Polishing behavior of PS/SiO$_2$ Core-Shell nanoparticles with different shell thickness on fused silica Chemical Mechanical Polishing

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Abstract. The core-shell PS/SiO$_2$ composite nanoparticles as abrasives with different shell thickness was researched in fused silica chemical mechanical polishing (CMP) for the first time. The polystyrene nanoparticles were prepared by using emulsifier-free polymerization method first, then the PS/SiO$_2$ with different shell thickness were synthesized by modified Stöber method. The morphologies of PS/SiO$_2$ monodisperse nanospheres were characterized with scanning electron microscopy (SEM). The elastic moduli of single nanoparticle was measured by atomic force microscopy (AFM). The CMP results indicated that the material remove rate (MRR) has been obviously improved with as-prepared nanospheres (21 $-$ 31 nm/min). There was a trend that MRR is rising when the shell thickness is between 200 and 50nm and then falling when the shell thickness is 35nm. Based on the small deformation theory, the finite element analysis was used to simulate the indentation depth and radius of the contact area between the individual particle and the wafer. Then a reasonable explanation for the experimental results was put forward. This research pave a way for realizing the optimization of CMP and material precise removal in the future.

1. Introduction
Recently, the core/shell structured nanoparticles has been drawing more and more attention due to their special properties. These nanocomposites exhibit many excellent properties like catalytic, ferromagnetic and suitable elasticity[1-3]. Because there are two or three materials to synthesis the nanoparticles, the properties of them can be modified by changing the components or structure. Thus the nanoparticles can be used in many fields such as biological, medicine, surface engineering and microelectronic industry[4-6]. For example, Torchilin et al. prepared a SiO$_2$ shell nanospheres which showed excellent biocompatibility[7]. Zhang et al. synthesized a new electromagnetic interference (EMI) shielding material with PS/TGO/Fe$_3$O$_4$ and they found the as-prepared material have much higher electrical conductivity compared with other materials[8].

As for the field of chemical mechanical polishing (CMP), composite nanoparticles have attracted more and more attention. As we known, there is a growing trend in the performance of CMP including small roughness, excellent surface quality, minimizing defects, high material removal and so on. Single particle has been no longer able to meet all of these requirements. So there have been many researchers were studying on the core/shell structured nanoparticles like CeO$_2$/PS, SiO$_2$/PS and so on. And it can be obtained different properties of particles through changing the materials of core or
shell[9-11]. Zhang et al. synthesized ceria-coated silica spheres by using ammonium cerium nitrate and urea as precipitant and the its polishing behavior on glass substrates showed that the MRR increased while the surface quality did not deteriorate[10]. Lee et al. synthesized CeO$_2$-coated silica spherical particles and the performance in the CMP showed that these novel spherical particles possessed a higher MRR compared with traditional pure CeO$_2$ and SiO$_2$ nanoparticles[11]. Chen et al. prepared PS/SiO$_2$ core/shell structured microparticles with diameters with different silica shell morphology (composite-A/composite-B) by using a modified Stöber method. The polishing results showed it can be obtained a lower root mean square roughness and higher material remove rate with these particles[12]. Chen et al. synthesized PS/CeO$_2$ composite abrasives by in situ decomposition reaction. The CMP performance on SiO$_2$ film layer with the as-prepared composite abrasives indicated that the core/shell structured nanospheres can enhance the oxide CMP performance. In addition, the shell thickness has a great influence on the oxide CMP performance[13].

Although, many researches have focused on the fabrication of core/shell structured nanospheres and their CMP performance, the application of core/shell structured nanospheres with different shell thickness for the polishing of fused silica (FS) has not yet been tried. At present, the common method for FS polishing is applying single commercial silica sol, but the MRR is low, about 20-80 nm/min[14]. During our research, we synthesized silica-coated core/shell structured polystyrene nanoparticles with different silica shell thickness and the Young’s moduli of these nanospheres were characterized with AFM. The polishing result of FS indicated that as-prepared nanospheres can obviously improve the MRR and shell thickness has significant influence on it. The contact state between the abrasives and polishing pad is different since these kinds of abrasives have different size. We used the finite element analysis to analyze the contact state and the result not only explains the experimental results well, but also provides some theoretical basis for polishing mechanism of abrasives with different shell thickness.

2. Experiment

2.1. Synthesis of the PS/SiO$_2$ composite nanospheres

**Materials:** All the original materials are obtained from Sinopharm Chemical Reagent Co., Ltd., China, including the styrene (St, ≥99.0%), potassium persulfate (KPS, ≥99.5%), ammonium hydroxide (NH$_3$·H$_2$O, 25%−28%), ethanol (≥99.7%), sodium dodecyl sulfate (SDS, 98%) and tetraethoxysilane (TEOS, 28.0%). It is better to distill the styrene (St) under the continuously reducing pressure condition before using. The wafer was a 2 inch fused silica with a 0.3 ± 0.05 nm original roughness approximately.

**Sample Preparation:** The emulsifier-free polymerization method was used to synthesize the PS nanospheres[15]. 25ml styrene and 0.1g KPS were dissolved into 200ml deionized water and mixed it with magnetic stirring for 5 minutes. 0.125g KPS was dissolved into 50ml deionized water. Both two homogeneous solution were transferred into a 250ml, three-necked flask and placed it in oil bath at 80°C. The mechanical stirring rotation speed was set at 300r/min. The dispersed PS nanoparticles were obtained after 12 hours of reaction. We used the ethanol to wash the samples with centrifugation and the rotation speed was 4000r/min, 3000r/min and 2000r/min respectively. Then, we used the modified Stöber method to synthesis the PS/SiO$_2$ core/shell nanoparticles. The specific steps are as follows: we poured the ethanol (50ml) and NH$_3$·H$_2$O (50ml) into a 250ml, three-necked flask mixed with the dispersed PS nanoparticles (5.5g). And placed the three-necked flask in oil bath at 40°C. A certain amount (1g, 2g, 4g, 6g, 8g) of TEOS mixed with ethanol (80ml) was poured into a buret (125ml). The mechanical stirring rotation speed was set at 300r/min. We control the flow rate of the buret at 0.5drop/s and purchase the PS/SiO$_2$ after 8h. The composite nanoparticles were washed by ethanol and deionized water three times respectively and were transferred into oven. White solid powder was obtained after 6h.
Slurry Preparation: The composite nanoparticles with different diameters were prepared as slurry for FS CMP. 20g white solid powder was put into a beaker (250ml) mixed with deionized water (200ml) and the pH was adjusted to 10.0 approximately.

2.2. CMP tests

The polishing experiment: The polishing testing was achieved through 1000S polishing machine (China Shenyang Science and Technology Instrument Co., Ltd) with a polyurethane polishing pad[16]. A 2 inch fused silica wafer was used and the experiment parameters as Table 1; The specimens were ultrasonic washed by ethanol for three times and dried by air spray gun after polishing. The MRR was calculated by mass loss as Eq. (1)[14]

\[
MRR = \frac{\Delta m}{\rho \pi r^2 t} = \frac{m_2 - m_1}{\rho \pi r^2 t}
\]

where

- \( m_1/m_2 \) — the mass of FS before polishing and after, mg;
- \( \rho \) — the density of FS, g/cm³ (2.2g/cm³);
- \( r \) — the radius of FS, cm (3.33cm);
- \( t \) — the polishing time, min (20minutes);

The mass of FS was the average value of FS by measuring three times with professional electronic balance (OHAUS DISCOVERY), its resolution is 0.0001g.

Table 1. Parameters of Polishing Process.

| Parameters                  | Value  |
|-----------------------------|--------|
| Downward pressure           | 6.2 kPa|
| Slurry supplying rate       | 10 ml/min |
| Work piece rotating speed   | 50 rpm |
| Down plate rotating speed   | 150 rpm |

3. Results and discussion

3.1. PS/SiO\(_2\) composite nanoparticles

The morphologies and sizes of PS and PS/SiO\(_2\) composite nanoparticles were investigated by SEM (FEI Quanta 200FEG, Holland) and the results was shown in Fig.1. The elastic modulus analysis of PS/SiO\(_2\) composite nanoparticles was carried out by atomic force microscopy (AFM, Bruker).

As shown in Fig.1(a), it was obvious to see that there was clear border between the PS nanoparticles in SEM of samples. The particles size distribution is uniform and the particles size were 300nm approximately. We also have prepared several kinds of composite nanoparticles PS/SiO\(_2\) core-shell structure with different shell thicknesses, as shown in Fig.1(b) to Fig.1(f), with the shell thickness of 35nm, 50nm, 80nm, 150nm and 200nm, respectively. The surface of the composite nanoparticles formed by silica coating was also relatively smooth and there was not obvious aggregation between particles.
3.2. CMP performance

Fig. 2 shows the polishing performance with as-prepared composite nanoparticles. The blue line represents the surface roughness of the FS after being polished by composite abrasives with different shell thickness. It can be seen that as the thickness of the shell layer decreases, in other words, as the particle size decreases, the surface quality gradually becomes better. The red line represents the polishing removal rate of the particles with different shell thicknesses. As the thickness of the shell layer gradually decreases, the polishing rate shows an upward trend, and an inflection point occurs when the thickness of the shell layer is 50 nm. The removal rate of the particles with 35 nm shell thickness begins to decrease.

In order to explain why the material removal rate would show such a trend, finite element analysis was used to simulate the contact state of the individual particle on fused silica to calculate the removal rate of individual particle. There are two key points here:

1) Nanospheres with different shell thickness have different elastic moduli;

2) The premise of replacing the polishing effect of the slurry with the material removal rate of the individual nanosphere is that the number of polishing nanospheres in the slurry is sufficient. In other words, the nanospheres can cover the entire polishing pad. Then we can eliminate the influence of the number of abrasives on the material removal rate.
3.3. Measurement of Elastic moduli of PS/SiO$_2$

The principle of measuring the elastic modulus according to the force-distance curves of AFM has been already explained in some literatures[17-20]. There also have been several theoretical models, such as Hertz model, Sneddon model and JKR model were used to calculate the elastic modulus of nanoparticles. Chizhik et al. used the scanning force microscopy to compare Hertz model and JKR model. And the results showed that there was more stable and precise value with Hertz model when the indentation depth was less than 200nm[21]. Cao et al. has proved that JKR model is more precise to calculate the elastic modulus of the composite nanospheres considering the adhesion force[15]. They calculated the elastic moduli of the nanospheres according to the Hertz theory because there was not obvious adhesion process in force-distance curves. At the same time, the error caused by not thinking about the adhesion force can be acceptable. The parameters of the probe used here were showed in Table 2. According to Hertz contact theory, a circular contact area will be created on the interface between nanosphere and substrate when they contact. The radius of circular area $a$ and indentation depth $\delta$ can be calculated by the following equations[22]:

\[
 a = \left( \frac{3RF}{4E'} \right)^{\frac{1}{3}}
\]

(2)

\[
 \delta = \frac{a^2}{R'} = \left( \frac{9F^2}{16R'E'^2} \right)^{\frac{1}{3}}
\]

(3)

And:

\[
 \frac{1}{R'} = \frac{1}{R_1} + \frac{1}{R_2}
\]

(4)

\[
 \frac{1}{E'} = \frac{1}{E_1} + \frac{1}{E_2}
\]

(5)

Where $R'$ and $E'$ are the relative radius of curvature and combined Young’s moduli of the two materials, respectively. $F$ is the applied load, $E$ is the Young’s moduli, $R$ is the radius, $\tau$ is the Possion ratio, and the subscripts 1 and 2 represent the probe and the nanospheres, respectively.

According to the above simultaneous equations, the elastic moduli of the composite nanoparticles $E_2$ can be obtained:
\[ E_z = \frac{3F \left(1 - \tau_z^2\right)}{4\delta^2} \left(\frac{R_1 + R_2}{R_1 R_2}\right)^{\frac{1}{2}} \]  

(6)

The parameters of the materials can be searched from the literatures: the Young’s moduli of the probe is 1141 GPa, and \( r_1 = 0.07 \)[23]. And the Possion ratios of the \( \text{SiO}_2 \) and PS are 0.19 and 0.33, respectively [24].

The results are showed in Fig.3. From the results, we can see that the elastic moduli of the composite nanospheres is rising gradually with the increasing of the shell thickness.

Table 2. Parameter Value of Probe.

| Probe type     | DT-NCHR-10 |
|----------------|-------------|
| Resonance frequency | 404 kHz    |
| Spring constant      | 62.4 nm\(^{-1}\) |
| Tip radius          | 87 nm      |
| Tip material        | Diamond-coated silicon |

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Figure 3. The elastic moduli of PS/ \( \text{SiO}_2 \) composites nanoparticles with different shell thickness.

3.4. Sum nanospheres in slurry

Fig.4 showed the cross-sectional state of polishing pad (\( r = 12 \)cm). We can see that as-used PU polishing pad was flat with no obvious peak shape. The area \( S \) of the pad which can carried nanoparticles can be approximately assumed be as the following equation:

\[ S = \pi r^2 \]  

(7)

At the same time, the maximum cross-sectional area \( A \) of nanospheres can also be obtained. Further, the number of nanospheres \( n \) required to fill the entire polishing pad side by side can be calculated:

\[ n = \frac{S}{A} \]  

(8)

And the number of nanospheres in slurry \( w \) can be calculated as following equation:
\[ w = \frac{M}{m} \]  

Where \( M \) is the overall mass (20g) of the nanospheres in slurry, \( m \) denote the mass of single nanoparticle. The results showed in Table 3. We can draw a conclusion that the number of composite nanospheres in slurry is a negligible factor.

3.5. Finite element analysis

According to small deformation contact theory, the contact state can be characterized by the indentation depth and the radius of contact area when a single spherical particle contact with planar fused silica. Therefore, Ansys software was used to simulate contact state of the PS/SiO\(_2\) nanoparticles with different shell thicknesses on fused silica. And the simulation results was showed as follows:

### Table 4. Indentation Depth and Contact Radius of Particles.

| Shell thickness | Elastic moduli | radius of contact area( \( a \) ) | indentation depth( \( \delta \) ) |
|-----------------|---------------|-----------------------------------|-------------------------------|
| 200nm           | 50GPa         | 10.48nm                           | 0.1395nm                      |
| 150nm           | 43GPa         | 10.45nm                           | 0.1439nm                      |
| 80nm            | 30GPa         | 9.988nm                           | 0.1472nm                      |
| 50nm            | 20GPa         | 10.48nm                           | 0.1422nm                      |
| 35nm            | 12GPa         | 10.97nm                           | 0.1228nm                      |
So we can calculate the radius of contact area and the indentation depth and further more the material remove rate of single nanospheres can be deduced by the following equation:

\[ \text{MRR} = a \delta U \]  \hspace{1cm} (10)

Where \( U \) represent the mean line speed of polishing pad. Since we only need to compare the relative size relationships, we need not to assign specific values. And the result is showed in Fig. 5. Compared with Fig. 2 we can find that there is a very good agreement with the actual polishing results.

![Figure 5. Calculation results simulated by finite element software.](image)

As for the surface roughness, it is easily to explain such a changing trend. As the size and elastic moduli of the nanospheres decrease, the damage of surface of wafer caused by abrasive particles is reduced gradually. It is worth noting that there is an inflection point at the PS nanoparticles. The reason is that PS has no polishing ability because PS is not have enough elastic moduli. It means that the surface quality after polished by PS nanoparticles in Fig. 2 is the original surface quality of fused silica. And the original surface quality of each fused silica is different. The original surface quality of fused silica polished by PS nanospheres is relatively coarser than previous sets of result. So this inflection point does not mean that the surface of fused silica was getting worse polished by PS nanospheres.
4. Conclusions
This work is first to apply PS/SiO$_2$ core/shell structured nanospheres with different shell thickness for CMP of FS. The composite nanospheres were synthesized via two-steps process: synthesis of PS through emulsifier-free polymerization method and the process of coating SiO$_2$ via a modified Stöber method. And the performance of polishing indicate that the MRR is first rising and then falling with decreasing of shell thickness. But the surface roughness is getting better. And the finite element analysis results have a good fit with the experimental results.

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