

## Chapter 2

### Fundamental Concepts of Post-Cu CMP Cleaning

#### 2.1 Mechanisms for Particle Contamination

##### 2.1.1 Particle-Wafer Interaction

Particle contamination results from the interaction between the abrasive particle and the wafer surface. There are several mechanisms for adhering to a wafer surface including van der Waals force, electrostatic force [28][29], chemical bonding [30], etc. The forces of adhesion depend upon a lot of factors like size of the suspended abrasive particles in the slurry, slurry chemistry that induces electrostatic and electrochemical effects, zeta-potential, etc. These forces need to be overcome in order to achieve effective particle removal from the surface.

##### 2.1.1.1 Van der Waals forces

Most of the particle contaminations are generated from a combination of sources including particles from the abraded surface, pad material, abrasive particles suspended in the slurry. These particles adhere to the surface as a result of physical attractive forces, between the particles and the wafer surface and also between the particle molecules and the surface, called the van der Waals forces. These are relatively weaker than the chemical bonds. The intensity of these forces depends upon the particle size and the distance between from the surface. The van der Waals force between a spherical particle and a flat surface could be expressed as:

$$V_A = -A_{123} \frac{R}{6H^2} \quad (\text{Eq.2-1})$$

Where  $A_{123}$  is the Hamaker constant for surfaces 1 and 2 in a dispersion medium 3,  $R$  is the radius of the spherical particle, and  $H$  is the separation between two surfaces. Based on the theory, it can be stated that the increasing distance between the particle and the wafer surface results in weaker forces. Therefore, wet cleaning is effectual than dry cleaning. This

interaction energy has to be overcome by the external forces to remove the particles off the wafer surface to achieve contamination free wafer surface.

### 2.1.1.2 Electrostatic Forces

During the CMP process, wafer and the pad surfaces develop surface charges thereby attracting the ions immersed in the slurry. Two layers of charge that develop in the liquid, balance the charge on both the surfaces. This is called electrical double layer (EDL), as shown in Figure.2-1. The potential of this layer that forms a boundary for these layers is termed and measured to be zeta-potential. This zeta potential is a measure of the charge of the layer, which determines the magnitude of attraction or repulsion and could be expressed as:

$$V_R(H) = \frac{64\pi\epsilon Rk^2T^2\gamma_1\gamma_2}{e^2z^2} \exp[-kH] \quad (\text{Eq.2-2})$$

$$\gamma = \frac{\exp[ze\psi_d/2kT]-1}{\exp[ze\psi_d/2kT]+1} \quad (\text{Eq.2-3})$$

where  $\epsilon$  is the permittivity of the dispersion medium,  $k$  is the Boltzmann constant,  $T$  is the temperature.  $z$  is the counter ion charge number,  $R$  is the particle radius, and the debye length  $1/k$  is  $(8\pi n v^2 e^2 / \epsilon k T)^{1/2}$ , while  $\psi_d$  is the zeta potential of the surface. Manipulating the pH, electrolytic concentration and adding various surfactants, magnitude of the zeta potential can be varied. If a high zeta potential value is maintained, the cleaning process becomes easier. If a large potential with the same sign as that of the particle is maintained, then the repulsion of the particles from the surface is large, resulting in separation of the particle easier removal of the particles and effective cleaning.

### 2.1.1.3 Chemical Bonding

Chemical or hydrogen bonds can be formed between the slurry particles and the wafer surface. Several different effects during CMP can promote bonding of the slurry particles to the film surface. First, the chemical component of the slurry can alter the surface chemistry of

the particle and the wafer, causing them to bond to each other. Also, during CMP there is a localized increase in the wafer's surface temperature. This elevated temperature may increase the rate of the chemical reactions between the slurry particles and the wafer surface. Water surrounding particles that settle on wafer surfaces may promote hydrogen bonding between the particle and the surface.

### 2.1.2 Embedding of Particles

During CMP pressure is applied through the wafer onto the slurry, which is between the wafer and the pad. Because abrasive particles are usually harder than the film being polished, particles can be embedded into the wafer surface to a certain extent, causing particle contaminations after CMP process. The mechanics of particle embedding is schematically shown in Figure.2-2. The penetration depth could be expressed as:

$$\delta = \frac{3}{4}d \left( \frac{P}{2cE} \right)^{\frac{2}{3}} \quad (\text{Eq.2-4})$$

where  $d$  is the diameter of the particle,  $P$  is applied pressure on abrasive particles,  $c$  is the particle fill factor at the surface which is equal to unity for fully filled close packing, and  $E$  is the Young modulus of the surface being polished. The typical value of the penetration depth of abrasive particles during CMP ranges approximately from a couple of angstroms to several hundred angstroms. Particle embedding may play a critical role in assisting the material removal during CMP. With regard to particle contamination, it seems that not all the embedded particles stay on the surface after CMP. It has been reported that the embedding of particles depends on the shape of the particle and the impact angle.

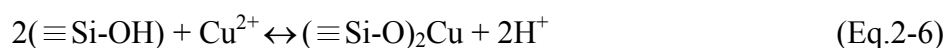
### 2.2 Particle Contamination Removal

Efficient particle removal is extremely difficult because of the wide variety of particle contaminations and strong adhesion forces [31]. Generally, harsh accelerations or high

pressure sprays are not able to remove the fine particles. In order to remove particles, the van der Waals forces first must be overcome to separate the particle from the substrate using mechanical effects such as scrubbing or by chemically etching the particle [32][33]. Then the electrostatic interaction must be turned into favorable conditions to avoid particle readhesion. A common practice during post-CMP cleaning is to manipulate electrostatic forces to prevent dislodged particles from redeposition on wafer surfaces by maximizing the zeta-potential repulsion between the particles and surfaces. The zeta-potential depends on the pH of the chemical solution used for cleaning. It can be manipulated by changing the pH as mentioned in earlier sections, thus resulting in the repulsion force between the surface and the adhering particles.

### 2.3 Mechanisms for Metallic Contamination

Figure.1-6 shows the Pourbaix diagram of Cu-H<sub>2</sub>O system [24]. It indicated that in acidic solutions with pH<5, copper oxide does not form and copper dissolves Cu<sup>2+</sup> at high potentials and is immune from oxidation at low potentials. In highly alkaline solutions with pH<13, it would form CuO<sub>2</sub><sup>2-</sup> at high potentials. For pH values ranging from 7 to 13, Cu<sub>2</sub>O formation is likely at low potentials. CuO forms on copper at higher potentials. Therefore, copper is corroded in acidic and alkaline solutions easily. In general, the CMP slurry chemistry is usually designed such that the metallic materials removed from the metal film can be dissolved. Therefore, the metallic contamination on oxide surfaces can be due to both the adsorption of dissolved metal species and the precipitation of insoluble metal compounds on the wafer surface. The mechanism for this copper ion-oxide surface interaction can be interpreted by using the following reactions:



## 2.4 Metallic Contamination Removal

Metal chelators are known to form stable complexes with Cu ions [26][27]. They could be used for Cu contamination removal from wafer surface. Mechanisms of copper contamination removal could be known by the distribution equilibrium [34]. The distribution equilibrium could be expressed by the following equations. Metal ions deposited on the wafer surface are dissolved into the aqueous phase (Eq.2-7). The complex reaction occurred between metal ion and chelator molecule (Eq.2-8). Metal-chelator complex might adsorb again on the wafer surface (Eq.2-9). Chelator molecule might adsorb on the wafer surface (Eq.2-10).



where M=metal ion, L=chelator, ML=metal-chelator complex, (aqueous)= dissolved in water phase, (solid)= adsorb on the surface.

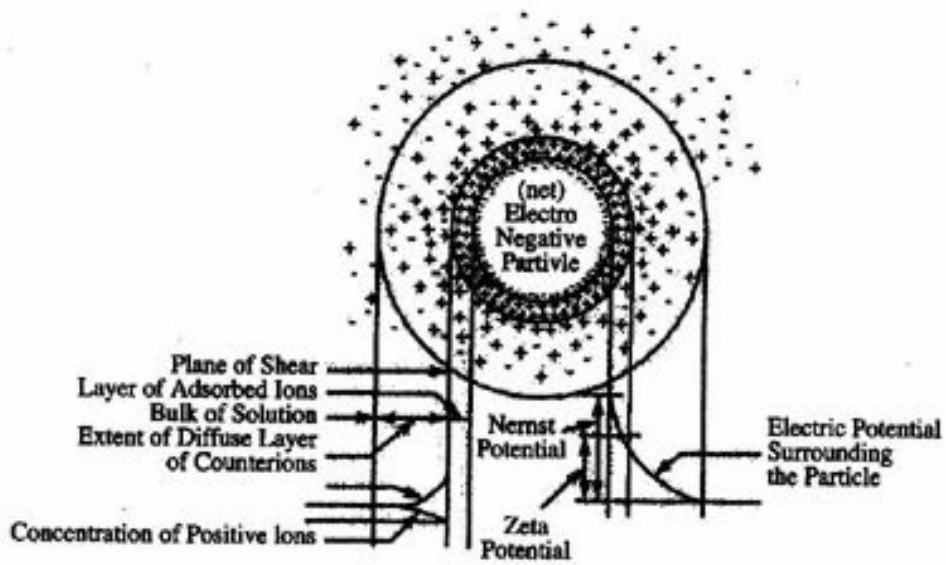


Figure.2-1 Electrostatic double layer around a particle.

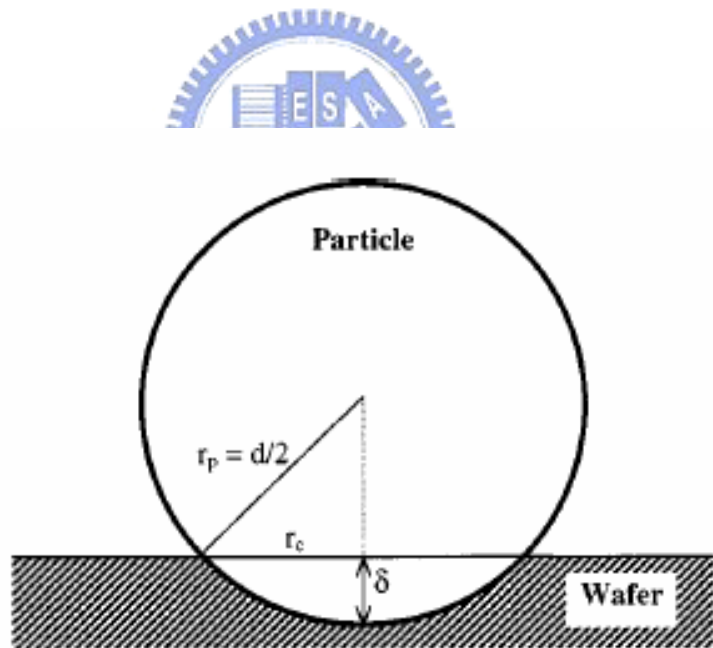


Figure.2-2 Geometry of an embedded particle into the wafer surface during CMP