Vol. 31, No. 11 Journal of Semiconductors November 2010

Modeling and experimental research on a removal mechanism during chemical mechanical polishing at the molecular scale*

An Wei(安伟)†, Zhao Yongwu(赵永武), and Wang Yongguang(王永光)

(School of Mechanical Engineering, Jiangnan University, Wuxi 214122, China)

Abstract: In order to understand the fundamentals of the chemical mechanical polishing (CMP) material removal mechanism, the indentation depth of a slurry particle into a wafer surface is determined using the *in situ* nanomechanical testing system tribo-indenter by Hysitron. It was found that the removal mechanism in CMP is most probably a molecular scale removal theory. Furthermore, a comprehensive mathematical model was modified and used to pinpoint the effects of wafer/pad relative velocity, which has not been modeled previously. The predicted results based on the current model are shown to be consistent with the published experimental data. Results and analysis may lead to further understanding of the microscopic removal mechanism at the molecular scale in addition to its underlying theoretical foundation.

Key words: chemical mechanical polishing; model; molecular scale; experimental
DOI: 10.1088/1674-4926/31/11/116005 **EEACC:** 2550E; 2570

1. Introduction

Chemical mechanical polishing (CMP) has become a critical technology for future integrated circuit (IC) fabrication. At present, the material removal mechanism of CMP has not been clearly explained [1,2].

Several mechanisms of material removal in CMP have been attempted for many years to express the material removal. One of the most popular mechanisms in the CMP proposed by Kaufman[3] is indentation/scratching removal. This is described as a process of alternation of chemical formation and mechanical removal of the reaction species on the wafer surface. This proposed mechanism has gained wide support and is the foundation for the recent modeling of material removal in CMP[4,5]. However, some theoretical studies[6–8] reveal that the above envisioned mechanism of material removal has been questioned. As the knowledge of the CMP process and role of consumables has improved over the years, some subsequent work has investigated the material removal from a molecular scale perspective[9,10].

In the preceding paper[10], a mathematical model for the material removal rate (MRR) in CMP was presented based on a molecular scale removal mechanism. The comprehensive model qualitatively describes the above three different abrasive size-MRR trends clearly. However, the effect of wafer/pad relative velocity was not explored.

2. Molecular scale removal mechanism

In this article, the indentation depth of a slurry particle into the SiO_2 wafer surface was investigated using a nanomechanical testing system tribo-indenter (NTST) by Hysitron with a diamond round tip of diameter 150 nm, as illustrated in Fig. 1. Samples were cut from SiO_2 wafer. The wafer surfaces were prepared for study by placing them for 5 min in HCL (conc.) + H_2O_2 (40%) + $6H_2O$ to remove contaminants from the surface. The hardness of the SiO_2 wafer used in the current experiment is 7.91 GPa. The NTST indentation was done with a load force of *ca.* 0–100 μN at 20 ℃. These forces are higher than the estimated force (106 nN)[4,11] of a single particle in the CMP. Based on a linear regression mechanism, Figure 1 shows the indentation depth to be around 0.04 nm at the estimated force. Finally, it is pointed out that, in the CMP process, the wafer acts with the chemicals, leading to a chemical thin film on the wafer surface. However, during the short chemical reaction time, the thickness of the chemical film was on the atomic scale[8]. Even now, it is a tough job to obtain the hardness of the thin film[4,7]. Therefore, in this paper, the chemical effect was not considered. There are more open questions with the consideration of chemical thin film in the CMP process.

Depending on the result of Zhang's research[12] on the molecular dynamics simulation of diamond abrasive's penetration into the silicon wafer, if the relative indentation depth (indentation-depth/particle diameter) of a particle into a wafer

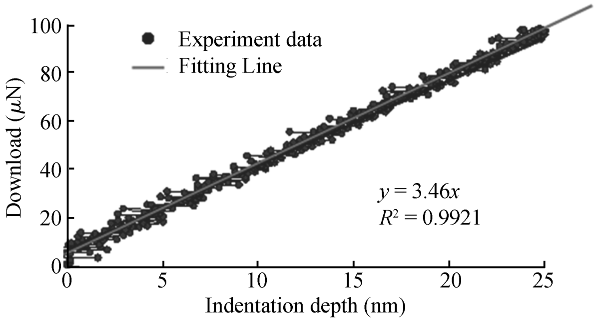

Fig. 1. Relationship between the indentation and the down load.

---

* Project supported by the National Natural Science Foundation of China (No. 51005102), the Natural Science Foundation of Jiangsu Province in China (No. BK2004020) and the Fundamental Research Funds for the Central Universities (No. JUSRP10909).

† Corresponding author. Email: anwei@jiangnan.edu.cn

Received 29 April 2010, revised manuscript received 2 July 2010

surface is smaller than 0.0075, the removal mechanism during the CMP process may be successfully explained by a molecular-scale removal mechanism. During the present experiment, the indenter tip is around 150 nm, and the indentation depth of the indenter into the wafer surface is estimated to be 0.22 nm by testing 10 different points on the wafer surface. Accordingly, the relative indentation depth is around 0.0015, which is smaller than the critical depth, 0.0075. Therefore, a conclusion can be drawn that, during the CMP process, the movement of the abrasives does not cause plowing but an atomic removal on the wafer surface.

Furthermore, the tip of an atomic force microscope (AFM) as an abrasive test apparatus to evaluate the scratch depth of a single slurry particle into the wafer surface was reported by Katsuki[13]. The experimental result shows that the scratch depth by a single abrasive particle on the SiO_2 wafer surface is around 0.042 nm at the normal contact load of 106 nN between the surface of the particle and the wafer. Several researchers[14, 15] also independently reported that few abrasive grooves are found in high quality polishing wafer surfaces. Accordingly, accompanied by this small scale of indentation/scratch depth as well as surface roughness, the removal mechanism in CMP is probably not a scratching/indentation mechanism but most likely a molecular scale removal theory. Moreover, the data gathered from the literature show that the decrease in the abrasive particle size from 2 μm to 10 nm leads to an enhancement of the MRR in CMP[4, 5, 11, 14]. This potentially allows the curtailment of the particle size to obtain higher polishing quality in practice during the CMP process. Nowadays, the abrasive particle size provided by Cabot Company is around 10 nm. With this decrease in particle size, the material removal mechanism may be more sensibly clarified by molecular scale theories.

3. Modeling

On the basis of a molecular scale removal mechanism, the MRR for CMP in the former paper is expressed as[10]

$$\mathrm{MRR} = \alpha \frac{V d_{\mathrm{m}} (3\sigma - d)\, d_{\mathrm{r}}}{1/\gamma + 1/\beta - 1} \frac{6 d_{\mathrm{s}} \rho_{\mathrm{s}} m_{\mathrm{s-a}}}{\pi \rho_{\mathrm{a}} D^3}, \tag{1}$$

where α is the real wafer/pad contact area ratio, V is the wafer/pad relative velocity, d_{m} is the average diameter of the molecule of the wafer surface material, σ is the standard deviation of the pad asperity height and d is the distance between the wafer and the mean plan of the pad asperity. The reference plan is assumed to pass through the mean of the asperity height distribution. d_{s} is the dilution ratio of the slurry, ρ_{s} is the density of the slurry before dilution, $m_{\mathrm{s-a}}$ is the concentration of the slurry before dilution, ρ_{a} is the density of the abrasive particles, D is the average diameter of the abrasive particles and d_{r} is the average contact diameter of the wafer with the particle.

β fraction of the unreacted surface sites in A that undergo the chemical reaction after the action of the first particle and before the action of the second;

γ fraction of the reacted surface sites in A that are converted (i.e. surface molecules removed) to the unreacted state during the action of the second slurry particle.

Given the first-order approximation of the chemical reaction, Zhao[8] proposed that the value of β is proportional to the concentration of the oxidizer C at the wafer surface. Thus,

$$\beta \propto C. \tag{2}$$

In addition, Zhao[8] reported that the ratio of the removal γ is a function of the mechanical removal energy E_{m} and the binding energy E_{r}, which can be expressed as

$$\gamma = f\left(\frac{E_{\mathrm{m}}}{E_{\mathrm{r}}}\right). \tag{3}$$

For simplicity, it is assumed that the value of γ is proportional to the mechanical removal energy and inversely proportional to the energy E_{r}. Therefore, $\gamma = k_1 E_{\mathrm{m}}/E_{\mathrm{r}}$, and k_1 is a constant parameter related to the mechanical removal.

The binding energy E_{r} plays a significant role in the removal rate and interacts strongly with chemical effects. Chemical reactions convert strongly bonded surface molecules to weakly bonded molecular species. The parameter defining the decrease in the binding energy due to the chemical reaction is k_2. In addition, as mentioned earlier, only some reacted molecules are partially removed by the slurry abrasive particles. Therefore, with the consideration of the effects of the chemical reaction on the wafer surface, the binding energy could be regarded as $(1 - k_2)\beta E_{\mathrm{r}}$. Then, Equation (3) can be rewritten as

$$\gamma = k_1 \frac{E_{\mathrm{m}}}{(1 - k_2)\, \beta E_{\mathrm{r}}}. \tag{4}$$

Substituting Eqs. (2) and (4) into Eq. (1) yields

$$\mathrm{MRR} \propto \frac{1}{\dfrac{C E_{\mathrm{r}} (1 - k_2)}{k_1 E_{\mathrm{m}}} + \dfrac{1}{C} - 1}. \tag{5}$$

Equation (5) indicates that the increase in the mechanical energy E_{m} leads to an increase in removal rate. The increase in the chemical value of k_2 results in a decrease in the binding energy, thus enhancing the removal rate.

In the preceding paper[16], the values of β and γ can be derived from it, and submitting the two variables into Eq. (1) allows it to be restated as

$$\mathrm{MRR} = \frac{V}{Y + V}, \tag{6}$$

where Y is a parameter that can be deduced from Ref. [16]. Other related values are constant, and the relationship between the MRR and the polishing speed V can be derived.

4. Results and discussion

4.1. Effect of the chemical oxidizer concentration

Defining $\lambda = (1 - k_2)/k_1$, the relation between the removal rate and the oxidizer concentration is shown in Fig. 2 as $E_{\mathrm{r}} = E_{\mathrm{m}}$. Figure 2 shows that the removal rate is rapidly raised at low concentration and approaches a constant at high concentration. An explanation of the predicted trend is shown below. At a low oxidizer concentration, the surface occupied by the reacted molecules is low and any addition of chemical oxidizer in the slurry enhances the fraction of the reacted surface, contributing to the increase in the polishing rate. At high concentration, the unreacted surface is effectively all reacted and the

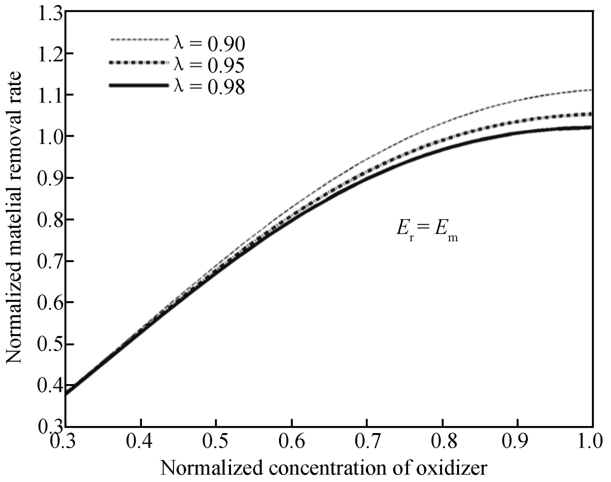

Fig. 2. Correlation between the concentration of oxidizer and the normalized removal rate.

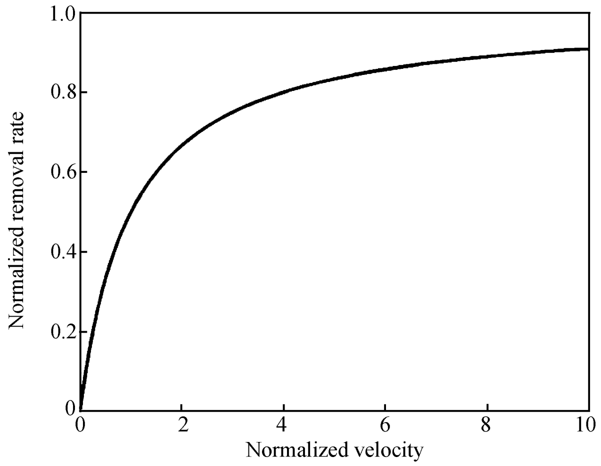

Fig. 4. Effect of normalized relative velocity on normalized MRR.

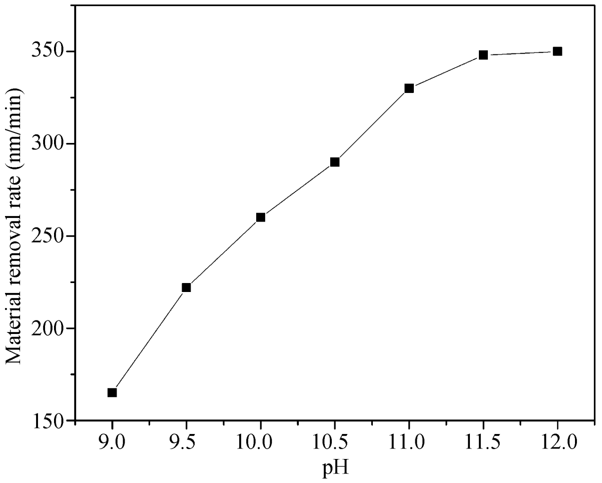

Fig. 3. Relation between pH and removal rate.

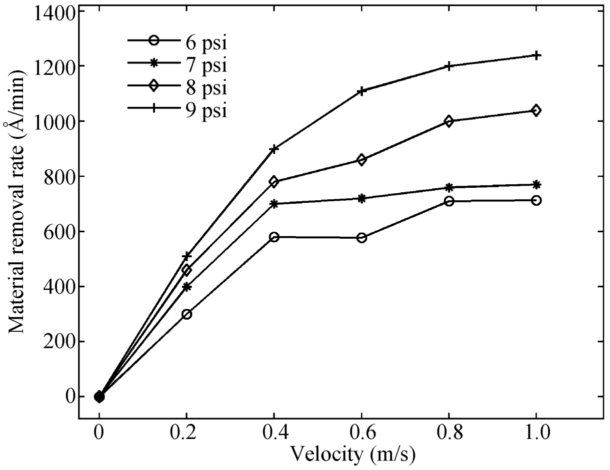

Fig. 5. Experimental data of the relation between the relative velocity and the removal rate.

increase in oxidizer concentration cannot find any more unreacted surface molecules to act upon. Furthermore, Figure 2 also shows that the removal rate falls with an increase in parameter λ. An interpretation of this phenomenon is that the mechanical parameter k_2 is reduced by an increase in the value of λ. In other words, the increase in the value of λ leads to a decrease in mechanical removal in CMP, contributing to the decrease in the MRR. Therefore, at constant oxidizer concentration, the polishing rate decreases due to the increase in the value of λ. Finally, it is pointed out that the qualitative comparison between the predicted results and the experiment data is based on the normalized method to predict the effective trends of oxidizer concentration on removal rate.

Experimental results of Tan[17] for the removal rate of a SiO_2 wafer using the organic oxidizer (NH_2RNH_2) in the slurry are shown in Fig. 3. The experiment was carried out at a pressure of 0.08 MPa with the pad and the wafer speeds of 60 rpm/min comprising the colloidal aluminum particles. Generally, the pH value is proportional to the oxidizer concentration of NH_2RNH_2. Therefore, Figure 3 reflects the qualitative relationship between the oxidizer concentration and the polishing rate. It is obvious that an initially rapid rise in the removal rate is followed by a slow approach to a constant rate with further increase in the NH_2RNH_2 concentration as the pH increases, which is in agreement with the model predictions.

4.2. Effect of velocity

Figure 4 shows that the MRR increases at the beginning and reaches stained and rough.

To verify the effect of the wafer/pad relative velocity on the removal rate, a wafer was put in a beaker with a Westech 372M CMP system for 150 mm wafers[18]. The head speed was 42 rpm, and the platen speed was varied from 10 to 50 rpm with variable pressures ranging from 4 to 9 psi. As shown in Fig. 5, the polishing rate increases rapidly at low velocity and approaches a constant at high velocity, which indicates that the variation in removal rate with polishing speed is non-Preston (nonlinear). Furthermore, the experimental results proposed by Forsberg[19] yield similar removal rate trends, which would most likely results from the limited chemical removal rate. This observation shows good agreement with the present model, as shown in Fig. 4. In other words, the current model exhibits a much better match with the experimental data shown in Fig. 5 than the original Preston equation.

5. Conclusion

In this study, the indentation depth of a slurry abrasive particle into wafer surface was evaluated by NTST to offer a fundamental understanding of a discrete removal mechanism at molecular scale during CMP. Based on this molecular-scale removal mechanism, a comprehensive mathematical model was modified and used to study the effects of the oxidizer and velocity on the removal rate. The model successfully fits the experimental data on polishing rates. Finally, the reasonable theoretical predictions appear to lend further evidence of the molecular scale removal mechanism of CMP.

References

[1] Evans C J, Paul E, Dornfeld D, et al. Material removal mechanisms in lapping and polishing. CIRP Annals-Manuf Technol, 2003, 52: 611

[2] Wang Y G, Zhao Y W, An W, et al. Modeling the effects of cohesive energy for single particle on the material removal in chemical mechanical polishing at atomic scale. Appl Surf Sci, 2007, 253: 9137

[3] Kaufman F B, Thompson D B, Broadie R E, et al. Chemical mechanical polishing for fabricating patterned W metal features as chip interconnects. J Electrochem Soc, 1991, 138: 3460

[4] Luo J F, Dornfeld D A. Material removal mechanism in chemical mechanical polishing: theory and modeling. IEEE Trans Semicond Manuf, 2001, 14: 112

[5] Jeng Y R, Huang P Y. A material removal rate model considering interfacial micro-contact wear behavior for chemical mechanical polishing. J Tribol, 2005, 127: 190

[6] Wang Y G, Zhao Y W. Research on the molecular scale material removal mechanism in chemical mechanical polishing. Chinese Sci Bull, 2008, 53: 2084

[7] Chang L. On the CMP material removal at the molecular scale. J Tribol, 2007, 129: 436

[8] Zhao Y W, Chang L, Kim S H. A mathematical model for chemical-mechanical polishing based on formation and removal of weakly bonded molecular species. Wear, 2003, 254: 332

[9] Paul E. CMP or M-C(P): the balance in chemical mechanical polishing. Electrochem Solid State Lett, 2007, 10: H213

[10] Wang Y G, Zhao Y W, Li X F. Modeling the effects of abrasive size, surface oxidizer concentration and binding energy on chemical mechanical polishing at molecular scale. Tribol Int, 2008, 41: 202

[11] Zhao Y W, Chang L. A micro-contact and wear model for chemical-mechanical polishing of silicon wafers. Wear, 2002, 252: 220

[12] Zhang L C, Tanaka H. Atomic scale deformation in silicon monocrystals induced by two-body and three-body contact sliding. Tribol Int, 1998, 31: 425

[13] Katsuki F, Watanabe J. The atomic scale removal mechanism during chemomechanical polishing of silicon: an atomic force microscopy study. In: Wahl K J, Huber N, Mann A B, et al. ed. Fundamentals of nanoindentation and nanotribology III, vol. 841. 2005: 253

[14] Bielmann M, Mahajan U, Singh R K. Effect of particle size during tungsten chemical mechanical polishing. Electrochem Solid State Lett, 1999, 2: 401

[15] Zhou C H, Shan L, Hight J R, et al. Influence of colloidal abrasive size on material removal rate and surface finish in SiO_2 chemical mechanical polishing. Tribol Trans, 2002, 45: 232

[16] Wang Y G, Zhao Y W, Jiang J Z, et al. Modeling effect of chemical-mechanical synergy on material removal at molecular scale in chemical mechanical polishing. Wear, 2008, 265: 721

[17] Tan B M, Yuan J Y, Niu X H, et al. Study on CMP slurry and technique of silicon dioxide dielectric for ULSI. Key Eng Mater, 2008, 373/374: 798

[18] Tseng W T, Wang Y L. Re-examination of pressure and speed dependences of removal rate during chemical-mechanical polishing processes. J Electrochem Soc, 1997, 144: L15

[19] Forsberg M. Effect of process parameters on material removal rate in chemical mechanical polishing of Si (100). Microelectron Eng, 2005, 77: 319