

Interaction between nanoparticles during chemical mechanical polishing (CMP)

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Nanoparticles have been widely used in polish slurries such as those in the Chemical Mechanical Polishing (CMP) process. For understanding the mechanisms of CMP, an Atomic Force Microscope (AFM) is used to characterize polished surfaces after a set of polishing experiments. To optimize the CMP polishing process, one needs to get information on the interaction between the abrasive slurry particles and the surface being polished. CMP slurry of the solid surfaces is slurry with large particle size colloidal silica nanoabrasive. Silica sol nanoabrasives with large particle are prepared and characterized by Transmission Electron Microscopy (TEM), Particles Colloidal Size (PCS) and Zeta potential in this paper. Results show that the silica sol nanoabrasives about 100 nm are of higher stability (Zeta potential is -65 mV) and narrow distribution of particle size. Then alkali CMP slurries for the solid surfaces containing self-made silica sol nanoabrasives are prepared and applied. The movement of nanoparticles in liquid and the interaction between nanoparticles and solid surfaces are very important to obtain an atomic alloy smooth surface in the CMP process. We investigate the nanoparticle adhesion and removal processes during CMP and post-CMP cleaning. The mechanical interaction between particles and the wafer surface was studied using a microcontact wear model. This model considers the particle effects between the polishing interfaces during load balancing. Experimental results on polishing and cleaning are compared with numerical analysis. This paper suggests that during post-CMP cleaning, a combined effort in chemical and mechanical interaction (tribochemical interactions) would be effective in removal of small particles during cleaning. For large particles, more mechanical forces would be more effective. CMP results show that the removal rate has been improved to 367 nm/min and RMS of roughness has been reduced.

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1. Introduction

Interaction of the nanoparticles with solid surfaces is of great interest for polishing processes used in the modern semiconductor industry.

What will occur when nanoparticles collide on a solid surface is an important problem in the ultra-smooth surface manufacturing industry, e.g. computer hard disk drives and ultra-large scale integration manufacturing. It would also provide valuable insights for a general understanding of collision which is critical to control and prevent solid surface damage generated by nanoparticles collision in nanomodification.

In recent years, there have been a great deal of simulations and tests of collisions between energetic (nanoparticles) clusters and surfaces are performed to explore the interactions between energetic clusters and solid surfaces [1-5].

However, research on nanoparticles collisions on solid surfaces is quite rare.

One major concern in CMP is nanoparticle adhesion on the substrate surface. These nanoparticles can be abrasive nanoparticles from the slurry, debris from the pad material, and nanoparticles of the polished film.

In this paper, we focus on the nanoparticle removal, using tribochemical interactions (a combined effort in chemical and mechanical interaction) during cleaning.

The cleaning method used in this paper is a direct micro contact with the substrate surface through brush sweeping, because this micro contact considers the nanoparticle effects between the polishing interfaces during load balancing.

To enhance the cleaning process, an anionic surfactant containing alcohol ether sulfates (AES) was added in the cleaning solution. This is to weaken the van der Waals (vdW) forces and electrostatic forces that bind the nanoparticles to the substrate surface. In order to show the effectiveness of using AES surfactant, the result is compared with the cleaning solution without surfactant.

When surfactant is mixed with deionized water, the molecules will dissolve and form a layer on the surface.

The bond strength of substrates is weakened and will in turn reduce the surface tension. At this level, the surfactant can form small colloidal sized nanoparticles called micelles, to react with the nanoparticles in the substrate surface by changing the surface charge of the substrates. This will increase the Zeta potential or repulsive charge between the nanoparticles and the substrate.

Also if surface tension is reduced, the van der Waals (vdW) forces present in the system will be weakened, thus increasing nanoparticle removal during brush sweeping.

2. Experiments

Based on the methods of nanoparticle growing by ion-exchange and hydrothermal synthesis, a silica sol nanoabrasive with large nanoparticles was prepared.

First the active silica is synthesized by water glass through ion exchange. The silica sols nanoabrasive with large nanoparticles is the prepared in turn through the process of preparing seeds, growing nanoparticles and maturing and so on.

Results show that the silica sol nanoabrasives have a grain diameter about 100 nm and are of higher stability (Zeta potential is about - 65 mV) and narrow distribution of nanoparticle size.

The colloidal silica nanoabrasives are characterized by Transmission Electron Microscopy (TEM), Laser Particles Size Analyzer (LPSA) and Zeta Potential Analyzer (ZPA). The polishing slurry contained 10 wt% and colloidal silica (about 100 nm).

Alkali slurries containing colloidal silica with large nanoparticles and non-ion oxidants (H_2O_2 was chosen as oxidizer for polishing) have become interesting for industry and academia.

However commercial colloidal silica abrasives are of smaller nanoparticle size, for example 50...70 nm, even 20...30 nm, which results in less removal rate because they can not provide enough mechanical abrasion. In order to resolve the above questions, alkali slurry containing silica with large nanoparticle size are proposed for the solid surface CMP.

CMP is the unique method amongst the global planarization/polishing technologies, which makes CMP be research emphasis among the Integrated Circuit (IC) key process technology, especially for 0.25 μm and IC process [6-8].

The samples used for CMP were silicon wafers with a 0.3 μm layer of saturation formed on the surface. H_2O_2 was chosen as oxidizer for polishing. The pH was adjusted to 9-10 using organic hydramine. The polishing slurries contained 10 wt% colloidal silica (about 100 nm). All the CMP tests were performed with a CP-4 CMP polisher. Four point sheet resistivity measurements were used to measure the thickness of the layer. Atomic Force Microscopy (AFM) was used to characterize the surface morphology of the sample.

3. Results and discussion

The nanoparticle size of silica sols with large nanoparticles is shown in Fig. 1.

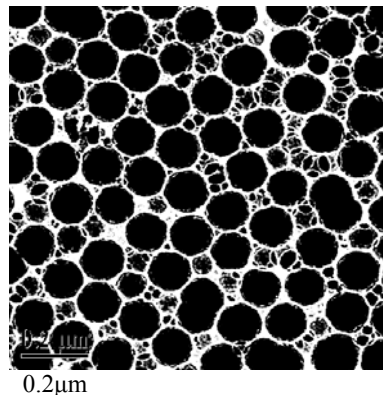


Fig. 1. TEM photograph of silica sols with large nanoparticle size silica.

Results of TEM show that the nanoparticles of the silica sols are spherical and the average nanoparticle size by number is about 100 nm.

The distribution of nanoparticle size for abrasives is one of the important performance indexes. In this paper, the distribution of nanoparticle size for silica sols abrasives is seen in Fig. 2.

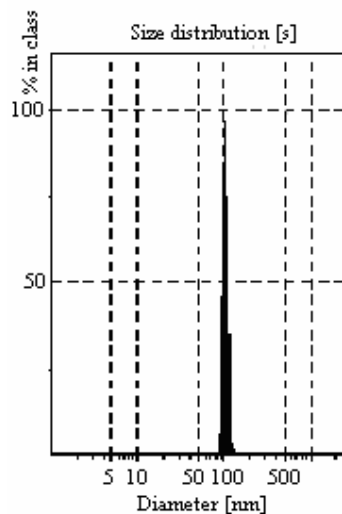


Fig. 2. Size distribution of silica sols with large nanoparticle size silica.

The average nanoparticle size of abrasive by number is about 100 nm, which is in accordance with TEM results. The narrow distribution peak shows the self-made silica sol abrasives are of higher uniformity for nanoparticle size.

The unstable Zeta potential region of colloid abrasives is commonly considered to be from - 30 mV to 30 mV. The Zeta potential of self-made silica sol abrasives are shown in Fig. 3, and the average zeta potential of silica sols is about - 65 mV, which illustrates that the silica abrasive sols are of higher stability. The CMP results show that removal rate has been improved

to 367 nm/min, which has met the industry requirement (more than 300 nm/min) [9].

How, in this paper we focus on the nanoparticle interaction and removal processes during CMP and post-CMP cleaning using tribochemical interactions (a combined effort in chemical and mechanical interaction) would be effective in removal small nanoparticles during cleaning [9]. The cleaning method used in this paper is a direct microcontact with the substrate surface through brush sweeping. An anionic surfactant containing alcohol ether sulfates (AES) was added in the cleaning solution, to enhance the cleaning process.

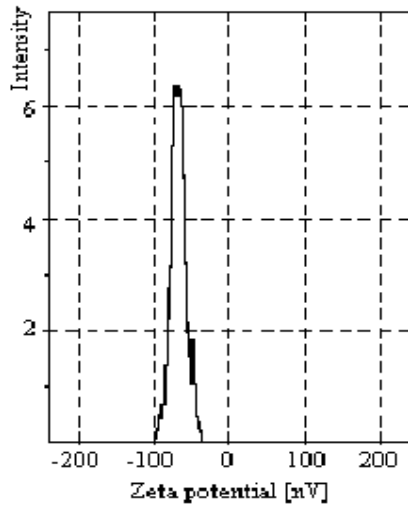


Fig. 3. Zeta potential of silica sols with large particle size.

Fig. 4 show bond breaking of big cluster nanoparticles during post-CMP cleaning with surfactant.

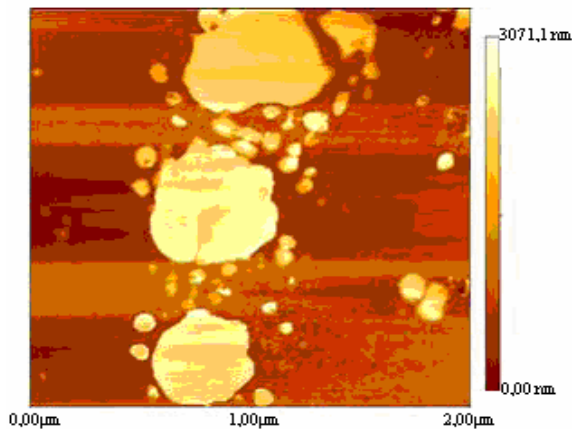


Fig. 4. Bond breaking of nanoparticles during post-CMP cleaning.

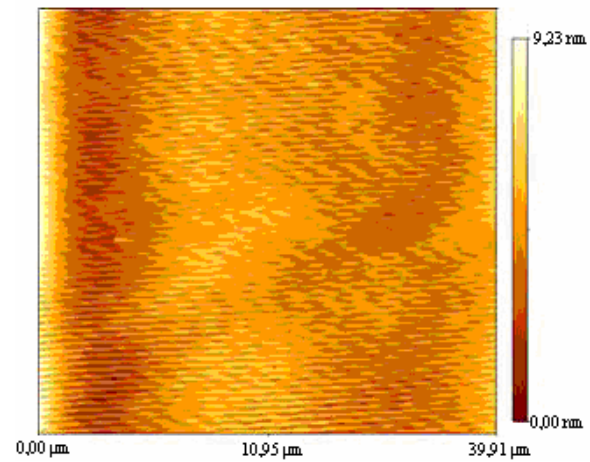
During this process, surfactant forms a layer on the substrate surface thereby reducing the friction on the substrate surface, which results in bond breaking of nanoparticle during nanoparticle removal during brush sweeping. The van der Waals force is weakened due to

lower surface tension thus reducing the average size of the nanoparticle cluster from 1.180 to 1.062 μm .

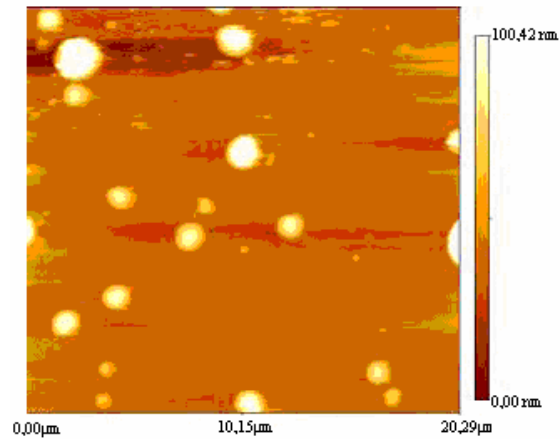
For small nanoparticles, brush sweeping with surfactant proved to be effective as shown in Fig. 5 a, where we observed artefacts, because the apparatus and of the zones with higher asperities than the size nanoparticles.

Note that in this process the hydrodynamic force will not be considered since substrate is immersed in the solution. The reason we neglect the hydrodynamic force is to be able to focus on the contact force first of all. This force has been reported as higher than the hydrodynamic drag force [9, 10].

For post-CMP cleaning the brush and nanoparticle must come into contact for complete nanoparticle removal. In the case of Fig. 5 b, where the sample has previously polished silica sols, large nanoparticles may be observed after the cleaning process.



(a)



(b)

Fig. 5. AFM image of silicon surface after post-CMP cleaning: a) small nanoparticles, brush sweeping with surfactant; b) large nanoparticles may be observed after the cleaning process.

To achieve a better result, it is necessary to increase the cleaning parameters such as concentration of surfactant, cleaning temperature, cleaning time and the mechanical force (brush sweeping) for an effective nanoparticle removal.

Without using surfactant in a cleaning solution, there will be no reduction in bond strength as there are no micelles to react with the cleaning solution.

Using the brush will have no effect in the van der Waals process in this case, since the nanoparticles will not be affected and removed by brush sweeping.

The contact force between the brush and nanoparticle was simulated using a continuum mechanical method. The results are shown in Fig. 6.

The force needed to remove nanoparticles change with nanoparticle size. From the experimental results discussed, can be concluded that using surfactant is possible to reduce the force needed to remove a smaller nanoparticle.

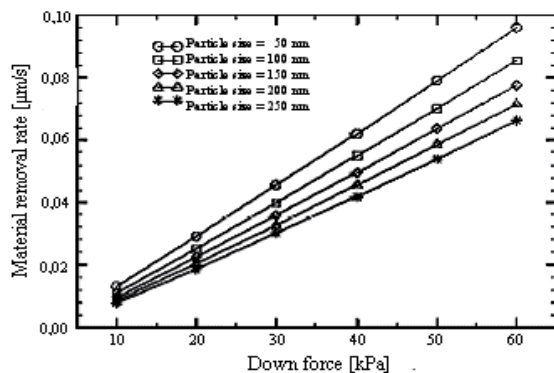


Fig. 6. Variation of material removal rate with down force for different nanoparticle size.

4. Conclusions

The self-made silica sol nanoabrasives sized about 100 nm are of higher stability (Zeta potential : - 65 mV) and narrow distribution of nanoparticle size. CMP results show that the removal rate has been improved to 367 nm/min and RMS of surface roughness has been reduced.

In sum, one kind of alkali slurry containing 100 nm silica sol for the solid surface CMP is studied, which has effectively resolved the lower removal rate and acidic corrosion questions.

Nanoparticles removal mechanisms during post-CMP cleaning were investigated. Results showed that using surfactant can reduce the adhesion between nanoparticles.

Numerical simulation shows that with mechanical sweeping alone, the nanoparticle removal is not as efficient as for chemical-mechanical cleaning.

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