Novel Pure Organic Particles for Copper CMP at Low Down Force

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Abstract

It is generally accepted that there is a minimum hardness requirement for abrasive particles to be used in CMP (Chemical Mechanical Polishing) slurries. For copper CMP, the common abrasives are various types of alumina and silica. It has also long been suspected that a softer organic based abrasive could significant reduce the defects during polishing. In this study, for the first time, we demonstrated the usefulness of an organic particle as abrasive in formulating copper CMP slurry. The unexpected consequence of using such soft hydrophilic particles is its low sensitivity of material removal rate for copper towards polishing down force and platen speed. In addition, due to its unique particle surface properties, the slurry gives high selectivity in removal rate for copper over barrier, cap, and dielectric materials. In this paper, some basic physical and chemical characteristics of the particles and slurry will be first presented. The performance of this new slurry in relation to conventional slurries on blanket and patterned wafers will be discussed.

Introduction

With the integration of copper as interconnect and low k materials as dielectric, the CMP community is facing an ever increasing demand on reducing defectivity without scarifying production throughput. One approach to meet such challenge is to lower the polishing pressure to below 1 psi.[1] Such a move has placed tremendous challenges to the tool manufactures, consumable suppliers (especially the slurry vendors), and end-users. It is generally difficult to remain high throughput (MRR and selectivity) at low down force without using harsh abrasives. It is commonly accepted that a minimum hardness is required for the abrasive particles in order to achieve the desirable performance in removal rate.[2] In addition, the colloidal stability of the particles are also very important in reducing surface defects.[3] For these and other reasons, the commonly used abrasive particles are those inorganic abrasive particles including silica, alumina, ceria, etc. Soft organic particles have not been considered as a key component in slurry formulation except previous work on the use of vesicles and micelles in an abrasive free systems.[4]

It is important to point out that the function of particles in slurry is not limited the enhancement of the abrasiveness of the pad. A more prominent role of the particles, at least in some cases, is related to its ability to interact with key chemical components found in the slurry due to its high surface area. For example, at pH = 5, a simple analysis based on isoelectric points (IEP) for a silica based copper CMP slurry indicates that the negatively charged silica particles and slightly positively charged copper oxide surface to be polished should have fairly strong interactions. In some instances, this interaction may lower the static etch rate for copper film.[5] For passivating agent benzotriazole (BTA), before polishing, the adsorption mainly occurs at the copper oxide surface due to its ability to form strong complex. The surface adsorption to silica is minimal due to the fact that BTA is a neutral molecule and silica is negatively charged. As soon as the polish starts, however, the dissolved copper ions form water soluble complex with BTA which is positively charged. The BTA-copper complex then will have a much greater tendency to adsorb onto silica particles thus reduced the effective concentration of BTA on copper surface, which in turn lowered the passivating efficiency.[6] In addition, the abrasive particles also play an important role to carry the polishing debris away from the space between the pad and the wafer. For example, when a similar chemistry was employed to formulate slurry that contains either silica or hexagonal boron nitride particles, the much softer BN slurry gives greater degree of scratch than its counterpart using silica. The scratch is mainly caused by the polishing debris that were not effectively removed by BN due to its low hydroxyl content on the surface and poor adsorption of polishing debris.[6]

In this study, we designed and prepared pure organic particles for metal CMP. Unlike conventional abrasive particles such silica or alumina, these unique particles are designed to specifically interact with the metal surface to be polished and significantly modify the rheological behavior of the slurry. The obvious advantage of using such particles is the reduction of defects during CMP. The consequence of using such particles is also its ability to provide unsurpassed high selectivity in removal rate for copper over barrier and dielectric materials due to their weak interaction with these particles. The added benefit for slurry that uses such particles is to allow CMP process to be conducted at a lower down force without compromising the throughput.

Experimental

Slurry Preparation

Desired amount of water is added to a Nalgene® beaker and placed on a stir plate. A magnetic stirrer bar is used to mix in the chemicals as well as aid the dispersion of the particles. To the beaker described above, desired amount of passivating (0.1 – 5.0 mM) and complexing (0.1 – 1.0 wt %) agents are added and allowed to completely dissolve. To the resultant mixture the organic particles (AeroCol slurry provided by Dynea) are added in the desired amount (0.1 – 10 wt %). Once the particles are dispersed the oxidizing agent, such as hydrogen peroxide, is added to the system in the desired concentration (0.1 – 8.0 wt %). The slurry is stirred for additional 5 minutes to aid in the dispersion of all components and the pH is adjusted to the desired value using 37% HCl or 10 wt % sodium hydroxide stock solutions. When performing the CMP experiments the slurry was stirred at all time to ensure that there is no settling or aggregation of the particles. The particle size of the slurry was obtained on a high angle dynamic scattering instrument (ALV-HPBS).

Copper Disk Polishing

A copper disk with 1” diameter was attached to a stainless-steel carrier and then mounted on a single side polishing machine (Struers Labopol-5 Grinding Table and Struers LaboForce Arm, Westlake, Ohio). A polyurethane IC1400 polishing pad was used for the study. A typical polishing lasts 2 minutes under a pressure of 6 psi by supplying the slurry at 120 mL/minute between the Cu disk and the pad. The Cu disk and the pad have a relative rotating speed of 150 rpm. After polishing the disk is cleaned with a DI water rinse followed by an isopropyl alcohol rinse. This disk is dried with a steady stream of house air and the material removal rate was calculated based on net weight loss and polished surface area.

Static Etch Measurements

After the slurry is prepared based on the method described above approximately 120ml is place in a 150 ml Pyrex beaker. Using Teflon coated tongs the pre-weighed copper disk is placed in the solution. The sample is stirred in the vessel at 100 rpm for 2 minutes at the desired temperature (25 or 42 C). The disk is then cleaned with DI water followed by an isopropyl alcohol rinse and dried with a steady stream of house air. The static etch rate was calculated based on net weight loss and the surface area of the disk.

Polishing Blanket and Patterned Wafers

Blanket copper, Ta and oxide wafers obtained from International SeMaTech (Austin, TX) were polished using a IPEC Westech 372M polisher. A design of experiment (DOE) was performed to determine a set of optimum polishing conditions such as down force (1-6 Psi), back pressure (0-2.5 psi), slurry flow rate (100-200 ml/min), platen and carrier speeds (15-90 rpm). After polishing, the removal rate profile was determined using a sheet resistant four-point probe. For patterned wafer evaluation, SeMaTech 854 patterned wafers based an MIT testing mask were used. The step-height reduction, dishing, and erosion results were obtained using an Ambios XP2 profilometer.

Results and Discussion

Among all organic particles available as aqueous dispersions, we designed and selected the particles that meet the following criteria. The particles are hydrophilic in nature and easily dispersed in an aqueous environment. The particles are rich in amino functional groups on the surface and chemically stable in the presence of common oxidizers such as hydrogen peroxide. In addition, the particles must be relatively easy to manufacture. As shown in Figure 1, the particles as received are smaller than 300 nm and have relatively narrow particle size distribution.

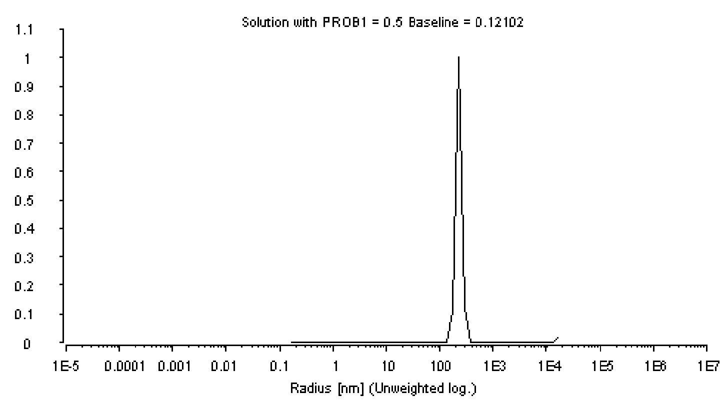

Figure 1. Particle sizing data obtained on a high angle dynamic light scattering instrument (ALV HPBS) for slurry sample prepared using pure organic particles ready for CMP.

As shown in Figure 2, the native particles have an isoelectric point (IEP) at about 8 due to the presence of amino functional groups. The particles are stabilized with an anionic surfactants and show strong negative zeta potential at a wide pH range. A benefit of having high zeta potential across a wide pH range may translate to a wider window for formulation and less sensitive to pH variation.

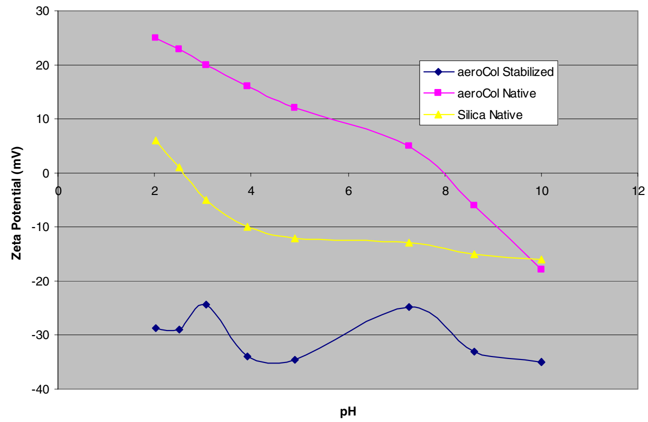

Figure 2. Zeta potential measurement for the slurries in which solid squares illustrate the native Aerocol organic abrasive particles, upper triangles depict typical silica particles as a reference, and the diamonds show the zeta potentials for those Aerocol particles stabilized by a negatively charged surfactant.

The organic abrasive particles are formulated into a copper CMP slurry that contains hydrogen peroxide as an oxidizer, a passivating agent, and a complexant. The material removal rate (MRR) and static etch rate (SER) are directly proportional to the amount of hydrogen peroxide as shown in Figure 3. This is consistent with the fact that, in this formula, hydrogen peroxide plays a stronger role in etching than passivating .

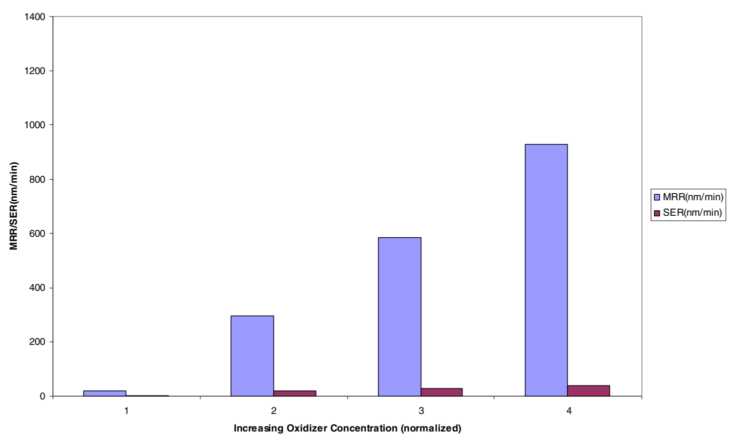

Figure 3. Material removal rate (MRR) and static etch rate (SER) for the slurry that contains Aerocol organic abrasive particles, an oxidizer, a passivating agent, and a complexing agent.

When the concentration of the complexing agent is reduced, both MRR and SER are lowered as shown in Figure 4. This is quite similar to a slurry with the same chemistry and other conventional abrasive particles.

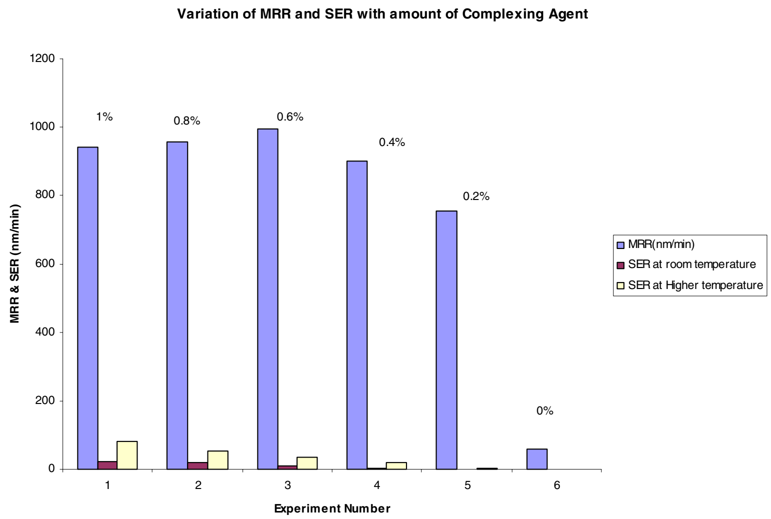

Figure 4. The MRR and SER of a slurry that contains hydrogen peroxide as oxidizer, a complexing agent, and a passivating agent.

For wafer polishing, the slurry that is formulated with the organic abrasive particles does behave differently in comparison with other abrasive particles. As shown in Figure 2, the organic particle based slurry gives high MRR at all down forces. In comparison, a silica-based slurry with similar chemistry gives significantly lower removal rate at lower down force. Furthermore, the organic particle based slurry gives adequate removal rate (> 4000A/min) at much lower platen speed (< 30 rpm). This property is unexpected if one considers the softness of organic particle. It is important to point out that the comparison data shown in Figures 5 were obtained with the same abrasive content for organic and silica particles. The low sensitivity towards down force and platen speed is a direct result of the unique design and nature of the organic abrasive particles. It is the functionality built into the abrasives that dominates the interaction between the particles and the surface to be polished and enhances the removal rate under low down force.

Using the optimized slurry formulation described above a blanket wafer evaluation was conducted to determine the blanket film removal, WIWNU, surface quality, and selectivity. As shown in Table 1, polished at 2 psi and 75 rpm platen speed, the removal rate for copper is significantly higher than that for barrier, cap, and dielectric materials. Therefore, the slurry has an excellent capability to stop at the desired layer. In addition, the surface quality of the polished copper wafer is excellent (Figure 6). It shows no corrosion and macro-scratches. Due to the fact that the organic particles are designed to specifically interact with copper surface, the copper slurry has very high removal rate selectivity over other films such as oxide, low k caps, and barrier metals. As shown in Figure 6a, when a copper wafer with Ta as a barrier layer is over polished with a silica based copper slurry, the barrier layer is often broken through at the edges due to wafer non-uniformity and poor copper to barrier selectivity. When the same wafer was polished and over polished with a slurry using organic abrasives, the barrier layer stays in tact without any sign of broken through.

Table 1. Material removal rate for various film materials using organic abrasive slurry.

Film Materials	Cu	PETEOS	SiCN	Ta
MRR (A/min)	8000	<50	<25	<25

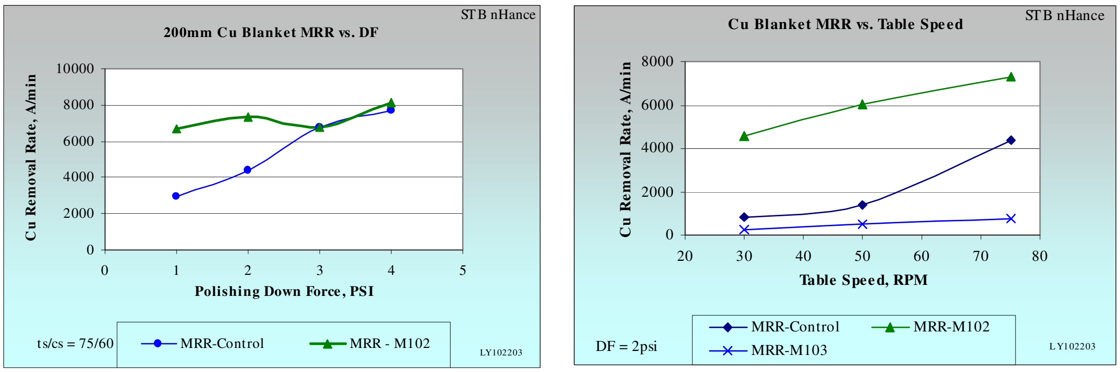

Figure 5. Material removal rate of copper films at various down forces (left) and platen speed (right). M102 is organic based slurry. Control slurry is silica based slurry with similar chemistry.

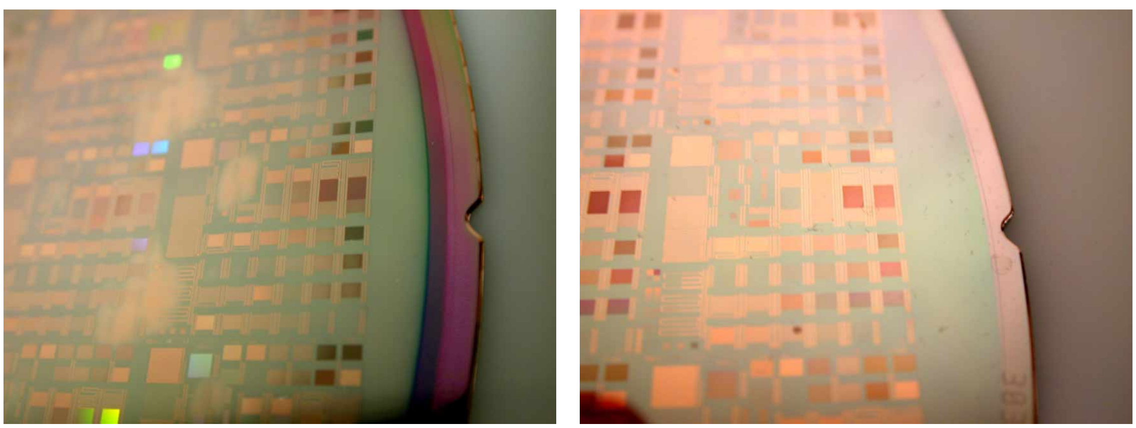

Figure 6. Photogragh of a wafer edge polished using a silica based slurry (left) and organic abrasive slurry (right). The purple color shown in the left photograph indicates a break through of the barrier layer exposing the oxide under layer.

On one most critical evaluation of a potential copper CMP slurry is its ability to achieve high step height reduction efficiency and low dishing values on larger copper lines (>50 um). As shown in Figure 7, the efficiency for a polish conducted on a standard SEMATECH 854 patterned testing wafer is nearly 100%. The dishing value at clear of over burden copper (80 seconds) is ca. 200 Å. A long over polishing window is also observed. For organic abrasive slurry, an increase of 300A dishing is observed for a 45 second over polish. In comparison, a silica based slurry yielded 800A dishing for the same length of over polish.

Conclusions

Copper CMP slurry based on pure organic abrasive particles has been developed. The novel slurry gives excellent material removal rate for copper and high copper to barrier selectivity. In addition, the unique chemical functional groups on these particles interact specifically with the copper surface and allow copper CMP to be conducted at a much lower down force and table speed without sacrificing the throughput. The soft nature of the particles may also reduce pad wear and extend its lifetime.

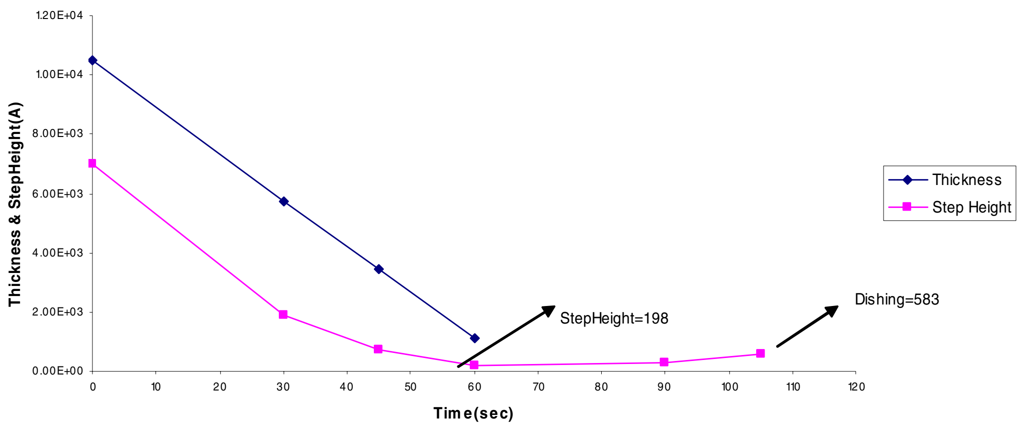

Figure 7. SEMATECH 854 patterned wafer polished with an organic based slurry on 372M. The overall average over-burden copper thickness and step height at 100um copper in the 50% metal density region are shown.

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