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Particle – Wafer Interactions in Semiaqueous Silicon Cleaning Systems

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Introduction

Interfacial interaction forces between particulate contaminants and semiconductor wafer surfaces play a key role in the understanding of post-CMP and post-lapping cleaning processes. In order to facilitate removal and prevent re-deposition of submicron particles on wafer surface, understanding, measurement, and manipulation of these forces is required.

The theory of interaction forces in liquids that includes DLVO forces (van der Waals, electrical double layer) and non-DLVO (solvation, hydration, hydrophobic, steric and bridging forces) is well established and is studied elsewhere.[1-4] Short range interaction forces between silica surfaces in alcohols have been successfully measured before using AFM.[5-7]

The normal forces to the surface, before contact, are measured by the colloidal probe technique.[8] These forces are important in designing effective barriers to prevent contaminant particle attachment to a semiconductor surface and in contaminant re-deposition phenomena. To understand the physical forces required to detach a contaminant particle from a wafer surface, however, the lateral force required to slide or roll a particle on a wafer surface are measured. Such measurements are then directly compared with the lateral force required to damage oxide structures on a semiconductor wafer.

Instead of providing specific numerical values obtained for certain cleaning systems, this article will provide a scientific procedure leading to successful design of a post-CMP cleaning solutions.

In order to understand what is happening close to the surface the molecular dynamics simulation (MDS) has been applied. The AFM colloidal probe technique provides data at the nanometer level, whereas MDS predicts what is happening at the interface just angstroms away from the surface. In this regard these two techniques are complementary.

Materials and Methods

The AFM force measurements include the colloidal probe technique and the lateral force technique. A fused silica (SiO_2) coupon from Harrick Scientific was used as the substrate for colloidal probe measurements. A bare silicon wafer with native oxide was used as the substrate for lateral displacement measurements of silica particles. Structured 200mm and 300mm silicon wafers were used for lateral force damage measurements, as provided by Micron Technologies. The spherical fused silica particles (TECO-SPHERE grains) were purchased from C-E Minerals.

The colloidal probe force measurement technique requires attachment of a spherical particle (probe) to a tip-less AFM cantilever. In these measurements, triangular NP cantilevers from Veeco and rectangular TL-NCH cantilevers from Nanosensors were used. The probe preparation process includes following steps: particle cleaning, tungsten wire etching (to selectively pick up a particle),

T0) and after

application of glue to the cantilever, placement and attachment of the particle to the cantilever tip with glue. An example of the colloidal probe attached to the AFM cantilever is shown on Figure 1

The colloidal probe measurements were done according to the procedure described by Ducker[8] and Cappella[3] with PicoSPM II (Mollecular Imaging) AFM. The cantilever with the attached probe was treated with UV light for 20 min just prior to the measurement in order to remove any organic contamination. The cantilever spring constants were verified by the thermal noise method[9,10] as measured with the MI AFM system.

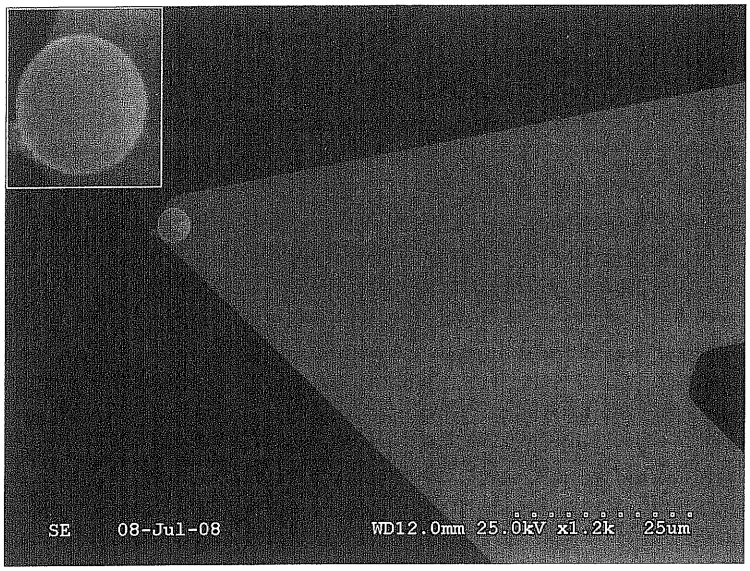

Figure 1. SEM image of 4 μm silica particle glued to the 0.13 N/m AFM cantilever.

Before measurements in a hydrophilic environment, the silica surface was cleaned with acetone, ethanol and DI water, and boiled in concentrated SC1 (5:1:1 mixture of DI water, 30% hydrogen peroxide and 27% ammonium hydroxide, respectively, by volume) at 80°C for 20 min. The surface was rinsed with MilliQ water. After such treatment the silica surface was found to be completely wetted.

In order to make silica hydrophobic the CVD (chemical vapor deposition) method was employed involving (Tridecafluoro-1,1,2,2-tetra-hydrooctyl) dimethylchlorosilane from Gelest. The silanation conditions were optimized with respect to amount of silane used, CVD time, temperature and the obtained contact angle based procedures described in the literature [11-13]. In the final silanation run, the silica surface and the spherical silica particle attached to cantilevers (colloidal probes) were silanated together, in the same chamber, to ensure the same surface coverage and the same degree of hydrophobicity (contact angle).

The contact angles were measured using the sessile drop technique.[14] For this purpose RAME'-HART Inc. NRL C.A. Goniometer, model no. 100-00-115 was used. The silanated silica substrate was placed on the flat stage. A clean microsyringe with stainless steel needle was filled with MilliQ water and was mounted in the goniometer. A sensile drop size which ensures no size effect on the measurement is reported to be of base size 7-9 mm.[15] To measure receding contact angle, the volume of the drop was decreased until the drop base receded to around 7 mm and the measurement was taken in about 30 s. To measure the advancing contact angle the volume of the drop was increased to cause the three-phase line of contact to advance to 8-9 mm and the measurement was taken in 30 s. The contact angles for silica coated with (Tridecafluoro-1,1,2,2-tetra-hydrooctyl)

dimethylchlorosilane were found to be equal to 87.0°+/-2.6° for the receding angle and 100.1°+/-4.3° for the advancing contact angle.

The interaction forces in different liquid systems, containing 2-propanol and MilliQ water with 10^{-4} M KCl as a background electrolyte, were measured. Colloidal probe measurements were taken with both the hydrophilic and hydrophobic silica particles in 0%, 10%, 40%, 70% and 100% 2-propanol for both hydrophilic and hydrophobic substrates for symmetric systems. For each system a total of at least 30 measurements in 3 different places around the sample were taken to achieve statistical significance.

The lateral force measurements (LFM) were performed with AFM Dimension 5000, Nanoscope IV (Veeco). Tapping mode was used to look at the structures and the contaminant particles at the wafer surface. The AFM lateral force measurement was done following the technique described by Yuan[16], which procedure is based on scanning of the same particle repeatedly, while increasing the normal force gradually, until the particle is displaced from its location on the wafer. The lateral (friction) force curve obtained for that scan is then used to determine the force needed to displace the particle. The lateral spring constants of the cantilevers used were calculated according to the procedure provided by Cannara.[17]

The AFM images were processed with freeware software WSxM for scanning probe microscopy.[18]

The temperature in the laboratory was around 21-22°C.

Contaminant removal vs. wafer damage

As the wafer structures become smaller and more fragile it is crucial to understand the impact of different manufacturing steps, especially the process of physical cleaning. The force required to remove a contaminant should be close to the structure damage force in order to maximize PRE, but not higher than this force in order to avoid structure damage. Therefore the first step in designing a wafer cleaning procedure is to determine the range of forces involved: forces that are effective for contaminant removal, but below the critical load that will damage sensitive wafer structures.[19,20]

Figures 2 and 3 show examples of lateral force measurements done with AFM. The measurement of the lateral force required to slide or roll a 250 nm silica particle is illustrated on Figure 2. There, a topography image (A) and 3D image (C) show the presence of silica particles on the silicon wafer surface. The inset (B) is a friction image that was created by scanning the particle along the dotted line with incrementally larger normal forces, (represented along the y-axis). The image D represents the 3D topography of image B. When the applied lateral force is not sufficient to overcome the adhesion forces, the AFM tip simply glides over the particle, as imaged on Figure 2 B and D. Using this methodology, it is easy to know when the particle is moved, as demonstrated by a missing particle, and at what lateral force.

The lateral forces required to move 250 nm spherical silica particles was correlated with the lateral force required to damage selected 200 mm and 300 mm wafer structures.

Figure 2 shows an amplitude image of sensitive hard mask features that have been scanned with known lateral force until structural damage was observed.

The magnitude of damaging force differs from structure to structure according to structure size (aspect ratio) and material type. Generally, the lateral force required to damage a wafer structures was 10 to 100 times grater than the lateral force required to roll/slide a 250 nm silica particle on the wafer surface.

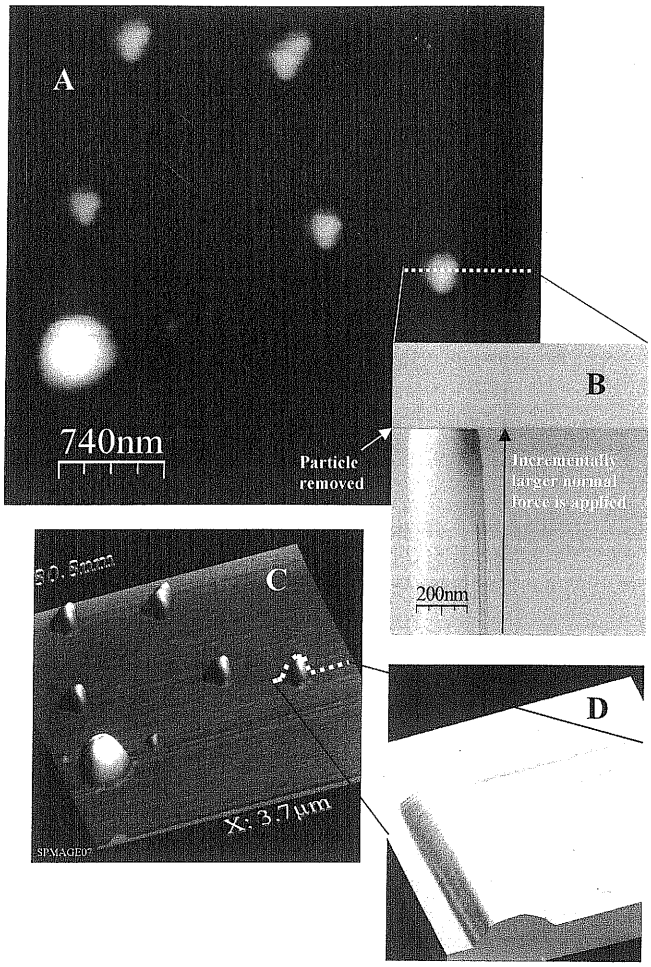

Figure 2 Measurement of the lateral force required to slide/roll a contaminant particle. A – 250 nm spherical silica particles on a wafer surface (topography), B – the indicated particle is scanned repeatedly with increasing normal force until the particle is displaced from its location on the wafer (marked as *particle removed*), C – 3D image of the 250 nm particles, D - 3D topography image of B.

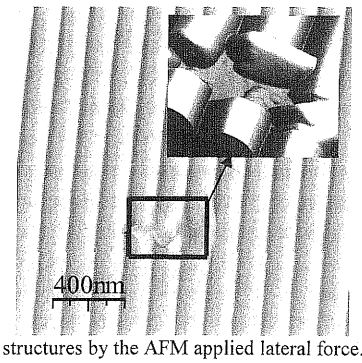

Figure 3. Damage of the spacer oxide structures by the AFM applied lateral force.

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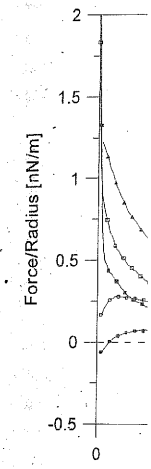

Figure 4. Force-
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Nonaqueous component and other additives

The influence of the nonaqueous content of semiconductor wafer cleaning solution on interaction forces was investigated under both hydrophilic (silica - silica) and hydrophobic (silanated silica – silanated silica) symmetric conditions. In the case of the hydrophilic system, Figure 4A, it is evident how the interaction forces, especially the electrical double layer component, diminishes as more 2-propanol is introduced into solution. The following two reasons may explain the results for the hydrophilic case: a) dilution of the electrolyte solution with non-aqueous agent results in weaker electrical double layer, b) gathering of 2-propanol molecules at the liquid-solid interface further diminishes the repulsion.

In the case of the hydrophobic system, the hydrophobic force dominates and masks all the other forces. It can be seen that hydrophobic forces are very significant for solutions containing 10% (by weight) alcohol or less. For concentrations of 40% and higher of the non-aqueous component hydrophobic attraction is highly diminished. It is completely extinct in pure 2-propanol and the interaction appear to be governed by the ever present van der Waals forces.

Based on analysis of these results, it is evident that the hydrophobic force was decreasing gradually as more of the less polar isopropanol was introduced into the solution. The hydrophobic attraction was shifting to smaller distances indicating weakening of the force. At 0% isopropanol it occurred around 30 nm from the surface. When only 10% of isopropanol was added the attraction was cut in half, occurring at 15 nm from the surface. At 40% isopropanol the distance is reduced to 8 nm, at 70% it is 6 nm and in isopropanol it is 4 nm from the wafer surface.

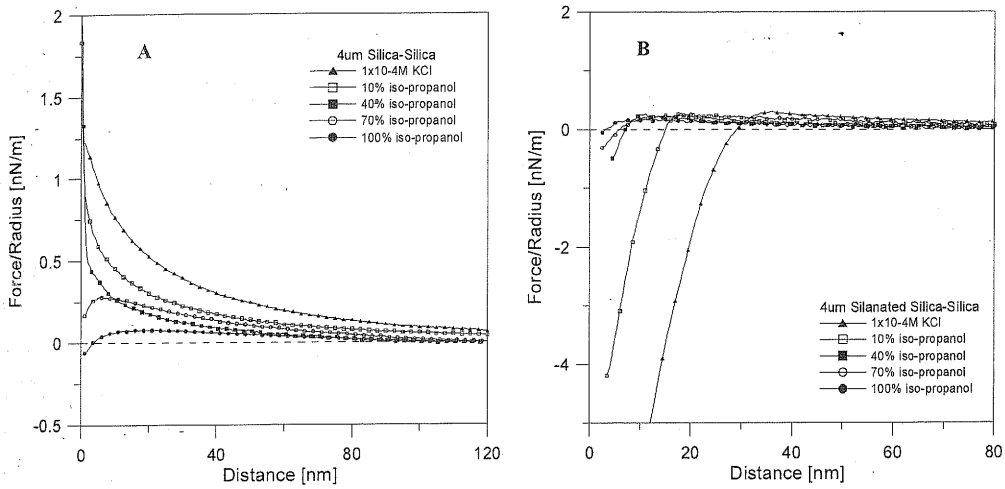

Figure 4. Force-distance curves measured for the hydrophilic (A) and hydrophobic (B) systems for different 2-propanol concentrations (by weight %) with $1x10^{-4}$M KCl. A - Presence of iso-propanol molecules weakens electrical double layer (EDL) and decreases surface charge. As a result diminishes repulsion between the hydrophilic surfaces. B - The strong attractive hydrophobic force is gradually extinguished as more 2-propanol is added into the system. This is due to decrease of interfacial tension of bridging cavity (at low alcohol concentrations) and subsequent lack of bridging cavity formation (at higher alcohol concentrations).

Molecular dynamics simulations

For molecular dynamics simulations atomically smooth quartz was used as a hydrophilic surface and atomically smooth graphite was used as a hydrophobic surface. The liquid environment was modeled to be similar to the experimental setup. The objective of the MD simulation was to look at

behavior of water molecules and isopropanol molecules in the vicinity of the hydrophilic and hydrophobic surface.

At a typical hydrophilic surface, i.e. silica particle, due to the presence of surface hydroxyl group, which is an ideal hydrogen bonding donor, water molecules interact strongly with the surface through hydrogen bonding, and are stabilized at the quartz surface. The interfacial water molecules exhibit specific orientation as a consequence of particle/water interaction. See Figure 5A. The hydrated sides of the quartz crystal are completely surrounded by the water molecules, which suggest complete wetting of the quartz surface. When two silica surfaces approach each other, no water exclusion between the surfaces is observed even when the distance between the particles is less than 10 angstroms. The density of water molecules between the particles is similar to that of in the bulk, suggesting the compatibility between the hydrophilic quartz surface and the water molecules. The simulation results satisfactorily complement the AFM force measurement results, which conclude that when two hydrophilic silica particles approach each other in water, only repulsion is measured (Figure 5A).

On the other hand the presence of isopropanol in a hydrophilic system dilutes electrical double layer (EDL) surrounding the surface and weakens the repulsion as more isopropanol is introduced into the system. In fact isopropanol molecules partially replace some of the water molecules at the silica surface (Figure 5B). The same conclusion can be drawn from AFM measurements, EDL repulsion between the hydrophilic surfaces is decreased as more isopropanol enters the system (Figure 5A).

At a typical hydrophobic surface (such as graphite which is characterized by a contact angle of 88 degrees), due to the absence of hydrogen bonding sites, water molecules are excluded from the surface. When two such surfaces approach each other, at a distance of less than 10 angstroms, water repellency is observed (Figure 6A). No water molecules enter the space between the two hydrophobic surfaces. Moreover, if the water molecules are already present near a hydrophobic surface and another hydrophobic surface approaches from the opposite side the water molecules are removed from between the surfaces.

The exclusion of water molecules between the two graphite surfaces produces significant liquid drainage and further capillary pressure, which is believed to be the origin of the short range hydrophobic attractions that have been observed in AFM force measurements.[21-23] See Figure 6A.

The MDS results suggest that the presence of isopropanol molecules significantly changes the interaction between the hydrophobic surfaces. It appears that the isopropanol molecules are accommodated at the hydrophobic graphite surface to minimize hydrophobic interactions. From Figure 6B it seems that the isopropanol molecules arrange themselves in such a way that the hydrogen atoms are in the nearest vicinity of graphite surface. Consequently, when the two surfaces are close to each other, no hydrophobic attraction is expected due to substitution of the interfacial water with isopropanol, and the structural barrier originates from the isopropanol molecules between the particles, as seen in Figure 6B.

Again, this observation from molecular dynamics is in good agreement with AFM force measurement results, which conclude that the addition of isopropanol eliminates the attraction between hydrophobic surfaces (Figure 6B). On the other hand the presence of isopropanol in a hydrophilic system replace some, but not all interfacial water molecules. Presence of isopropanol molecules dilutes electrical double layer (EDL), surrounding the silica surface and weakens the repulsion as more isopropanol is introduced into the system.

The molecular dynamics simulation (MDS) results are complementary to the AFM colloidal probe force measurement results. The molecular dynamics simulations contribute to the research by revealing the arrangement of water and alcohol molecules at the interface and their influence on the interaction forces between the two surfaces.

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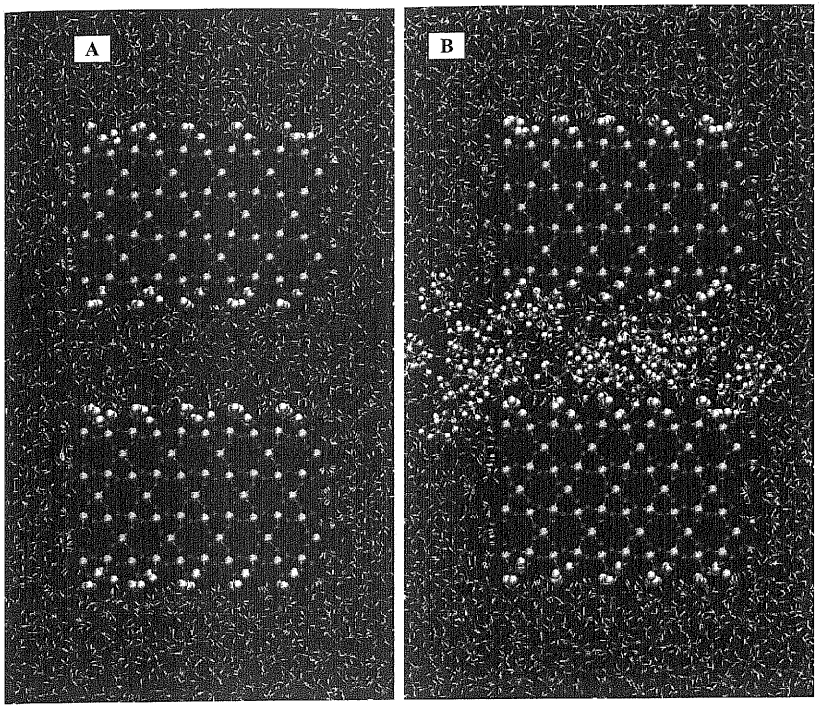

Figure 5 MDS snapshot of two hydrophilic silica surfaces interacting in pure water. The red color corresponds to oxygen atoms (small spheres), white to hydrogen (large spheres at the surface), yellow to silicon (large spheres in the lattice) and blue to carbon atoms (small spheres between the surfaces). The distance between the two surfaces is 10 Angstrom. A - Water molecules are stabilized between the surfaces due to the hydrogen bonding of these water molecules with the surface hydroxyl groups. B - The isopropanol molecules dilute electrical double layer (EDL) surrounding the surface and weakens the repulsion between the two silica surfaces.

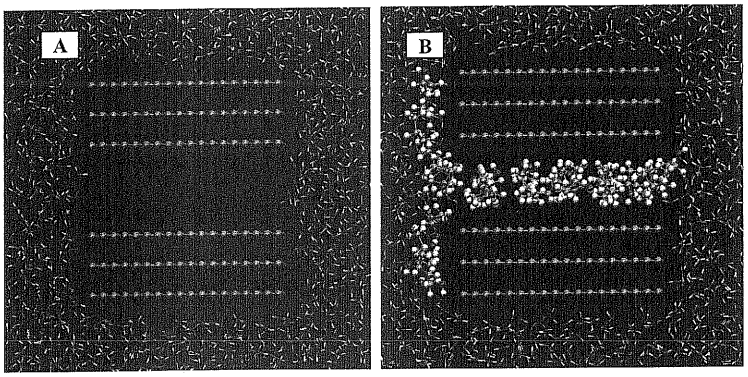

Figure 6 MDS snapshot of two hydrophobic graphite surfaces interacting in water. The red color corresponds to oxygen atoms (small spheres between the surfaces), white to hydrogen (large spheres between the surfaces) and blue to carbon atoms (small spheres in the lattice and between the surfaces). The distance between the two surfaces is 10 Angstroms. A - The exclusion of water molecules from between the two graphite surfaces is shown. B - Isopropanol molecules are accommodated between the surfaces decreasing the hydrophobic attraction.

Summary and conclusions

The lateral force damage to wafer structures was correlated with the lateral force necessary to move contaminant particles from the wafer. The differences in the measured forces were one to two orders of magnitude, depending on the semiconductor structures considered. Knowledge of such forces is essential to design effective cleaning procedures.

The addition of a nonaqueous component diminishes both the repulsive interactions in the case of the hydrophilic silica/silica system and the attractive forces in case of the hydrophobic silanated silica/silanated silica system.

Molecular dynamics simulations helped to explain the arrangement of water and isopropanol molecules between hydrophobic and hydrophilic surfaces. Such arrangement influences the interaction forces between the two solid bodies in semiaqueous mixtures.

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