material defect tool Complus 3T which will be introduced later in Section 3.6.

From Table 3.1, two different defect maps appeared. The result of the defect inspection is divided into seven categories, which included a cluster type cylinder supporting Si_3N_4 peelings defect; cluster type particles; random distribution big peeling particles; random distribution small particles with size smaller than 0.5µm; random distribution organic type residues and penetration. The scanned defects are classified into these categories accordingly. Without NH_4OH treatment, defects are worst on the wafer surface, especially near the wafer edge. Cluster particles which are defined as having more than 100 particles, with a size larger than 0.1μm per die, distribute most near the surface of the wafer edge. Then, without NH_4OH treatment, wafers contain 400 percent more random small particles (particles with size smaller than 0.5μm) than those with NH_4OH treatment. Figure 3.12 shows the SEM image for particle categories that mentioned earlier.

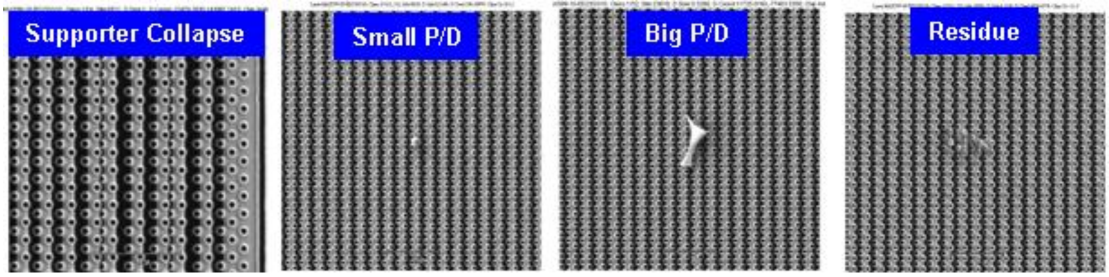
Table 3.1 and Graph 3.1 show that wafers with NH_4OH treatment have better performance than ones without. NH_4OH solution has changed the zeta potential on the particles and the wafer surface, which enhances the effect of particle removal. In order to get a better wafer yield, wafers with NH_4OH treatment were chosen for the next experiment.

Table 3.1 Defect counts summary for condition 1 and condition 2.

Lot Slot	MAX599 #10	MAX99 #20	MAX599 #6	MAX599 #7
3S Crown Wet Etch Condition	49% HF 27"			
	Without NH_4OH		NH_4OH 600sec	
Defect Map				
Cluster supporter SiN collapse	7	6	60	42
Cluster Particle Defect	100	60	0	0
Random Big Peeling	265	309	357	141
Random Small Particle	1552	2092	396	462
Random Residue	227	295	278	100
Penetration	10	0	12	6



Graph 3.1 Defect counts for condition 1 and condition 2.



(a) (b) (c) (d)

Figure 3.12 (a) cylinder supporter collapse (b) small particle (<0.5µm) (c) big particle (>0.5µm) (d) residue. (SEM 10K magnification)

3.3 Experimental Design: Single Wafer Type Tool

The surface material of the specimen exposed is mainly Titanium, therefore, strong oxidation chemicals and concentrated acids are avoided. The most noted chemical property of titanium is its excellent resistance to corrosion, capable of withstanding attack by dilute sulfuric acid and hydrochloric acid as well as chlorine gas, chloride solutions, and most organic acids. Thus, dilute chemicals are targeted. And in order to be compatible with Perfluoroalkoxy (PFA) copolymer resin material in SEZ DV38-DS experimental tool, chemicals EKC6800 and Rezi-38 are chosen to be investigated. The single-wafer spin processor rinses from the wafer center to the edge, there are fewer inherent defectivity transfer pathway.

3.3.1 Chemical Selection :

3.3.1.1 EKC6800 [5]

EKC technology, Inc., part of DuPont Electronic and Communications, is the leading manufacturer of patent specialty chemicals used in the manufacturing of wafers for the semiconductor and related industries. EKC6800, one of the chemicals used in the Back End of Line (BEOL) for advanced interconnect applications was chosen in this experiment. EKC6800 contains 55~85 percent of N,N-Dimethylacetamide and 0~5 percent of Ammonium bifluoride, and with a pH value varied from 6 to 8. The main reason for this chemical being chosen is that, the contained fluoride can react with polymer residues. Polymer residues are then reformed into a low molecular structure that is soluble in water.

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3.3.1.2 Rezi-38 [6]

Rezi-38, a product of Baker Incorporate, is an aqueous ash residue remover, which effectively cleans a wide variety of metal-organic residues from substrates, including sensitive metal alloys like copper and low k dielectrics. With a pH around 13, this product is 80 percent aqueous, which requires no special rinse and is effective at room temperatures (as low as 23 degrees°C). In addition, Rezi-38's aqueous composition also offers a variety of environmental benefits. It does not contain SARA 313[7] specified components or hazardous air pollutants (HAPs), and has a less than 5 percent concentration of volatile organic compounds (VOCs). In addition, the high water content of the product allows easier disposition that is environment free. Table 3.2 below compares Rezi-38 and EKC6800.

Table 3.2 Comparison of REZI-38 and EKC 6800 chemicals.

Chemical	**REZI-38**	**EKC 6800**
Maker	Baker	Dupont
Formulation	>85% Aqueous	Fluoride salt
	<3% TMAH	Organic solvent
Acid/base	Base	Alkalescent
pH	13	7.8 ~ 8.2
Viscosity @ RT	1.2 cSt.	---
Solubility in Water	Complete	Complete
Surface Tension	72 dyne/cm	---
Etch Rate (A/min)		
TiN	~0	0
W	2.3	0.41
Ti	0.103	0

3.4 Experimental Design: Batch Type Process Tool

As stated above, the majority of defect particles distributed are Titanium rich compounds. We targeted a few chemicals that are compatible with the equipment material, that is stainless steel SUS 316 that has a good resistance to heat and corrosion : EKC265[8], ELM C30[9] and EcoPeeler [10].

3.4.1 Chemical Selection : EKC265, ELM C30 & EcoPeeler

3.4.1.1 EKC265 [8]

Also invented by EKC technology, Inc., EKC265 is the initial product of Dupont™ PlasmaSolv® series formulated to remove photoresist residue generated after via and metal etch processes. EKC265 post-etch residue removers are made with Hydroxylamine (HDA) high performance hydroxylamine-based cleaning technology. HDA technology comprises aqueous organic mixtures formulated to effectively remove residues from substrate surfaces after via, poly and metal etch processes used in the microelectronics industry.

3.4.1.2 ELM C30 [9]

A product of Mitsubishi Gas Chemicals, the ELM series cleaning chemical specialize in cleaning and removing etch residue with inorganic chemicals. However, ELM C30 contains Dimethylformamide (DMF) as a chemical solvent. Dimethylformamide is the organic compound with the formula $(CH_3)_2NC(O)H$ which is a common solvent for chemical reactions, unfortunately, this is always linked to cancer in humans, and is also thought to cause birth defects.

3.4.1.3 EcoPeeLer[10]

EcoPeeler is a transparent and inorganic chemical which does not contain any HDA (Hydroxylamine), hazardous, toxic or organic solvents. A product of Fine Polymer, the pH of EcoPeeler can be controlled to required levels so as to be comparable with various processes. It is also a cost effective chemical as there is no necessity for additional facilities or cost associated with its disposal. But most important of all, EcoPeeler is eco-friendly and provide a low CoO (Cost of Ownership) advantage.

Table 3.3 summarizes the differences between these three chemicals for batch type spray process tool.

Table 3.3 Comparison of batch type spray tool chemical.

Chemical	**EKC265**	**ELM C30**	**EcoPeeler**
Maker	Dupont	MGC	Fine Polymers
Formulation	1) 2-(2-aminoethoxy)ethanol 50~100% 2) Hydroxylamine (HDA) 10~25% 3) Pyrocatechol 2.5~10%	1) Dimethylformamide (DMF) 69% 2) Fluoride compound 2% 3) Water 29%	1) Ammonium phosphate (NH_3H_2PO) 2) Condensed ammonium phosphate ($-(OPNH_3)_n-$) 3) Urea ($OC(NH_2)_2$) 4) Water
Acid/base	Base	Neutral	Acid
pH	11.5~12.5	7~8	3~4
Solubility in Water	Completely	Completely	Well Mixed
Etch Rate (A/min)			
TiN	2.0	0.7	0.9
W	0.7	1.9	0.3
Ti	34.2	3.6	5.4
TEOS	0.1	197	0.1

3.5 Process Variables Investigated

A lot of aqueous chemistries are available for cleaning wafers; their effectiveness in providing a contamination-free surface depends upon a number of variables, including the sequence of chemistries used, the ratio of the chemicals, the processing temperature, the age of the solution, etc. However, we will only focus on three variables in this work, including both chemical reactions and physical reactions.

1. Chemical dependency.
2. Chemical process time dependency.
3. Rotation speed dependency.

3.6 Detection and Analysis of Particle Defects

In order to detect particles adhered to the surface of a specimen, the defect inspection tool by Applied Material, Complus 3T was used (Figure 3.13). This wafer surface inspection equipment utilizes the dissolution phenomenon of the direct polarized light component of the laser, which can distinguish scattered light from a particle and scattered light from a pattern edge. Furthermore, by utilizing the regularity of repeated circuit patterns, the diffracted light from the patterns can be spectroscopically blocked using a space filter [11]. There is a method developed in Complus 3T which eliminates detection signals from circuit patterns by comparing the scattering signals from adjacent chips and then subtracting these signals (Figure 3.14). In this work , a die-to-die pattern image comparison with a random mode settings and 100% step coverage recipe is setup to inspect the result.

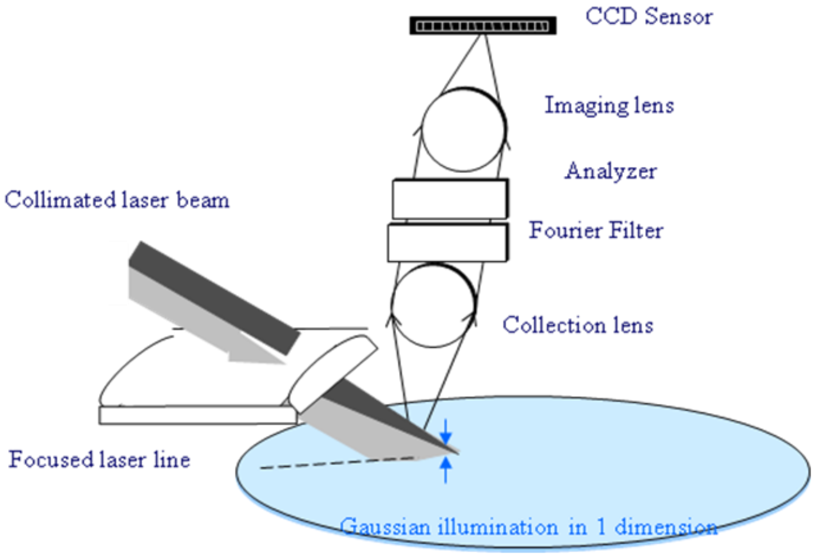

Figure 3.13 Schematic of detectors chamber of Applied Materials Complus 3T.

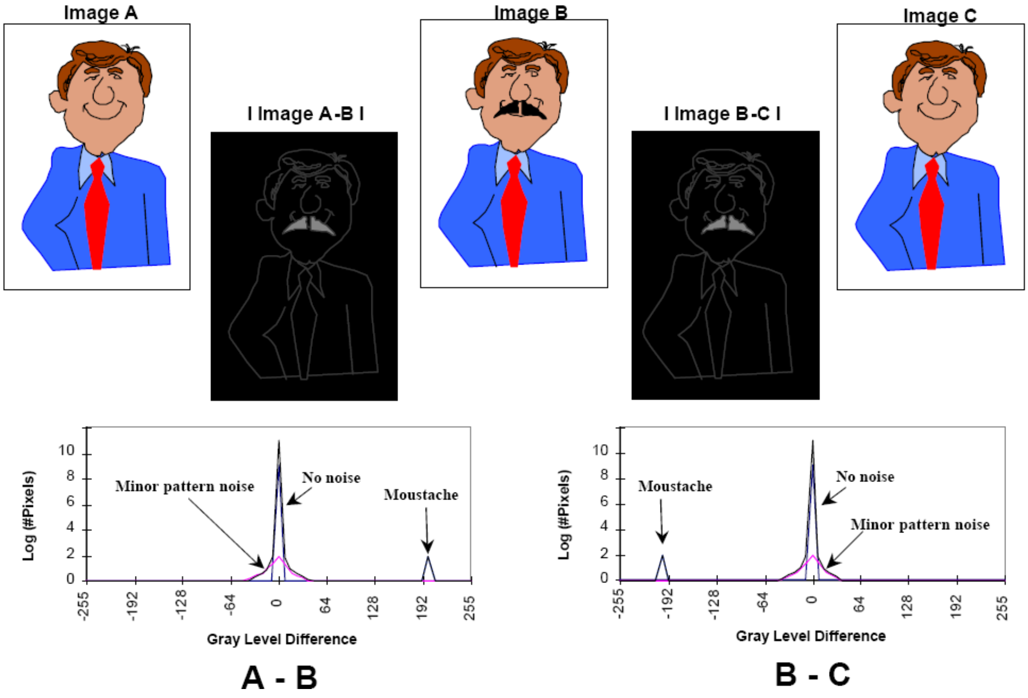

Figure 3.14 Detection signals eliminates from circuit patterns by comparing the scattering signals.

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Chapter 4: Impact of Process Variables Towards Wafer Surface Cleaning

The main variables in semiconductor device production are process technologies such as film deposition, photolithography, and etching. However, without the wet process which supports these three essential steps, semiconductor devices cannot be manufactured. In the previous Chapter, specimens with a crown capacitor structure were prepared. The wafers after the crown capacitor wet treatment are covered with big sheet particles and residues. These particulates defects and residues are proven to have a high impact on yield loss. Thus, a cleaning step has to be added in order to remove all these by-products. The following topic will discuss various cleaning process variables, to find which will have the highest particle removal ability, and in addition, without any side-effects like penetration and pattern collapse.

4.1 Introduction to Experimental Design

The requirement for an "ultraclean Si wafer surface" on which ultra-fine patterns are fabricated is defined as a surface which satisfies the following eight requirements [1].

1. Free from particles.
2. Free from metallic impurities.
3. Free from organic impurities.
4. Free from unintended native oxide.
5. Maintaining atomic-order "microroughness".
6. A top surface completely terminated with hydrogen.
7. Free from moisture absorption.
8. Free from charge-up.

However, the Si wafer goes through a wet cleaning process before and after each cycle of film deposition, photolithography, and then etching steps. The requirement for a clean wafer surface varies according to the device and its structure. In this work, the wafer surface is covered with crown capacitor, thus the requirement for its cleanliness is targeted as below.

1. Free from big sheet particles > 1μm.
2. Free from residues / organic impurities.
3. Free from unintended native oxide.
4. No pattern penetration or pattern collapse.
5. Free from random and cluster type particles > 0.5μm.
6. No water mark form during drying process.

This study approach includes three phases of analysis with four controllable factors. These factors will be assessed in the following sections: chemical dependency (4.1.1), chemical and intermediate rinse process time dependency (4.1.2) and rotation speed dependency (4.1.3). Result of these phases is discussed accordingly in each section. Then, result and discussion is elaborated in section 4.2, chemical reaction and physical reaction of each phase will be analyzed and discussed. A final optimized condition model is setup in section 4.3. At last, to ensure the feasible of mass production, reproducibility test is performed for the optimum condition in section 4.4.

4.1.1 Chemistries Dependency On Crown Capacitor Particle Defects

Five ready-to-use chemical solutions are assessed in this work. These solutions contain chemistries that are effective in removing residual photoresist, post-etch, and ash residues. The typical chemical cleaning sequence for each chemical in this work was depicted as below.

1. EKC6800 [3]→ DIW rinse → N_2 Dry.
2. REZI38 [4]→ DIW rinse → N_2 Dry.
3. EKC 265 [5] → IPA rinse → DIW rinse → IPA Dry.
4. ELM C30 [6]→ DIW rinse → IPA Dry.
5. EcoPeeler [7]→ DIW rinse → IPA Dry.
6. Without any cleaning treatment.

Chemicals EKC265, ELM C30 and EcoPeeler is used in the wet batch type spray process tool TEL PR300z; meanwhile, Rezi-38 and EKC6800 are used in the single wafer type tool, SEZ DV 38 DS. A defect inspection is conducted within 2 hours after the wafer cleaning treatment, in order to avoid time effects on wafers, which might confuse the experiment result. Particles generated from the waiting hours are basically ignored in this discussion. Another wafer piece without any cleaning treatment will also be inspected to check the baseline of defects.

Some process steps are different for each chemical, due to the chemical's characteristics itself, and the limitation of the process tool applied. As for an HDA-based chemical like EKC265, the residual HDA mixed with water will release $[OH^-]$ and induce metal corrosion. The purpose of an Isopropanol (IPA) rinse after the EKC265 step is to dilute HDA concentration and reduce the [OH-] amount to minimize metal loss. For the chemical EKC265, ELM C30 and EcoPeeler, IPA drying is used; meanwhile N_2 drying is applied on EKC6800 and Rezi38 due to the single wafer tool limitation.

4.1.1.1 Experimental Result

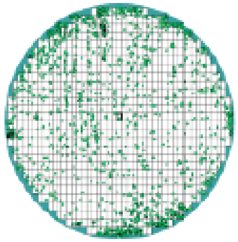
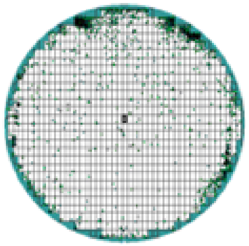
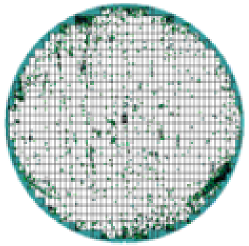
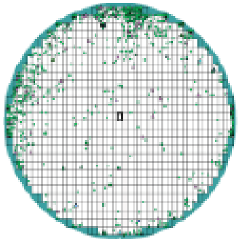
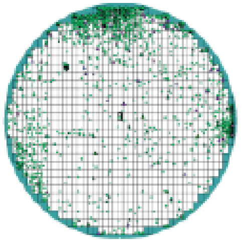
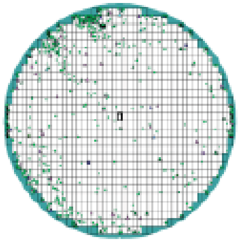
The result of this experiment is inspected by the AMAT Complus 3T tool. This work only focuses on the killer defects, which are bigger than 0.5μm The defects of interest have been categorized into four classifications according to size, shape and component.

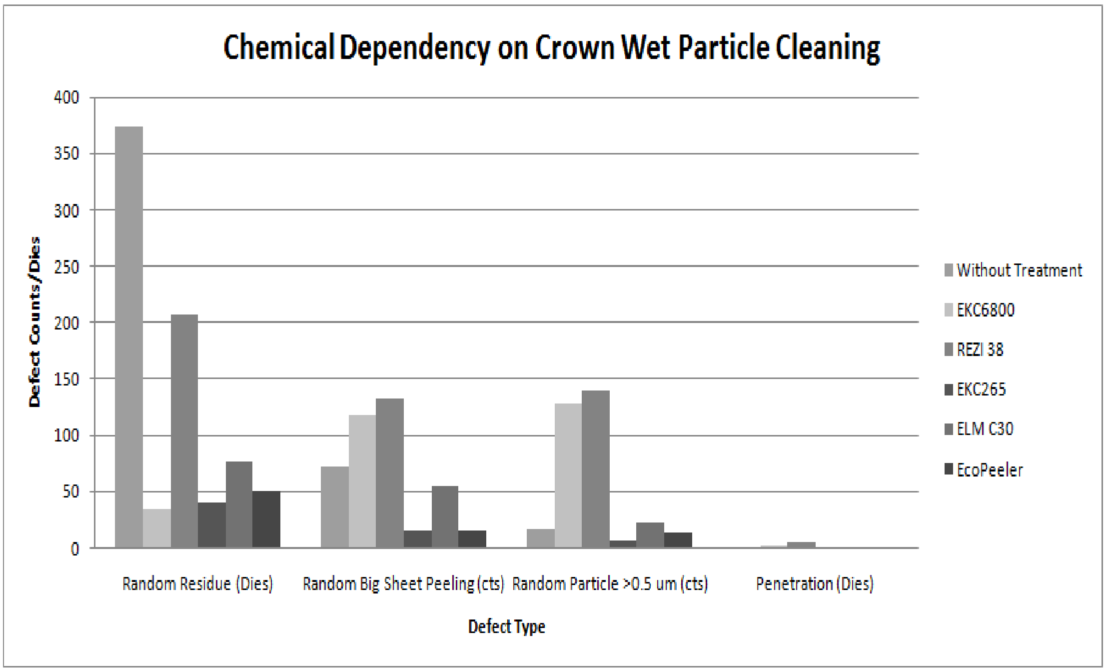
1. Random size residues (organic type particles with various shapes).
2. Random sheet type peeling particles (>1 μm).
3. Random type particles (>0.5 μm).
4. Penetration or cylinder collapse.

Table 4.1, it can be seen that EKC6800 and Rezi38 has penetrated the guard ring oxide due to the cylinder collapse. This kind of cylinder collapse has a serious yield impact, thus the first priority of the whole work is to avoid cylinder collapses. For the organic residues, Rezi38 has the highest distribution over the wafer, proof that the removability of Rezi38 is relatively difficult for the residues generated after the crown wet capacitor process. Meanwhile EKC265 has the lowest distribution for organic residues.

As for the Titanium rich big sheet particles (Figure 4.1), EKC265 and EcoPeeler have the lowest counts; meanwhile EKC6800 and Rezi38 have the highest. The same is prone to happen to particles larger than 0.5 μm too. EKC265 performance is the best (Graph 4.1). Thus, the chemical EKC265 was chosen for the next process time dependency experiment.

Table 4.1 Defect analysis for chemical dependency on crown wet particles.

	Without Treatment	EKC6800	REZI 38	EKC265	ELM C30	EcoPeeler
						
Random Residue (Dies)	374	34	207	40	76	50
Random Big Sheet Peeling (cts)	73	117	133	15	55	15
Random Particle >0.5 um (cts)	16	128	139	6	22	14
Penetration (Dies)	0	2	5	0	0	0



Graph 4.1 Defect analysis for chemical dependency on crown wet particles.

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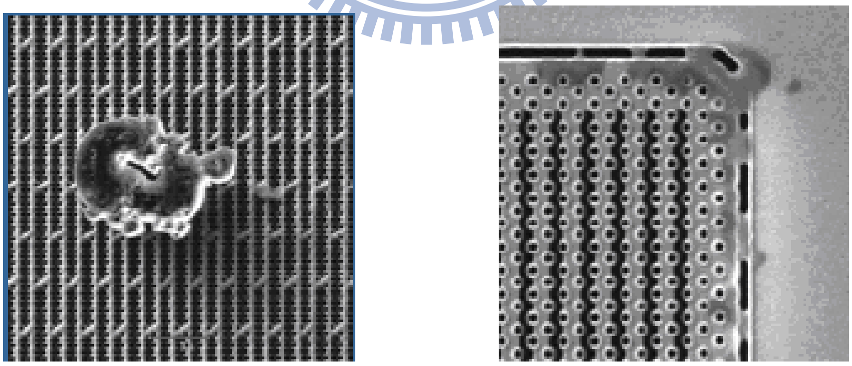


(a)	(b)

Figure 4.1 (a) Sheet particle (SEM magnification 5K) (b) residue (SEM magnification 10K).

4.1.2 Chemical Process Time Dependency On Crown Capacitor Particle Defects

In this section, we chose the chemical with the lowest particle defect count for all four defects categories from the results in chapter 4.1.1; that is, EKC265. For EKC265, a HDA-based chemical, an intermediate rinse with IPA is needed. Thus, there are two variables in this experiment: the EKC265 chemical itself, and the intermediate rinse IPA. The following experiment technically analyzes how EKC265 and the IPA rinse process time affect the defect counts.

In the first experiment, the dependency of the EKC265 chemical process time on crown capacitor particle defects will be checked. The following conditions are investigated:

1. without treatment.
2. EKC265 3 minutes → IPA 12 minutes → IPA dry.
3. EKC265 6 minutes → IPA 12 minutes → IPA dry.
4. EKC265 9 minutes → IPA 12 minutes → IPA dry.
5. EKC265 12 minutes → IPA 12 minutes → IPA dry.

Next, the IPA process time dependency on crown wet particles is derived in combination with a fixed EKC265 chemical time of 12 minutes. IPA plays an important role in the chemistry of HDA- based EKC265. In a base solution, HDA served as a reducing agent. If HDA reacts with water directly, a strong alkali solution will be formed and corrode the metal. The following conditions are tested:

1. without treatment.

2. EKC265 12 minutes → IPA 3 minutes → IPA dry.
3. EKC265 12 minutes → IPA 6 minutes → IPA dry.
4. EKC265 12 minutes → IPA 9 minutes → IPA dry.
5. IPA 12 minutes → IPA dry.

4.1.2.1 Experimental Results

The first experiment of chapter 4.1.2, the IPA process time remained 12 minutes whereas with EKC265 treatment time varies, in the second experiment, we fixed the EKC265 process time to 12 minutes and varied the IPA process time.

From Figure 4.2, it is observed that treatment with EKC265 is very efficient at removing organic type residue defects. This scatter plot shows a trend of decreasing residue amount according to EKC265 treatment time. EKC265 with a treatment time above 3 minutes can remove at least 80% of the residue adhered on wafers. On the other hand, IPA also contributes to the removal ability of organic residue, but only in small amounts. However, decreasing IPA time does not affect the residue defect much. Without EKC265 treatment, a long IPA treatment time of 12 minutes is useless. Most residues still remain on the wafer surface without EKC265 treatment, with or without IPA rinse.

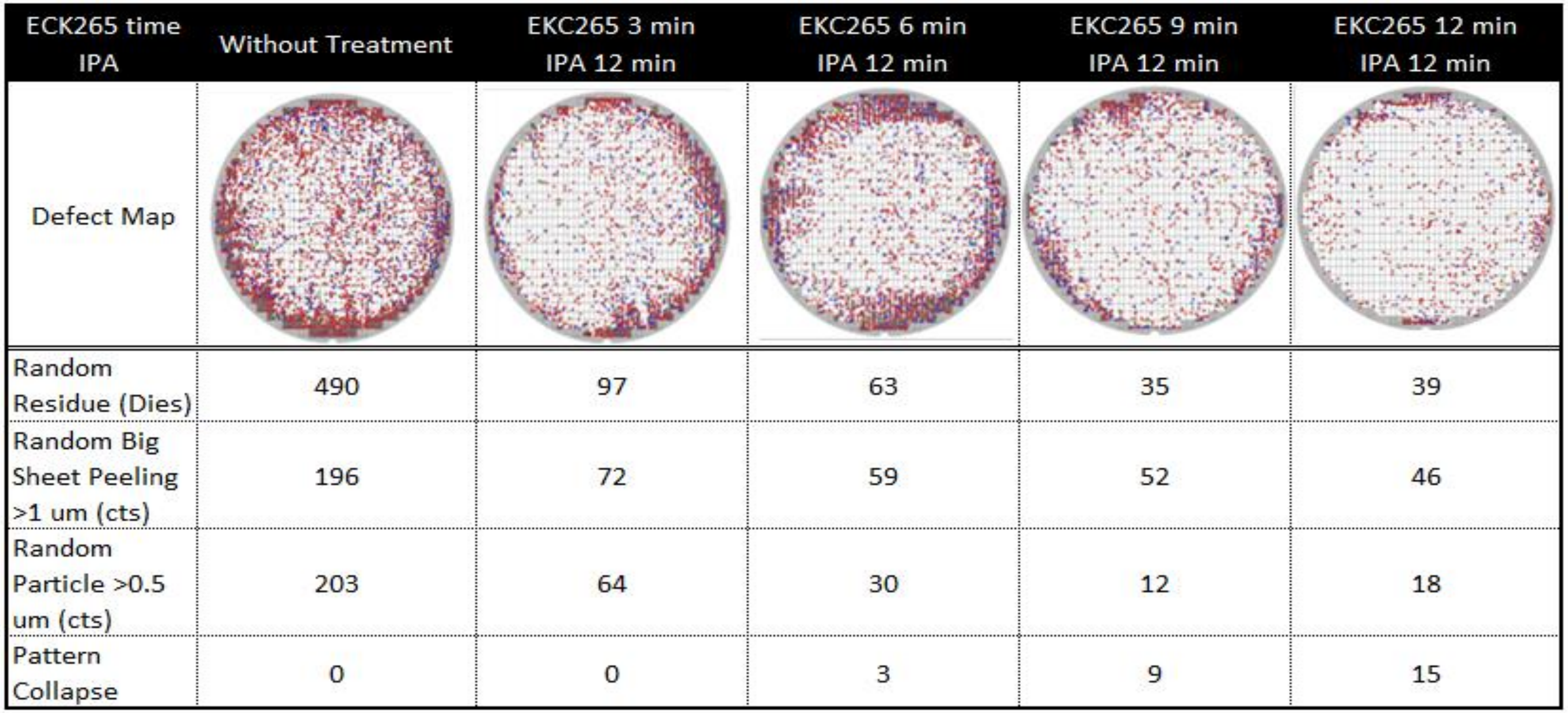
Figure 4.3 and Figure 4.4 show that for big sheet particles bigger than 1 μm and random size particles bigger than 0.5μm, their defect count is inversely proportional to the EKC265 treatment time. In contrast, IPA treatment time seems to have no impact on the defect count. This proves that the reduction of IPA treatment time does not cause an increment in total amount of particle defects. Therefore, the impact on

IPA rinse time for particle removal can be ignored.

In Figure 4.5, the pattern collapse amount increased significantly with EKC265 process time, however, the result is irrelevant to the IPA process time. It can be concluded that IPA only usefully functions as an intermediate rinse for chemical EKC265, and does not influence any particle or residues removal.

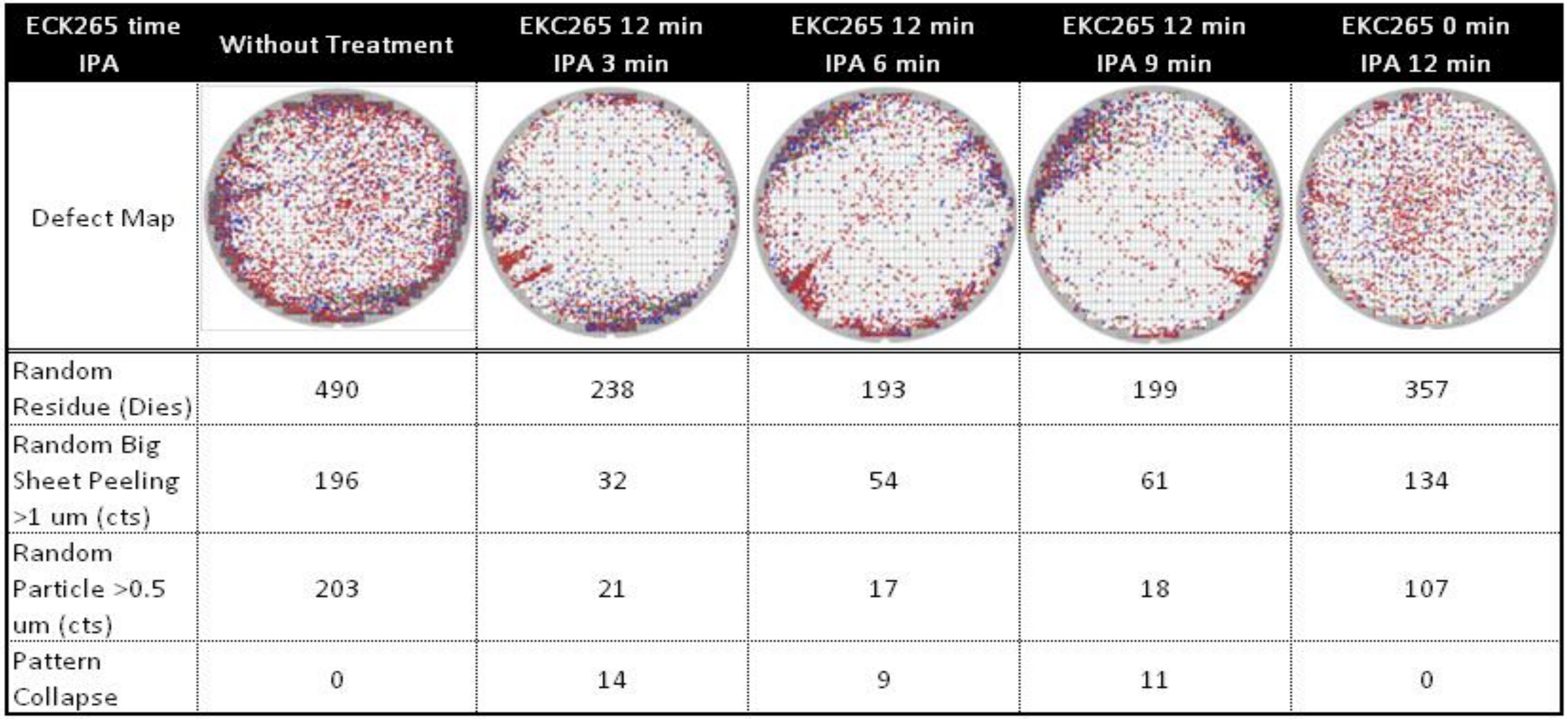
From Figure 4.2 to 4.5, we chose the best condition from the result of experiment 4.1.2.1: (EKC265 6 minutes and IPA 6 minutes) to check the physical reaction impact on particles defects for the next experiment.

Table 4.2 Defect analysis for chemical process time dependency on crown wet particles.

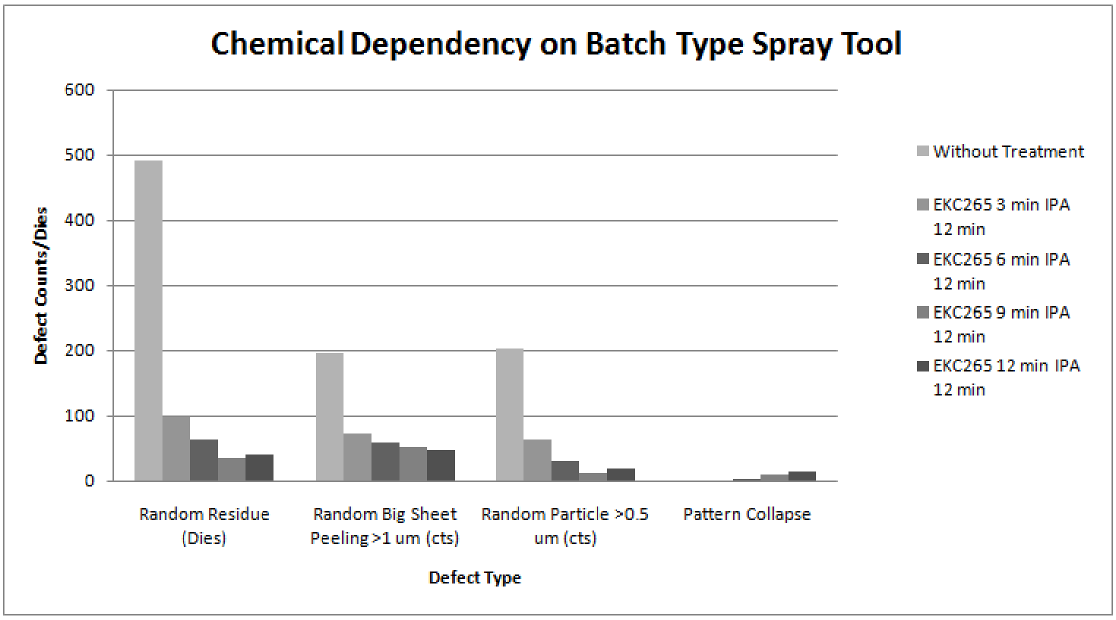


ECK265 time IPA	Without Treatment	EKC265 3 min IPA 12 min	EKC265 6 min IPA 12 min	EKC265 9 min IPA 12 min	EKC265 12 min IPA 12 min
Defect Map					
Random Residue (Dies)	490	97	63	35	39
Random Big Sheet Peeling >1 um (cts)	196	72	59	52	46
Random Particle >0.5 um (cts)	203	64	30	12	18
Pattern Collapse	0	0	3	9	15

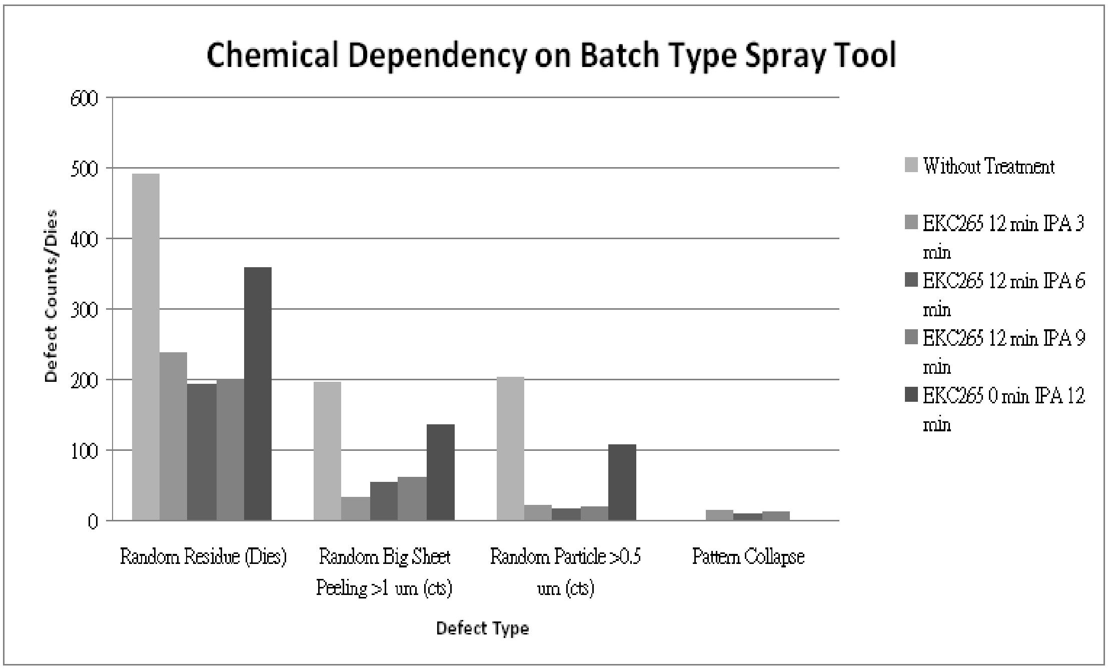
Table 4.3 Defect analysis for IPA process time dependency on crown wet particles.



ECK265 time IPA	Without Treatment	EKC265 12 min IPA 3 min	EKC265 12 min IPA 6 min	EKC265 12 min IPA 9 min	EKC265 0 min IPA 12 min
Defect Map					
Random Residue (Dies)	490	238	193	199	357
Random Big Sheet Peeling >1 um (cts)	196	32	54	61	134
Random Particle >0.5 um (cts)	203	21	17	18	107
Pattern Collapse	0	14	9	11	0



Graph 4.2 Defect analysis for chemical process time dependency on crown wet particles.



Graph 4.3 Defect analysis for IPA process time dependency on crown wet particles.

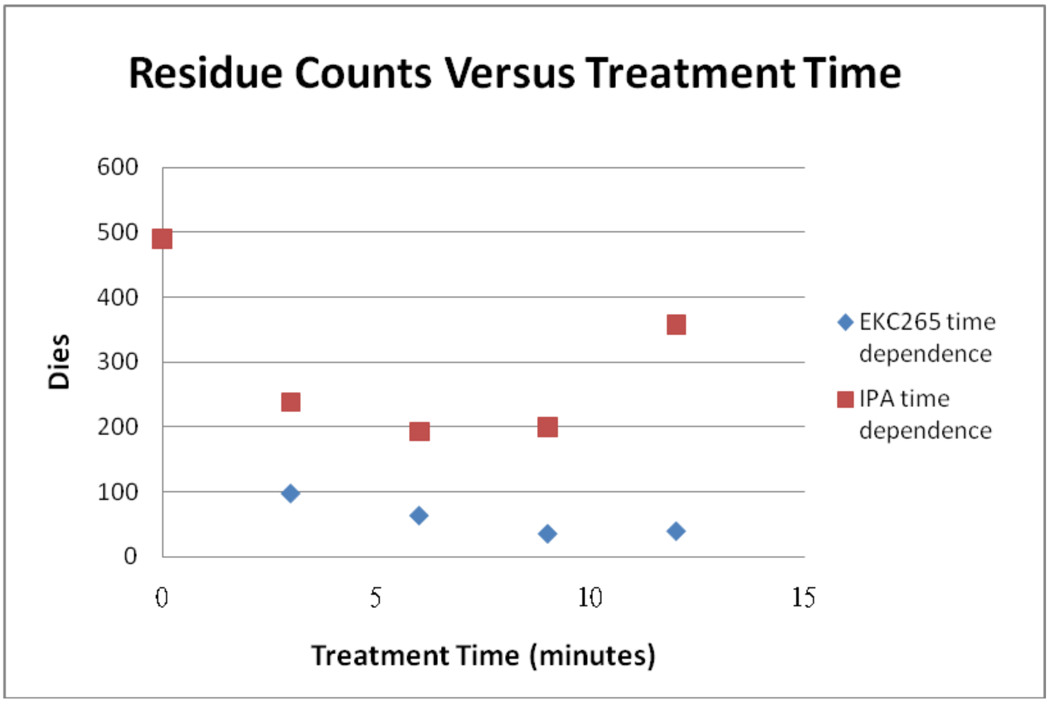


Figure 4.2 Scatter plot for residue counts versus EKC265 and IPA process time variation.

IES

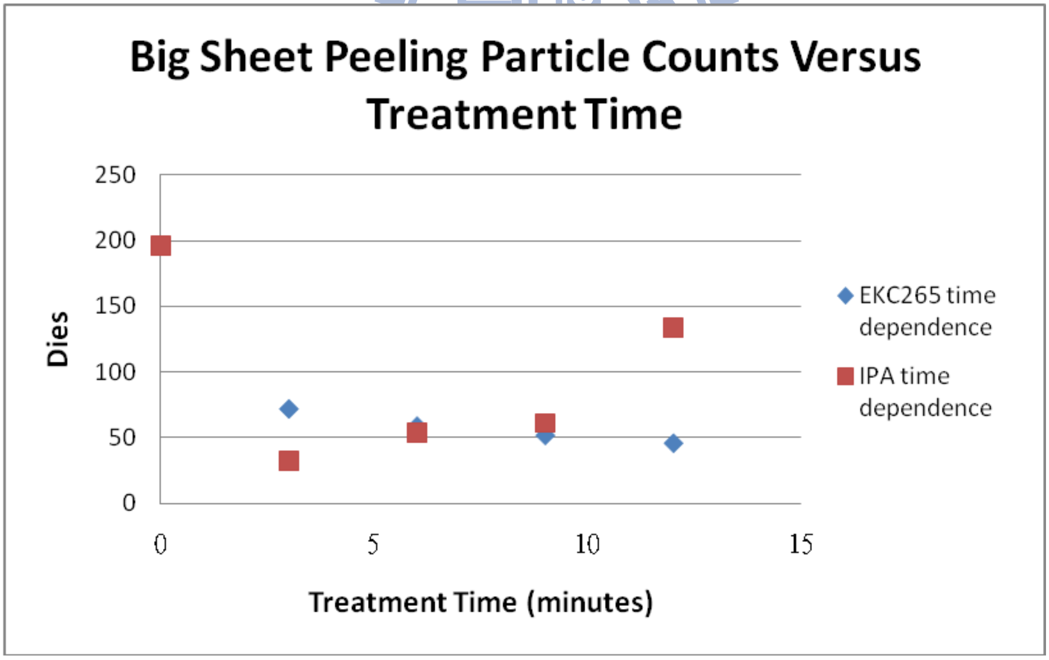


Figure 4.3 Scatter plot for big sheet particles counts versus EKC265 and IPA time variation.

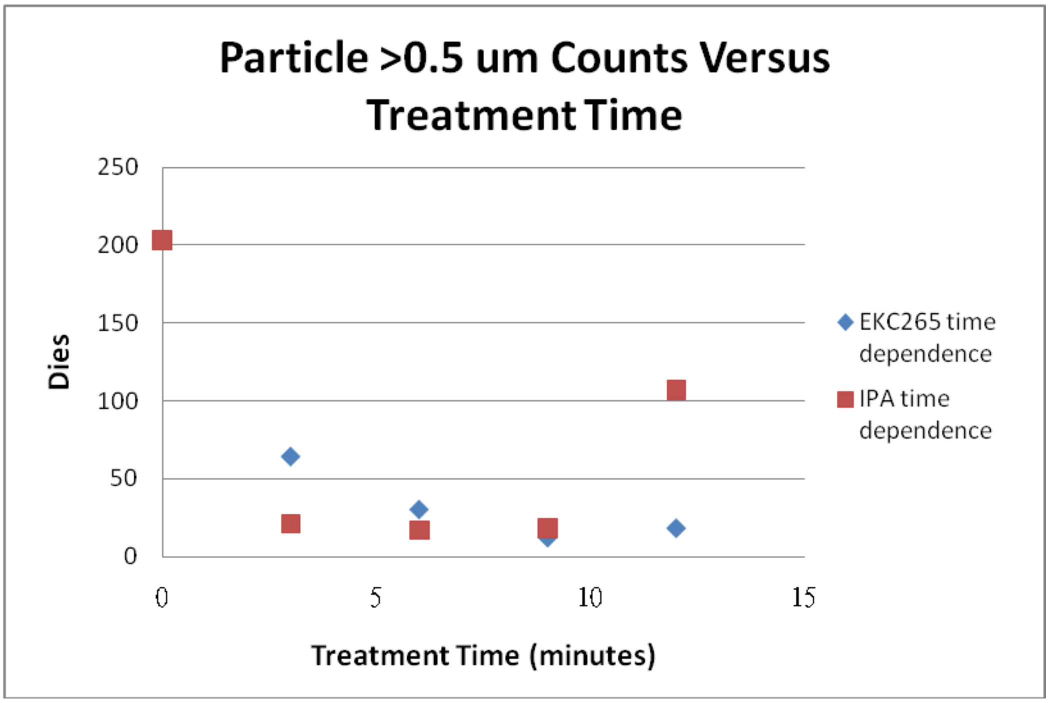


Figure 4.4 Scatter plot for particles > 0.5μm counts versus EKC265 and IPA time variation.

ESA

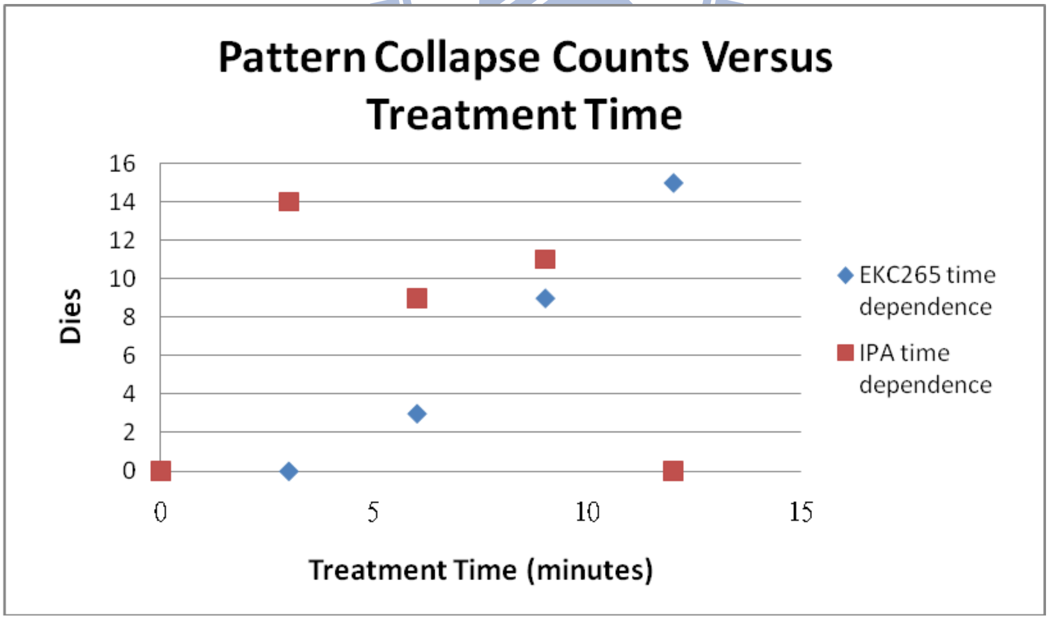


Figure 4.5 Scatter plot for pattern collapse counts versus EKC265 and IPA time variation.

4.1.3 Chemical Rotation Speed Dependency On Crown Capacitor Particle Defects

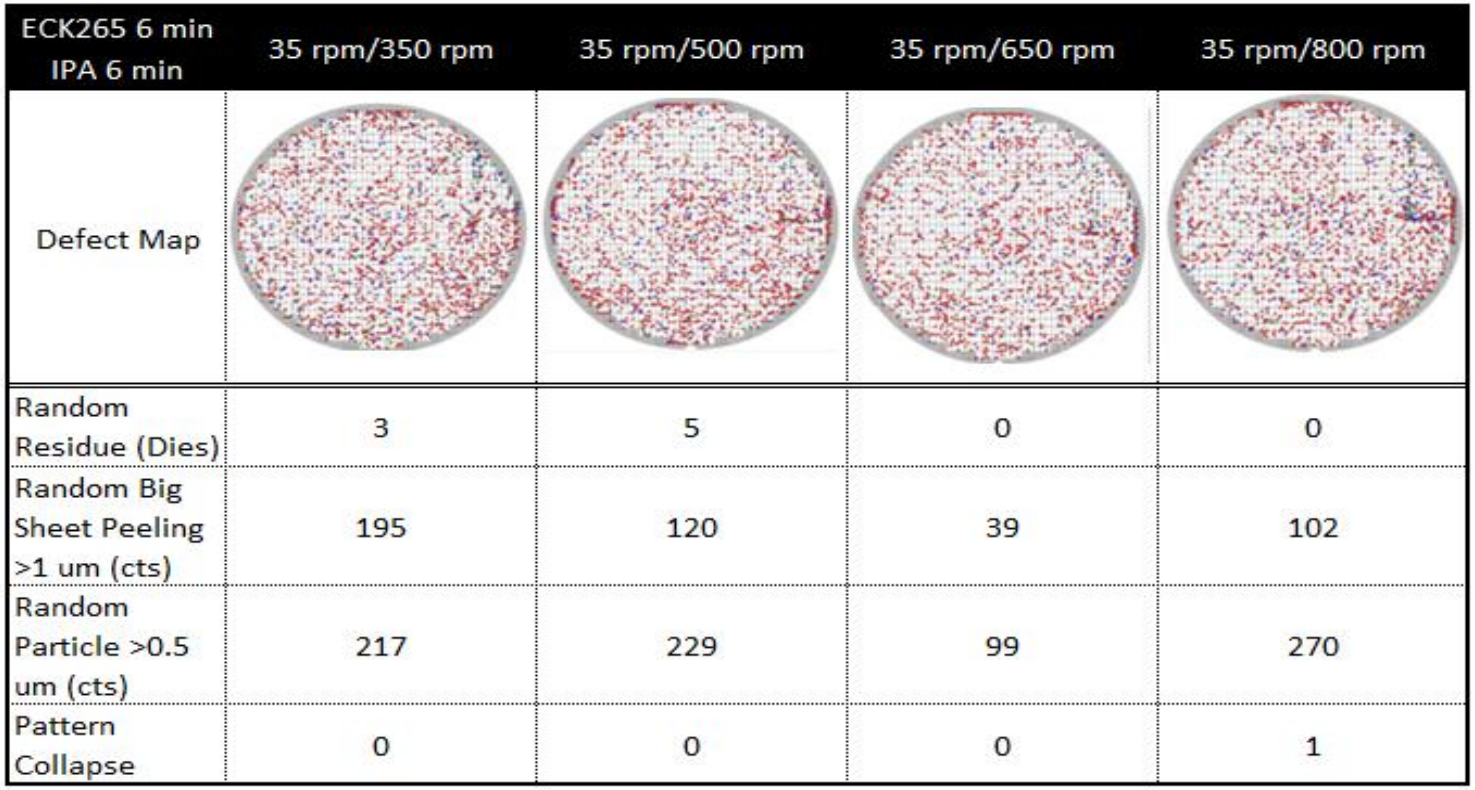
Section 4.1.2 thoroughly reviews the impact of EKC265 and IPA process time on particle defects. This section will apply EKC265 6min and IPA 6 min as the center condition due to its lowest particle defects distribution. The purpose of this section is to examine the dependency of chemical rotation speed on the crown capacitor particles. The following rotation speed is analysed.

1. EKC265 6 minutes, hybrid rotation speed 35 rpm/350 rpm → IPA rinse 6 minutes → IPA dry.
2. EKC265 6 minutes, hybrid rotation speed 35 rpm/500 rpm → IPA rinse 6 minutes → IPA dry.
3. EKC265 6 minutes, hybrid rotation speed 35 rpm/650 rpm → IPA rinse 6 minutes → IPA dry.
4. EKC265 6 minutes, hybrid rotation speed 35 rpm/800 rpm → IPA rinse 6 minutes → IPA dry.

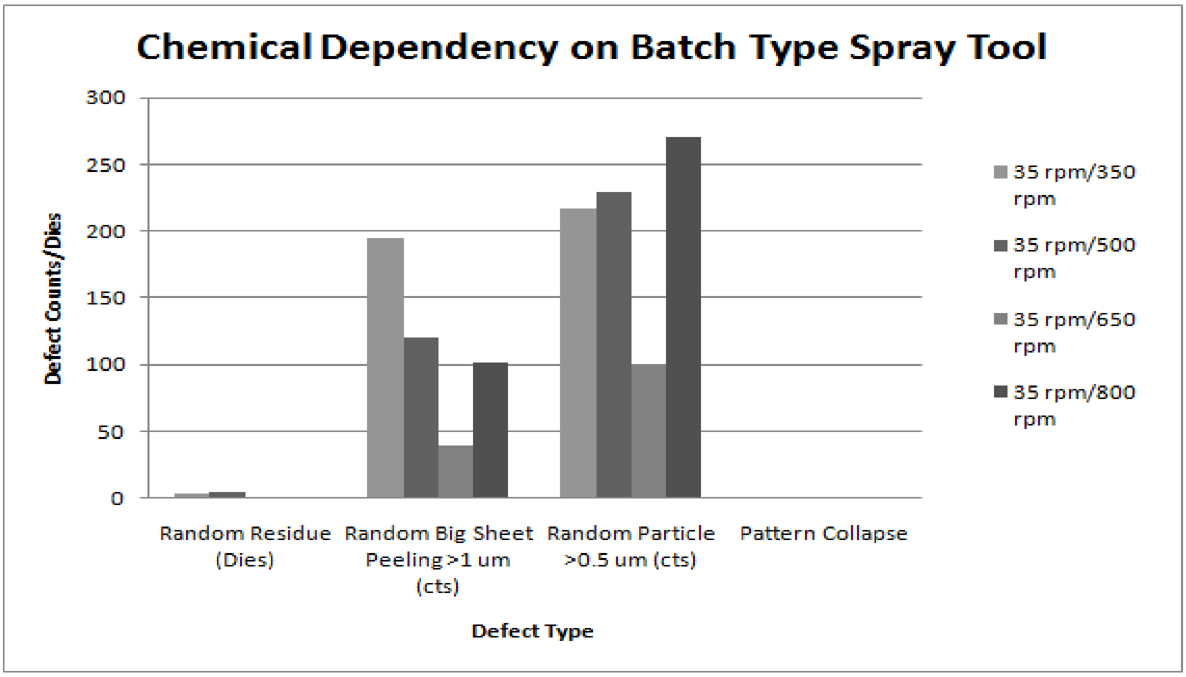
4.1.3.1 Experimental Result

Notably, the wafer treated with a hybrid rotation speed of 35/650 rpm has the lowest big sheet particles and random type particle defects, as shown in Table 4.4, Graph 4.4, and Figure 4.6. Interestingly, the particle count appears to be inversely proportional with rotation speeds in the range of 350rpm and 650 rpm, and then became proportional for 800 rpm. We will elucidate more in the next section.

Table 4.4 Chemical rotation speed dependency on crown capacitor particle defects.



ECK265 6 min IPA 6 min	35 rpm/350 rpm	35 rpm/500 rpm	35 rpm/650 rpm	35 rpm/800 rpm
Defect Map				
Random Residue (Dies)	3	5	0	0
Random Big Sheet Peeling >1 um (cts)	195	120	39	102
Random Particle >0.5 um (cts)	217	229	99	270
Pattern Collapse	0	0	0	1



Graph 4.4 Chemical rotation speed dependency on crown capacitor particle defects.

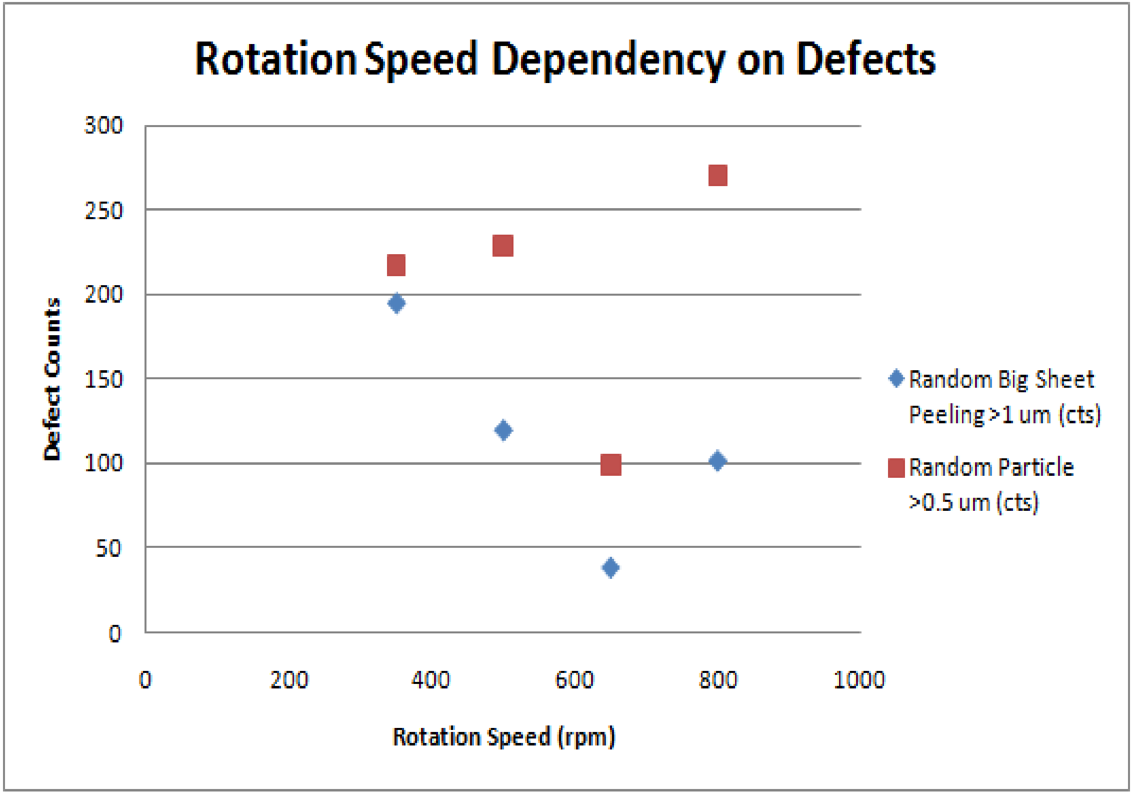


Figure 4.6 Rotation speed dependency on big sheet peeling particles and random type particles.

4.2 Discussion

Particle removal methods are generally divided into two categories: wet chemical procedures and mechanical techniques. Wet chemical methods are the traditional ways that performed cleaning via surface etching. Mechanical techniques clean through the application of a hydrodynamic force or other physical force. This work shows the greatest promise since we have the greatest potential to combine mechanical and chemical effects advantageously.

The particles distributed over the wafer comprises mainly of the compound of titanium oxide, carbon rich residues and silicon dioxide (as explained in the previous chapter two). In this section, a comprehensive understanding for both chemical and mechanical factor is elucidated.

4.2.1 Chemical Reaction

Although chemical reaction for each candidate is rather complex and hard to be entirely defined, we can infer from some of the chemical components and derive a model.

4.2.1.1 EKC6800

EKC6800[3], a ready-to-use semi-aqueous solution from EKC Technology, Inc, contains Ammonium Fluoride that can dissociate into ammonium and fluoride ions, and setting up a complex series of equilibrium's, as shown below.

.

The three potential active species were HF, HF_2^{-is} and F^- . In this solution, the dominant species is F^-. F^- reacts with polymer residue on the wafer and reformed. $(TiF_6)^{2-}$ is water soluble, so during the water rinse step polymer residue can be removed (Equation 4-7). Meanwhile, the oxide-like polymer residues react with HF and form a water soluble compound $H_2[SiF_6]$. The water rinse step then removes the soluble compound (Equation 4-8). HF_2^- is barely involved in the reaction with EKC6800 pH, hence, SiO_2 like material loss is minimumal.

$NH_4F \leftrightarrow NH_4^+ + F^-$ (Equation 4-1)

$NH_4 + F^- \leftrightarrow NH_3\ (g) + HF$ (Equation 4-2)

$2HF \leftrightarrow HF_2^- + H^+$ (Equation 4-3)

$NH_4F + H_2O \leftrightarrow NH_4OH + HF$ (Equation 4-4)

$HF + H_2O \leftrightarrow H_3O^+ + F^-$ (Equation 4-5)

$HF + F^- \leftrightarrow HF_2^-$ (Equation 4-6)

$Ti(s) + 6HF \rightarrow (TiF_6)^{2-} + 3H_2\ (g)$ (Equation 4-7)

$SiO_2\ (s) + 6HF\ (aq) \rightarrow H_2[SiF_6]\ (aq) + 2H_2O\ (l)$ (Equation 4-8)

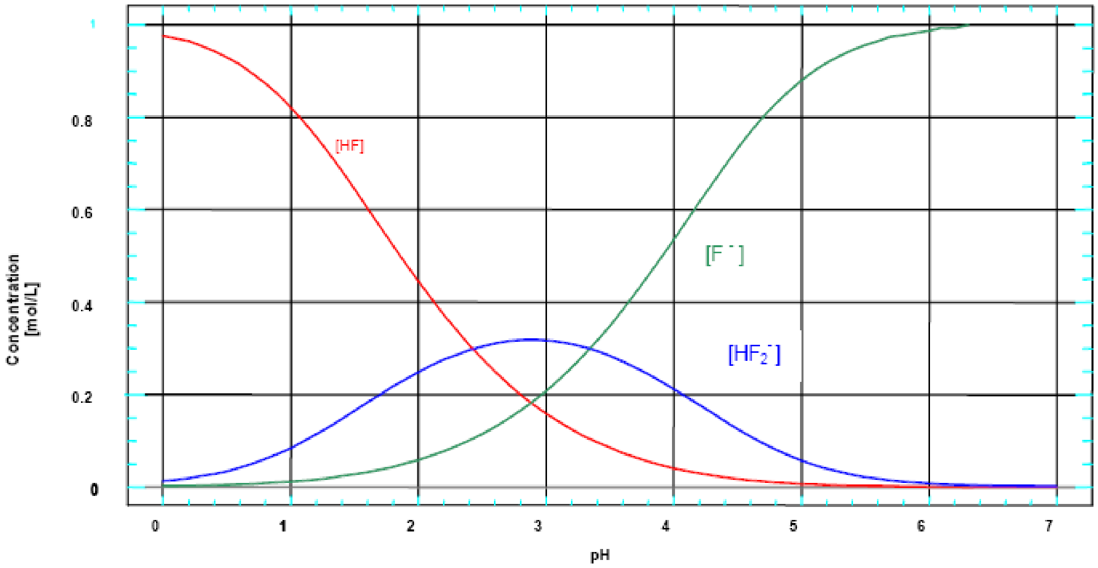


Figure 4.7 Schematic of HF, HF_2^- and F^- concentration relatives to pH [2].

4.2.1.2 REZI-38

As for the REZI-38[4] chemical, the potential active species for reaction were OH^- and HO_2^-.

$2[(CH_3)_4NOH] \rightarrow N_2 + 2OH^- + 2(CH_3)_4$ (Equation 4-9)

$H_2O_2 \rightarrow HO_2^- + H^+$ (Equation 4-10)

$Ti + 3H_2O_2 \rightarrow [Ti(OH)_3O_2]^- + H_2O + H^+$ (Equation 4-11)

$Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + OH^- + \cdot OH$ (Equation 4-12)

$R\text{-}COOH + OH^- + HO_2^- \rightarrow R\text{-}COO^- + H_2O + O_2$ (Equation 4-13)

$SiO_2 + 2OH- \rightarrow SiO_2(OH)_2^{2-}$ (Equation 4-14)

The first reaction to happens is dissolution. Hydroxide ion (^-OH) and hydrogen peroxide (H_2O_2) attacks the metallic residues and forms a highly water-soluble complex. As mentioned in chapter 2, most particle distribute contains a high concentration of Titanium (Ti). For Ti rich particles, hydrogen peroxide (H_2O_2) is the only chemical (other than hydroxylamine or fluoride) identified to date that will effectively remove post-etch residues with a high titanium content without damaging the exposed metal or dielectric. The mechanism of dissolution of the Ti-rich residues is not well understood, however, it may proceed according to one of the oxidation reaction above (Equation 4-11) & (Equation 4-12). In chemical reaction (Equation 4-11), a water-soluble-complex $[Ti(OH)_3O_2]^-$ formed, meanwhile in reaction (Equation 4-12), Ti^{3+} could be $Ti(F)_3$ or TiN or Ti_2O_3.

As for other types of Si-rich particles, water soluble $[SiO_2(OH_2)]^{2-}$ complex formed.

For carbon rich particles or polymers, OH^- and HO_2^- react with alkyl compound and formed $RCOO^-$ (Equation 4-12). Both $[SiO_2(OH_2)]^{2-}$ and $RCOO^-$ complex can be removed by the next water rinse step.

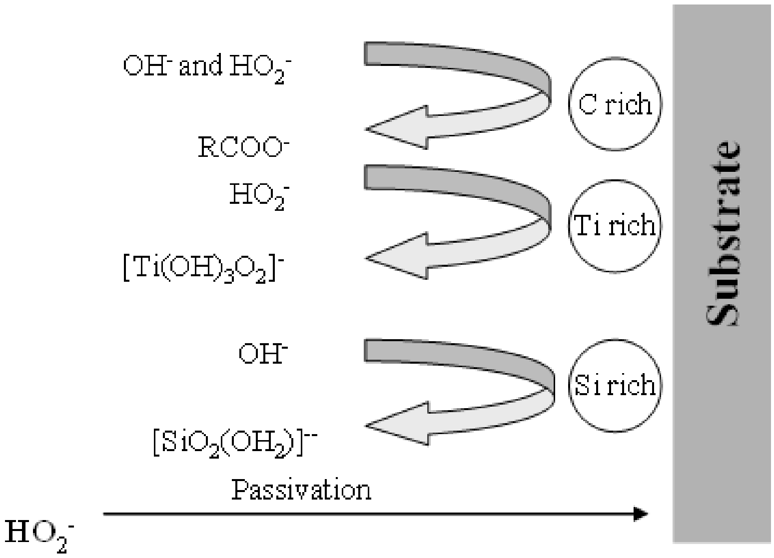


Figure 4.8 Cleaning Mechanism of Rezi38.

REZI-38 contains one or more chelating or complexing agents. These agents can sequestrate the dissolved metallic residue to prevents it’s re-deposition on the wafer. Also, there were one or more metal corrosion inhibitors in REZI-38 that can help prevents excessive attack of the metal by the hydroxide ion.

Hinges Table 4.1 and Graph 4.1 verify that EKC6800 has a better organic residue removal ability than REZI-38 for the single wafer tool chemical category. Meanwhile, there is no difference for Ti rich big sheet particle removal rate.

4.2.1.3 EKC265

As for EKC265[5] , another semi-aqueous solution from EKC Technology, Inc, Hydroxylamine served as a reducing agent. Metal ions are reduced into lower oxidation states and formed a more stable soluble complex. The attack mechanism is a two step reaction starting with the formation of hydroxyl ions, when the amine component in the stripper is hydrolyzed with water (Equation 4-15).

$$RNH_2 + H_2O \rightarrow RNH_3^+ + OH^- \qquad \text{(Equation 4-15)}$$

Amine plays several assisting roles in EKC265. First, it can act as a solvent, extremely effective at removing organic materials. Also, amine assists in keeping the soluble residues in solution so that they can be carried away from the water surface. It also creates hydroxide ions, OH^-: these species aid in the dissolution of post-etch residues. HDA removes resist by a process of penetrating, swelling, and reducing Van Der Waal forces. The solvent molecules solvate the polymer molecule and overcome the attractive forces that hold the polymer together.

After the crown capacitor etching, we believe that some metal oxides, e.g. TiO_2, TiO would be formed and left behind. Other stable metal halides, such as TiF_3 also remain on the wafer surface. These salts and oxides are insoluble in water, dilute acids, or bases, but they are removed in HDA solutions. Reduction of these metallic species and subsequent formations of chelating complexes play a role in the removal of metal oxides residues. Based on the oxidation/reduction potentials, the metallic species that can be reduced by hydroxylamine are listed in Table 4.5. [8]

The combination of HDA and an organic amine form a strong reducing and complexing (ligating) solution. The insoluble metal oxide could be reduced to a lower oxidation state and subsequently chelated with the ligand to form a more soluble metal complex which could ultimately end up in the solution. The proposed mechanism of reduction, chelation, and stabilization results in removal of a number of etching residues without attacking the pure metal surfaces.

We postulate the good performance of EKC265 is a result of HDA reaction. In addition, Titanium corrosion is averted due to the basic solution. Hence, EKC265 is chosen as the cleaning treatment chemical for crown wet capacitor post clean.

Table 4.5 Metallic Reduction By Hydroxylamine.

Metallic Reduction by Hydroxylamine
Ag (I) → Ag(0)
Au(II) → Au(I)
Co(III) → Co(II)
Cr(VI) → Cr(IV)
Cu(II) → Cu(I)
Fe(III) → Fe(II)
Pd (II) → Pd(I)
Ti(III) → Ti(I)
W(V) → W(III)

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4.2.1.4 ELM C30

ELM C30[6] consists of 69% of N-N Dimethylformamide (DMF) and 1% of Fluoro-compound. DMF acts as the solvent to organic compounds; meanwhile, fluoride functions as oxygen-silicon, oxygen-metal, carbon-silicon and carbon-halogen bond attacks. The reaction for ELM C30 fluoride-based chemical is basically the same with EKC6800 (Equation 4-4 & Equation 4-5).

By figure 4.9, metal oxides and organic particles react with F^- and HF_2^- at a pH around 3 to 4 (figure 4.6), the compound formed is dissolved in DMF. The water rinse step is required to rinse away the water soluble complex compound.

Like the results for EKC6800, ELM C30 succeeds in removing most of the organic like residues, but the removal of big sheet particles and small particles is not significant enough.

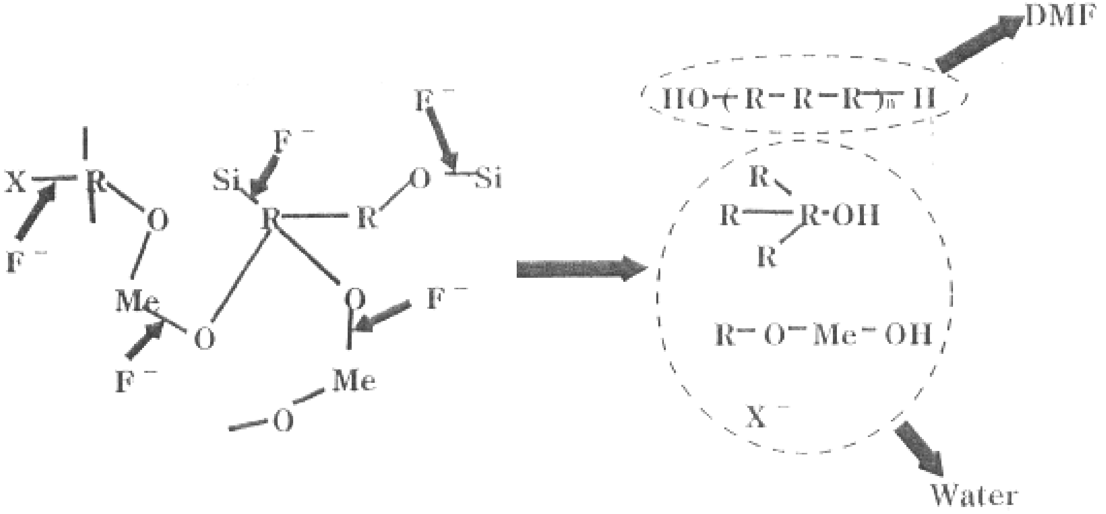


Figure 4.9 Schematic of ELM C30 reaction of removing fluoro compound and organic carboxylate.

4.2.1.5 EcoPeeler

Ammonium phosphate (NH_3H_2PO) is the major reactant in EcoPeeler(7). It plays the role of removing metal polymer. Figure 4.10 shows that by controlling NH_3, pH value can be controlled. The polymer removal ability of ammonium phosphate is different under different pH values. In Figure 4.11, the cleaning mechanism of EcoPeeler is explained. Ammonium Phosphate breaks the interface between metal and polymer then the polymer reacts with condensed ammonium phosphate and becomes water soluble.

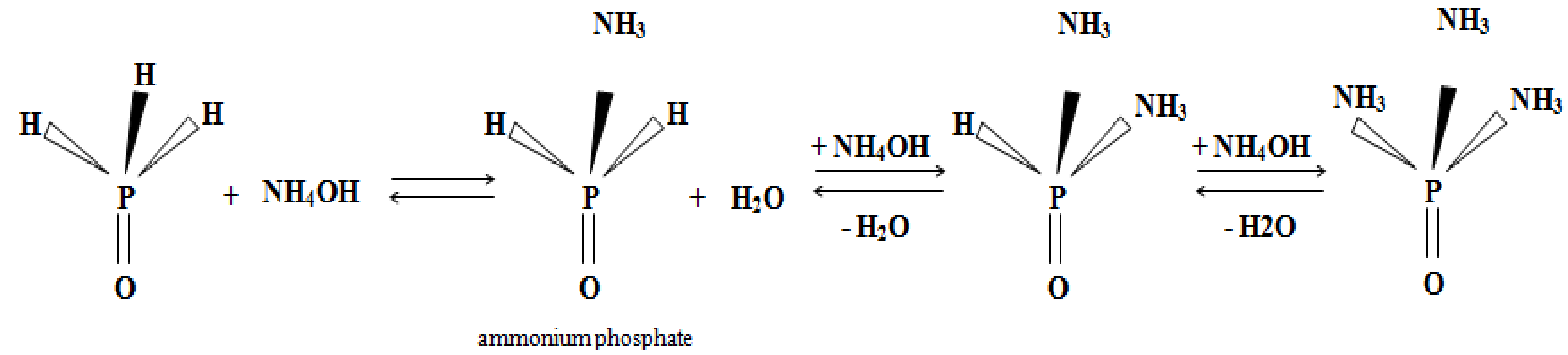


Figure 4.10 Ammonium phosphate preparation.

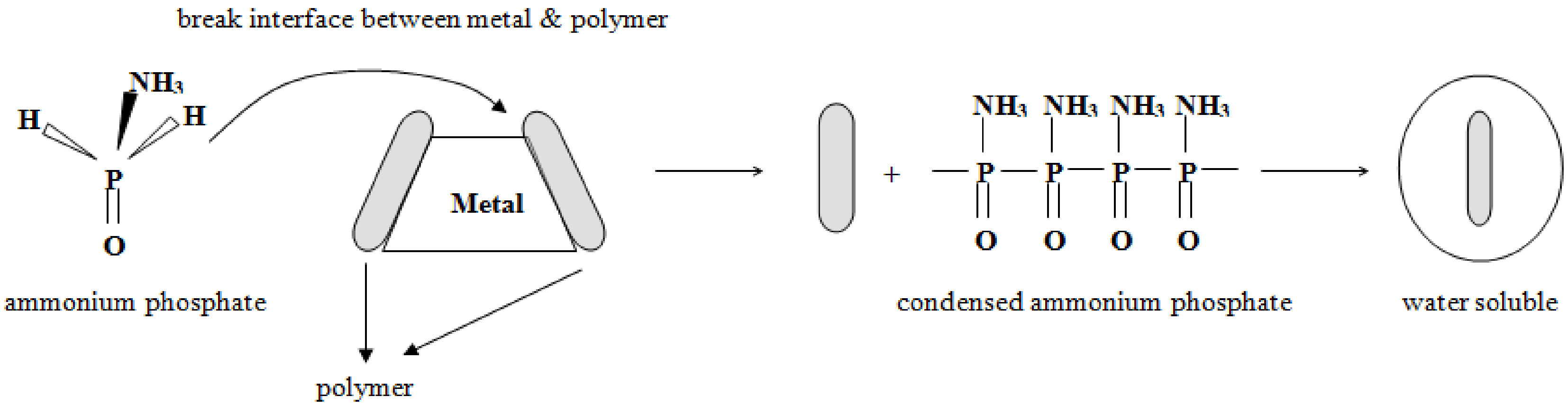


Figure 4.11 Cleaning mechanism of EcoPeeler.

4.2.1.6 Summary for Chemical Reaction

Single wafer tool chemicals have poor performance in removing organic type polymer residues; meanwhile batch type tool chemicals EKC 265, ELM C30, and EcoPeeler are rather good in terms of dissolving the organic residues. However, from defect result shown in Figure 4.1, EKC265 has the best removal rate for Titanium rich particles than the others. These kind of particles are more easily removed by a HDA based chemical. As shown in the Pourbaix diagram (Figure 4.11), $Ti(OH)_3$ is easily formed in solutions with high pH.

In conclusion, particle defects removal for the crown capacitor process is more easily achieved in an alkali solution than in a neutral or acid solution. EKC265 is the best particles for the cleaning treatment.

From the result of section 4.1.2, a longer EKC265 treatment time implies a lower particle defect count, but a higher penetration and collapse count. This phenomenon can be infered from the etch rate of Titanium and Titanium oxide in HDA based chemistry. Longer treatment time brings a higher Titanium and Titanium oxide etch rate. Consequently, the capacitor cylinder built from Titanium risks cracking and collapsing. Depending on the bottom titanium cylinder film thickness, EKC265 treatment time can be adjusted.

On the other hand, IPA treatment time is completely irrelevant to the result of the experiment. We conclude that the IPA treatment time is not a factor that will impact particle defect removal ability.

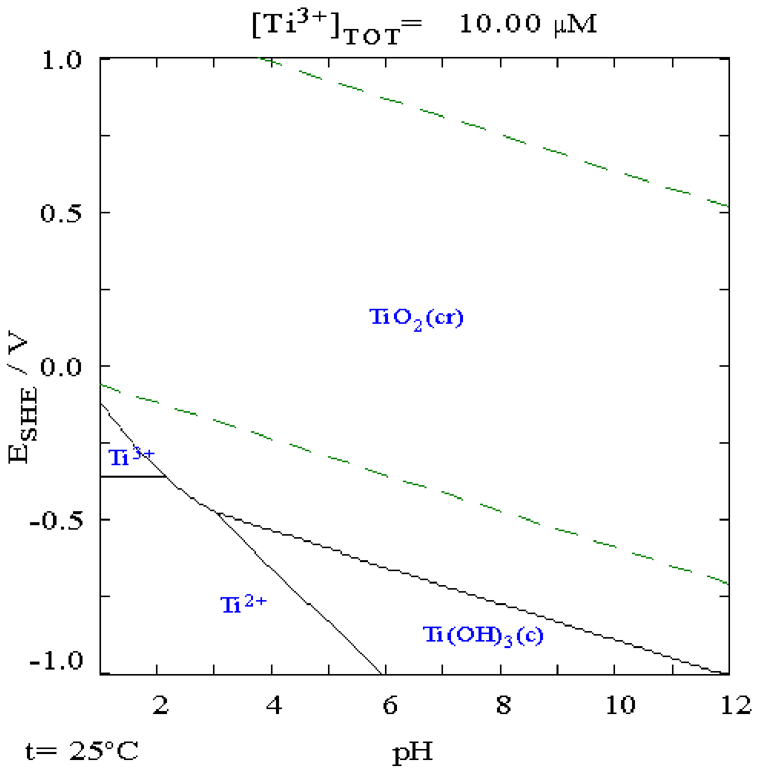


Figure 4.12 Pourbaix diagram [9] for Titanium in pure water, perchloric acid or sodium hydroxide.

4.2.2 Physical Reaction

From the result of section 4.1.3.1, we found that the rotation speed has direct impact on the particle removal. The physical mechanism of a particle removal by hydrodynamic and centrifugal force is studied in this section. It is important to understand the detachment of particles with hydrodynamic drag force and from a practical point of view know the advantages and the limitations of this cleaning technique[10,11].

There are two classes of traditional particle removal: 1) Lift away from substrate: particles move vertically through an ever-weakening force field. The applied force dislodges particle and immediately brings it through field. 2) Translate along substrate and off edge: once the particles are dislodged, they roll over substrate without being pulled through the force field, often occurs in fields at substrate edge.

The fundamental processes related to the removal of fine particles from surfaces in a hydrodynamic flow field are not adequately understood. Beaudoin had proposed a model of hydrodynamic particle removal from surfaces by using the particle Reynolds number [12]. In his approach, particle removal is assessed based on a critical particle Reynolds number: particle removal occurs at and above the critical particle Reynolds number, while particles remain attached to the surface when below the critical value.

Figure 4.13 shows a general model for a deformable particle, of diameter *d*, adhering to a surface in a hydrodynamic flow field. There are three forces – adhesion (F_A), drag (F_D), and lift (F_L)- and one external moment (M_D) acting on a particle (Figure 4.12)

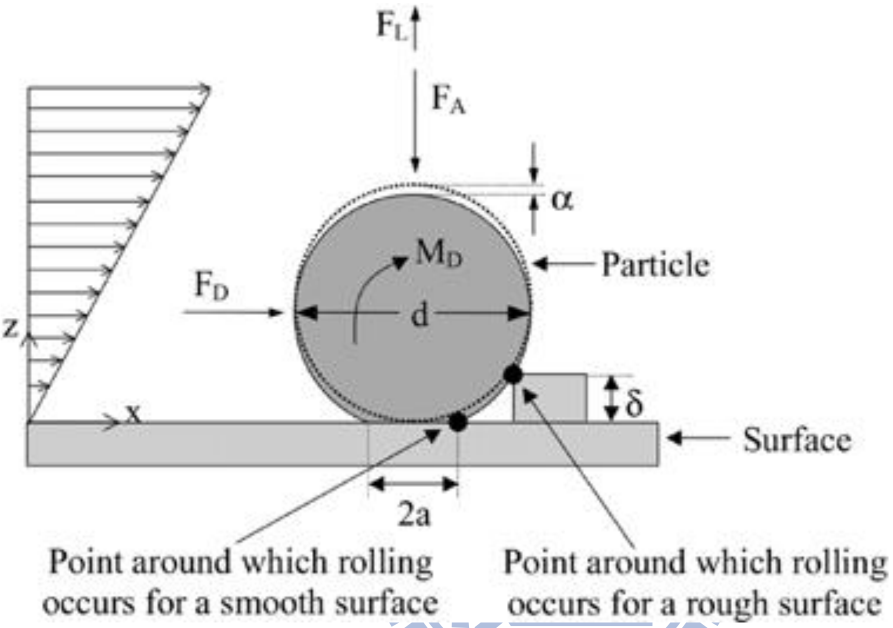


Figure 4.13 Particle adhesion/removal model used in the critical particle Reynolds number model.

The particle Reynolds number (Re_p) is defined as [13] :

$$Re_p = \frac{d \rho V_p}{\mu} \qquad \text{(Equation 4-15)}$$

The use of particle Reynolds number provides a means for scaling the removal criteria to different particle diameters and cleaning systems, as well as taking into account the flowing conditions near an adhering particle.

When the vectors sum of external moment, drag force, and lift force exceeds adhesion force, particle is removed (Figure 4.13) [14]. All forces and moments except adhesion force are functions of Re_p.

$$M_D + F_D \cdot I_1 + F_L \cdot I_2 \geq F_A \cdot I_2 \qquad \text{(Equation 4-16)}$$

$$M_D \propto d\, Re_p \qquad \text{(Equation 4-17)}$$

$$F_D(Re_p < 1) \propto Re_p \qquad \text{(Equation 4-18)}$$

$$F_L \propto d \frac{dy}{dx} Re_p \qquad \text{(Equation 4-19)}$$

I_1 : Vertical lever arm

I_2 : Horizontal lever arm

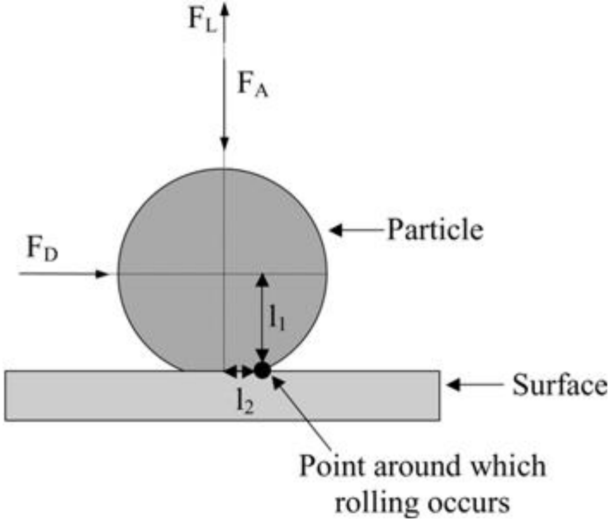


Figure 4.14 Schematic showing the definition of the lever arms as related to rolling particle removal.

Some particles were removed when Re_p(flow) $\geq$ Re_p(Rolling).

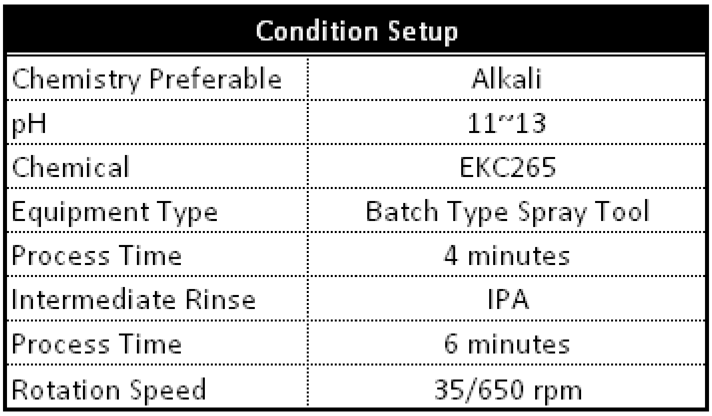
However, there should a balance between chemical reaction and physical reaction in order to have the lowest particle distribution. When the rotation speed reaches 800 rpm, the chemical reaction will be limited. Higher rotation speed implies less chemical reaction on the wafer due to the turbulent flow. It is noted that the design of high aspect ratio structure of the specimens can withhold the maximum external forces applied (rotation speed 800 rpm with chemical flow rate 1.2 liter/minute) without any structure collapses.

4.3 Summary for Physical Reaction and Optimal Condition Setup

In this study, we can conclude that the batch type spray cleaning process tool is suitable for a high aspect ratio structure cleaning. Meanwhile, for the titanium film exposed area, it is suggested to process it with an alkali solution, rather than concentrated acid. Thus, a stripping and cleaning chemical solution based on hydroxylamine (HDA) chemistry, EKC265 , has been proven to effectively remove organic type residue, big sheet type particles and small particles after the crown capacitor wet etch process. The solution contains hydroxylamine, a metal ion free reducing agent, mixed in an alkaline buffer. The cleaning mechanism is postulated to be a two step reducing and complexing reaction process. In addition, an appropriate rotor rotation speed applied enhances the particle removal abililty.

Defect inspection results reveal that the condition of EKC265 with a rotation speed of 35/650 rpm removes a number of polymer residues and particles. Compared to the wafers without treatment, 90 percent of the particle defects were removed. As for the chemical process time, the final condition adopted is not the longest process time due to the pattern collapse and penetration. EKC265 with a process time of 4 minutes combined with an IPA of 6 minutes is chosen in order to have a wider process window. Table 4.6 summarizes the final condition of this study.

Table 4.6 Final optimal condition for stacked crown capacitor cleaning.



Condition Setup	
Chemistry Preferable	Alkali
pH	11~13
Chemical	EKC265
Equipment Type	Batch Type Spray Tool
Process Time	4 minutes
Intermediate Rinse	IPA
Process Time	6 minutes
Rotation Speed	35/650 rpm

4.4 Reproducibility Test and Yield Improvement Result

At the end of this work, a reproducibility test with the setup condition was carried out.

The reproducibility test is to qualify the optimal condition before mass production. Figure 4.15 and Figure 4.16 show a significant improvement for crown capacitor defect counts with and without EKC265 treatment. The horizontal axis of these figures represented the tested wafers. Defect inspection is performed only after the cleaning process, thus, only final mean and median value will be considered as some of the pre-process difference will impact the distribution of defect counts.

For organic type residues, 50% of overall counts less for wafers with EKC265 treatment; meanwhile; for particles with size > 0.5 µm, the remove rate is larger than 80%. As for big sheet particles, wafers with EKC265 treatment are 60% lower than without.

The most important purpose of this study is to gain the wafer yield for 60 nm DRAM. The wafer yield is defined as the percentage of good chips over the total chips on a wafer. Figure 4.16 presents an outstanding yield improvement using EKC265. EKC265 yield is 3% higher than those without cleaning. In other term, with the cleaning process applied, there is an extra 50 good chips per wafer to be sell in the market. In addition, there is no electric characteristic: I_{CC2} (standby current) change by using EKC265 treatment (Figure 4.17). The impact of EKC265 on the surface characteristic of the crown capacitor's bottom electrode is assumed to be compatible with the device characteristic. Both CP1 marginal fail and typical fail are lower in our work.

From the above result, it cleary shows that the final optimal condition of this work is robust and applicable in factory mass production in terms of defect reduction and yield improvement.

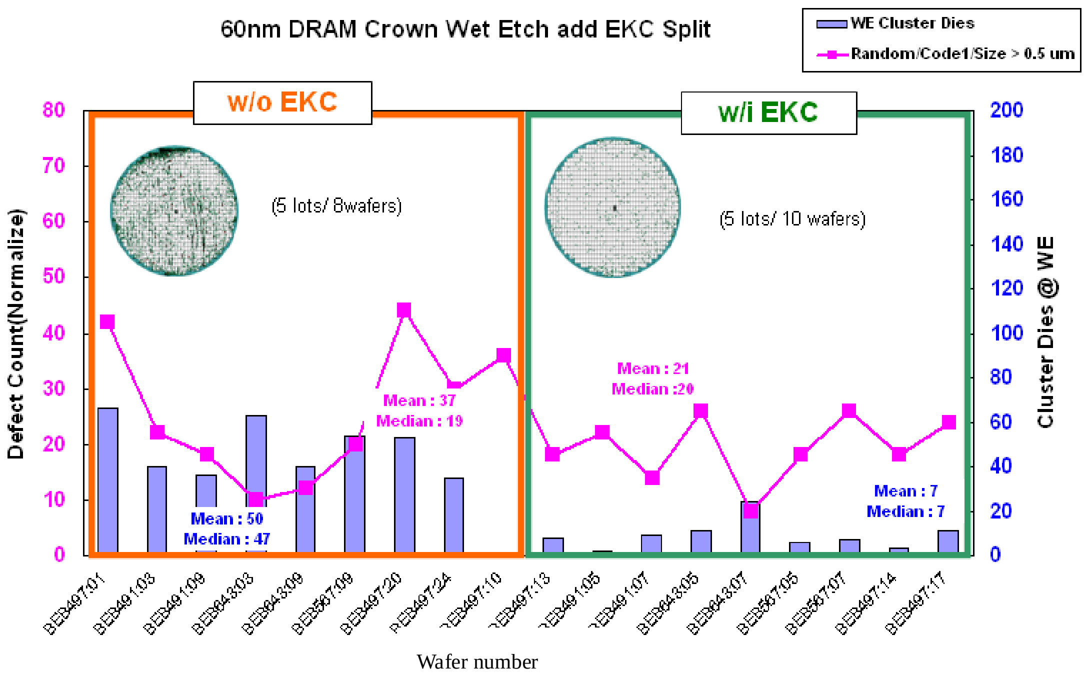


Figure 4.15 Comparison of organic residues and small particle > 0.5 μm for wafer with and without EKC265 treatment.

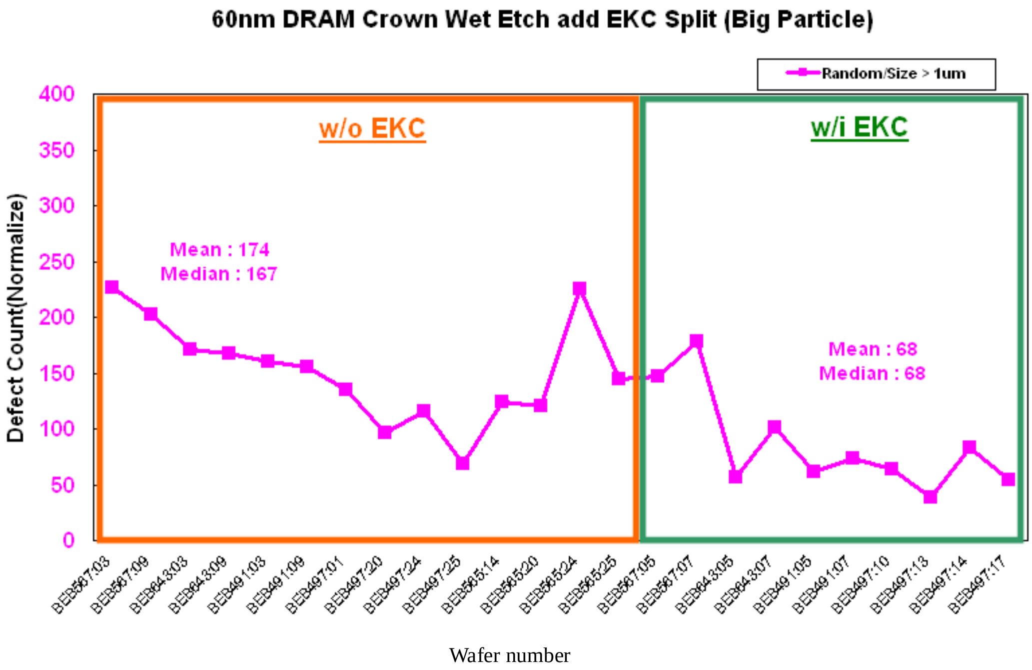


Figure 4.16 Comparison of big sheet particle > 1.0 μm for wafers with and without EKC265 treatment.

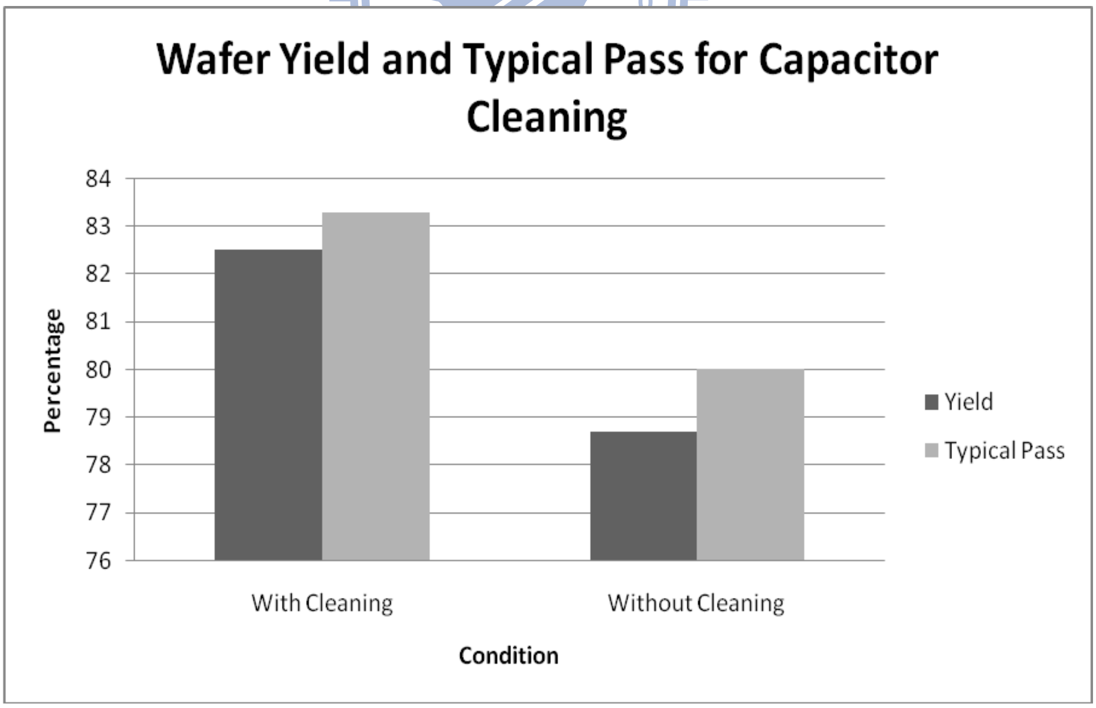


Figure 4.17 Comparison of wafer yield and typical pass for lot with and without EKC265 cleaning.

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Chapter 5: Conclusions and Future Development

5.1 Conclusions

Crown wet capacitor process plays an important role for increasing capacitance in 60nm DRAM. The main yield killer in 60nm DRAM is identified to be particle defects from the capacitor node. From defect source analysis evaluation results, the majority of particulate defects that have direct yield impact come from the crown capacitor wet etch back process that proceeds from the wet bench with concentrated HF. In low pH liquid solution, the specimen surface, which is Si_3N_4 and TiN exposed, is keen to attract major particulate defects that are negatively charged via strong van der Waals bondings. These particulate defects are divided into big particle defects larger than 0.5μm and residues. Titanium, Oxide, Carbon and Fluoro are the major elements contained in these defects. Thus, there is an urgent need to remove these defects in order to gain higher wafer yield.

It is surprising to see that the traditional spray type batch tool has a higher particle removal rate than the single wafer type tool. The main issues for the single wafer tool are 1) the insufficient drag force and detach momentum during chemical process, 2) the DI water rinse for particles and pattern collapse during N_2 drying. During processing, relevant chemicals, DI water and dry N_2 flow are parallel to the process wafer for single wafer tool; while, for the batch type tool, direction of wafer is proportional to the process wafer flow. The differences in physical removal ability tend to favor the traditional spray type batch tool.

Out of five chemicals tested in this work, the HDA-based chemical EKC265 with a high pH has the best particle removal ability. This is because the zeta potential of particles on the specimen surface is negative under alkali solutions, so the electric double layer repulsion is stronger, which tends to repel particles from the wafer surface. With EKC265, processing conditions are optimized, such as process treatment time and rotation speed. Long chemical process times are better for particle removal but will cause more material loss which induces pattern collapses. As for the rotation speed, a lower RPM will lead to insufficient physical momentum for particles to dislodge, while a higher RPM will tend to have a relatively shorter chemical process time due to the flow pattern that keeps chemicals from attaching. Thus, a moderate condition with the largest process window will be finalized as the best condition. Also, the repeatability of the final condition proved to be consistent. The final wafer yield is improved by 2% due to the defect reduction.

The optimal condition of crown wet capacitor post cleaning: HDA based chemical EKC265 4 minutes with rotation speed 600 rpm and IPA 6 minutes performed with a batch type spray tool is proved to have a consistent performance for capacitor post cleaning for 60nm DRAM and beyond.

5.2 Future Development

As mentioned in chapter 1, the cleaning process is required to achieve: (i) ultraclean surface, (ii) without any side effects, (iii) within a short period of time, (iv) with high reproducibility, and (v) at low cost [1]. These requirements get increasingly demanding year by year as the device density goes up and device price goes down. At the same time, challenges to be overcome get diversified more than ever before, along with rapid diversification of device materials, manufacturing processes and production systems.

For the cleaning of metallization, a HDA-based chemical might still be suitable to be applied in a metal-via-hole cleaning process, however the solvent, due to its toxicity, is not easy to dispose and so is not environmentally viable. The solvent application is expected to continue to weaken because of environmental and health regulations that restricting solvent emissions [2]. Thus, alternate processes that either reduce or replace chemical usage are being sought because of the current challenges of submicron particle removal, environmental impact from high consumption of water and chemicals, integration into cluster tools, as well as increasing costs [3]. The future development of chemicals will need to focus on environmentally friendly green products, like aqueous based chemical without solvent. However, semi aqueous or aqueous based chemicals are relatively weak in reaction in comparison to fluoride based or solvent based chemicals. Researchers are still working hard in developing a material loss limited, non-corrosive, disposable, environmentally friendly, low cost and low consumption for metallization cleaning.

This study shows that single wafer equipment performance is quite limited for the high aspect ratio structure process. An important aspect of wet cleaning is the final drying step. Conventional N_2 centrifugal spin dryers can leave water marks, induce stress on the wafers, redeposit particle recontamination from static charges and cause the collapse of high aspect ratio structures which will lead directly to yield loss. During the wafer drying step, surface tension can pull together neighboring pairs of tall, narrow structures. To prevent these issues, engineered drying that use isopropyl alcohol (IPA) drying or low surface tension fluids is introduced. However, IPA drying requires high temperatures and high pressure environments, which adds to the chemical consumption, and poses an environmental hazard [3]. Thus, the use of low surface tension fluid is one of the new approaches being evaluated. In another perspective, the development of dry cleaning for high aspect ratio structure should also be considered.

As a conclusion, before the new technologies are mature, batch type equipment and HDA based chemistries will remain irreplaceable for high aspect ratio structures metal cleaning.

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