Preparation of Ag₂O modified silica abrasives and their chemical mechanical polishing performances on sapphire

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Abstract: The chemical mechanical polishing (CMP) process has become a widely accepted global planarization technology. The abrasive material is one of the key elements in CMP. In the presented paper, an Ag-doped colloidal SiO₂ abrasive is synthesized by a seed-induced growth method. It is characterized by time-of-flight secondary ion mass spectroscopy and scanning electron microscopy to analyze the composition and morphology. The CMP performance of the Ag-doped colloidal silica abrasives on sapphire substrates is investigated. Experiment results show the material removal rate (MRR) of Ag-doped colloidal silica abrasives is obviously higher than that of pure colloidal silica abrasives under the same testing conditions. The surfaces that are polished by composite colloidal abrasives exhibit lower surface roughness (Ra) than those polished by pure colloidal silica abrasives. Furthermore, the acting mechanism of Ag-doped colloidal SiO₂ composite abrasives in sapphire CMP is analyzed by X-ray photoelectron spectroscopy, and analytical results show that element Ag forms Ag₂O which acts as a catalyst to promote the chemical effect in CMP and leads to the increasing of MRR.

Keywords: chemical mechanical polishing; Ag-doped colloidal silica abrasive; sapphire; material removal rate

1 Introduction

Sapphire possesses excellent optical and mechanical properties with good corrosion resistance and high hardness, and is widely used in solid lasers, infrared windows, semiconductor chip substrates, precision anti-friction bearings, and other high-tech fields [1–5]. Sapphire is well known as the substrate for gallium and indium nitride films and is used for fabricating light emitting diode devices [6]. With the rapid development of photoelectron technology, improvement of planarization efficiency and the study of planarization mechanism of sapphire have become more and more important to meet the increasing demand of higher surface quality [7]. As is known to all, sapphire substrates are difficult to be polished for their physical and chemical properties, such as high hardness, brittleness and so on. Chemical mechanical polishing (CMP) is used as one of the most effective

ways to produce an atomic-level smooth surface [8–14].

During the CMP process, the abrasive was the most important factor that influenced the sapphire quality [15]. To improve surface planarization and the material removing rate (MRR) of sapphire, several polishing abrasives were studied. Xiong et al. [16] adopted silicon carbide, alumina, and silica sol as polishing abrasives for CMP on sapphire. Under the same condition, the results showed the Ra of sapphire polished with silica sol abrasive was lower than that with silicon carbide and alumina abrasives. The effect of the hardness of the abrasives on CMP of (0001) plane sapphire was researched by Zhu et al. [17], and the results showed that hard abrasives (such as monocrystalline and polycrystalline diamond, α -Al₂O₃) improve MRR of sapphire, but surface average roughness (Ra) increased. However, a lower Ra value could be reached by using silica sol as the polishing abrasive for sapphire,

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but the MRR of sapphire was lower too. It could be concluded from the above examples that colloidal silica was widely regarded as the ideal polishing abrasive for sapphire CMP since it could achieve a better surface quality, but the MRR of sapphire with colloidal SiO_2 as a polishing abrasive still needed further research.

Silica-based composite particles were paid increasing attention on because the production process of silica was controllable and mature to combine with other materials. Xu et al. [18] reported the slurry of colloidal silicon dioxide (SiO_2) containing Fe- N_x /C exhibited higher MRR than the slurry containing pure SiO_2 abrasives in the CMP of sapphire substrates under the same conditions. Bai et al. [19] synthesized a kind of core-shell SiO_2 /CeO₂ composite abrasive by calcining of the precursor under appropriate temperature and was used for sapphire CMP. The MRR decreased since the silica core had no direct contact with the sapphire CMP. In our previous work, silica/ceria nano composite abrasives [20] and alumina/silica core-shell abrasives [21] were prepared for hard disk CMP. Both showed high planarization efficiency and better planarization quality than pure silica abrasives under the same conditions. The examples above indicated silica-based composite abrasives resulted in both high planarization efficiency and good planarization quality. Recently, several kinds of abrasives were investigated to polish sapphire substrate, such as Mg-doped colloidal SiO_2 abrasives [22] and SiO_2 /CeO₂ composite abrasives [19]. To further improve the sapphire CMP performances, new silica composite abrasives needed to be explored. In this paper, argentum ions modified silica (Ag-doped colloidal SiO_2) abrasives were synthesized by seed growth method, and the CMP performances on sapphire were investigated.

2 Materials and methods

Ag-doped colloidal SiO_2 abrasives were synthesized by a seed growth method.

A certain amount of sodium silicate (40 wt%, Jinan Dewang Chemical Industry Co., LTD, China) was diluted with water and passed through a column filled with 2 L of a strong cation exchange resin to produce silicic acid. During the ion exchange process,

the sodium ions in the sodium silicate solution were replaced by hydrogen ions gradually. Finally, the 2.5 wt% silicic acid solution was obtained.

2.20 g silver nitrate (AgNO_3 , Analytical Reagent (99.8%), Sinopharm Chemical Reagent Co., LTD, China) was dissolved in 1,395 g DI water to obtain a 0.01 mol/L silver ion solution. Then, the silver nitrate solution was mixed with the same weight of silicic acid. Next, the solution was added in drops into the crystal silica seed solution (40 wt%, Zhejiang Delixin Micro/Nano Science and Technology Co., LTD, China) to prepare a 0.5 wt% Ag-doped silica abrasive. The reaction took place in a four-neck flask under a 100 °C environment with constant stirring. During the reaction, sodium hydroxide (1 wt% NaOH, Analytical Reagent (96%), Sinopharm Chemical Reagent Co., LTD, China) was added to the basic solution to adjust the pH. Different Ag-doped contents of colloidal SiO_2 abrasives (0.5 wt%, 1.0 wt%, 1.5 wt%) were obtained by adding different amounts of silver nitrate during the reaction. When silver nitrate was dropped into the flask, argentum ions (Ag^+) of different amounts of silver nitrate combined with hydroxyl (OH^-) to form Ag_2O with different contents (0.5 wt%, 1.0 wt%, and 1.5 wt%) ($2\text{Ag}^+ + 2\text{OH}^- = \text{Ag}_2\text{O} + \text{H}_2\text{O}$). The experimental flow chart was shown in Fig. 1.

After the preparation of the slurry, it was used to polish the sapphire substrate. The substrate (sapphire crystals, Jiangsu Haohan Sapphire Science and Technology Co., LTD, China.) with c (0001) orientation was Φ 50.8 mm. The CMP experimental was performed on UNIPOL-1502 polishing equipment (Shenyang Kejing Instrument, Co. Ltd., China) with a Rodel

Fig. 1 The experimental flow chart of modified silica.

porous polyurethane pad. Then the sapphire was polished for 2 hours under 6 kg pressure with 60 rpm rotating speed and 180 mL/min slurry flow rate.

The Ag-doped colloidal SiO_2 was inspected with a scanning electron microscopy (SEM), time-of-flight secondary ion mass spectroscopy (TOF-SIMS), and X-ray photoelectron spectroscopy (XPS).

The SEM observations were performed with a JEOLJSM-6700F field emission scanning electron microscope with a voltage of 15.0 kV.

Elementary analysis of the modified silica was measured by time-of-flight secondary ion mass spectroscopy (TOF-SIMS, Model2100 Trift II) with a pulsed gallium ion beam with the energy of 15 kV. The analytical region was $200\ \mu\text{m} \times 200\ \mu\text{m}$ and post acceleration was 5 kV/5 kV (+/-).

Mechanism analysis was characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, 0.45 eV energy resolution and $3\ \mu\text{m}$ spatial resolution). XPS spectra were obtained by using focused monochromatized Al K radiation ($h\nu = 1,486.6\ \text{eV}$). The binding energy of C1s (284.6 eV) was used as reference.

The sapphire substrate was subjected to the MRR

and surface average roughness (Ra). The MRR and Ra were the important factors to evaluate the performance of the slurry on sapphire under the same conditions. The Ra and polishing surface topography were measured by an Ambios XI-100 surface profiler (Ambios Technology Corp., USA, ZYGO) with a vertical resolution of $0.1\ \text{\AA}$ in texture modes. The measuring area was $500\ \mu\text{m} \times 500\ \mu\text{m}$. The depth of focus was $3.0\ \mu\text{m}$, the working distance was 7.4 mm, and the numerical aperture was 0.3. The mass of the sapphire substrates was measured by the analytical balance and all data were the means of four tests. The equation below was used to calculate the MRR.

$$\text{MRR} = 10^6 \Delta m / (\rho \pi d^2 t) \quad (1)$$

(MRR—material removal rate ($\mu\text{m}/\text{h}$); m —mass of material removed (g); ρ —density of sapphire, $3.98\ \text{g}/\text{cm}^3$; d —diameter of sapphire, 50.8 mm; t —polishing time, 2 h)

3 Results and discussion

After the modification process, the colloidal silica particles, shown in Fig. 2(a), and Ag-doped silica

Fig. 2 The SEM images of colloidal silica abrasives and Ag-doped silica abrasives: (a) colloidal silica abrasives, (b) 0.5 wt% Ag_2O , (c) 1.0 wt% Ag_2O , and (d) 1.5 wt% Ag_2O .

abrasives with various contents of Ag_2O , shown in Figs. 2(b), 2(c), and 2(d), were observed by SEM. All particles were mono-dispersed with spherical appearance and were similar to the $\text{SiO}_2/\text{CeO}_2$ composite abrasives [19] and Mg doping colloidal SiO_2 abrasives [22].

To investigate whether the element Ag was absorbed into the abrasives, the colloidal silica abrasive and the modified silica abrasives were analyzed by TOF-SIMS (Fig. 3) to study the element composition of the compound which was an effect way to investigate the component of the abrasives. In Fig. 3, the X axis was the relative atomic mass, and the Y axis represented the intensity of the element in the sample. The argentum peak in Fig. 3(b) showed the evidence of surface modification of colloidal silica via this process by comparing it with Fig. 3(a).

Fig. 3 TOF-SIMS spectrum of the colloidal silica abrasive (a) and Ag-doped colloidal silica abrasive containing 1.5 wt% Ag_2O (b).

Figure 4 showed the relationship between the MRR and the mass content of Ag_2O . With an increased content of Ag_2O , the MRR increased rapidly. The MRR increased steeply from $0.324 \mu\text{m}/\text{h}$ to $0.724 \mu\text{m}/\text{h}$ when the content of Ag_2O ranged from 0 to 1.5 wt%. The MRR of sapphire substrates polished by pure colloidal SiO_2 abrasive was $0.324 \mu\text{m}/\text{h}$. When the content of Ag_2O reached 1.5 wt%, the MRR was two times greater than pure colloidal SiO_2 abrasive. In other words, the prepared Ag-doped colloidal SiO_2 composite abrasives possessed a higher MRR than pure colloidal SiO_2 abrasives. Meanwhile, when it was compared with the $\text{SiO}_2/\text{CeO}_2$ composite abrasive [19] and Mg-doped abrasive [22], the MRR of Ag-doped abrasive ($0.724 \mu\text{m}/\text{h}$) was much more than the $\text{SiO}_2/\text{CeO}_2$ composite abrasive ($0.295 \mu\text{m}/\text{h}$) and Mg-doped abrasive ($0.617 \mu\text{m}/\text{h}$). Ag-doped abrasive exhibited much better CMP performance on the MRR than the other two.

Surface roughness of sapphire was presented in Fig. 5. It was observed in Fig. 5 that surface roughness decreased linearly with the mass content of Ag_2O ranging from 0 wt% to 1.5 wt%. All Ra values of sapphire substrates polished by slurries containing Ag-doped silica composite abrasives obviously decreased when compared with the pure silica abrasive under the same testing conditions. When the content of Ag_2O reached 1.5 wt%, the sapphire substrate had the minimum value (0.854 nm). The result of the

Fig. 4 The relationship between MRR and the mass content of Ag_2O in abrasives (red line is the error bar).

Fig. 5 The relationship between Ra and the mass content of Ag_2O in abrasives (red line is the error bar).

MRR and Ra suggested that colloidal silica abrasives after Ag modifying not only increased the removal rate but also improved the surface quality.

Figure 6 showed the surface morphology analysis of the sapphire substrate. It was performed by the AMBIOS TECHNOLOGY XI-100 Optical Surface Profiler. The surface morphology of the sapphire substrate before polishing was shown in Fig. 6(a). Figure 6(b) depicted surface profiles of sapphire polished by colloidal silica abrasives. Figure 6(c) depicted surface profiles of sapphire polished by Ag-doped colloidal silica with the mass content of 1.5 wt% Ag_2O in abrasive. In Fig. 6, it was obviously that Figs. 6(a) and 6(b) demonstrated wavier behavior than Fig. 6(c) whose surface was smoother and the topography fluctuation could hardly be observed. The peak-valley values of Figs. 6(a) and 6(b) were bigger than Fig. 6(c). A better surface could be reached by using Ag-doped colloidal silica abrasive to polish the sapphire substrate.

To further study the removal mechanism of sapphire, the Ag-doped colloidal silica containing 1.5 wt% Ag_2O after polishing was subjected to XPS in Fig. 7. After the slurry was dried in the oven, the residuum was ground into powder in the agate mortar. Finally, it was analyzed by XPS.

The XPS spectrum of element Si 2p, Al 2p, and Ag 3d was presented above. The binding energy of various substances was displayed in Tables 1–3. The black line was the real total intensity measured by

Fig. 6 Surface profiles of sapphire (a) before polishing ($R_a = 3.62$ nm), (b) polished by colloidal silica ($R_a = 2.24$ nm), and (c) polished by Ag-doped colloidal silica containing 1.5 wt% Ag_2O ($R_a = 0.85$ nm).

XPS test, and the green line was the total intensity after curve fitting by using the Thermo Advantage software. The overlap ratio between the real result (black line) and the fitting result (green line) contributed to more accurate measurement results.

In Fig. 7, the peak at the binding energy (BE) of 102.3 eV (Fig. 7(a)) corresponded to Si 2p of SiO₂, which were the fundamental particles of the slurry [23]. The BE at 103.1 eV (Fig. 7(a)) was in conformity with Si 2p of Al₂SiO₅ here. At the same time, the peak at

Fig. 7 XPS spectra of element Si, Al, and Ag in abrasives containing Ag-doped colloidal SiO₂ with 1.5 wt% Ag₂O after polishing: (a) Si 2p, (b) Al 2p, and (c) Ag 3d.

Table 1 Binding energy of Si 2p.

Chemical state	Binding energy (eV)
Al ₃ N ₅ O ₃ Si ₃	101.7
SiO ₂	102.3
Al ₂ SiO ₅	103.1

Table 2 Binding energy of Al 2p.

Chemical state	Binding energy (eV)
Al ₂ O ₃	72.73
Al ₃ N ₅ O ₃ Si ₃	74.50
Al ₂ SiO ₅	74.91
Al(OH) ₃	75.77
AlOOH	76.63

Table 3 Binding energy of Ag 3d.

Chemical state	Binding energy (eV)
AgO	367.3
Ag ₂ O	368.6

74.91 eV in Fig. 7(b) which corresponded to Al 2p of Al₂SiO₅. This situation showed that SiO₂ might react with the sapphire, and Al₂SiO₅ might be the product. The possibility of chemical reaction during the CMP process was as follows:

That guess was proven by Vovk who revealed that aluminum silicate with the composition Al₂SiO₅ could be formed on the polished surface and the silicon-containing near-surface layer thickness was about 20 nm [24]. The CMP process occurred on the surface activated by the destruction of interatomic bonds after an amorphous silicon-containing layer was removed under the mechanical frictional action of silica particles on sapphire surface.

In Fig. 7(b), the peaks at the BE of 75.77 eV and 76.63 eV of Al 2p XPS spectra were intermediate products (Al(OH)₃ and AlOOH). The forming process could be described as

In addition, the peak at BE of 74.50 eV in Fig. 7(b) corresponded to Al 2p of Al₃N₅O₃Si₃, the peak at BE of 101.7 eV in Fig. 7(a) corresponded to Si 2p of

$\text{Al}_3\text{N}_5\text{O}_3\text{Si}_3$ [25]. In Fig. 7(c), the Ag 3d peak met with AgO at 367.3 eV. The peak at BE of 368.6 eV (Fig. 7(c)) corresponded to Ag_2O . Compared with the colloidal silica, Ag-doped colloidal silica abrasives were more effective on sapphire CMP. However, argentum did not form the new compound during the CMP process as referred to Fig. 7(c). Therefore, argentum might act as a catalyst to accelerate the reaction between sapphire and Ag-doped colloidal silica. The equations were deduced as follows:

Compared to polishing with pure silica abrasive, Ag-doped colloidal SiO_2 abrasives had a great enhancement in MRR and Ra which could be explained by the chemical equations above. The addition of argentum ions could promote the reaction between abrasives and sapphire.

4 Summary

Ag-doped colloidal SiO_2 abrasives were synthesized by a seed-induced growth method. The Ag-doped colloidal SiO_2 abrasive was effective and improved polishing performance of sapphire. At the content of 1.5 wt% Ag_2O , the MRR was two times greater than the pure SiO_2 abrasive. The Ra decreased from 3.62 nm to 0.85 nm. During the polishing process, Ag_2O was formed and acted as a catalyst to accelerate the reaction between the slurry and sapphire during the CMP process.

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