Polydisperse spherical colloidal silica particles: Preparation and application*

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A new industrial method has been developed to produce polydisperse spherical colloidal silica particles with a very broad particle size, ranging from 20–95 nm. The process uses a reactor in which the original seed solution is heated to 100 °C, and then active silicic acid and the seed solution are titrated to the reactor continuously with a constant rate. The original seeds and the titrated seeds in the reactor will go through different particle growth cycles to form different particle sizes. Both the particles' size distribution and morphology have been characterized by dynamic light scattering (DLS) and the focus ion beam (FIB) system. In addition, the as-prepared polydisperse colloidal silica particle in the application of sapphire wafer's chemical mechanical polishing (CMP) process has been tested. The material removal rate (MRR) of this kind of abrasive has been tested and verified to be much faster than traditional monodisperse silica particles. Finally, the mechanism of sapphire CMP process by this kind of polydisperse silica particles has been investigated to explore the reasons for the high polishing rate.

Keywords: colloidal silica, polydisperse, chemical mechanical polishing, sapphire wafer

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1. Introduction

Colloidal silica as inorganic nano-materials have been applied in many industrial fields for centuries; e.g., as catalyst carrier, anti-slip agent for floor wax, stiffener for hard coating reagent, and especially as abrasive particles for chemical mechanical polishing (CMP) slurries in recent decades.[1] Colloidal silica can be prepared by various methods.[2–10] We focus attention on the preparation of colloidal silica from ion exchange method, which uses sodium silicate as preferred starting material because of its lower cost, compared to the other alkali silicates that are available commercially. With the increase of colloidal silica's production and application, products in different particle size distributions are needed in different fields. The literature[2–5,11–13] and patents[14,15] have paid more attention to form or use monodisperse and uniform colloidal silicas with controllable particle size. However, few studies were reported to prepare polydisperse silica particles to meet the new demands of the modern market, especially the booming sapphire CMP market.

Silica slurries are mostly used for the final polish process of a sapphire wafer since they can produce the required surface quality. But the polishing of these materials is often MRR limiting because the sapphire has high hardness. Monodisperse nano-scaled silicas, either fumed or amorphous, are often used as the abrasive particles in the slurry. The fumed silica-based slurry can remove hard sapphire wafer quickly but it leaves irreversible defects on the wafer surface after polishing because of its sharp edges. Amorphous silica-based slurry behaves better in preventing wafer surface defects, but the MRR is far below that of fumed silica. Therefore, it is urgent to develop a new kind of abrasive used in the sapphire CMP slurries with high polishing rate and fewer surface defects. Polydisperse colloidal silica is a good choice to solve this problem.

In this paper, we have produced one kind of polydisperse spherical colloidal silica particles with very broad particle size range 20–95 nm. The preparation method is very simple, controllable, and repeatable. We have examined the MRR of this kind of abrasive particles. Compared with traditional monodisperse spherical silica particles, the polydisperse silica particles can increase the MRR by 50%, without sacrificing the sapphire wafer's surface roughness after polishing. The mechanism of sapphire CMP process by this kind of polydisperse silica particles has also been investigated.

2. Experiment

2.1. Materials

Sodium silicate (or water-glass) was used as the main raw material, with SiO_2 content of 32 wt%, Na_2O content

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of 14 wt%, and the molar ratio of SiO_2:Na_2O is 2.36. Solid sodium hydroxide (analytical reagent) was also used. Colloidal silica (3.4 wt% sodium stabilized colloidal silica solution in water, 33.1 nm by dynamic light scattering method, Shanghai Xinanna Electronic Technology Co., Ltd) was used as the seed solution. Deionized (DI) water was used in all of the experiments, unless otherwise stated.

2.2. Preparation of the colloidal silica

Four hundred and seventy grams of sodium silicate were diluted with water to 3500 g. Diluted sodium silicate was passed through a bed of cation-exchange resin in a column for which hydrogen ions had been regenerated in advance to allow the sodium ions to be absorbed onto the resin bed and leave an aqueous solution of active silicic acid. The active silicic acid contained about 4.3 wt% SiO_2, which was calculated by gravimetric analysis measuring the weight loss of active silicic acid at a temperature of 800 °C in a muffle furnace for 30 min. 1500 ml water with 15 g solid sodium hydroxide (NaOH) was mixed to obtain 1.0 wt% NaOH solution.

To synthesize polydisperse colloidal silica, the original seed solution (1000 grams) was violently stirred and heated to 100 °C. Then, the active silicic acid and the seed solution were titrated to the 100 °C seed solution with constant rates under peristaltic pumps of BT300-1F Longerpump type, respectively. The titration rate of the active silicic acid was about 5.85 ml/min, the titration rate of the seed solution was 0.90 ml/min, and the sum titration rate of the active silicic acid and the seed solution was equal to the evaporation rate of the heated solution. After titrating with 3000 ml active silicic acid, 60 grams 1.0 wt% NaOH solution should be added to the heated solution to prevent gel. The total weight of the active silicic acid added to the heated solution is 24000 ml, while the total weight of the seed solution added to the heated seed solution is 3788 g. The general manipulation required is shown in Fig. 1(a). The prepared polydisperse colloidal silica here is marked as PCS-A.

For comparison, monodisperse colloidal silica (MCS-B) was also prepared. The experimental flowchart required is shown in Fig. 1(b). The difference of the synthesis method between PCS-A and MCS-B is that the titrating seed solution in the preparation of PCS-A was replaced by water in the preparation of MCS-B. Other preparation processes are identical.

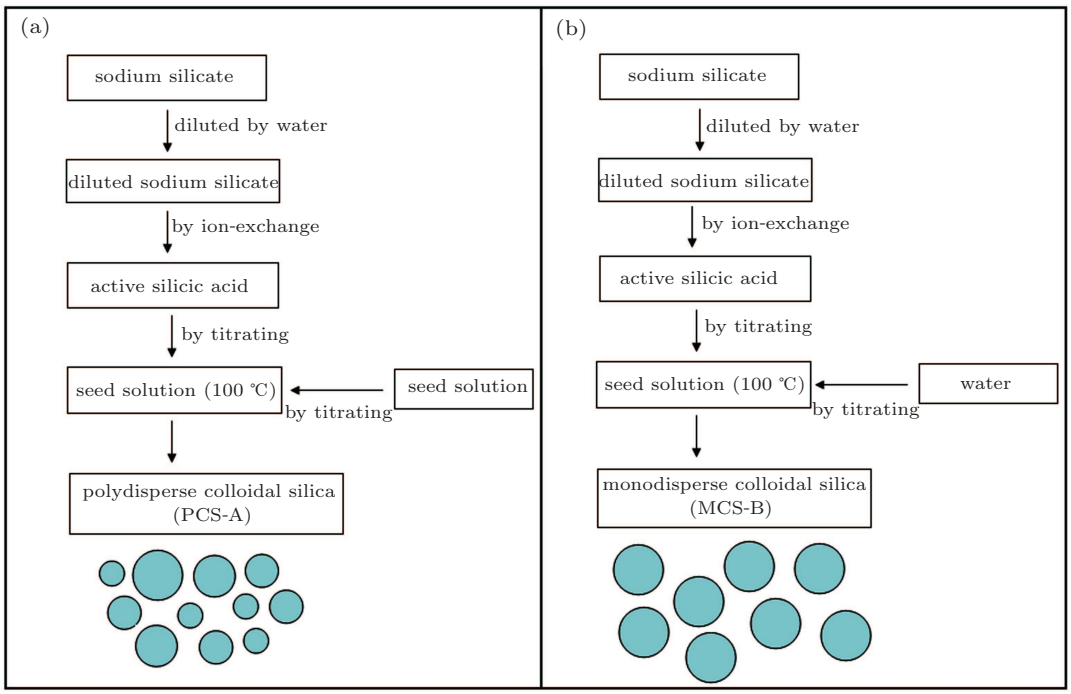


Fig. 1. (color online) Experimental flowchart from sodium silicate to (a) PCS-A and (b) MCS-B.

2.3. Characterization of the colloidal silica

The formed colloidal silicas were subjected to mean particle size, focus ion beam (FIB) system testing, pH value, and polishing testing.

Mean particle size of colloidal silica was measured by dynamic light scattering (DLS) method with Nicomp™ 380/ZLS instrument (PSS, America). The microstructure and morphology of prepared colloidal silica were examined by FIB techniques, all the measurements were carried out on DualBeam helios nanolab 600 (FEI, America) focus ion beam system at 5.0 kV voltage and 0.17 nA electric current. The pH value of colloidal silica was measured by FE20 pH meter (Mettler Toledo, Switzerland).

In polishing testing, PCS-A and MCS-B were used as

abrasives in the CMP slurries. 1.0 wt% NaOH solution was used to adjust the pH values of all colloidal silica-based slurries to be about 10.35. DI water was used to dilute silica slurries to the abrasive concentration of 15 wt%. No other chemical reagents were added to the slurries. Two inch sapphire wafers ((0001) oriented) were purchased commercially and used as work pieces. The polishing experiments were carried out using a CP-4 polisher (Bruker, America) with a suba 800 pad (Dow), which is equipped with an online coefficient of friction (COF) detector instrument. The polishing process parameters such as pad rotation speed, wafer rotation speed, down force, slurry feed rate, and polishing time are summarized in Table 1. The suba 800 pad was conditioned before each polishing for 5 min using a 4 inch diamond grit conditioner. The measurement of MRR has been reported in detail in other studies.[16,17] The weight of the sapphire wafers before and after polishing was measured by electron balance to calculate the MRR according to

$$\mathrm{MRR} = \frac{10^7 \Delta m}{2.54^2 \rho \pi t}. \quad (1)$$

Here, MRR (nm/min) is the material removal rate, Δm (g) is the mass variation of sapphire wafer before and after polishing, t (min) is the polishing time, and ρ (g/cm^3) is the density of sapphire.

The surface morphology of the polished samples was characterized using a 2.5 μm×2.5 μm atomic force microscope (AFM) (Park Systems, Korea).

Table 1. Process parameters used for sapphire polishing using CP-4 polisher.

Pad rotation speed/rpm	100
Wafer rotation speed/rpm	90
Down force/psi	6
Slurry feed rate/ml·min^{-1}	125
Polishing time/min	30

3. Results and discussion

3.1. DLS results

Figure 2 shows the mean particle size of the original seed solution, PCS-A and MCS-B by DLS, respectively. The mean diameter is 33.1 nm for the original seed solution, and 90.5 nm for MCS-B. However, PCS-A shows two different diameters (88.4 nm and 23.4 nm) due to its polydisperse distribution. Through adding the same amount of active silicic acid for the preparation of PCS-A and MCS-B, the particle size of MCS-B is larger than PCS-A. The reason is stated as follows. Firstly, the smaller mean particle size of PCS-A than that of MCS-B is contributed by the smaller individual particles, the formation of which is substantially dominated by the titrating seed solution (see Section 3.2.). Secondly, while the original seed number for both PCS-A and MCS-B is the same, the adding of outside titrated seed for PCS-A increases the total seed (both original seed and outside titrated seed) number, so the choice of particle growth for per seed in PCS-A is less than that in MCS-B, which makes a smaller particle size of PCS-A.

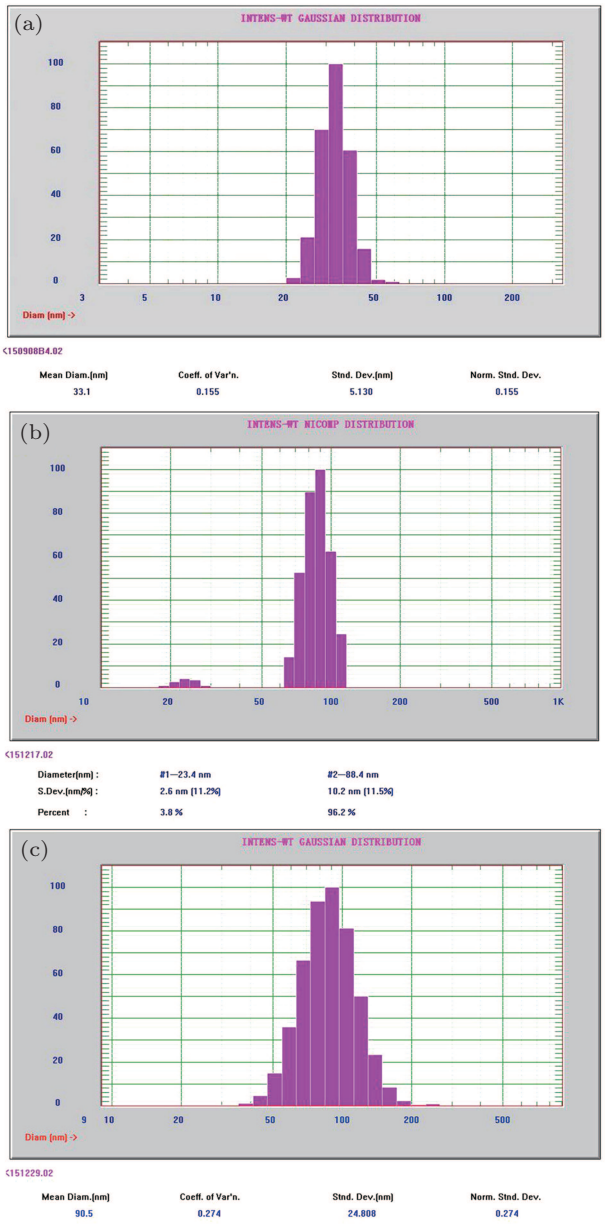


Fig. 2. (color online) The mean particle size of (a) the seed solution, (b) PCS-A, (c) MCS-B.

3.2. FIB results

The morphologies of the original seed solution, PCS-A and MCS-B are observed by FIB, as shown in Fig. 3. The original seed solution contains monodisperse and spherical particles with diameters of about 20–40 nm. MCS-B is also monodispersed and spherical with diameter about 85–95 nm. The process for the preparation of MCS-B used a reactor in which the original seed solution was heated to 100 °C. Active silicic acid was titrated continuously at a constant rate. The original seed acted as nuclei in the reactor, then active

silicic acid polymerized around the nuclei, and thus particles were formed. Small particles were not found in MCS-B, which means that no new nuclei were formed during particle growth stage. Hence, all of the incoming active silicic acid was deposited on the previous seeds, and the number of the particles in the reactor remained constant. PCS-A has a very broad particle size range and very large particles with a diameter about 95 nm. The process for the preparation of PCS-A also used a reactor in which the original seed solution was heated to 100 °C. Then active silicic acid was titrated continuously with a constant rate. Meanwhile, the seed solution was also titrated continuously to the original seed solution in the reactor. The amount of the seeds in the reactor increases with time because the outside seed was added continuously. Hence, all of the incoming active silicic acid was deposited both on the original seeds and the outside titrated seeds. Some of the original seed particles in the reactor experienced the maximum particle growth cycles to form the largest particles, some underwent partial growth cycles to form the middle size particles, while others (last titrated seeds) formed the smallest particles in the reactor after only a few cycles or even no growth cycles. The particle size distribution tends to be in a very broad particle size range from about 20 nm to 95 nm.

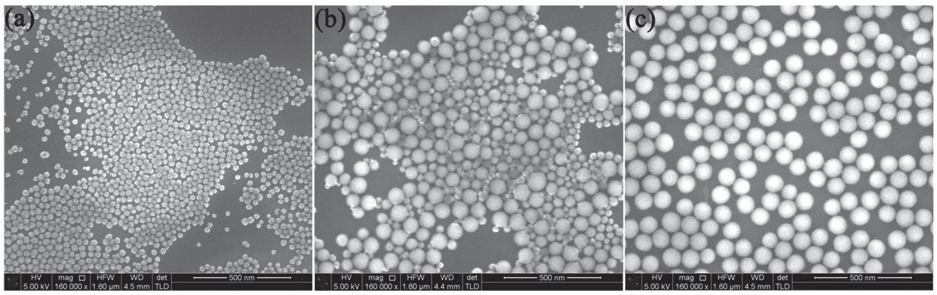


Fig. 3. The morphology of (a) the seed solution, (b) PCS-A, (c) MCS-B.

Figures 4(a)–4(c) further show the morphologies of PCS-A sample from three different regions by FIB. All particles in Figs. 4(a)–4(c) were divided into six different size ranges: 20–40 nm, 40–55nm, 55–65 nm, 65–75 nm, 75–85 nm, and 85–95 nm, respectively. Then, the number proportion of particles from each size range in all particles was calculated in order to further study the particle size distribution of PCS-A, as shown in Fig. 4(d). Figure 4(d) shows that the size range of 20–40 nm possesses the highest number proportion (about 38.23%), the size of 75–85 nm and 40–55 nm possess 18.65% and 17.75%, respectively, the size of 85–95 nm possesses about 10.21%, the size of 65–75 nm possesses 7.80%, and the size of 55–65 nm possesses the lowest number proportion (about 7.36%). It is interesting that the particles of 85-95 nm in PCS-A was from the original seed particles in the reactor which experienced the longest particle growth cycle. The original seed solution is 1000 grams, and the outside titrated seed solution is 3788 g, so the proportion of the original seeds in the total seeds is about 20.88%. However, particles with size of 85-95 nm possess only 10.21%, which means that only about half of the original seeds grew to 85–95 nm particles.

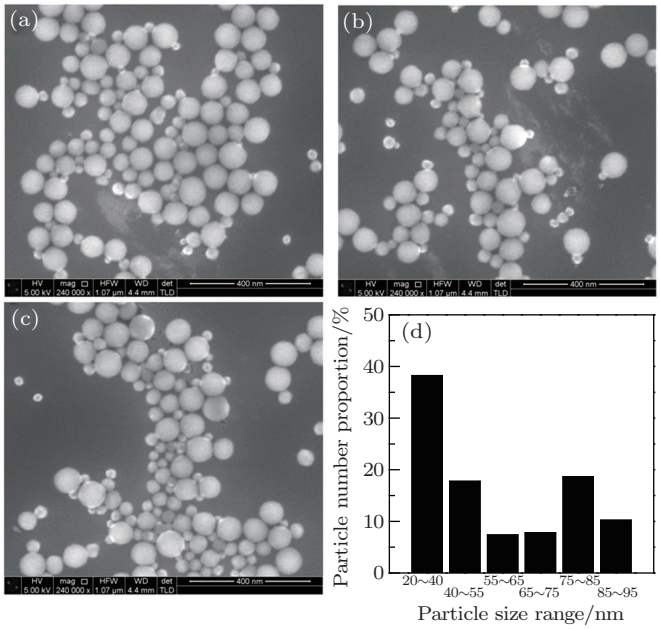


Fig. 4. (a)–(c) The morphologies of PCS-A from three different regions by FIB. (d) The particle size distribution of PCS-A calculated according to the average particle number proportion of Figs. 4(a)–4(c).

3.3. CMP results

In order to compare the MRR of polydisperse PCS-A with monodisperse colloidal silicas, MCS-B (with particle size 90.5 nm by DLS) here is chosen as baseline, as shown in Fig. 5(a). Under the same polishing conditions (solid content 15 wt%, pH values 10.35), polydisperse PCS-A shows a higher MRR than monodisperse MCS-B, and PCS-A can increase the MRR by 50%. This can be explained by mechanical abrasion of the abrasive abrasion and the chemical action of the abrasive.

The mechanical abrasion action can be explained by the coefficient of friction (COF) comparison graph in Fig. 5(b). The COF is defined as the ratio of the shear force (F_{shear}) to

the normal force (F_{normal}),

$$\text{COF} = \frac{F_{\text{shear}}}{F_{\text{normal}}}. \tag{2}$$

As the silica particles set onto the pad, mechanical actions such as rolling and sliding indentation are created between pad, particle and sapphire wafer surface by the relative velocity difference. The friction forces produced by rolling abrasive are much lower than those produced by sliding abrasive.[18–20] Under the same polishing down force (6 psi), higher COF means higher friction force among pad, slurry and sapphire surface in the CMP process. The COF of PCS-A is much higher than that of MCS-B, which indicates that polydisperse PCS-A particles lead to more sliding indentation action which removes more surface material by directly increasing the MRR.

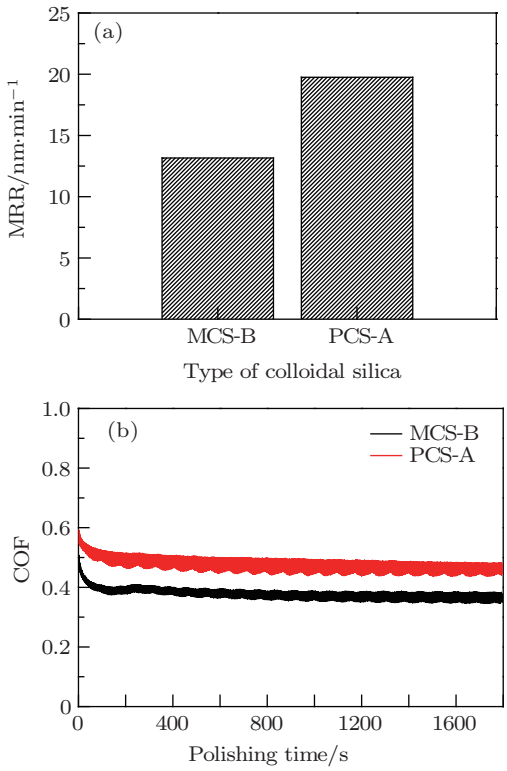


Fig. 5. (color online) (a) MRRs of polydisperse PCS-A and monodisperse MCS-B; (b) COF of polydisperse PCS-A and monodisperse MCS-B during CMP process.

The polishing of sapphire by colloidal silica is believed to follow a chemical reaction leading to aluminum silicate dihydrate as described by the following reaction:[21]

$$Al_2O_3 + 2SiO_2 + 2H_2O \Leftrightarrow Al_2Si_2O_7 \cdot 2H_2O.$$

Silica abrasive will be directly involved in the chemical reaction of CMP process. Under the same SiO_2 content (15 wt%), the number of particles per unit volume in PCS-A is much more than that in MCS-B. This happens because the majority of particles of PCS-A are smaller than those of MCS-B (as discussed in Section 3.2). Furthermore, small particles have larger specific surface area than large ones. Hence, PCS-A abrasive has more chemical active sites than MCS-B during CMP process, which makes the chemical reaction easier.

Figure 6 depicts the sapphire surface roughness (R_q) and AFM images after polishing using PCS-A and MCS-B. It can be observed that there is not much difference between the R_q in PCS-A (0.315 nm) and MCS-B (0.344 nm), which indicates that the surface roughness is not sacrificed, even though the polishing rate of PCS-A is much higher. The reason for this is that strong chemical and mechanical actions of PCS-A combined well with each other, which makes the softening layer of aluminum silicate dehydrate form and removed easily at the same time, and further produces higher MRR with good surface quality.

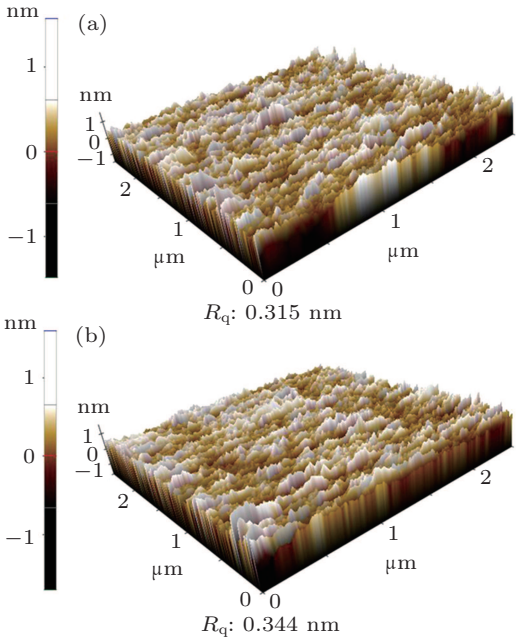


Fig. 6. (color online) AFM images of the polished surfaces using (a) polydisperse PCS-A and (b) monodisperse MCS-B.

4. Conclusion

In this paper, we have produced a kind of polydisperse spherical colloidal silica particles with very broad particle size range 20–95 nm by the ion exchange method. We have examined the MRR of this kind of abrasive particles. Compared with traditional monodisperse spherical silica particles, polydisperse silica particles can increase the MRR by 50% during sapphire wafer CMP process, without sacrificing the sapphire wafer's surface roughness after polishing. The mechanism of sapphire CMP process by this kind of polydisperse silica particles has been explained by both mechanical abrasion and chemical action of the abrasive. Polydisperse PCS-A particles lead to more sliding indentation action, which removes more surface material by directly increasing the MRR. Besides, PCS-A has more chemical active sites during CMP process, which makes the chemical reaction easier.

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