Research Article

Influence of the Molecular Adhesion Force on the Indentation Depth of a Particle into the Wafer Surface in the CMP Process

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By theoretical calculation, the external force on the particle conveyed by pad asperities and the molecular adhesion force between particle and wafer are compared and analyzed quantitatively. It is confirmed that the molecular adhesion force between particle and wafer has a great influence on the chemical mechanical polishing (CMP) material removal process. Considering the molecular adhesion force between particle and wafer, a more precise model for the indentation of a particle into the wafer surface is developed in this paper, and the new model is compared with the former model which neglected the molecular adhesion force. Through theoretical analyses, an approach and corresponding critical values are applied to estimate whether the molecular adhesion force in CMP can be neglected. These methods can improve the precision of the material removal model of CMP.

1. Introduction

During the course of chemical mechanical polishing (CMP) process and as the particle's diameter gets close to the nm scale and the particle's indentation depth into wafer's surface is around 0.01~1 nm, the attractive intermolecular forces acting at the particle/wafer interface and the external force applied on the particle may be close in magnitude. Ignoring the molecular forces will influence the accuracy of the model of CMP process and leads to errors. Therefore, in this paper in-depth study was conducted on the influential law of the molecular forces between particle and wafer surface on CMP process, and a more complete particle indentation depth model considering the effect of the molecular forces between particle and wafer surface is established. Several important modeling assumptions are as follows.

In the CMP process, the abrasive particles are in the liquid environment. According to DLVO theory [1], the molecular forces between particle and wafer surface are mainly the electric double-layer repulsion and van der Waals attraction; other intermolecular forces are smaller than them in the order of magnitude and therefore can be ignored.

DLVO theory also shows that double-layer repulsion is major, and van der Waals attraction can be ignored at large particle/wafer surface approaching distance. van der Waals attraction is dominant and electrical double-layer repulsion can be neglected, when the approaching distance is less than the critical value of 3 nm. In the CMP process, the indentation depth of particle into wafer surface is about 0.01~1 nm, so just van der Waals attraction is considered.

There will be molecular force between particle and polishing pad surface. Igor Sokolov found that in liquid environment the magnitude of the Hamaker constant of the particle/pad system is about 0.1×10^{-20} J, while the magnitude of the Hamaker constant of the particle/wafer system is about 1×10^{-20} J [2]. van der Waals attraction is proportional to Hamaker constant, so the van der Waals attraction between particle and wafer is ten times the magnitude of that between particle and pad. Hence, the van der Waals attraction between particle and pad can be neglected [3].

It is assumed that the particle and wafer surface is completely smooth; therefore, the molecular force between the particle and the asperities of wafer surface is negligible.

FIGURE 1: Schematic of pad/wafer/particle three-body contact.

2. Applied Forces Exerted on a Particle

2.1. Force Balance Equation of a Particle. In the CMP process, the abrasive particle is pressed into the contact area of pad/wafer under the external force, which forms a three-body contact. Pad is so soft that after wafer is pressed to contact pad asperities, pad asperities will wrap abrasive particles. In this case, the work pressure p is sustained by the pad asperities and the abrasive particle together [4]. The schematic diagram of a three-body contact of pad/wafer/particle is shown in Figure 1.

The applied forces exerted on abrasive particle include the external force F_Z conveyed by pad asperities, antiforce F_h by wafer surface, the molecular adhesion force F_a between particle and wafer surface, and abrasive particle gravity. As the abrasive particle diameter is in nanometer scale, taking Al_2O_3 abrasive whose density is larger in CMP as an example to calculate its gravity gives 1.88×10^{-9} nN, while the magnitude of the external force acting on abrasive particle generally can reach tens to hundreds of nN [5], and the abrasive gravity can be ignored. Small deformation takes place in the contact area between wafer surface and particle, as its indentation depth into wafer surface δ_w is far less than the particle diameter D ; the whole process is considered as a completely plastic deformation [4], and the total plastic contact stress between wafer and particle, that is, antiforce by wafer surface F_h , is given as

$$F_h = H_w \pi D \delta_w. \quad (1)$$

When a particle is in equilibrium state, the force balance equation is shown as follows:

$$F_h = F_Z + F_a. \quad (2)$$

The schematic diagram of the force applied on the particle is shown in Figure 2.

2.2. External Force F_Z . Fu and Chandra used a creative equivalent beam bending model to calculate the external force F_Z conveyed by pad asperities to particle during CMP [10]. In his model, the particles are assumed to be distributed uniformly in the contact area between pad and wafer and

FIGURE 2: Applied forces on the particle.

the part of the pad between two particles is reduced to a fixed-fixed bending beam. According to beam theory of mechanics of materials, F_Z can be expressed as

$$F_Z = \left(\frac{4^5}{3^3} \right)^{1/4} \left[E_p t_p^3 \frac{D}{2} \left(\frac{A_r}{N} \right)^2 p^3 \right]^{1/4}, \quad (3)$$

where E_p is Young's modulus of pad, t_p is the equivalent beam thickness, A_r is the effect contact areas between pad and wafer, and N is the number of effective particles embedded into the contact areas between pad and wafer.

According to Zhao and Chang [4], the number of effective particles embedded into the contact areas between pad and wafer N can be calculated by

$$N = A_r \left(\frac{6\chi}{\pi D^3} \right)^{2/3} = A_r \left(\frac{6C_a \rho_f}{\pi D^3 \rho_s} \right)^{2/3}, \quad (4)$$

where χ is abrasive particle volume concentration, C_a is abrasive particle mass concentration, ρ_f is slurry density, and ρ_s is abrasive particle density.

Factors affecting the thickness of equivalent beam t_p include particle diameter D , Young's modulus of pad E_p , and the working pressure p . Based on the theory of dimensionless unit analysis of the four variables, we have

$$\left(\frac{t_p}{D} \right)^{3/4} = k_2 \left(\frac{E_p}{p} \right)^{k_1}, \quad (5)$$

where k_2, k_1 are dimensionless constants.

Substituting (4), (5) into (3), we obtain

$$F_Z = \left(\frac{4^5}{3^3} \right)^{1/4} k_2 (E_p)^{1/4} \left(\frac{E_p}{p} \right)^{k_1} (p)^{3/4} D^2 \left(\frac{6C_a \rho_f}{\pi \rho_s} \right)^{-1/3}. \quad (6)$$

According to Qin's analysis [11], in the range of the working pressure p in a typical CMP, the average stress of the actual contact area between pad and wafer p_r approximately changes very slowly with the increase of the working pressure p . It is reasonable to assume that, with a wafer being pressed onto a polishing pad, p_r is independent of p , the increment of which is determined by the increase of abrasive particles being embedded into the contact area between pad asperities

FIGURE 3: Schematic of adhesion between a particle and a surface.

and wafer. Therefore, p_r can be considered as a constant. As a single particle is concerned, the applied force of pad on it F_Z keeps unchanged, so the indentation depth of the particle into the wafer δ_w is unchanged. This point of view is substantiated by Zhao and Chang [4], Qin et al. [11], and Jeng and Huang [12]. If the working pressure p does not affect the indentation depth δ_w , we can obtain $k_1 = 3/4$ in (6). And then rearranging (6) yields

$$F_Z = 2.48k_2 E_p D^2 \left(\frac{6C_a \rho_f}{\pi \rho_s} \right)^{-1/3}. \quad (7)$$

In (7) k_2 is a dimensionless constant and has no relation to a variety of the pad/wafer/particle and operating parameters during the course of CMP. Based on the study of Qin et al. [11] and Jiang et al. [9], k_2 is 0.078 in a typical CMP, so (7) is rearranged to (8). Equation (8) can be applied to every case of CMP:

$$F_Z = 0.19 E_p D^2 \left(\frac{6C_a \rho_f}{\pi \rho_s} \right)^{-1/3}. \quad (8)$$

2.3. Molecular Adhesion Force between Particle and Wafer F_a . As shown in Figure 3, during the course of a particle approaching a surface, when the approaching distance Z_0 is less than 3 nm, the van der Waals attraction between the particle and the surface is dominant. When the approaching distance is Z_0 , the van der Waals attraction F_0 between a particle with the diameter of D and a plane can be expressed as [3]

$$F_0 = \frac{AD}{12Z_0^2}, \quad (9)$$

where A is the Hamaker constant of the adhesion system.

An expression of the molecular adhesion force F_a between a particle and a plane is given by Bowling [13] as

$$F_a = \frac{AD}{12Z_0^2} \left(1 + \frac{2a^2}{DZ_0} \right), \quad (10)$$

where R is the diameter of the particle and a is the contact radius between particle and plane, as shown in Figure 4.

The geometric relationship equation in Figure 4 is given as

$$a^2 = \left(\frac{D}{2} \right)^2 - \left(\left(\frac{D}{2} \right) - \delta_w \right)^2 = D\delta_w - \delta_w^2. \quad (11)$$

FIGURE 4: Adhesion force considering particle deformation.

TABLE 1: Hamaker constant of Cu-Water- Al_2O_3 .

Materials	Water	Vacuum	Unit	Reference
Copper	30	40	10^{-20} J	[6]
Water	—	4.0	10^{-20} J	[6]
Al_2O_3	4.44	16.75	10^{-20} J	[6]
Polyurethane-water-silicon nitride		0.1–1	10^{-20} J	[6]

Substituting (11) into (10) gives

$$F_a = \frac{AD}{12Z_0^2} \left(1 + \frac{2(D\delta_w - \delta_w^2)}{DZ_0} \right). \quad (12)$$

Because the indentation depth of a particle into wafer surface δ_w is far less than the particle diameter D , (12) can be reduced as

$$F_a = \frac{AD}{12Z_0^2} \left(1 + \frac{2\delta_w}{Z_0} \right). \quad (13)$$

Assuming the particle and the wafer surface are completely smooth, Z_0 can be taken as 0.4 nm [14]. A is the Hamaker constant related to the material properties of the adhesion system of the particle/polishing slurry/wafer system, and the formula is shown as (14) to calculate the Hamaker constant of a three-component adhesion system [6]:

$$A = \left(\sqrt{A_{11} - A_{33}} \right) \left(\sqrt{A_{22} - A_{33}} \right), \quad (14)$$

where A_{11} is the Hamaker constant for a particle in a vacuum environment, A_{22} is the Hamaker constant for wafer in a vacuum environment, and A_{33} is the Hamaker constant for polishing slurry in a vacuum environment. As the abrasive particle and oxidant concentration in the slurry are not high, polishing slurry of CMP usually can be approximated as the water. The Hamaker constants of Cu-Water- Al_2O_3 system are listed in Table 1.

2.4. Comparison of F_Z and F_a . To further study the relationship between the external forces on a single particle F_Z by pad

TABLE 2: Parameters calculating forces between wafer and abrasive.

Parameter	Value	Reference
Young's modulus of wafer E_W (MPa)	130000	[5]
Poisson's ratio of wafer ν_W	0.26	[5]
Wafer surface hardness H_W (MPa)	5000	[7]
Young's modulus of particle E_S (MPa)	310000	[4]
Poisson's ratio of particle ν_S	0.26	[4]
Particle density ρ_s (kg/m ³)	3600	[4]
Young's modulus of pad E_P (MPa)	10	[8]
Poisson's ratio of pad ν_P	0.5	[8]
Mass concentration of particles C_a	0.034	[9]
Slurry density ρ_f (kg/m ³)	1000	[9]
Particle diameter D (nm)	200	[9]

FIGURE 5: Comparison of F_Z and F_a ($E_P = 10$ MPa, $\delta_W = 1$ nm).

and the molecular adhesion force between particle and wafer F_a , an example is used by theoretical calculation to compare F_Z and F_a that assumes an Al_2O_3 abrasive is pressed into the surface of Cu wafer. The Hamaker constant of Cu-Water- Al_2O_3 system is calculated as 9×10^{-20} J by (13), the indentation depth δ_W is taken as 1 nm, and other parameters are listed in Table 2.

Using (8), (13) to calculate the external forces on a single particle F_Z by pad and the molecular adhesion force between particle and wafer F_a , the results are shown in Figure 5.

As shown in Figure 5, the critical value when the external force F_Z is equal to the molecular adhesion force F_a is 33 nm. When the particle diameter is less than the critical value, F_Z is less than F_a . When the particle diameter is greater than the critical value, F_Z is greater than F_a , and, along with increase of the particle diameter, the increasing extent of F_Z is greater than that of F_a . The above analysis shows that when the particle diameter is small, the molecular adhesion force F_a may be greater than or close to the external force applied on a single particle F_Z . Therefore, CMP models ignoring the molecular adhesion force between particle and wafer will bring about

large errors. Only when the particle diameter is large enough and the external force F_Z is much greater than the molecular adhesion force F_a , F_a can be ignored. The critical values used to judge whether the molecular adhesion force in CMP can be neglected or not are related to Young's modulus of polishing pad, particle diameter, particle indentation depth, and particle volume concentration. In order to find the critical values, further study is needed.

3. Particle Indentation Depth considering the Molecular Adhesion Force

Substituting (1), (8), and (13) into (2) gives the specific force balance equation of the particle shown as

$$k_a E_P D + \frac{A}{12Z_0^2} \left(1 + \frac{2\delta_W}{Z_0}\right) = H_W \pi \delta_W. \quad (15)$$

In (15), a dimensionless parameter k_a is defined as

$$k_a = 0.19 \left(\frac{6C_a \rho_f}{\pi \rho_s} \right)^{-1/3}. \quad (16)$$

From (15), we have

$$\frac{\delta_W}{D} = \frac{(k_a E_P / H_W) + (A / 12Z_0^2 H_W D)}{\pi + (A / 6Z_0^3 H_W)}. \quad (17)$$

Two dimensionless parameters are defined as

$$\Pi_1 = \frac{A}{6Z_0^3 H_W}, \quad (18)$$

$$\Pi_2 = \frac{A}{12Z_0^2 H_W D}.$$

If the Π_1 , Π_2 items are ignored in (17), the particle indentation depth without considering the molecular adhesion force between particle and wafer surface can be expressed as

$$\frac{\delta_W}{D} = \frac{k_a E_P}{\pi H_W}. \quad (19)$$

The result of calculating by using (17), (19) is shown in Figure 6. Relative parameters are taken as follows: $E_P = 10$ MPa, $C_a = 0.01$, and the rest are listed in Table 2. In accordance with the analysis of Figure 6, when the particle diameter D is equal to 25 nm or so, the relative particle indentation depths calculated by (17), (19) are equal; when D is less than 25 nm, the relative particle indentation depth considering the molecular adhesion force is greater than that ignoring the molecular adhesion force, and with the decrease of the particle diameter, their deviation will increase; when D is greater than 25 nm they are in small deviation and can be seen as equal. Therefore, in case of large particle diameter, the influence of the molecular adhesion force between particle and wafer on the indentation depth δ_W of particle into wafer is negligible. From the analysis of (17), the critical values used to judge whether the molecular adhesion force in CMP can be neglected or not still have relation with the Hamaker constant of CMP system, the approaching distance between particle and wafer surface, and wafer surface hardness.

FIGURE 6: Comparison of relative indentation depth of abrasive particle.

4. Two Dimensionless Judicial Criteria

According to (17), when assuming $\Pi_1 < 0.1\pi$, $\Pi_2 < 0.1k_a E_p / H_w$; that is,

$$\frac{A}{Z_0^3 H_w} < 0.6\pi, \quad (20)$$

$$\frac{A (6C_a \rho_f / \pi \rho_s)^{1/3}}{E_p Z_0^2 D} < 0.231.$$

The Π_1 , Π_2 items in (17) can be neglected; that is, the influence of the molecular adhesion force between particle and wafer on the indentation depth δ_w of particle into wafer is negligible.

Substituting the Hamaker constant $A = 9 \times 10^{-20}$ J, the approaching distance $Z_0 = 0.4$ nm, into (20) gives

$$H_w > 746 \text{ MPa}, \quad (21)$$

$$\frac{E_p D}{(6C_a \rho_f / \pi \rho_s)^{1/3}} > 2.435. \quad (22)$$

From the above analysis, when a CMP system is under the condition shown in (21), (22), the molecular adhesion force between particle and wafer can be ignored. Substituting the parameters in a typical CMP $E_p = 10$ MPa, $C_a = 0.034$, $D = 200$ nm, $\rho_s = 3600$ kg/m³, and $\rho_f = 1000$ kg/m³ into (22) gives

$$\frac{E_p D}{(6C_a \rho_f / \pi \rho_s)^{1/3}} = 7.626 > 2.435. \quad (23)$$

What is more, $H_w = 500$ MPa < 746 MPa. Hence, Π_2 item can be neglected while Π_1 item cannot be neglected during

the course of this CMP. And then the relative indentation depth of the Cu-water-Al₂O₃ system can be simplified as

$$\frac{\delta_w}{D} = \frac{k_a E_p / H_w}{\pi + (A / 6Z_0^3 H_w)}. \quad (24)$$

From the above analysis, (20) are the two dimensionless judicial criteria that determine whether the influence of the molecular adhesion force between particle and wafer on the indentation depth δ_w of particle into wafer can be neglected or not. The two judicial criteria can apply to all CMP processes. It can be seen from these two criteria that the greater the wafer surface hardness H_w , the Young modulus of pad E_p , and the particle diameter D , the lower the particle concentration and the greater the possibility of neglecting the influence of the molecular adhesion force. It is by the inverse calculations indicated that, in typical metal CMP processes, if we take $E_p = 10$ MPa, $C_a = 0.034$, $\rho_s = 3600$ kg/m³, and $\rho_f = 1000$ kg/m³, average surface hardness of pure metal is generally less than 746 MPa, so Π_1 item cannot be ignored; when the particle diameter D is greater than 64 nm, Π_2 item can be neglected. For a typical nonmetallic oxide CMP processes, under the same conditions, the nonmetallic oxide surface hardness is generally greater than 746 MPa, so Π_1 item can be neglected; when the particle diameter D is greater than 64 nm, Π_2 item can be neglected.

5. Conclusions

By considering the influence of the molecular adhesion force between particle and wafer on the indentation depth δ_w of particle into wafer, the force equilibrium equation of a particle in wafer/particle/pad CMP system is established, and the external force on the particle conveyed by pad asperities and the molecular adhesion force between particle and wafer are compared and analyzed by quantitative calculation. The two dimensionless judicial criteria that determine whether the influence of the molecular adhesion force between particle and wafer on the CMP process can be neglected are deduced through theoretical deduction. They can be applicable to every CMP system, which are important to construct mechanical model of CMP. According to the two criteria, the greater the wafer surface hardness H_w , the Young modulus of pad E_p , and the particle diameter D , the lower the particle concentration and the greater the possibility of neglecting the influence of the molecular adhesion force.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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