Physical and chemical properties affected by temperature in copper films chemical mechanical polishing

Shih-Jyun Liao[1], NTai-Hao Kuo[2] , Wen-Shan Lin[2], Chia-Ling Liao[2], Ssu-Hua Chien[2], **Trung Kien Vi [1]** ,Tsung-Chieh Cheng[1*]

[1]Graduate Institute of Mechanical and Precision Engineering, National Kaohsiung University of Applied Science,Taiwan

[2]Microsystems Technology Center，Industrial Technology Research Institute South，Taiwan

Abstract

Chemical mechanical polishing (CMP) of copper films in is one of the most essential processes for the manufacturing of semiconductor devices, next-generation compact 3D microelectronic devices and integrated microelectromechanical system with through holes plating. In this paper, we firstly discuss the thermal bending effect for CMP process of 4 inch p-type silicon wafers. In our experiment, surface roughness and removal rate increased with polishing temperature because of wafer thermal bending. In order to avoid thermal bending effect, the softer pad - 545N polishing cloth which is better than IC 1000 was used in our CMP experiments because of its better polishing selectivity. Therefore, we also use 545N polishing cloth to experiment with many important fabrication conditions which involve physical and mechanical mechanisms such as pad rotation speed, down force, temperature, pad types and chemical additive concentration. The results indicated that the removal rate will increase with higher rotation speed and increasing loading pressure. Besides, higher polishing temperature will cause the higher removal rate and higher surface roughness and the slurry with 3wt% hydrogen peroxide has the highest removal rate for copper CMP process.

Keywords: chemical mechanical polishing, polishing temperature, thermal bending effect

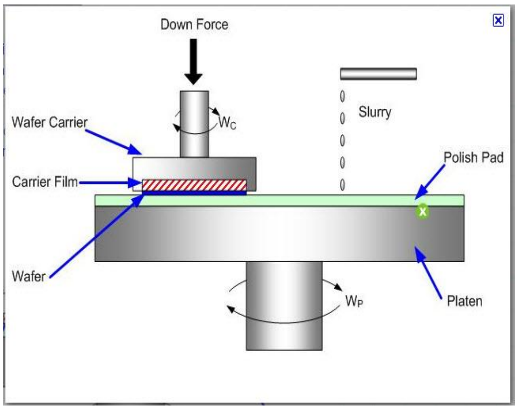
1. Introduction

The use of copper as an interconnect or wiring material in ultra large scale integration (ULSI) of microelectronic devices, vertical interconnections of 3D package or MEMS devices is being increasingly considered mainly due to its low resistivity and high resistance to electromigration compared to the widely used aluminium alloys [1,2]. For potential application of copper as interconnect material in many fabrication techniques such MEMs or semiconductor process, the wafer surface must be made planar on a global scale. Therefore, copper chemical mechanical polishing (CMP) has become one of the most critical and significant process in the manufacturing of state-of-the-art interconnects [3]. The role of CMP is to polish a patterned wafer for circuits planarization and to remove excess fill from the preceding deposition or electroforming step in such a way that it leaves a planarized surface having minimal roughness, defectivity, and no corrosion [4]. This technology is the most efficiency global planarization technology developed by International Business Machines Corp. (IBM) to solve the problem of layer nonuniformity at 1980s[5]. Although the process was initially developed for planarize interlevel dielectrics (ILD), CMP is also widely used in Tungsten, silicon, silicon oxide and several dielectric layer polishing. [6-10].

Compared to CMP for silicon dioxide, the metal (particularly copper) CMP process is poorly understood, due mainly to electrochemical interactions between the slurry and the metal film during polishing, and the coupled effect of these on the mechanical properties of the surface. Cu-CMP process involves several step such as chemical modification of the soft copper surface followed by mechanical abrasion [2], the dissolution of the metal passivation layer in the CMP solution, and the protection of recessed areas of the surface by using a corrosion inhibitor[11]. For typical CMP process, a pad and wafer are pressed together by a dynamic polishing head and held in place by a plastic retaining ring. The dynamic polishing head is rotated with different axes of rotation. This removes material and tends to even out any irregular topography, making the wafer flat or planar. In CMP process, the slurry which contains a colloidal suspension of abrasive particles such as alumina or silica and specific chemical additives is injected to the pad. Polishing pads were usually made by polymeric material (e.g. polyurethane) has porous surface or contains different pad grooves to liberate CMP slurry[12]. From previous literatures, many researches revealed that many factors may affect the polishing results such as pH value, loading pressure, rotation speed, pad rigidity, slurry flow, even slurry’s temperature. Du and Seal et al. found that the removal rate of copper decreased with increase in H_2O_2 concentration due to the formation of a less soluble copper oxide film and in 3wt% of hydrogen peroxide would get the maximum removal rate[4]. Du and Desai indicated the pH of the slurries plays a very important role in copper CMP removal and pH value at 2~3 was easy to generates soft passivation layer in CMP process[13]. Besides, sillca dispersion and its particle size and slurry stability were also changed accompany with pH value[14,15]. In addition, Tohru et al. used MnO_2 slurry to improve the delamination generation from the copper CMP process, and various layers would cause different critical pressure which was relation to the delamination of copper[16,17]. Defect of dishing is general problem which will be found in CMP process. Thomas et. al. indicated that the use of benzotriazole (BTA) provides a protective effect in H_2O_2 corrosion environments and stable film on copper surfaces.[18,19] Moreover, the slurry temperature effect in CMP on copper and SiO_2 films was also discussed by Subrahmanya[2], Seo[20], and Sorooshian[21]. The results indicated increasing trend for copper polishing with a rise in polishing temperature by coefficient of friction (COP) measurement. In general, chemical mechanical planarization (CMP) models have relied heavily on parameters such as pressure, velocity, slurry, and pad properties to describe material removal rates and wafer uniformity[9]. However, one key parameter, temperature, which can impact both the mechanical and chemical facets of the CMP process, is often neglected. Therefore, experimental data involving the effect of thermal bending of wafer, pad selectivity, removal rate, and surface roughness were investigated in this paper to avoid the effect of higher temperature of CMP process.

2. Experimental

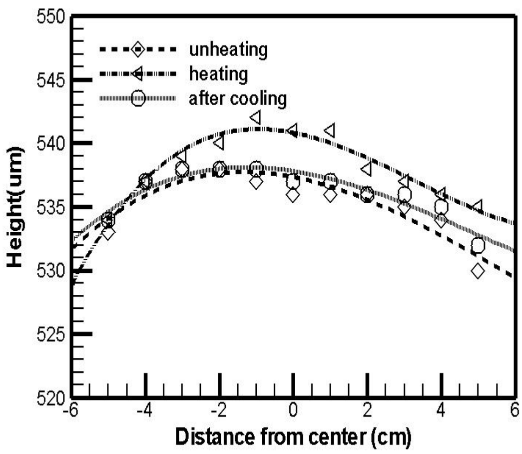
The polishing samples were two-layer structure of Cu/Ti with thicknesses of 500/20 nm, sputter deposited on a 4-in (~100mm) n-type (111) oriented silicon Si wafer which was covered with a 100-nm thick thermally grown SiO2. The under layer of 20-nm Ti was used as an adhesion promoter for the copper deposition, since copper does not adhere well on the thermal oxide. All polishing experiments were carried out by using R&D UNIPOL-1502 commercial polisher and the schematic diagram of CMP equipment was shown in Figure 1.



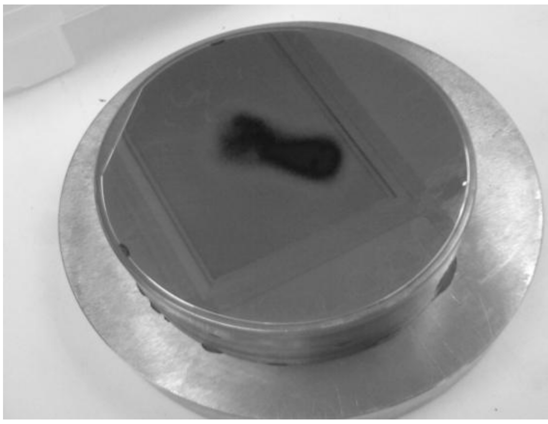
The down force was applied by cast iron cob placed on the wafer carrier. The base slurry used in the experiments was based ETERPOL EPL-2361, with the value of PH 4~4.4, 4~6% colloidal silica and 2~23nm particle sizes diluted with H_20_2. In order to determine the influence of the oxidizing agent and how this process really works, different amounts of H_20_2 were added. Besides, for investigating the effect of different pads for thermal bending wafer, we prepared two kinds of pad: (1) rigid polishing pad and (2) Soft polish cloth. The rigid polishing pad IC 1000 (polyurethane) with squarely grooves is offered by Rohm and Haas Electronic Materials Corp. and the soft polish cloth (545N) was provided from R&D HI-TECH. In our experiment, the wafer carrier was heated by hot plate to melt the wax, and the wafer was fixed on the wafer carrier by this wax. Then both the wafer carrier and the polishing table were rotated at different rotation speed 60rpm, 70rpm, 80rpm, 90rpm and a different down force of 21.9 kPa, 31.85g/cm^2、63.7g/cm^2、82.8g/cm^2 and 114.2g/cm^2 was applied to the carrier with a constant slurry flow rate of 100 cc/min constitute the experimental parameters. Furthermore, the wafer was heated by hot plate before the polishing process and the slurry container was heated with continuous stirring of the slurry contents to ensure uniform temperature rise of the wafer and slurry. Then the slurry was passed onto the polishing pad to achieve steady state temperature of the pad before starting the actual experiment. Post CMP metrology was performed by the thickness of 10 points from the center to the edge was measured on each wafer at different temperatures by using the surface profiler (Dektak 6M). AFM experiments were performed on a Digital Instruments Dimension Series 3100 AFM using Tapping Mode to determine the morphology of the Cu surface before and after the Cu-CMP process in this paper.

3. Results and Discussion

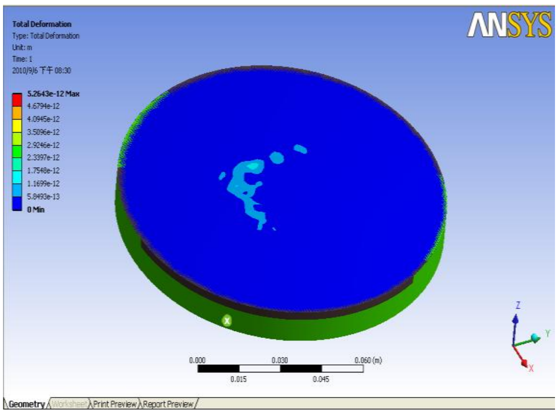
Temperature is an important issue of copper CMP. In CMP process, heat is generated at the interface of polishing due to friction and interaction of the asperities of wafer, pad and the abrasive particles. These heats will increase the temperature and induce the bending phenomena of wafer. In order to understand the thermal bending of wafer, the surface profile of unheated, heated, and cooling after heated wafer was measured by surface profiler as shown in Figure 2.



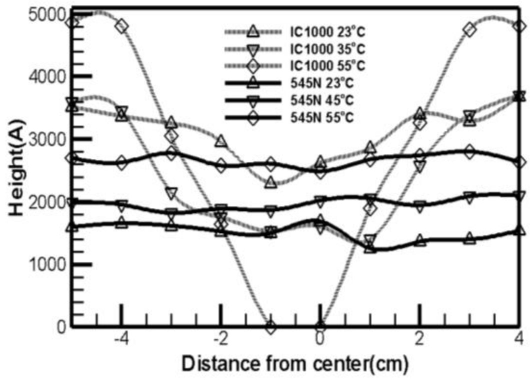
However, as shown in Fig.2, the wafer is subjected to bending at room temperature because Cu thin film which causes the inertial stress was grown on the silicon [22]. Then, if we heat the wafer continuously, the bending phenomena of wafer will be enhanced with increasing temperature. Finally, after we cool down the wafer to the room temperature, the bending will reduce with decreasing temperature and is closed to unheated wafer. This serious bending phenomena is caused by the deformation between silicon and copper film because of different thermal expansion coefficient of copper ($17*10^{-6}$1/^{o}C) and silicon wafer ($2.6*10^{-6}$ 1/^{o}C). Therefore, according to the results of Fig.2, it is interesting to understand the effect of thermal bending for Cu-CMP process. For this reason, thermal bending wafer (heated to23℃) which was polished with IC1000 at loading pressure of 82.8g/cm^2 was shown in Fig. 3(a).



Use Ansys software its analyse and shows overpolish phenomena by using IC 1000 pad polishing at polishing temperature23^{0}C in Fig.3 (b)



Over polished was observed near the center areas of the wafer. This result reveals that the removal rate is faster in the center than in the edge of wafer because of wafer bending effect. According to the Preston's function[1], the removal rate of material is a function of polishing pressure[23], which is directly proportional to real contact area. It also means that the local pressure in the center of wafer is greater than in the edge of wafer. Besides, higher loading pressure makes relatively high temperatures at the interface causing the increased chemical activity between the copper and the slurry at elevated temperatures [24] and higher temperature which is directly proportional to real contact area also reduce the hardness of pad asperity, thus pad and wafer increase the real contact area [23,25]. These are resulting in the increase of over polished phenomena near the center of wafer. Therefore, in order to finding the solution to avoid the thermal bending effect of Cu-CMP process, two different kind of pads: IC1000 rigid polishing pad and 545N soft polish cloth were used for Cu-CMP process at different polishing temperature as shown in Figure 3(c).



In this figure, the results, by using rigid polishing pad IC1000, showed that over polished was observed near the center of wafer and it becomes more and more serious with the increase of temperature because of thermal bending effect. Besides, with IC1000 polishing, the position of maximum removal rate is located at about 1cm near the center of wafer which is correspond with the maximum bending of the wafer as shown in Fig. 2. In addition, as also shown in Fig.3 (c), the softer pad 545N shows better uniformity than the rigid pad IC1000. These results indicate that the larger pad modulus will cause smaller contact area thus resulting in a smaller number of particles in contact with the wafer[26] and then resulting in the selective area polishing of the wafer. Therefore, in order to avoid the thermal bending effect of Cu-CMP process, we use the 545N polish cloth to be our polish pad in our following experiments.

Figure 4 shows the surface roughness before and after copper polishing process under the conditions of rotation speed 70rpm and pressure loading 63.7g/cm^2 with 545N polish cloth As also illustrated in Table 1,

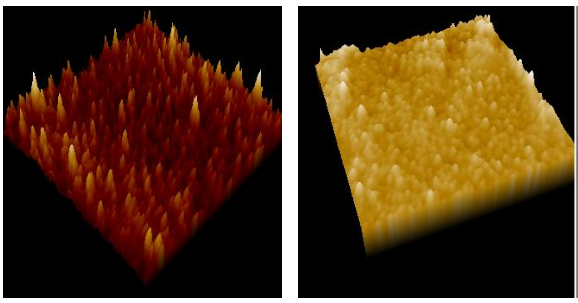
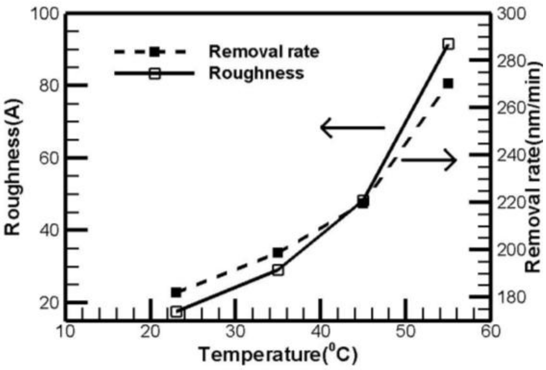


Table 1

	before polishing	after polishing
RMS	37.88A	26.03A
Ra	29.35A	19.09A

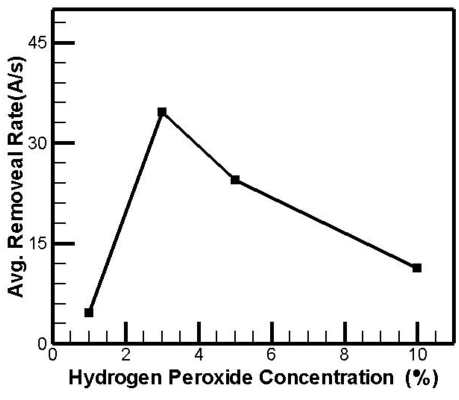
The root mean square (RMS) value of wafer was improved from 37.88A to 26.03A, and Roughness(Ra) was improved from 29.35A down to 19.09A. It shows that 545N polish cloth is a useful polish pad for Cu-CMP process.

Pad mechanical property will also have impact on CMP planarization performance. Figure 5 shows the removal rate improvement attained by raising the polishing temperature with 545N polish cloth at rotation speed 70rpm and loading pressure 63.7g/cm^2.



This could be due to the formation of a thick passivating layer which prevents further oxidation of the copper surface reducing the removal rate. The passivating layer gets dissolved into the slurry at high temperatures exposing fresh copper surface for further oxidation and hence high removal rates[27,28]. Besides, another reason for removal rate increased with polishing temperature can be attributed to increasing the number of abrasive particles coming in contact with the wafer surface and decrease in the viscosity of the slurry occurs with increasing temperature, which increases the friction at the interface and hence increases shear resulting in higher removal rates[29]. However, as shown in Fig. 5, the surface roughness of wafer also increases with increasing polishing temperature. In our previous experiment, higher temperature will cause the lager thermal bending of the wafer. Although the higher polishing temperature will cause the increase of coefficient of friction and play a significant role in affecting shear force, large thermal bending of wafer with high temperature will reduce the contact area and generate the uncertainty of polishing process resulting in the increasing roughness of the wafer.

Fig. 6 shows the dynamic and static removal rate of Cu as a function of H_2O_2 content.



The removal rate of copper increased initially with an increase in H_2O_2 content at 3% and finally decreased with increasing H_2O_2 content. The suppression of the removal rate with hydrogen peroxide content beyond 3% was probably attributed to the surface repassivation process [11]. This repassivation layer will decrease in the chemical reactivity at higher H_2O_2 concentrations which is possibly due to the formation of a copper oxide film on the copper surface, providing some protection to the copper surface from chemical attack. The formation of passive CuO film is represented by Eq. 1, accompanying related reactions shown in Eq. 2 and 3 to form $Cu(OH)_2$[30]

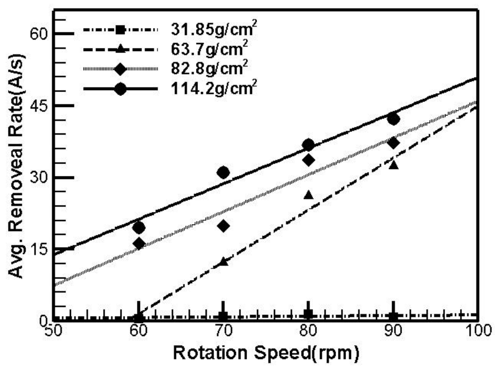
$$Cu_2O + H_2O_2 \leftrightarrow 2CuO + H_2O \tag{1}$$

$$Cu + H_2O_2 + 2H^+ \rightarrow Cu^{2+} + 2H_2O \tag{2}$$

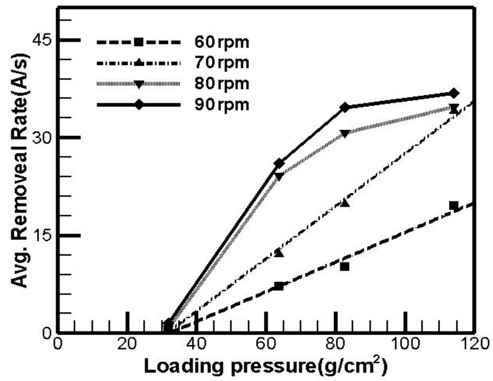
$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \tag{3}$$

Besides, another reason of the decreased removal rates at higher H_2O_2 concentrations is simply that the oxidation/passivation process is faster than mechanical removal, and an oxide layer is always present on the copper surface during CMP. It has also been suggested that at higher concentrations of hydrogen peroxide, the passive film changes characteristics, such as strength and porosity, thereby inhibiting further oxidation[31,32].

Figure 7 presents the effect of the removal rate along with various loading pressure and rotation speed with 2~23nm colloidal silica as the abrasives and 545N polishing cloth as the polishing pad. In Fig.7 (a),



The removal rate is a function of rotation speed and it continuously decreases with raising rotation speed at different pressure. This phenomena can be explain that as the head speed increases, the rotation speed of slurry particles in contact with the wafer surface and shear stress acted on the wafer surface is also increased, thus the removal rate increases. Besides, as shown in Fig. 7(b)



The CMP load pressure is dependences of removal rate at four different rotation speeds. The results reveals that the removal rate with polishing pressure did not all follow the Preston behavior, which the removal rate was proportional to the pressure[33,34]. In the low loading pressure region, the removal rate-loading pressure relations show that the higher the rotation speed, the larger the slope, indicating that for a softer pad surface, the size of the valleys between the pad and the wafer is easier to be reduced with increasing loading pressure. This smallest valley decreased as the down force increased and thereby increased the contact ratio in the polishing interface thus increasing the removal rate. Therefore, in this low loading pressure region, removal rate linearly increasing along with the pressure increasing, i.e., fit for the original Preston's theory. However, at the high loading pressure region, the data show that the removal rate becomes slowly increasing or saturated at the higher rotation speeds of wafer, indicating that on a softer pad surface, the size of the valleys reaches its minimum value at higher loading pressure[6].

4. Conclusions

The thermal bending effect of Cu-CMP process was investigated in this paper. Higher temperature will induce the larger thermal bending of wafer. In order to avoid overpolish phenomena resulting from the thermal bending effect, the softer 545N polish cloth which is better than rigid polish pad-IC1000 was used to be our polish pad for Cu-CMP process. In our experiment, the removal rate dramatically increased with higher polishing temperature, because of the increasing coefficient of friction and the increasing shear stress between the pad and copper film. However, higher polishing temperature also induces the larger thermal bending effect which reduces the polishing contact area and generates the uncertainty of polishing process that increases the surface roughness of copper directly. In addition, the effect of the removal rate along with various loading pressure and rotation speed are investigated. The results indicated that the removal rate which decreases continuously with raising rotation speed and increases linearly along with the loading pressure increase until it reaches the saturation region

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6. References

1. F.W. Preston, "The Theory and Design of Plate Glass Polishing Machines", *Journal of the Society of Glass Technology*, Vol. 11, , pp.214-247, 1927.
2. Subrahmany Mudhivarthi, and Ashok Kumar "Effect of Slurry Temperature on Cu Chemical Mechanical Polishing with Different Oxidizing Agents" *Materials Research Society*, Vol. 867 pp. w6.6.1-w6.6.6, 2005.
3. M. saif islam, ,G.Y. Jung, T. Ha, D.R. Stewart, Y. Chen S.Y. Wang, R. Stanley Williams, "Ultra-smooth platinum surfaces for nanoscale devices fabricated using chemical mechanical polishing" Applied Physics A Vol.80 pp.1385–1389, 2005
4. S. Seal, S.C. Kuiry, B. Heinmen "Effect of glycine and hydrogen peroxide on chemical– mechanical planarization of copper" *Thin Solid Films*, Vol.423 pp.243–251, 2003.
5. Pei-Lum Tso, Chih-Lung Huang "Development tendency of chemical mechanical polishing technique" *Machinery Industry Magazine*, Vol.206 pp.131-145, 1996.
6. Weidan Li , Dong Wook Shin, Minoru Tomozawa, Shyam P. Murarka,"The effect of the polishing pad treatments on the chemical-mechanical polishing of $Si0_2$ films", *Thin Solid Films* Vol.270 pp.601-606, 1995
7. Kei-Wei Chen, Ying-Lang Wang and Yungder Juang, "Optimized Process Improvement for Tungsten CMP Throughput" *Journal of Scientific and Technological Studies*, Vol.41, pp.65-72, 2007
8. Thomas F.A. Bibby, Randy Harwood, Dennis Schey, Kevin McKinley " Cartesian coordinate maps for chemical mechanical planarization uniformity characterization", *Thin Solid Films* Vol.308 pp.512–517, 1997
9. .J. G. Park_, H. I. Jungy and T. Katoh, U. G. Paik, H. Jeon "Effects of Film Type and Wafer Shape on Oxide CMP Characteristics" *Journal of the Korean Physical Society*, Vol. 39, pp. S296-S301, 2001
10. Jea-Gun Park and Takeo Katoh "Nanotopography impact in shallow-trench isolation chemical mechanical polishing-analysis method and consumable dependence", *Journal of Materials Research* Vol. 19, 2004
11. S. Deshpande, S. C. Kuiry, M. Klimov, Y. Obeng, and S. Seal "Chemical Mechanical Planarization of Copper: Role of Oxidants and Inhibitors" *Journal of The Electrochemical Society*, Vol.151 pp.G788-G794, 2004.
12. G. Helen Xu and Hong Liang "Effects of Electric Potential on Chemical-Mechanical Polishing of copper" *Journal of Electronic Materials*, Vol.31 pp.272-277, 2002.
13. T. Du, v. Desai "Chemical mechanical planarization of copper: pH effect" *journal of materials science letters*, Vol.22 pp.1623-1625, 2003.
14. Arno nennemann, matthias voetz, gabriele hey, lothar puppe, stephan kirchmeyer "Colloid chemical Interactions of Silica Particles in the Cu-CMP-Process" *Progress in Colloid and Polymer Science*, Vol. 133 pp.159-168, 2006.
15. Nam-Hoon Kim, Jong-Heun Lim, Sang-Yong Kim, Eui-Goo Chang, "Semi-abrasive free slurry with acid colloidal silica for copper chemical mechanical planarization", *Journal of Materials Science: Materials in Electronics* Vol.16 pp.629-632, 2005.
16. Tohru Hara, S. Balakumar "Chemical mechanical

polishing of copper layer employing MnO_2 slurry" *Thin Solid Films*, Vol.462 pp.186– 191, 2004.

17. Shimura, "Peeling and delamination in Cu/SiLKk process during Cu-CMP", *Thin Solid Films* Vol.462 pp.161- 167, 2004
18. Thomas Laursen, and Malcolm Grief, "Characterization and Optimization of Copper Chemical Mechanical Planarization", *Journal of Electronic Materials*, Vol. 31, 2002.
19. M.T. Wang, M.S. Tsai, C. Liu, W.T. Tseng, T.C. Chang, L.J. Chen, M.C. Chen "Effects of corrosion environments on the surface finishing of copper chemical mechanical polishing" *Thin Solid Films*, Vol.308 pp.518–522, 1997.
20. Yong-Jin Seo, "Oxide-chemical mechanical polishing characteristics using silica slurry retreated by mixing of original and used slurry", *Microelectronic Engineering* Vol.77 pp.263–269, 2005
21. Nam-Hoon Kim, Pil-Ju Ko, Gwon-Woo Choi, Yong-Jin Seo, Woo-Sun Lee "Chemical mechanical polishing (CMP) mechanisms of thermal SiO_2 film after high-temperature pad conditioning" *Thin Solid Films*, Vol.504 pp.166-169, 2006.
22. Subrahamany Mudhivarthi, Norm Gitis, Suresh Kuiry, Michael Vinogradov, and Ashok Kumar "Effects of slurry flow rate and pad conditioning temperature on dishing, erosion, and metal loss during copper CMP" *Journal of The Electrochemical Society*, Vol.153 pp.G372-G378 2006.
23. J.M. Steigwald, Chemical Mechanical Planarization of Microelectronic Materials, Wiley, New York, pp. 74–83 1997.
24. T.K. Yu, C.C. Yu, M. Orlowski, "A statistical polishing pad model for chemical mechanical polishing", Proceedings of the IEDM'93, pp. 35.4.1–35.4.4. 1993
25. Kuide Qin, Brij Moudgil, Chang-Won Park "A chemical mechanical polishing model incorporating both the chemical and mechanical effects" *Thin Solid Films* Vol.446 pp.277–286, 2004
26. H.J. Kim, H.Y. Kim, H.D. Jeong, E.S. Lee, Y.J. Shin "Friction and thermal phenomena in chemical mechanical polishing" *Journal of Materials Processing Technology* Vol.130 pp.334–338, 2002
27. J. Sorooshian, D. Hetherington, and A. Philipossiana, "Effect of Process Temperature on Coefficient of Frictionduring CMP" *Electrochemical and Solid-State Letters*, Vol.7 pp. G222-G224, 2004
28. Subrahmany Mudhivarthi, Parshuram B. Zantye, Arun Kumar, Ashok Kumar, Martin Beerbom, and Rudy Schlaf "Effect of Temperature on Tribological, Electrochemical, and Surface Properties during Copper CMP" *Electrochemical and Solid-State Letters*, Vol.8 pp.G241-G245, 2005
29. D. DeNardis, D. Rosales-Yeomans, L. Borucki, A. Philipossian "Characterization of copper-hydrogen peroxide film growth kinetics" *Thin Solid Films* Vol.513 pp.311–318, 2006
30. Q. Luo, S. Ramarajan, and S. V. Babu, "Modification of the Preston equation for the chemical–mechanical polishing of copper"*Thin Solid Films*, Vol.**335**, pp.160-167, 1998
31. D. Zeidler, Z. Stavreva, M. Plotner, K. Drescher "Characterization of Cu chemical mechanical polishing by electrochemical investigations" *Microelectronic Engineering*,Vol.33 pp.259-265, 2003
32. Jeng-Yu Lin, Chi-Chao Wan, Yung-Yun Wang, Jui-Chin Chen, Jiun-Yu Lai, Yuh-Da Fan, and Jui-Ping Chuang "Effect of Impurity Distribution on Corrosion Behavior of Electrodeposited Copper in H_2O_2-Based Slurry "*Journal of The Electrochemical Society*, Vol.154 pp.H530-H535, 2007
33. E. Paul and R. Vacassy, "A model of CMP" *Journal of The Electrochemical Society*, Vol.**150** pp.G739-G743, 2003.
34. Kei-Wei Chen and Ying Lang Wang "Study of Non-Preston Phenomena Induced from the Passivated Additives in Copper CMP" *Journal of The Electrochemical Society*, Vol.154 Vol.1 pp. H41-H47, 2007

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