Polishing Mechanism of TEOS-CMP with High-temperature Slurry by Surface Analysis

Nam-Hoon Kim
Research Institute of Energy Resources Technology, Chosun University,
Seoseok-dong, Dong-gu, Gwangju 501-759, Korea

Yong-Jin Seo
Department of Electrical and Electronic Engineering, Daebul University,
Samho-eup, Yeongam-gun, Chonnam 526-702, Korea

Pil-Ju Ko and Woo-Sun Lee[a]
Department of Electrical Engineering, Chosun University,
Seoseok-dong, Dong-gu, Gwangju 501-759, Korea

[a]E-mail : wslee@chosun.ac.kr

(Received July 27 2005, Accepted August 10 2005)

Effects of high-temperature slurry were investigated on the chemical mechanical polishing (CMP) performance of tetra-ethyl ortho-silicate (TEOS) film with silica and ceria slurries by the surface analysis of X-ray photoelectron spectroscopy (XPS). The pH showed a slight tendency to decrease with increasing slurry temperature, which means that the hydroxyl (OH^-) groups increased in slurry as the slurry temperature increased and then they diffused into the TEOS film. The surface of TEOS film became hydro-carbonated by the diffused hydroxyl groups. The hydro-carbonated surface of TEOS film could be removed more easily. Consequently, the removal rate of TEOS film improved dramatically with increasing slurry temperature.

Keywords : Chemical mechanical polishing (CMP), Tetra-ethyl ortho-silicate (TEOS), Slurry temperature, Removal rate, pH, X-ray photoelectron spectroscopy (XPS)

1. INTRODUCTION

Chemical mechanical polishing (CMP) is the planarization method that has been selected by the semiconductor industry today[1]. The CMP process must provide high removal rate (RR), good global and local planarity, high selectivity, and a clean post-CMP surface [2,3]. It is generally known that several process parameters including equipment and consumables (pad, backing film and slurry) can optimize and improve the CMP performance[4]. Among the consumables for CMP process, especially, slurry and its properties play a very important role in the removal rates and planarity for global planarization ability of the CMP process[5]. There are several slurry properties that affect the material removal procedure such as slurry chemicals, potential of hydrogen (pH), size and hardness of abrasive particles, slurry viscosity, stability of the abrasive suspension in the slurry, etc.[6]. Polishing temperature is one of the most important factors that affect the material removal process. The CMP performance and the characteristics of slurries by high-temperature were investigated by our research group[7]. However, the accurate reason for the increase of removal rate in TEOS-CMP could not be clearly presented[7]. In this study, the mechanism of TEOS-CMP by the high-temperature slurry was investigated using X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL DETAILS

The CMP polishing of all test wafers was performed with a G&P POLI-380 CMP polisher[8]. Rodel IC-1300 and Suba IV were glued by a bonding agent of PSA II to make a double pad[8]. The parameter ranges of design of experiments (DOE) technique for the optimized CMP process are summarized as follows: table speed, head speed, slurry flow rate, and down force were 40 rpm, 60 rpm, 90 ml/min, and 300 gf/cm^2, respectively[9]. CMP processing time was 60 seconds. The conditioning pressure was fixed at 2 kg/cm^2 to exclude the effects of pad-conditioning. The polishing pad was used without change because of its good stability. A commercial silica-based oxide slurry (silica slurry) and ceria-based oxide slurry (ceria slurry) were used as CMP slurries. To prevent aging effects, the slurries were dispersed by using a Sonic Tech ultrasonic wave homogenizer before polishing. Temperature of slurries at room temperature was 20 °C. Polishing was carried out with the slurries cooled or heated from 10 °C to 90 °C at intervals of 10 °C by chiller and hot plate. All temperatures in this experiment were measured by IR (infrared rays) sensor. Post-CMP cleaning proceeded using a sequence of 3 minutes in SC-1 chemicals ($NH_4OH:H_2O_2:H_2O=1:2:7$), 2 minutes in diluted HF (DHF) of 1:10, and 4 minutes in ultrasonic cleaning. All the samples in this paper were prepared on 4-inch n-type (111) oriented silicon wafers with resistivity of 3-6 Ωcm. For cleaning and removal of native oxide, the substrate was rinsed with the solution of $H_2SO_4:H_2O_2$ (1:4), H_2O:HF (DHF; 10:1), and deionized water (DIW), consecutively. TEOS film of 1900 nm was deposited on the silicon by plasma enhanced chemical vapor deposition (PECVD). Film thickness at 9 points from the center to the edge was measured clockwise on each wafer using a spectroscopic ellipsometer (J.A woollam, M-2000V). In order to understand the effects of temperature on chemical reactions between slurry and TEOS film, the variations of chemical composition of a surface was analyzed by XPS (VG-Scientific ESCALAB 250) measurement. The sample was immersed in slurries with a specific temperature for 60 minutes. Then it was transferred to analysis chamber for the XPS after air-drying. For XPS analysis, Al kα (1486.6 eV) was used as an X-ray energy source. A scan interval was 1 eV (wide scan spectrum) and 0.05 eV (narrow scan spectrum), respectively. All binding energy (BE) values were compensated as C 1s (284.5 eV).

3. RESULTS AND DISCUSSION

In order to investigate the origin of increase of removal rates in the preceding research[7], the slurry properties as a function of temperature were studied. Figure 1 shows the pH lowering resulting from raising the temperature of slurry in both silica and ceria slurries [7]. As shown in Fig. 1, the pH of silica slurry decreases with the temperature of slurry from 10.60 at 20 °C to 9.63 at 90 °C. A similar trend was also observed using ceria slurry; pH of ceria slurry decreased from 7.77 at 20 °C to 6.50 at 90 °C. The pH showed a slight tendency of decrease while the removal rates increased with temperature. The pOH, although not used as commonly, can be clearly defined by the simple formula: pH + pOH = 14[10]. The decreased pH means that the hydroxide ion molar concentration (pOH) increased in the slurries. This increasing hydroxyl (OH^-) groups diffused into the TEOS and then weakened the TEOS surface in a hydrolyzing process[10,11]. The weakened TEOS surface was more easily removed by the mechanical force of CMP process. While the measured pH is due to the amount of hydrogen (H^+) and hydroxyl (OH^-) ions present in the slurry, the measured conductivity is a result of a combinations of the above-mentioned ions and other dissolved ions[12].

TEOS samples were immersed in silica and ceria slurries at the different temperatures for 60 minutes in order to examine the slurry attacks. According to the proposed models of TEOS-CMP, the slurry solution weakens the Si-O bonds in TEOS film and softens the surface as it becomes hydrated with Si-OH bonds[11].

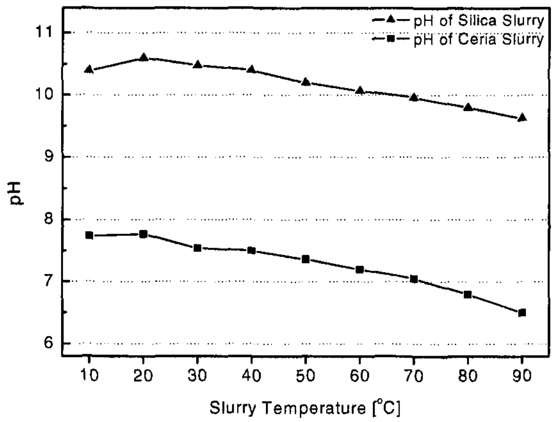

Fig. 1. Changes of pH as a function of temperature in silica and ceria slurries[7].

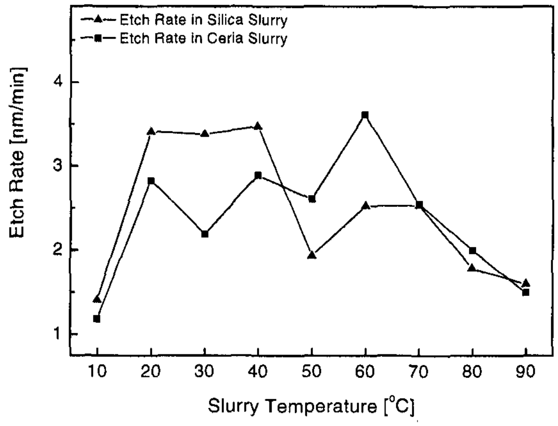

Fig. 2. Etch rates of TEOS film after immersed in silica and ceria slurry with the different slurry temperatures for 60 minutes.

Then the subsequent removal of softened surface is achieved by the mechanical actions of the abrasive slurry and polishing pad. The results of etch rates shows in Fig. 2 as increasing slurry temperature. The etch rate generally shows the tendency to rise with slurry temperature; however, it is very low under 3.0 nm/min at all temperatures with the both slurries while the removal rates are from 183.0 nm/min to 832.2 nm/min. It does not make a difference that the values of etch rate with both slurries are within the measurement error of ellipsometer. This result indicates that the chemical etch does not directly affect the removal rate. It is thought that the passivation layer on the TEOS surface by reactions with slurry was not desorbed from the surface.

The XPS analysis was performed to characterize the surface change for TEOS immersed in the both slurries with the different temperatures for 60 minutes. Figure 3(a) and Fig. 3(b) show the XPS measurements of the O 1s narrow scan for the samples dipped in different temperatures of ceria slurry and silica slurry for 60 minutes, respectively. First, the no-dipped specimen spectrum at the BE of 533.05 eV shows that most O elements existed in SiO_2. The immersed samples spectra show the changes of surface characterization. Both peaks at the BEs of 533.05 and 532.74 eV, corresponding to SiO_2 and $H_6C_2Si_2O_3$[13], were detected on the specimen spectrum dipped in 20 °C slurry. Then, the peaks shift to the lower BE levels of 532.74 and 532.50 eV, corresponding to $H_6C_2Si_2O_3$ and $H_{16}C_{10}OSi_2$[13], in the specimen spectrum immersed in 80 °C slurry. Figure 4(a) and Fig. 4(b) show the narrow scan spectra of C 1s for the specimens immersed in different temperature of the both slurries for 60 minutes, respectively. It is generally known that the peak at BE of 284.5 eV correspond to C-C bonding[14]. It is observed that the two peaks at 283.4 eV and 286.3 eV correspond to CSi and H_4C_{20} bonding[14-16]. The BEs from 288.6 to 289.14 eV are attributed to H-C-O bonding[17-20]. For the specimens immersed in ceria slurry, XPS peaks at BEs of 283.4 and around 288.7 eV increased due to C-Si

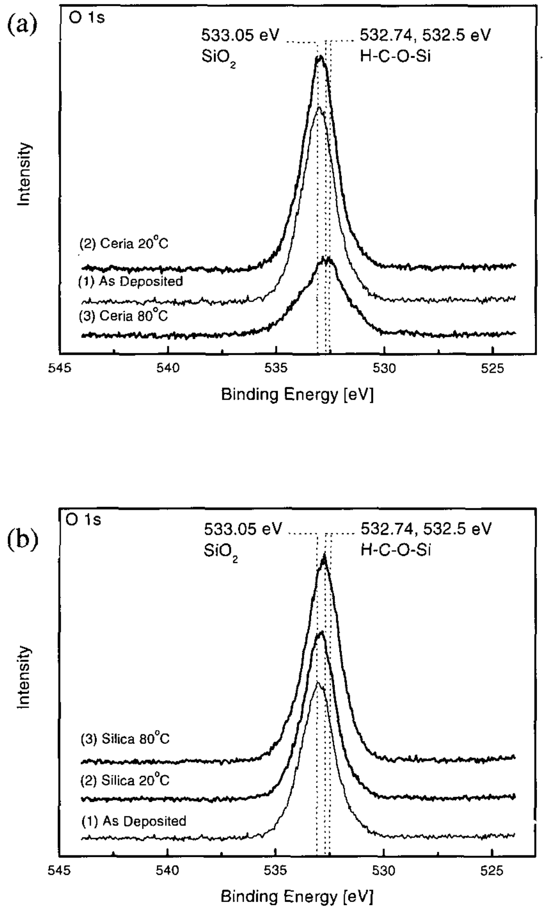

Fig. 3. XPS narrow scan analysis on TEOS film of O 1s dipped in (a) ceria slurry and (b) silica slurry with the various temperatures.

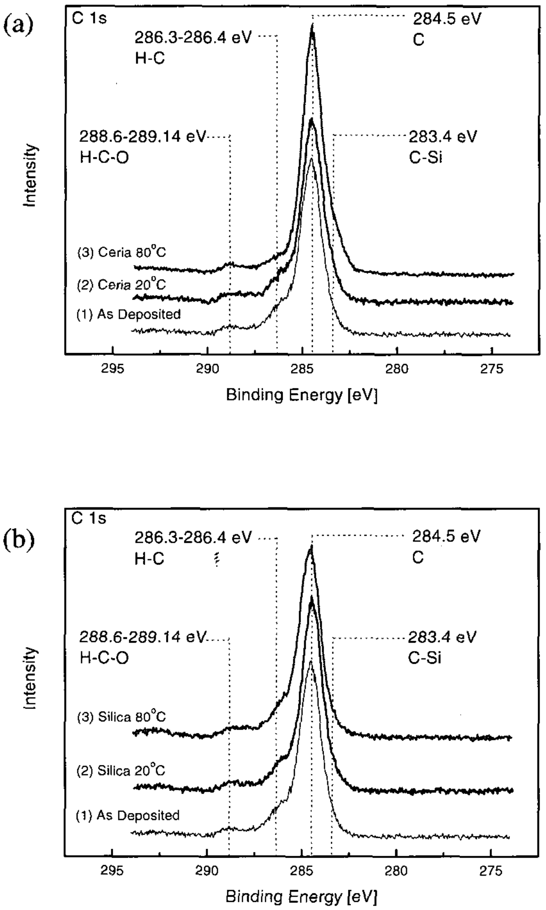

Fig. 4. XPS narrow scan analysis on TEOS film of C 1s dipped in (a) ceria slurry and (b) silica slurry with the various temperatures.

and H-C-O bonds when XPS peak at BE of 286.3 and 286.4 eV due to H-C bond decrease by increase of slurry temperature as shown in Fig. 4(a). For the samples dipped in silica slurry, the changes of XPS peaks were similar to that in ceria slurry. The peaks at BEs of 283.4 and around 288.7 eV assigned to C-Si and H-C-O bonds increased when the samples immersed in silica slurry as shown in Fig. 4(b). However, the shoulder at BE of 288.3 eV due to H-C bond still more increased as the slurry temperature increased. It is though that the abundant H-C-O-Si bonds were formed on the surface of TEOS film when the sample was polished by high-temperature slurry. Figure 5(a) and Fig. 5(b) show the narrow scan spectra of Si 2p for the samples dipped in different temperatures of the both slurries for 60 minutes, respectively. The peaks of all temperature conditions at BEs of 103.75 and 103.9 eV were assigned to SiO_2[21]. The each peak for the all specimens had a small shoulder at a BE of 102.9 eV which was reported by Wagner, et al. to $H_6C_2Si_2O_3$[13]. The shoulder increased with an increase of slurry temperature. As results of XPS, slurry actively reacts with the TEOS surface leading dissolution of Si-O bonds to H-C-O-Si bonds as the process temperature increased[11]. This hydro-carbonated surface of TEOS film was easier to be removed by mechanical parts of CMP process.

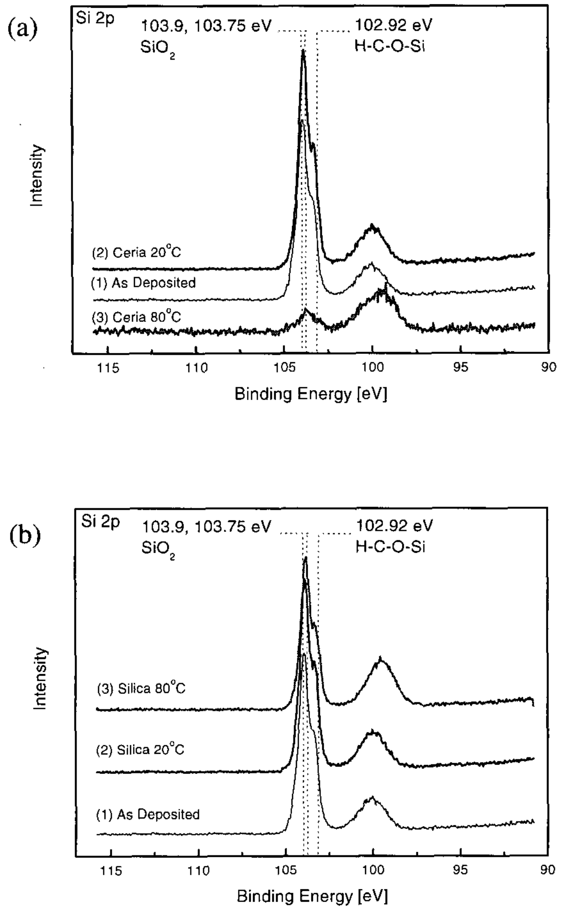

Fig. 5. XPS narrow scan analysis on TEOS film of Si 2p dipped in (a) ceria slurry and (b) silica slurry with the various temperatures.

4. CONCLUSION

Chemical mechanical polishing of TEOS films with silica and ceria slurries has been examined as a function of slurry temperature. The pH showed a slight tendency to decrease with temperature in both slurries. The increasing hydroxyl (OH^-) groups diffused into the TEOS and then weakened reactants such as H-C-O-Si bonds on the surface of TEOS film were actively generated with the slurry temperature. These soft reactants on the surface of TEOS film could be removed easily by mechanical parts of CMP.

ACKNOWLEDGMENTS

This work was supported by a Korea Research Foundation Grant(KRF-2004-005-D00007).

REFERENCES

[1] P. B. Zantyea, A. Kumara, and A. K. Sikder, “Chemical mechanical planarization for micro-electronics applications”, Mat. Sci. Eng. R, Vol. 45, Iss. 3-6, p. 89, 2004.

[2] M. Biemann, U. Mahajan, and R. K. Singh, “Effect of particle size during tungsten chemical mechanical polishing”, Electrochem. Solid St., Vol. 2, Iss. 8, p. 401, 1999.

[3] M. Bielmann, U. Mahajan, R. K. Singh, D. O. Shah, and B. J. Palla, “Enhanced tungsten chemical mechanical polishing using stable alumina slurries”, Electrochem. Solid St., Vol. 2, Iss. 3, p. 148, 1999.

[4] Y. J. Seo, S. Y. Kim, Y. O. Choi, Y. T. Oh, and W. S. Lee, “Effects of slurry filter size on the chemical mechanical polishing (CMP) defect density”, Mater. Lett., Vol. 58, Iss. 15, p. 2091, 2004.

[5] G. B. Basim, J. J. Adler, U. Mahajan, R. K. Singh, and B. M. Moudgil, “Effect of particle size of chemical mechanical polishing slurries for enhanced polishing with minimal defects”, J. Electrochem. Soc., Vol. 147, Iss. 9, p. 3523, 2000.

[6] J. M. Steigerwald, S. P. Murarka, and R. J. Gutmann, “Chemical Mechanical Planarization of Micro-electronic Materials”, John Wiley and Sons, New

York, p. 40, 1997.
[7] P.-J. Ko, S.-W. Park, N.-H. Kim, Y.-J. Seo, and W.-S. Lee, "Polishing properties by change of slurry temperature in oxide CMP", J. of KIEEME(in Korean), Vol. 18, No. 3, p. 219, 2005.
[8] Y. J. Seo and W. S. Lee, "Chemical mechanical polishing of $Ba_{0.6}Sr_{0.4}TiO_3$ film prepared by sol–gel method ", Microelectron. Eng., Vol. 75, Iss. 2, p. 149, 2004.
[9] S. W. Park, C. B. Kim, S. Y. Kim, and Y. J. Seo, "Design of experimental optimization for ULSI CMP process applications", Microelectron. Eng., Vol. 66, Iss. 1-4, p. 488, 2003.
[10] M. R. Oliver, "Chemical-mechanical Planarization of Semiconductor Materials", Springer-Verlag, Heidelberg, p. 217, 2004.
[11] J. M. Steigerwald, S. P. Murarka, and R. J. Gutmann, "Chemical Mechanical Planarization of Microelectronic Materials", John Wiley and Sons, New York, p. 137, 1997.
[12] W. Li, D. W. Shin, M. Tomozawa, and S. P. Murarka, "The effect of the polishing pad treatments on the chemical-mechanical polishing of SiO_2 films", Thin Solid Films, Vol. 270, Iss. 1-2, p. 601, 1995.
[13] C. D. Wagner, D. E. Passoja, H. F. Hillery, T. G. Kinisky, H. A. Six, W. T. Jansen, and J. A. Taylor, "Auger and photoelectron line energy relationships in aluminum-oxygen and silicon-oxygen compounds", J. Vac. Sci. Technol., Vol. 21, No. 4, p. 933, 1982.
[14] K. L. Smith and K. M. Black, "Characterization of the treated surfaces of silicon alloyed pyrolytic carbon and SiC [artificial heat values]", J. Vac. Sci. Technol. A, Vol. 2, No. 2, p. 744, 1984.
[15] J. J. Pireaux, J. Riga, R. Caudano, J. J. Verbist, J. Delhalle, S. Delhalle, J. M. Andre, and Y. Gobillon, "Polymer primary structures studied by ESCA and EHCO methods", Phys. Scripta, Vol. 16, No. 5-6, p. 329, 1977.
[16] J. M. Burkstrand, "Copper-polyvinyl alcohol interface: a study with XPS", J. Vac. Sci. Technol., Vol. 16, No. 2, p. 363, 1979.
[17] D. T. Clark and H. R. Thomas, "Applications of ESCA to polymer chemistry. XI. Core and valence energy levels of a series of polymethacrylates", J. Polym. Sci. Pol. Chem. Ed., Vol. 14, No. 7, p. 1701, 1976.
[18] D. T. Clark and H. R. Thomas, "Applications of ESCA to polymer chemistry. XVII. Systematic investigation of the core levels of simple homopolymers", J. Polym. Sci. Pol. Chem. Ed., Vol. 16, No. 4, p. 791, 1978.
[19] J. S. Hammond, J. W. Holubka, J. E. deVries, and R. A. Dickie, "The application of x-ray photo-electron spectroscopy to a study of interfacial composition in corrosion-induced paint de-adhesion", Corros. Sci., Vol. 21, Iss. 3, p. 239, 1981.
[20] F. C. Burns and J. D. Swalen, "X-ray photoelectron spectroscopy of cadmium arachidate monolayers on various metal surfaces", J. Phys. Chem., Vol. 86, Iss. 26, p. 5123, 1982.
[21] F. P. J. M. Kerkhof, J. A. Moulijn, and A. Heeres, "The XPS spectra of the metathesis catalyst tungsten oxide on silica gel", J. Electron Spectrosc., Vol. 14, Iss. 6, p. 453, 1978.