Chemical Mechanical Polishing of Oxide Layers using Novel Ceria-Polymer Microcomposites

Cecil A. Coutinho[a], Subrahmanya R. Mudhivarthi[b,c], Ashok Kumar[b,c], and Vinay K. Gupta[a*]

[a]*Department of Chemical and Biomedical Engineering*
[b]*Nanomaterials and Nanomanufacturing Research Center*
[c]*Department of Mechanical Engineering*
University of South Florida, Tampa, FL – 33620

ABSTRACT

To meet the stringent requirements of device integration and manufacture, surface defects and mechanical stresses that arise during chemical mechanic planarization (CMP) must be reduced. Towards this end, we have synthesized multiple hybrid and composite particles on micron length scales consisting of siloxane co-polymers functionalized with inorganic nanoparticles. These particles can be easily tailored during synthesis, leading to softer or harder abrasion when desired. Upon using these particles for the planarization of silicon oxide wafers, we obtain smooth surfaces with reduced scratches and minimal particle deposition, which is an improvement from conventional abrasive materials like pure silica, ceria and alumina nanoparticle slurries. Tribological characteristics during polishing were examined using a bench top CMP tester to evaluate the in situ co-efficient of friction. Characterization of the hybrid and composite particles has been done using infrared spectroscopy, dynamic light scattering, and electron microscopy. Surface roughness of the wafers was examined using atomic force and optical microscopy while removal rate measurements were conducted using ellipsometry at multiple angles.

INTRODUCTION

Chemical mechanical polishing (CMP) is quickly becoming one of the most critical processing steps due to the reduction in feature sizes and increasing layers of metallization[1, 2]. With the advance of the semiconductor industry into the 45 nm technology node, achieving planar wafers with fewer defects after CMP is essential. Besides global planarization and high polish rate, the CMP process needs to also achieve high material selectivity and a superior surface finish. The advantages of using CMP as a global planarization technique can be nullified due to contamination from slurry chemicals, scratches, pattern related defects (dishing/erosion), delamination and dielectric crushing due to mechanical damage[3, 4]. Thus, making improvements in the CMP process to reduce the surface defects is an important engineering challenge.

Towards this end, we developed novel inorganic-organic composite microparticles that can be used in slurries and lead to improved surface characteristics after CMP. This was done by using microspherical hybrid polymeric networks, consisting of poly(N-Isopropylacrylamide) (PNIPAM) microgels with siloxane functional groups. Within these hybrid microgels are embedded nanoparticles of ceria. The presence of ceria nanoparticles has proven to be highly beneficial for oxide CMP, both in terms of removal rate and selectivity for silicon oxide[5, 6]. Incorporating the ceria nanoparticles within a polymer network reduces the friction at the polishing interface between the abrasive microparticles and the wafer surface, resulting in much fewer scratches and negligible particle embedment on the polished wafer. The combination of inorganic (e.g., siloxane and ceria) components with polymer latex particles represents a

* Author to who correspondence should be addressed: vkgupta@eng.usf.edu

promising alternative for the synthesis of abrasive particles necessary for highly planar wafer surfaces.

EXPERIMENTAL SECTION

Experimental conditions for slurry testing:

The composite microparticles were used to polish thermally grown oxide wafers, using a CETR CP-4 CMP bench top tester. The testing of the slurry was carried out at a 7 psi downward pressure with a 200 rpm rotation of the IC1000K groove polishing pad and a slider velocity and stroke of 3mm/s and 7mm respectively. The polishing pad was conditioned using a commercially available 3M diamond disk conditioner with a 400 grit size. The slurry flowrate was maintained at 75ml/min using a standard analog peristaltic pump.

Characterization:

The synthesis of polymer-siloxane-ceria (PSC) microcomposite particles was described elsewhere[7, 8]. The particle were examined using TEM to visually determine the extent of CeO_2 loading and dispersion within the polymer matrix. A drop of the sample solution was placed on a Formvar-coated Cu TEM grid that was examined using a FEI Morgagni 268D. The inorganic-organic composition of the composite microparticles was determined using a TA SDT Q600 thermal gravimetric analyzer (TGA). Samples were heated in air heated at a rate of 2°C/min from room temperature to 500°C.

RESULTS AND DISCUSSION

To create a robust particle, hybrid polymer-siloxane microparticles were first synthesized that contained ~10wt% silica (by TGA). As detailed in a prior publication[9], although the surfaces polished with these hybrid particles were smooth with no visible particle contamination or scratches, the oxide removal rate was low (~10-15nm/min) and needed improvement. Toward this end, we focused on the incorporation of ceria nanoparticles within the microgels. While nanoparticles of ceria are well known for their selectivity and removal of oxide from a wafer surface, they can also produce major and minor scratches that hamper further metallization[10, 11]. Therefore, microcomposites of ceria nanoparticles and microgels are attractive route towards significant improvements in the surface finish while achieving practical rates for oxide removal.

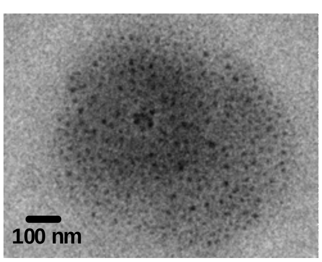

Figure 1: TEM of microcomposite

To promote incorporation of ceria nanoparticles in the microgels, we used a strategy that was successfully used in the past to form microcomposites of titania nanoparticles and PNIPAM based microgels[12]. Interpenetrating chains (IP) of poly(acrylic acid) within the hybrid microgel lead to significant fractions of carboxylic acid moieties in the microgel without altering the temperature responsive behavior and also facilitate the incorporation of ceria nanoparticles within the microgels[12]. By simply controlling the mixing ratios of the IP-hybrid microgel and ceria solutions, the mass fraction of ceria within the polymer-ceria composite particles can be easily tailored. Here the composite particles that were prepared contained approximately 50wt% ceria, which was confirmed using TGA.

The TEM image of the PNIPAM-ceria microcomposite particles (Figure 1) shows dark spots corresponding to the ceria nanoparticles (~20nm). It is evident that the PSC microcomposite particle is heavily loaded with ceria that is well dispersed and largely unaggregated within the microgels. Also, high mass loading of ceria into the IP-hybrid microgel composite, prevents free-floating ceria in the surrounding solution as shown in the above TEM image. These microcomposites were used for the planarization of 2” thermal oxide wafer. Polishing using a suspension containing 0.5wt% of the composite was compared to polishing by suspensions that contained 0.5wt% of only ceria nanoparticles. Polishing with only ceria resulted in major scratches on the wafer surface. In contrast, polishing with the composites showed no scratches and removal rates (~100nm/min) were comparable to the rates obtained with slurries containing only ceria. The lack of scratches and particle deposition on the silicon oxide wafer surface can be attributed to the cushioning effect of the polymer surrounding the inorganic oxides. The polymeric network, plausibly, helps to reduce the friction at the wafer-slurry interface and thereby, reduces surface scratches. The presence of the polymer chains can also reduce particle agglomeration that adversely affects CMP performance. Lower surface defects during polishing are useful in eliminating rigorous post CMP cleaning stages and in enabling environmentally benign CMP processes[13-15].

Quantitative thickness measurements of the oxide film on the wafer were performed using ellipsometry at multiple angles (Table 1). The PSC microcomposite particles yielded removal rates of approximately 100nm/min that was nearly 10 times higher that past studies where only hybrid microgels with no ceria were used[9]. This increase in removal rate makes it feasible to use the microcomposite particles for polishing in the final stages of CMP process where only moderate amounts of material needs to be removed but superior surface quality is required.

Table 1

Slurry	COF	Removal Rate(nm/min)
0.5wt% Ceria-Polymer Composites	0.155	98
0.5wt% CeO_2	0.215	236
0.25wt% CeO_2	0.108	111

Table 1 also lists the coefficient of friction (COF) data measured during polishing. The COF was obtained from the ratio of lateral and normal forces measured in-situ using a dual force sensor installed to the upper carriage of the machine carrying the wafer carrier. The average coefficient of friction after the process had reached the steady state was been used. The average values of COF in Table 1 reveal that the slurry containing 0.25wt% ceria particles resulted in lower coefficient of friction as compared to the slurry containing 0.5wt% of ceria particles, which is presumably due to lower particle concentration. Interestingly, the composite particles lead to reduced friction at the polishing interface even though a 0.5wt% slurry of these particles should contain a higher particle concentration given the lower mass density of the organic polymer. Thus, the lower COF supports the expectation that the composite particles should have a milder abrasive interaction with the surface.

The results presented above clearly indicate that the composite particles with controlled softness/hardness can be beneficial and can be successfully implemented for polishing in the final stage of CMP process where only moderate amounts of material needs to be removed but superior surface quality is required. Fewer surface defects and particle residue[7] will aid in the elimination of rigorous post CMP cleaning stages and consequently, will help in achieving environmentally benign CMP process.

CONCLUSIONS

Composites consisting of a polymer modified with inorganic components and nanoparticles of ceria were successfully synthesized and used for low defect oxide CMP slurry applications. These particles produced a superior surface quality after polishing with very few surface scratches and no particle residue on the oxide wafer surface thereby making these particles potential candidates for next generation stringent polishing requirements.

ACKNOWLEDGEMENT

Financial support in the form of a graduate teaching assistantship from a NSF grant on Curriculum Reform (EEC-0530444) to CAC is gratefully acknowledged. The authors would also like to thank Jonathon Mbah for help with TGA analysis. Support from the University of South Florida is also acknowledged.

REFERENCES

1. Oliver, M. R., *Chemical Mechanical Planarization of Semiconductor Materials*. 2004.
2. Steigerwald, J. M.; Murarka, S. P.; Gutmann, R. J., *Chemical Mechanical Planarization of Microelectronic Materials*. 1996.
3. Teo, T. Y.; Goh, W. L.; Lim, V. S. K.; Leong, L. S.; Tse, T. Y.; Chan, L., Characterization of scratches generated by a multiplaten copper chemical-mechanical polishing process. *Journal of Vacuum Science & Technology* 2004, 22, (1), 65-69.
4. Zhang, L.; Raghavan, S.; Weling, M., Minimization of chemical-mechanical planarization (CMP) defects and post-CMP cleaning. *Journal of Vacuum Science & Technology* 1999, 17, (5), 2248-2255.
5. Evans, D. R., Cerium oxide abrasives - observations and analysis. *Materials Research Society Symposium Proceedings* 2004, 816, 245-256.
6. Koyama, N.; Ashisawa, T.; Yoshida, M. Cerium oxide CMP (chemical mechanical polishing) agents and method for polishing of substrates. JP Patent 2000109814, 2000.
7. Coutinho, C. A.; Subrahmanya, M. R.; Kumar, A.; Gupta, V. K., Novel Ceria-Polymer Microcomposites for Chemical Mechanical Polishing. *Applied Surface Science* 2008, doi:10.1016/j.apsusc.2008.08.093.
8. Gupta, V. K.; Kumar, A.; Coutinho Cecil, A.; Subrahmanya, R. M. Novel Ceria-Polymer Microcomposites for Chemical Mechanical Polishing. WO 2008052216, 2007.
9. Subrahmanya, R. M.; Cecil, C.; Ashok, K.; Vinay, G., Novel Hybrid Abrasive Particles for Oxide CMP Applications. *ECS Transactions* 2007, 3, (41), 9-19.
10. Lee, J. W.; Yoon, B. U.; Hah, S.; Moon, J. T., A planarization model in chemical mechanical polishing of silicon oxide using high selective CeO2 slurry. *Materials Research Society Symposium Proceedings* 2001, 671, (Chemical-Mechanical Polishing 2001--Advances and Future Challenges), M5 3/1-M5 3/5.
11. Tateyama, Y.; Hirano, T.; Ono, T.; Miyashita, N.; Yoda, T., Study on ceria-based slurry for STI planarization. *Proceedings - Electrochemical Society* 2001, 26, 297-305.

12. Coutinho, C. A.; Gupta, V. K., Formation and properties of composites based on microgels of a responsive polymer and TiO2 nanoparticles. *Journal of colloid and interface science* 2007, 315, (1), 116-22.
13. Chen, J. J. Method of fabricating a shallow trench isolation. TW Patent: 9988115709, 2001.
14. Chiou, H.-W.; Chen, L.-J., One-step effective planarization of shallow trench isolation. *IEEE International Interconnect Technology Conference Proceedings* 1998, 199-201.
15. Jang, S.-m.; Chen, Y.-h.; Yu, C.-h. Formation and planarization of shallow trench isolation in an integrated circuit. US Patent: 97810390, 1997.