Study of Several Silica Properties Influence on Sapphire CMP

Haibo Wang*, Zhongxiang Zhang* and Shibin Lu[†]

Abstract – Colloid silica using as abrasive for polishing sapphire has been extensively studied, which mechanism has also been deeply discussed. However, by the requirement of application enlargement and cost reduction, some new problems appear such as silica service life time, particle diameter mixing, etc. In this paper, several influences of colloid silica usage on sapphire CMP are examined. Results show particle diameter and concentration, pH value, service life time, particle diameter mixing heavily influence removal rate. Further analysis discloses there are two main effect aspects which are quantity of hydroxyl group, contact area for abrasive density stacking between abrasive and sapphire. Based on the discussions, a dynamic process of sapphire polishing is proposed.

Keywords: Sapphire, Chemical mechanical polishing, Colloid silica, Removal rate, Mechanism

1. Introduction

Sapphire has many special characteristics such as high hardness, great thermal stability, chemical inertness and good light transmission. It is widely used in a range of applications such as optics, electronics and temperature sensing[1]. In manufacturing light emitting diodes (LED), sapphire is widely used as substrates for gallium and indium nitride films [2]. The development of LED technology leads to an exponential increase in device efficiency and light output over past thirty years, which promotes the LED to become light sources of choice for virtually all applications. All applications require sapphire no damaged near-surface layer, no surface defects as well as low working surface roughness. To achieve the surface quality, technique of chemical mechanical polishing (CMP) should be applied to manufacture sapphire wafer.

Over past few years, researchers focused on the use of colloid silica as abrasives for polishing sapphire by the advantage of good dispersity and stability. Particularly, silica can supply acceptable removal rate because of solid phase reaction generation between sapphire hydrolysis product and colloid silica during polishing process [3]. Thus, several techniques were proposed to improve polishing method based on colloid silica. Zhang [4] disclosed two step polishing process by using alumina solution as the first step and using silica as the second, which improved machining efficiency and obtained good surface quality. Other studies were also executed based on silica sol by further adding chemical reagents to improve polishing rate [5-9]. To further improve polishing rate, influence of silica properties and modifications were also studied. Silica doped with Fe, Cu and La elements were

studied in the performance of sapphire polishing process [10-12], results showed better polishing efficiency and lower surface roughness were obtained by the reason of solid phase reaction enhancement to promote the conversion of polishing products. Silica with different size was studied by using X-ray photoelectron spectroscopy which shows a complex mechanism [8, 9]. Also useful mixed silica with different particle size were studied to improve the polishing rate, the mechanism is still not very clear [13]. Therefore, there is still a dearth of detailed research on sapphire CMP such as investigations on the effect of colloidal aspects and the mechanism of CMP process.

In this paper, we investigate several properties of colloid silica for sapphire CMP. New phenomenon of removal rate along with parameters variation of colloidal silica is found. Based on the measurements, a possible reason is discussed.

2. Experimental

The polishing tests were carried out using a CP-4 polisher (Bruker, USA) with pressure 7psi and rotation rate 100rpm, and the feed rate of slurry was set as 120ml/min. The using slurry contained 5wt%, 80nm, KOH stabilized colloid silica, which pH value was finally adjusted by diluted 8wt% KOH and 8wt% H_2SO_4. The polishing time for each run was one hour. The weight of sapphire before and after polishing were measured by an electronic balance to calculate removal rate (RR) according to function (1)

$$RR = \frac{M_2 - M_1}{\rho \cdot s \cdot t} \cdot 10^7 \qquad (1)$$

Here RR is the removal rate, $M_2(g)$ is the weight of wafer before CMP, $M_1(g)$ is the weight of wafer after CMP, $\rho(3.98g/cm^3)$ is the density, s is the wafer area(2inch sapphire wafer, Φ=50.8mm), t(hour) is polishing time.

Dynamic light scattering (DLS, Zetasizer ZS90, Malvern) was used to measure particle size distribution and zeta potential. Particles were diluted in de-ionized (DI) water at pH 10.0 and then sonicated for 5 minutes before size analysis. Scanning electron microscopy (SEM, Hitachi S-4700) was used to observe silica particle morphology.

3. Results and Discussion

3.1 Effect of particle size and concentration on removal rate

Fig. 1 shows removal rate variation as a function of the particle size of colloid silica. The removal rate appears as a linear relationship with silica diameter and increases steeply from 2.02μm/hour to 3.64μm/hour with particle size increasing from 20nm to 100nm.

Fig. 2 shows removal rate variation as a function of colloid silica concentration. It can be seen the removal rate increases gradually from 0 to 4.97μm/hour with the concentration increasing from 0 to 40wt%.

The above evolution rules are consistent with other reports [14-16]. Removal rate increases with abrasive concentration for the probability increases at a high abrasive concentration regarding to the contacts between sapphire wafer and active abrasives. Similarly, Removal
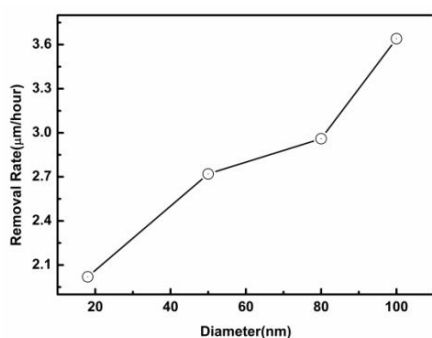
rate increases with the abrasive diameter increasing for the indentation depth increases under a same pressure.

3.2 Effect of pH on removal rate

It is well known that pH value provides a different chemical solution for colloidal silica discussed everywhere. Silica surface chemical bond presents as $Si-O^-$ or $Si-OH$ structure depending on OH^- concentration. Usually, surface has a more intensive $Si-O^-$ structure with a higher pH value. For another aspects, OH^- can dissolve sapphire forming gibbsite, boehmite and diaspore by hydrolysis reaction at high temperature [17]. Thus, the pH value seriously influences sapphire polishing process. Fig. 3 shows the removal rate as a function of pH value. It can be observed removal rate is at the range from 3.5 to 3.6 μm/hour with pH value below 10.0 and sharply decrease to 2.63μm/hour with pH further increasing to 11.5. The results are almost the same as other report [18]. Basically, effect of pH on sapphire polishing is a contradiction of hydrolysis and abrasive-substrate contact. By increasing the pH, the sapphire hydrolysis is enhanced resulting in a high removal rate, but the abrasive-substrate contact may also changes which are further proved by the zeta potential tests.

Fig. 4 shows zeta potential of silica and sapphire as a function of pH value. It can be obviously seen zeta potential gradually decreases with pH going to a higher one both of silica and sapphire indicating enhancement of repulsive force between silica and sapphire during CMP. Therefore, removal rate changes caused by different
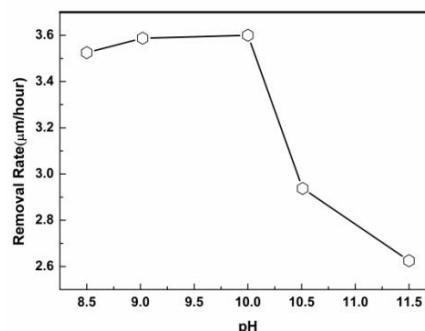

Fig. 1. RR variation as a function of the particle size with concentration 20wt%
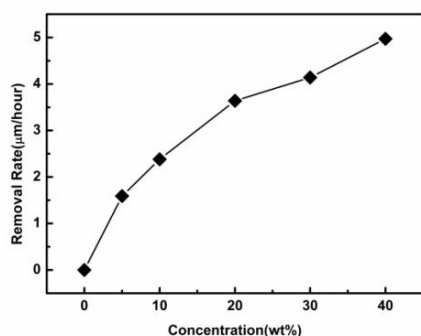
Fig. 2. RR variation as a function of concentration using 100nm diameter silica
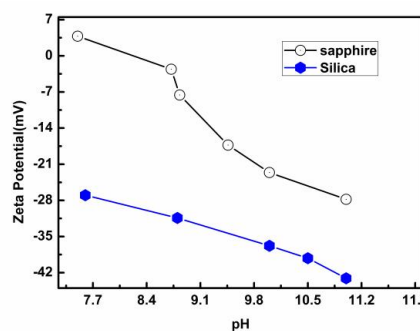

Fig. 3. Effect of pH on removal rate
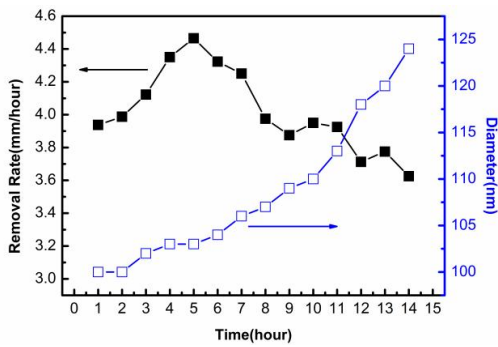

Fig. 4. Zeta potential as a functional of pH value

**Fig. 5.** Effect of colloid silica service life time on removal rate and diameter

pH can be understood as following. When pH<10.0, electrostatic repulsive force would be weaker leading to relatively higher removal rate; when pH>10, colloidal silica presents as Si-O⁻ structure in water which has a same electrical property as well as sapphire [3]. Further increasing pH value can make a stronger repulsive contact resulting in a lower removal rate.

3.3 Effect of colloid silica service life time on removal rate

For commercial slurry, it is traditionally required a very long time usage such as 10 hours. During the polishing time, removal rate maintains a certain range by the best. Typical parameter for describing usage time can be called service life time. However, it is seldom reported about the effect of colloid silica service life time on removal rate.

Fig. 5 shows 14 hours recycling polishing rate using one kind of 100nm colloid silica based slurry. For each hour, polishing process is terminated to calculate removal rate, adjust pH (10.0) and measure mean particle size. From the figure, we can clearly see removal rate increases for initial 5 hours and decreases from 6th hour to 14th hour, meanwhile, mean particle size continuously increases from 100nm to 124nm.

It is well known that colloid silica can react with sapphire in alkaline solution during polishing as Eq. (2)

$$Si(OH)_4 + 2AlO_2^- = Al_2Si_2O_7.2H_2O + 2OH^- + H_2O \quad (2)$$
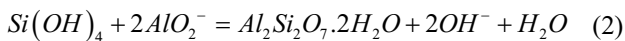
Thus, the polishing process may consume Si-OH of active surface structure on silica by reacting with sapphire hydrolysis product of Al(OH)$_3$ or AlOOH, which could cause particle grow-up to be a larger one as shown Fig. 5. Mean particle size is 100nm in the initial polishing, and gradually increases to 124nm by 14 hours polishing. Additionally, we do not observe stratification and precipitate which also indicates silica growing.

3.4 Effect of colloid silica mixing on removal rate

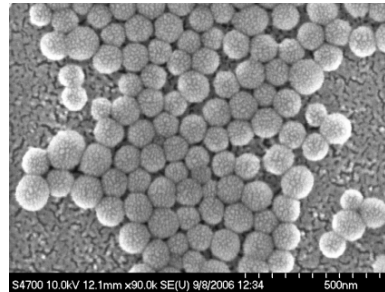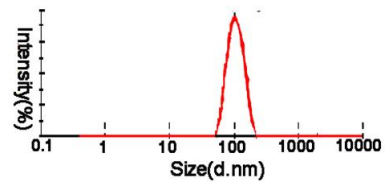We know that so-called particle size traditionally points

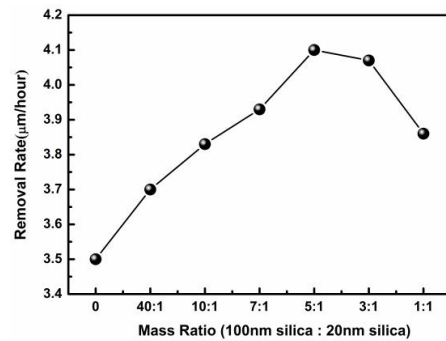**Fig. 6.** Particle size of 100nm silica measured by DLS(a) and SEM(b) respectively

Fig. 7. Effect of colloid silica mass ratio on removal rate (total concentration is 20wt %)

to mean particle size which is always measured by dynamic light scattering method [19]. Fig. 6 shows 100nm silica for sapphire polishing respectively measured by DLS and SEM. It can be seen that the particle distribution is broad, and presents so many small silica (d<30nm) which may influence sapphire polishing behavior. To test the effect, we add small particle to large one according to a certain ratio.

Fig. 7 shows removal rate as a function of 20wt% slurry using 100nm and 20nm mixed abrasive with different mass ratio. The removal rate gradually increases with the increases of mass ratio, the value reaches maximum at ratio 5:1, further increases the concentration of 20 nm silica, the removal rate turns to decrease. Another phenomenon is that removal rate obtained using mixed abrasive is larger than that obtained using single diameter particle. To further study the mixing effect, we test different diameter particle mixed with 20nm silica with fixed mass ratio 10:1 as shown in Fig. 8(a).

We can see the removal rate increases with the particle size increases from 60nm to 120nm. Fig. 8(b) shows the different diameter particle mixed with 100nm with fixed

mass ratio 10:1 as shown in Fig. 8(b). The removal rate decreases with particle size increases from 10nm to 40nm. Compared to the two results, it is found that if two particles are mixed, larger diameter difference may result in bigger removal rate.

3.5 Possible mechanism

For polishing, there is a typical model using function *RR=KPV*, and chemical removal process is analyzed as production $Al_2Si_2O_7.2H_2O$ [20]. But the dynamic processes are often complicated. For colloidal aspects, there are chemical reaction interaction, static electronic force and mechanical force conduction in sapphire polishing. Under alkaline solution, colloidal silica surface present as Si-OH or Si-O$^-$ according to pH value [21], while the sapphire can hydrolyze to gibbsite, boehmite and diaspore [3]

(a)

(b)
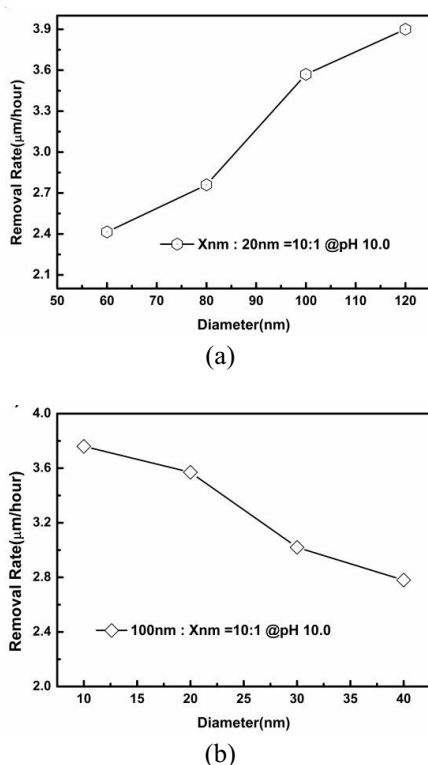
Fig. 8. Effect of colloid silica mixing on removal rate, different larger particle mixed with 20nm on removal rate (a) and different smaller particle mixed with 100nm on removal rate (b)

(a)   (b)
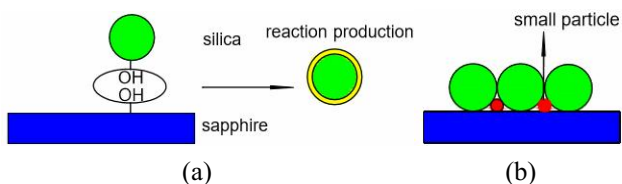
Fig. 9. Schematic of dynamic processes for contact model (a) and density stacking (b)

which also present a negative charge proved by the zeta potential measurement [22]. The same charge causes a repulsive force for abrasive-sapphire contact in polishing process resulting in a relative low removal rate. Thus, by the pH increasing, the removal rate decreases which is shown in Fig. 3. The reaction product is polished away from the sapphire surface, then link to particle surface resulting in silica diameter increasing. This process may decrease the total Si-OH quantity which causes the removal rate to decrease and finally decrease silica service life time which is shown as Fig. 9(a).

The colloid silica concentration and particle size heavily affect the mechanical force according to polishing model proposed by Luo[23]. Under a uniformity pressure, a large particle may indent into sapphire surface indicated a bigger contact area resulting in higher removal rate illustrated by a solid-solid contact model. By increasing the abrasive concentration, effective polishing particle increases for abrading sapphire surface. Unfortunately, traditionally used silica is non-ideal one which has a diameter distribution. This may affect the polishing results. In polishing process, we know that massive particles disperse between sapphire surface and pad. Three large particles approaches to form a space which can be squeezed by small particles forming intensive stacking which can increase contact area between sapphire and abrasive shown as Fig. 9(b). Through qualitative analysis, enhancement of the diameter difference between large particles and small ones, contact area will increase which may cause a higher removal rate as shown in Fig. 7. Also, increasing particle ratio still increases silica-sapphire contact area.

4. Conclusions

In this paper, four aspects of particle diameter and concentration, pH value, service life time, particle diameter mixing on the effect of sapphire polishing were studied. The following results were obtained. (1) Removal rate gradually increases with both concentration and particle size increase; (2) Removal rate is at the range from 3.5 to 3.6μm/hour with pH value below 10.0 and sharply decrease to 2.63μm/hour with pH further increase to 11.5; (3) Removal rate gradually decrease from 6th hour by a long time polishing(14hours); (4) Multi-diameter mixed particle can efficiently increases removal rate, and make the removal rate reach maximum at a mass ratio 1:5(120nm : 20nm).These results indicate two reasons of quantity of hydroxyl group, contact area between abrasive and sapphire for abrasive density stacking were considered for sapphire polishing. Based on consideration, a dynamic process of polishing using colloid silica is assumption. These results can give an introduction for slurry development to improve polishing efficiency by increasing silica hydroxyl content on surface and increasing contact area between silica and sapphire.

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Haibo Wang He received pH.D degree in microelectronic engineering from SIMIT, CAS. His research interests are IC design and manufacturing.

Zhongxiang Zhang He received pH.D degree in electromagnetic field and microwave from USTC. His research interests are IC design and manufacturing.

Shibin Lu He received M.S degree in circuits and systems from Anhui University. His research interests are integrated circuit design and device simulation.