

Composite Nanoparticles for Defectivity Reduction during CMP

Silvia Armini ^{*†‡}, Valentina Terzieva [†], and Karen Maex ^{†‡}

[†] IMEC, Kapeldreef 75, B-3001 Leuven, Belgium.

[‡] Department of Electrical Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 1, B-3001 Heverlee, Belgium.

^{*} corresponding author: Silvia Armini, IMEC, SPDT/ADRT Division, Kapeldreef 75, B-3001 Leuven, Belgium. Tel. + 32 (0) 16 28 86 17. Fax. : +32 (0) 16 28 13 15. E-mail: silvia.armini@imec.be

Abstract

The synthesis and characterization of nanoparticles comprising a polymer core and a silica shell, with and without a silane-coupling agent between the core and the shell, is presented in this paper.

The first step in the nanoparticle synthesis is a “surfactant free” radical suspension polymerization in water of monomeric units of methylmethacrylate in the presence of methoxypolyethylene glycol methacrylate, as a co-monomer, and 4-vinylpyridine. Vinylpyridine provides electrostatic stabilization in the form of functional basic amino groups located at the polymer surface, as confirmed by FTIR analysis. In the second step of the procedure, the Polymethyl Methacrylate (PMMA) spheres were mixed with silica spheres.

Dynamic Light Scattering (DLS) measurements were used to correlate particle size to pH or ionic strength, while Electrophoretic Light Scattering (ELS) measurements revealed the dependency of the zeta potential on pH or ionic strength (I). Since the interaction between the abrasives and the wafer surface in the CMP process is expected to be dependent also on the particle morphology and structure of the polymer core, N₂ adsorption isotherms on PMMA were taken to evaluate porosity and total surface area using the Brunauer-Emmett-Teller (BET) method.

Introduction

Chemical Mechanical Planarization (CMP) combines chemical and mechanical interactions to planarize metal and dielectric surfaces using a polishing solution (slurry) composed of chemicals and sub-micron-sized particles. It removes material by rotating a metal or dielectric-coated wafer and pressing its active surface against a rotating polymer-based pad filled with the slurry [Steigerwald *et al.*, 1997]. CMP is a complex process dependent on numerous parameters. The two principal factors in the process are slurry and pad. Slurry chemical composition includes concentration of oxidizers, surfactants, corrosion inhibitors, and buffers, while slurry

mechanical properties are dependent on abrasive type, concentration, charge, and size [Moinpour *et al.*, 2002].

According to micro-electronic fabrication standards, the critical issue in CMP is process-induced defectivity on the polished wafer surface, comprising micro defects, such as residual slurry, particles, pits and micro-scratches [Chen *et al.*, 2001]. Microscratch generation mechanisms are not yet understood, but the presence of hard inorganic abrasive particles (silica, alumina,...) in the slurry seems to be one of the main reasons for defects observed after CMP [Doyen *et al.*, 2002]. CMP-related defects can lead to fatal long-term reliability failures in microelectronic devices [Varadarajan *et al.*, 2002]. Therefore, defectivity observed after CMP, especially in Cu Damascene technology, can be considered a bottleneck in IC Manufacturing [Gotkis *et al.*, 2002].

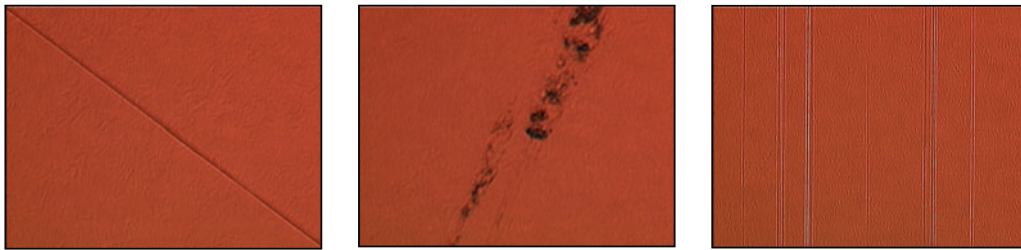


Fig. 1 Confocal Review Station images of scratches on a blanket Cu wafer after CMP (magnification 150 x, scratch depth ~ 50-100 nm, scratch length ~ 1 μ).

The key challenge in microscratching is control of the hardness, concentration, size and size distribution of the abrasive particles in the slurry [Singh *et al.*, 2002]. The importance of hardness can be easily explained considering, in a first approximation, the model for the Hertzian indentation used in hardness testing, showing the penetration depth (δ) that increases together with the size of the abrasive (ϕ):

$$\delta = \frac{3}{4}\phi\left(\frac{P}{2KE}\right)^{\frac{2}{3}},$$

where K is the slurry fill factor and E is the Young's modulus of the material polished [Kaufman *et al.*, 1991]. Also, the presence of large particles in the slurry ($> 1\mu$ [Lee *et al.*, 2002]), even in parts per million concentrations, is extremely harmful to surface quality after CMP [Pohl *et al.*, 1996]. In addition, concerns, regarding time-dependent aggregation of particles, pH drift, and long-term stability of the slurry, should be taken into account. If the slurry is unstable, and, in the case of Cu CMP composition, this instability may be accentuated by the presence of salts that increase the ionic strength,

the particles may settle on the wafer surface thus increasing the density of microscratches [Sing *et al.*, 2002].

In selecting the abrasive for each CMP process, the abrasive particle should ideally be softer than the substrate material [Singh *et al.*, 2002]. The material of choice is not so straightforward in the case of Cu as it is a relatively “soft” material.

Therefore, our study is focused on the synthesis of abrasive composite organic/inorganic materials obtained by coating an individual polymeric core with a (mono)layer shell of inorganic nanoparticles (Fig. 2 a).

According to us, CMP-induced defectivity is affected by the main abrasive-related variables, including particle size, shape, concentration, dispersion, hardness, pH, chemical additives and particle surface functionalization. In order to decrease defectivity, while at the same time maintaining acceptable Removal Rate (RR) and planarization parameters, monodispersed, spherical particles, with decreased size and hardness are targeted.

The novelty of this polishing mechanism is that, assisted by the cushion-like effect coming from deformable abrasives, with a polymeric core acting as a spring when a pressure is applied, the recessed Cu area is protected and polished at a lower removal rate. This should result in a lower defectivity and less damage to the polished surface. An improved polishing mechanism with the newly synthesized slurry is based on the fact that the more elastic and softer composites can adapt their shapes to the pad asperities reducing the stress concentration that facilitate particle penetration [Zhong *et al.*, 1999].

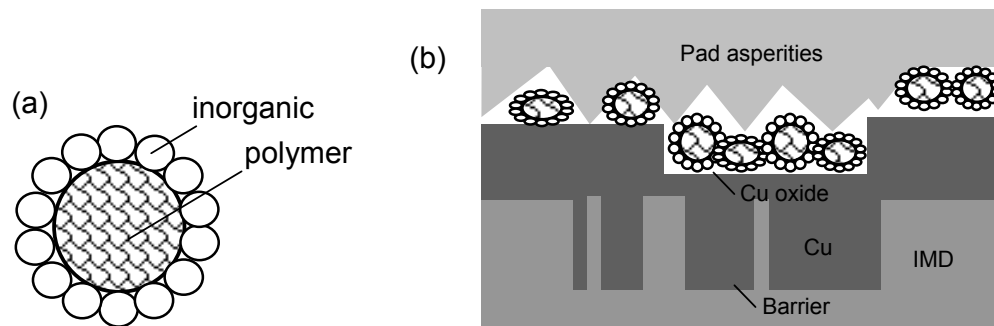


Fig. 2 Schematic diagrams of the composite abrasive (a) and of the polishing mechanism with the newly synthesized slurry (b).

Experimental

Materials

Methyl methacrylate (99% purity, Aldrich), Methoxypolyethylene glycol 5,000 acrylate (Aldrich), 4-Vinylpyridine (95% purity, Aldrich), 2,2'-Azobis(2-methylpropionamide) dihydrochloride (97%, Sigma-Aldrich), (Chloromethyl)trimethylsilane (98% purity, Aldrich), Triethoxy(vinyl)silane (\geq 98% purity, Fluka), Tetraethoxysilane (TEOS) (99+% purity, Alfa Aesar) were used as received without further purification.

The colloidal silica particles used in the synthesis of the composite (30 wt %, mean diameter (80 ± 5) nm) were provided by H.C. Stark.

Preparation of the polymeric core

Poly-methyl-methacrylate (PMMA)-based spheres, used as core particles, were synthesized by a suspension radical free polymerisation, using a slight modification of the procedure described by K. Nishimoto *et al.* [Nishimoto *et al.*, 2000]. 50 ml of Methyl methacrylate, 3 ml of Methoxypolyethylene glycol acrylate, 0,45 g of the azo-type polymerization initiator 2,2'-Azobis(2-methylpropionamide) dihydrochloride (pre-dissolved in 50 ml of water), and 300 ml of ion-exchanged water were charged in a 1 dm³ round-bottomed three-necked flask. In order to prevent aggregation of the core particles 3 ml of 4-Vinylpyridine were added to the system. This solution was heated to 343 K while stirring. To eliminate the effects of oxygen, the solution was purged with nitrogen before the process was initiated and the reaction was carried out under nitrogen gas atmosphere for 6/8 hours, until the conversion exceeded 70%-80%, as determined thermogravimetrically.

Preparation of composite particle A (with a silane coupling agent between PMMA core and silica particle shell).

105 ml of an aqueous dispersion containing 5 wt% of PMMA particles previously synthesized was charged in a 1 dm³ round-bottomed three-necked flask, 1 ml of (Chloromethyl)trimethylsilane was added, and the mixture was stirred at 313 K for 2 hours at low pH. This first step allowed us to obtain an aqueous dispersion of silanized PMMA-based particles that could be added to a colloidal silica particle suspension, to obtain a dispersion of particles in which silica particles had adhered to the polymer ones. To achieve this, 70 ml of an aqueous dispersion containing 5wt % of colloidal silica particles (pH 8) were added over 2 hours to 105 ml of the former solution. 2 ml of Vinyltriethoxysilane was added to this aqueous dispersion, the mixture was stirred for 1 hour, and then 1 part of TEOS was added, heated to 333 K, stirred for 3 hours, and then cooled in a cold water bath. Thus, an aqueous dispersion containing composite particle A was obtained.

Post-synthesis treatment

The dispersions resulting from the previous two syntheses were centrifuged at 5,000 rpm for 45 min, the supernatant solutions discarded, and the particles re-suspended in deionised water using ultrasonic treatment (1 hour). This process was repeated 3 times (PPMA 1 and Composite A).

To compare two different post-synthesis treatments, 10 ml of the polymer colloidal suspension was dialyzed for two days against deionised water. The dialyzate was changed every 12 hours (PMMA 2).

Preparation of composite particle B (with an electrostatic interaction between PMMA core and silica particle shell).

105 ml of an aqueous dispersion containing 5 wt % of PMMA particles (pH 2) were mixed with 70 ml of an aqueous dispersion containing 5 wt % of colloidal silica, to obtain an aqueous dispersion (pH 5), and the mixture was stirred for 2 hours to obtain an aqueous dispersion containing the composite particles B.

Analyses

The particle size and size distribution were measured by Dynamic Light Scattering (DLS) using a Nicomp particle sizer (model 370, PSS, Santa Barbara, CA) at a fixed scattering angle of 90°. To fit the experimental data an Inverse Fourier Transform (Nicomp) algorithm was applied.

The zeta (ζ) potential measurements were performed on a Nicomp 380/ZLS by Electrophoretic Light Scattering (ELS) at 298 K, at a scattering angle of 14.8°, and with λ (HeNe laser) = 632.8 nm. Diluted solutions of colloidal particles as synthesized, at different pH in the range between 2 and 11 (constant ionic strength of 0.001 M), and at different ionic strengths in the range between 0 and 0.001 M (constant pH of 6-7), were measured.

Scanning Electron Microscopy (SEM) (Philips XL-30 FEG) studies on the dried particles were also carried out. For the PMMA latexes it was necessary to use a lower electron beam voltage of 3 eV with a spot size of 2 due to exposure induced sample damage.

The specific surface area and the pore size for the PMMA-based particles were studied using a BET analyser (OmniSorb 360CX, Coulter Electronics Inc., Luton, UK). The adsorbed gas volume was calculated by measuring the pressure change resulting from adsorption of a known volume of gas. The adsorbate used was nitrogen at 77.36 K. The physisorption of nitrogen was measured in a chosen range for the ratio P/P_0 from 0.05 to 0.2 (the pressure range from 0.05 P_0 to 0.03 P_0 is the linear region of the BET data) [Berry et al., 1967].

The freeze-dried PMMA latex (1.0 g) was outgassed at 373 K overnight under vacuum ($1.4 \cdot 10^{-3}$ Pa).

Results and Discussion

Particle characterization

The synthesis of PMMA, after 3 post-synthesis purification cycles, gave an aqueous dispersion containing PMMA-based particles carrying as functional group a cation of an amino group and a polyethylene glycol chain. This was concluded from FTIR analysis (data not shown). Functionalization was also confirmed by ζ potential measurements. In fact, for both PMMA 1 and PMMA 2, the isoelectric point was found to be at around pH 6 (Fig 4). This indicates that the basic amino functionality ($pK_a \sim 6$) is located at the surface of the composite particles. Similar results were reported for 4-Vinylpyridine-silica and for polypyrrole-silica nanocomposites derivatized with surface amino groups [Butterworth *et al.*, 1995, Barthet *et al.*, 1999]. These specific groups are covalently bound or adsorbed on the particle surface and are ionizable. They carry a net positive or negative charge, or are neutral, depending on the pH of the surrounding aqueous solvent. The extent of the surface charge is directly related to the ζ potential value as well as the pK_s of the ionizable groups on the surface. Hence, the pH of the suspension strongly influences the net charge of the colloidal particles and therefore their stability against aggregation [Hunter]. This is confirmed by the fact that the mean diameter for the PMMAs and composite A is dependent on pH and I values and show oscillations. The latter observation requires further investigation.

Understanding and preventing colloid agglomeration is important for our work in CMP defectivity reduction, because the presence of scratches and pitting after CMP can be attributed either to hard foreign matter in the polishing solution or to particle coagulation [Basim *et al.*, 2002]. Measuring the ζ potential is an efficient way to monitor colloid stability. While for silica the isoelectric point (i_{ep}) is around pH 2, for the PMMAs the i_{ep} is around pH 6. The “s-shaped” curve for both the composites indicates a pH-dependent coverage, since it is not completely identical to the curve obtained for the silica particles. Unexpectedly, both composites A and B have shown the same trend (Fig. 3). With increasing I of the solution by adding electrolytes (NaCl or KNO_3), the ζ potential of the colloidal particles tends to zero with a decrease in stability (Fig. 4). This phenomenon was expected and is due to the fact that the addition of electrolytes increases the concentration of ions in the vicinity of charged surfaces causing the potential to decrease more rapidly with the distance. This is explained by the compression of the double layer. In this way, the particles can come closer to each other, with the result that the short-range attractive Van der Waals forces are relevant and the agglomeration energy barrier becomes lower [Hunter].

As expected, the average polymer particle size in aqueous solution measured by DLS is strongly dependent on the pH of the solution. A mean diameter of 584.6 (± 66) nm is observed at pH 11 while pH 2 results in a

mean diameter of $327.2 (\pm 43)$ nm (Fig. 5). The static radius (SEM) is smaller than the hydrodynamic one (DLS) for the PMMA colloids. This phenomenon can be attributed to the swelling of the polymer particles in aqueous solution and to the penetration of solvent molecules into the entangled structure [Chen *et al.*, 1999]. The mean diameter, taken as an average value of 100 measurements determined by SEM, is 370 ± 15 nm and the particles are monodispersed and spherically shaped (Fig. 6 a). The DLS mean diameter of composite A is 766.5 ± 89.5 nm at pH~8 (Fig.5), while the SEM diameter is confirmed to be smaller, with an average of 550 ± 30 nm (Fig.6 b). The average particle size of composite B (DLS) is 912.2 ± 80.0 nm (Fig. 5), while the SEM diameter is 550 ± 30 nm (Fig. 6 c). For both composites the coverage is promising, as evident from Fig. 6.

The SEM inspection allowed us to investigate shape and monodispersity of the particles and the coverage of the composites. The shape of the dry PMMA is spherical and the size distribution is monodisperse. The difference between 100 measurements of the particle diameter in the x direction vs the y direction is $\pm 0,4\%$. For both composite A and B (with an optimised mixing ratio silica/PMMA 1/1.5), the coverage is optimal (Fig. 6 b and Fig. 6 c).

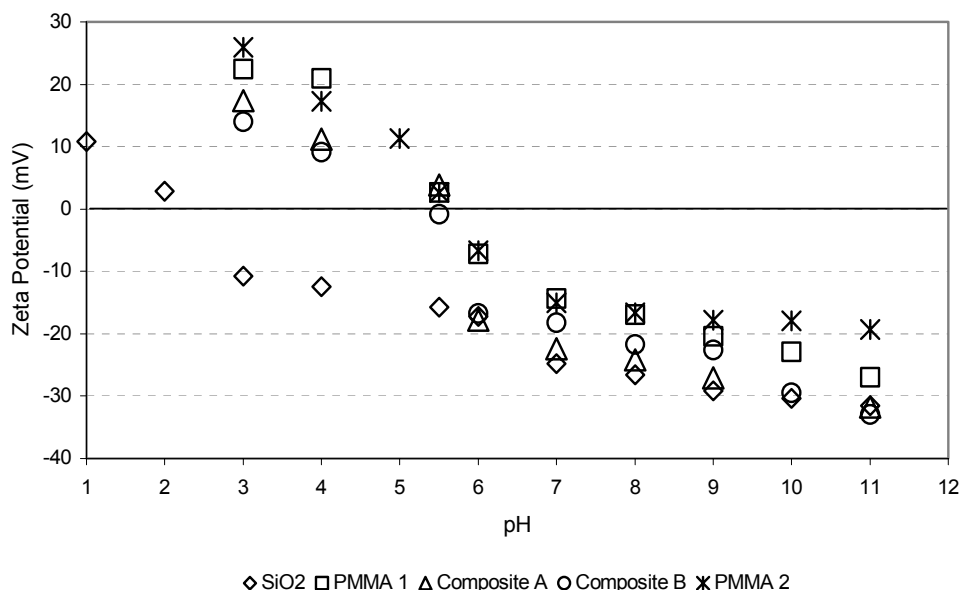


Fig 3. Zeta potential vs. pH (constant $I = 10^{-3}M$) for SiO₂, PMMA, Composite A, and Composite B.

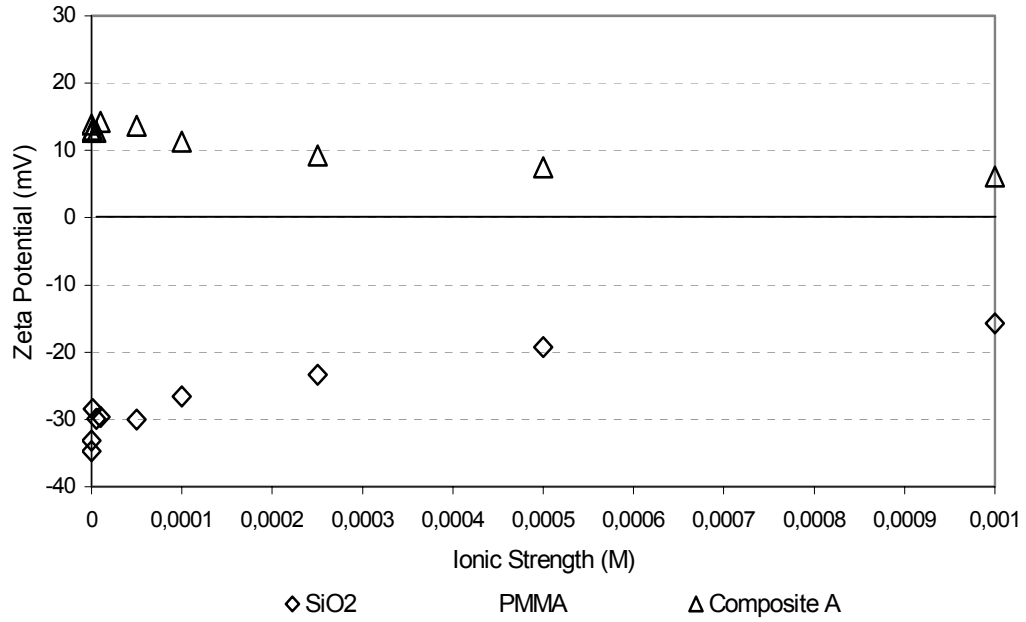


Fig 4. Zeta potential vs. ionic strength (I) (constant pH of 6) for SiO₂, PMMA, and Composite A.

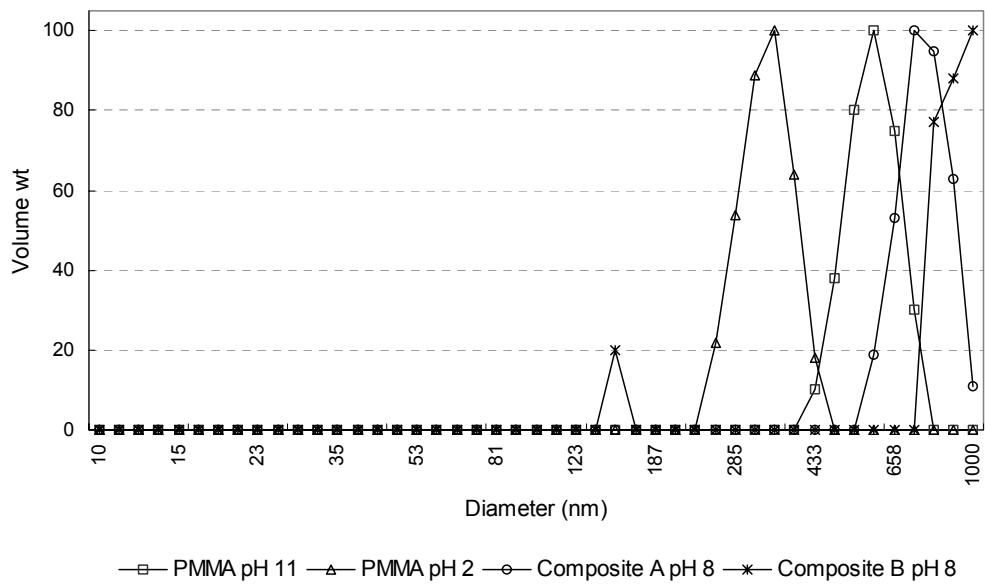


Fig 5. Particle DLS Nicomp size distributions (volume weight) at different pH values for PMMA, Composite A, and Composite B.

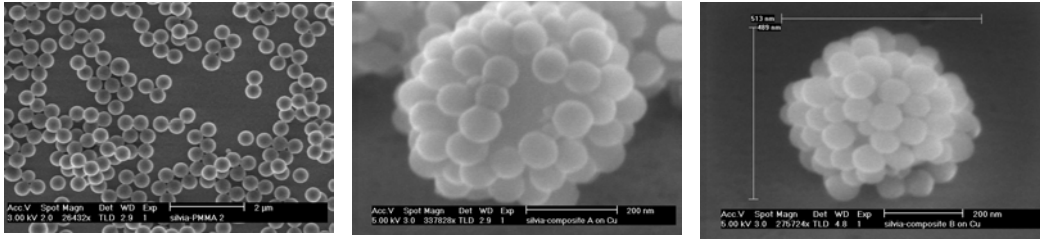
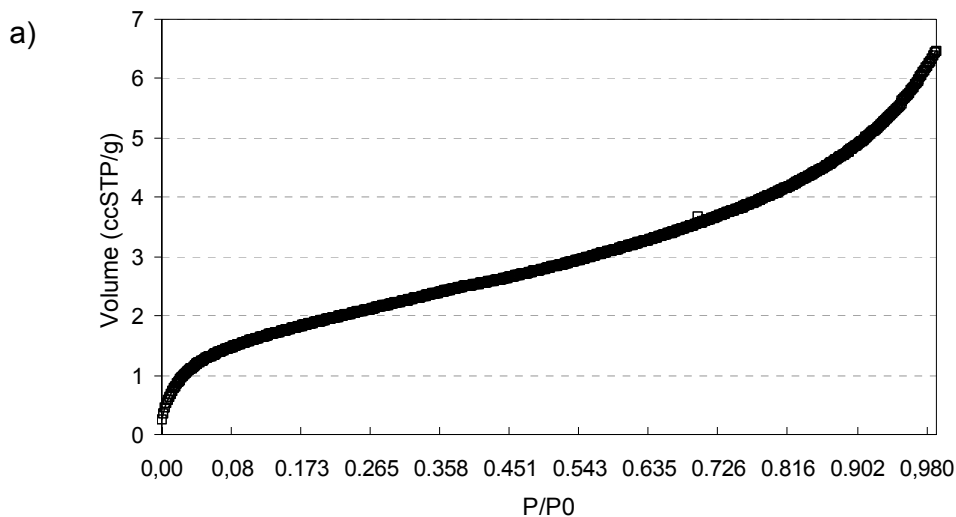


Fig 6. SEM images of (a) PMMA, (b) composite A, (c) composite B particles.

The effect of abrasive particle hardness on the polish process is significant [Li *et al.*, 2000]. The bulk density of the particle can be varied by altering the porosity and morphology of the material [Babu *et al.*, 1998]. In particular, the interaction between the composite abrasive and the wafer surface in the CMP process is expected to depend also on the morphology and structure of the polymer core. N_2 adsorption isotherms on PMMA were obtained, in order to evaluate porosity, and total surface area. For the determination of the surface area, the BET method was used [Brunauer *et al.*, 1938]. According to the International Union of Pure and Applied Chemistry, pores of less than 2 nm in diameter are classified as "micropores", and those with diameters between 2 and 50 nm are termed "mesopores". The Barrett-Joyner-Halenda (BJH) model for mesopore volume was not appropriate. However, Horwath-Kazakoe (HK) calculations were made for the micropore volume and pore size distribution. In the chosen range of the ratio pressure of the adsorbate/vapor pressure of the pure condensed adsorbate (P/P_0) and at a temperature of 77 K, the nitrogen volume adsorbed was 1,658 ml/g. Thus, under the reported experimental conditions, the particles showed a very low surface area in the range $5\div 7 \text{ m}^2/\text{g}$ ($\pm 20\%$) (Fig. 7 a) and the presence of micropores (HK model fitting) of 0,7-0,8 nm in diameter (Fig. 7 b). This could be due to fact that the analysis temperature was quite low so that the PMMA structure has collapsed and is very dense.



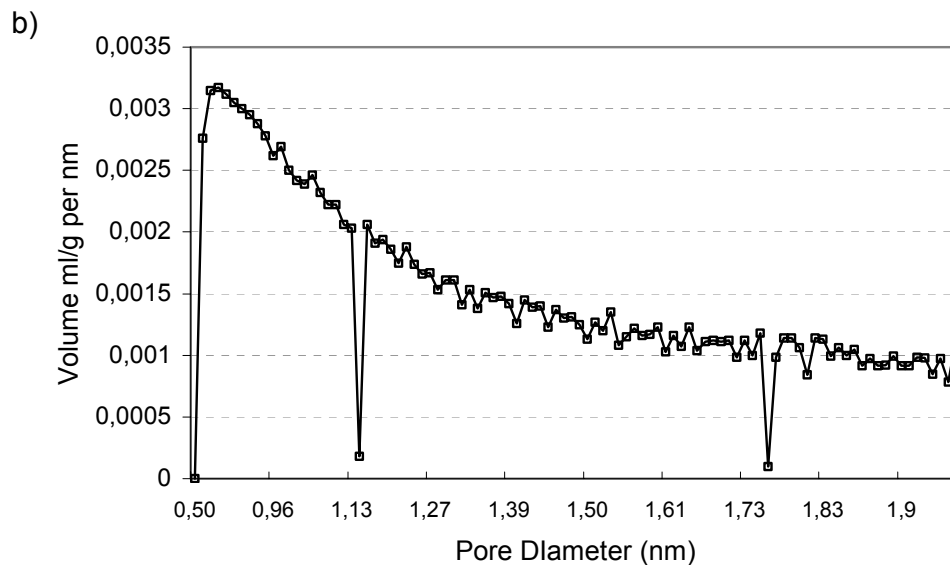


Fig.7. a) Adsorption Isotherm (T=77 K) for PMMA; b) Differential HK porosity model for PMMA.

Conclusions

In the Cu interconnects fabrication process, soft abrasion is the most promising approach to decreasing defectivity during Cu CMP. In order to satisfy this concept, spherical nanometer-sized particles comprising a polymer core and a silica shell, with and without silane coupling agent between the core and the shell, have been synthesized. Under the described experimental conditions, the presence of amino and carboxyl groups on PMMA surface, has been confirmed by FTIR and ζ potential measurements. The static radius, as evaluated by SEM, is smaller than the hydrodynamic one, evaluated by DLS, which depends on the pH value for PMMA and composites. This phenomenon has been attributed to the swelling of the polymer particles in aqueous solution and to the penetration of solvent molecules in the entangled structure. The IEP for the composite particles was found to be at a pH of between 5-6 similar for the one of the pure PMMA particles.

Acknowledgements

The author thanks Caroline Whelan, Mikhail Baklanov, and Geoffrey Pourtois for their valid scientific support and useful comments, Jose' Luis Hernandez for his support and availability, and the Center for Surface Chemistry and Catalysis (COK) of the Katholieke Universiteit of Leuven for the BET nitrogen adsorption measurements.

References

- S. V. Babu, M. Hariharaputhiran, S. Ramarajan, Y. S. Her, and M. M. Mayton, ***"The role of particulate properties in the Chemical-Mechanical Polishing of Copper"***, February 19-20, 1998 CMP-MIC Conference, 1998 IMIC-300P/98/0121
- C. Barthet, A. J. Hickey, D. B. Cairns, and S. P. Armes, ***"Synthesis of Novel Polymer-Silica Colloidal Nanocomposites via Free-Radical Polymerization of Vinyl Monomers"***, Advanced Materials, 1999, 11, N. 5, 408-410.
- G. B. Basim, B. M. Mudgil, ***"Effect of Soft Agglomerates on CMP Slurry Performance"***, Journal of Colloid and Interface Science, Vol. 256, N. 1, 137, December 2002.
- G. C. Berry, T. G. Fox, ***"The Viscosity of Polymers and their Concentrated Solutions"***, Adv. Polym. Sci. 1967, 5, 261.
- S., Brunauer, P. H., Emmet, E., Teller, ***"Adsorption of gases in multimolecular layers"***, J. Am. Chem. Soc. 1938, 60, 309.
- M. B. Butterworth, S. Maeda, J. Johal, R. Corradi, S. F. Lascelles, S. P. Armes, ***"Zeta Potential Measurements on Conducting Polymer-Inorganic Oxide Nanocomposite Particles"***, J. Colloid Interface Sci. 1995, 174, 510.
- H-C. Chen, T-C. Tsai, Y-M. Huang, C-H. Huang, C-H Chen, Y-T. Wei, M-S. Yang, J-Y. Wu, T-R. Yew, and J-K. Chen, ***"Defect Reduction of Copper BEOL for Advanced ULSI Interconnect"***, IEEE 2001.
- W.L. Chen, K.R. Shull, ***"Equilibrium Swelling of Hydrophilic Polyacrylates in Humid Environments"***, Macromolecules, 1999, 32, 136-144
- L. Doyen, D. Vacher, K. Tarutani, P. Bouard, F. Picore and D. Girard, ***"Analyzing Large Particles in CMP Slurries"***, Semiconductor International 8/1/2002.
- Y. Gotkis Lam Research Corporation, CMP/Clean Division, ***"Surface heterogeneity and vulnerability of the copper inter-grain boundary bring up new demands to post-cmp cleaning in Dual Damascene technology"***, Centre for Microcontamination Control, Northeastern University, First International Surface Cleaning Workshop, November 2002.
- R. J. Hunter, ***"Fundation of Colloid Science"***, Vol.1, Clarendon Press Oxford.

F. B. Kaufman, D. B. Thompson, ***“Chemical-Mechanical Polishing for Fabricating Patterned W Metal Features as Chip Interconnects”***, J. Electrochem. Soc., **138** (1991), 3460.

C. Lee, M. Federau, D. Ligocki, T. Myers, S. Lesiak, M. Diaz, M. Maxim, ***“Point-Of-Use Filtration Lifetime for CMP Slurries”***, presented at the February 2000 CMP-MIC Conference in Santa Clara, CA.

Y. Li, S. Ramarajan, M. Hariharaputhiran, Y. S., Her, and S.V. Babu, ***“Planarization of Cu and Ta Using Silica and Alumina Abrasives-A Comparison”***, Mat. Res. Soc. Proc. 2000, 6134, E2.4.1-E2.4.6

M. Moinpour, A. Tregub, A. Oehler, and K. Cadien, ***“Advances in Characterization of CMP Consumables”***, MRS Bulletin October 2002, Vol. **27**, N. 10.

K. Nishimoto, M. Hattori, N. Kawahashi, US patent 6,582,761, November 21, 2000.

M. Pohl, D. A. Griffiths, ***“The Importance of Particle Size to the Performance of Abrasive Particles in the CMP Process”***, Journal of Electronic Materials, Vol. **25**, N. 10, 1996.

R. K. Singh, S-M. Lee, K-S. Choi, G. B. Basim, W. Choi, Z. Chen, and B. M. Moudgil, ***“Fundamentals of Slurry Design for CMP of Metal and Dielectric Materials”***, MRS Bulletin October 2002, Vol. **27**, N. 10.

J. M. Steigerwald, S. P. Murarka, and R. J. Gutmann, ***Chemical-Mechanical Planarization of Microelectronic Materials*** (John Wiley & Sons, New York, 1997).

S. Varadarajan, D. Kalakkad, and T. Cacouris, ***“Understanding and Reducing Copper Defects”***, Semiconductor International, 6/1/2002.

L. Zhong, J. Yang, K. Holland, J. Grillaert, K. Devriendt, N. Heylen, and M. Meuris, ***“A static Model for Scratches Generated during Aluminum Chemical-Mechanical Polishing Process: Orbital Technology”***, Jpn. J. Appl. Phys. Vol. 38 (1999), 1932-1938.