Effect of ammonium molybdate concentration on chemical mechanical polishing of glass substrate*

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Abstract: The effect of the ammonium molybdate concentration on the material removal rate (MRR) and surface quality in the preliminary chemical mechanical polishing (CMP) of a rough glass substrate was investigated using a silica-based slurry. Experimental results reveal that the ammonium molybdate concentration has a strong influence on the CMP behaviors of glass substrates. When the ammonium molybdate was added to the baseline slurry, polishing rates increased, and then decreased with a transition at 2 wt.%, and the root mean square (RMS) roughness decreased with increasing ammonium molybdate concentration up to 2 wt.%, after which it increased linearly up to 4 wt.%. The improvement in MRR and RMS roughness may be attributed to the complexation of hydrolysis products of the glass substrate with the ammonium molybdate so as to prevent their redeposition onto the substrate surface. It was found that there exists an optimal ammonium molybdate concentration at 2 wt.% for obtaining the highest MRR and the lowest RMS roughness within a particular polishing time.

1. Introduction

With the rapid popularization and improvement of home electronic products, such as VCDs, DVDs, CVDs and HDVDs, the demand for digital compact discs (CDs) is growing at an astounding rate[1]. As the mastering substrate in the manufacture of CDs, glass substrates must reach a high surface quality, which influences the accuracy of data transferred to the CD and the number of times that the glass substrate can be used. Chemical mechanical polishing (CMP), which combines mechanical friction and chemical corrosion, arising from the abrasives and the slurry chemicals, respectively, has become an accepted planarization technology in manufacturing CD glass substrate due to its high surface quality[2−4]. In the CMP of a glass substrate, ceria (CeO₂) is the most widely used abrasive due to its high material removal rate (MRR) and relatively good surface quality[5]. However, blue ray technology is now entering the CD market, and this requires an even better surface quality that is defect free and exhibits low roughness and dynamically stable substrates at increasing rotation speeds. Ceria particles may not satisfy the surface quality required for blue ray series glass substrates due to its broad size distribution and irregular shape[6]. Silica (SiO₂) abrasive is suitable candidate because it can be prepared as monodispersed spheres with a narrow size distribution. In addition, silica abrasive is cheaper than ceria abrasive. In spite of these advantages, silica abrasive has not yet gained widespread commercial acceptance in the field of glass CMP since its glass polish rate is very low[7].

In this study, we have selected ammonium molybdate as the chemical to increase the glass polishing rate. It is found that the addition of ammonium molybdate can enhance the MRR and improve the surface quality, and there is an optimal ammonium molybdate concentration to obtain the highest MRR and the lowest root mean square (RMS) roughness within a particular polishing time.

2. Experimental methods

The slurry used for this study was a colloidal silica solution (10 wt.%) supplied by Shanghai Xinanna Electronic Science & Technology Co., Ltd. The colloidal silica had a mean particle size of about 50 nm (as shown in Fig. 1), which was investigated by scanning electron microscopy (SEM). Ammonium molybdate was used as a polishing rate accelerant and the concentrations studied were 1 wt.%, 2 wt.% and 4 wt.%. The original pH of the slurry was around 9. After ammonium molybdate was added to the slurry and dissolved, the pH decreased, but pH 9 was restored by adding 0.1 M NaOH.

Two inch pristine Soda Lime glass substrates of constant surface roughness were polished using a CMP tester (CETR, CP-4) with a polyurethane (PU) pad (Universal Photonics, LP66). The polishing process parameters used in this study are given in Table 1. The pad was conditioned prior to each pol-
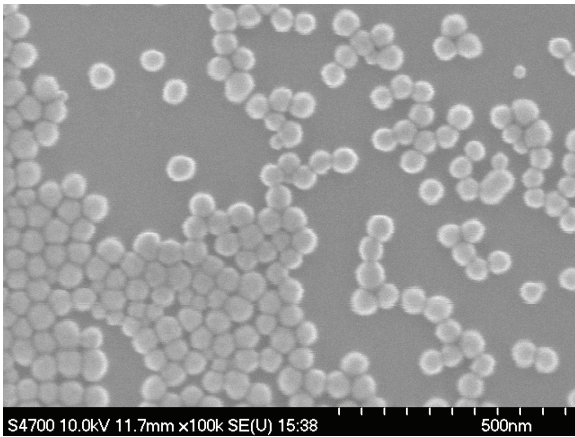
Fig. 1. SEM image of silica particles used in this study.
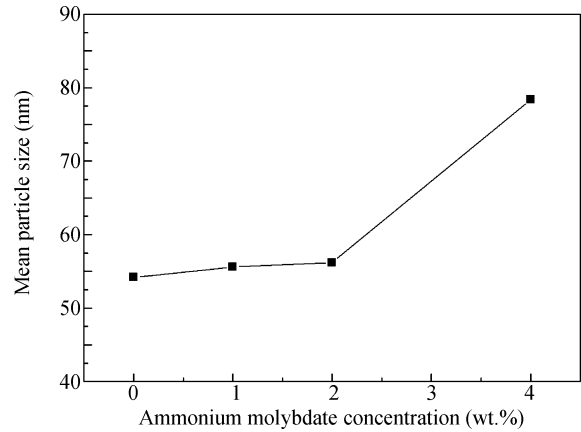
Table 1. Process parameters used for glass polishing using a CP-4 polisher.

Parameter	Value
Pad rotation speed	100 rpm
Wafer rotation speed	100 rpm
Down force	5 psi
Slurry feed rate	100 mL/min
Polishing time	30 min

ishing for 5 min using a 4 inch diamond grit conditioner. After polishing, the substrate was rinsed in an ultrasonic bath of deionised water and dried with N_2 gas.

The weight of glass substrate before and after polishing was measured with an electron balance to calculate the MRR according to Eq. (1),

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

Here, Δm (g) is the mass variation of glass after polishing, t (min) is the polishing time, ρ is the density of glass substrate and the MRR (nm/min) is the corresponding removal rate. The polished surface topography and RMS were measured by a Quesant Q-Scope 250 atomic force microscope (AFM). The AFM operating mode was contacting mode, and the scan area was $10 \times 10 \ \mu m^2$. The MRR and RMS roughness were the average of 3 individual polishing tests.

3. Results and discussion

Particle size analysis via light scattering was selected to detect the agglomeration of silica particles as the ammonium molybdate concentration was increased. Figure 2 shows the mean particle size of colloidal silica as a function of ammonium molybdate concentration. The mean particle size of colloidal silica in the baseline slurry was found to be 54.2 nm. This demonstrates that the silica was well dispersed in the absence of ammonium molybdate. When the ammonium molybdate concentration was below 2 wt.%, the mean particle size was almost unchanged. This result suggests that the electrostatic repulsion force was sufficient to maintain a well-dispersed slurry when the ammonium molybdate concentration was low. When 4 wt.% ammonium molybdate was added to the baseline slurry,

Fig. 2. Mean particle size of colloidal silica as a function of ammonium molybdate concentration.
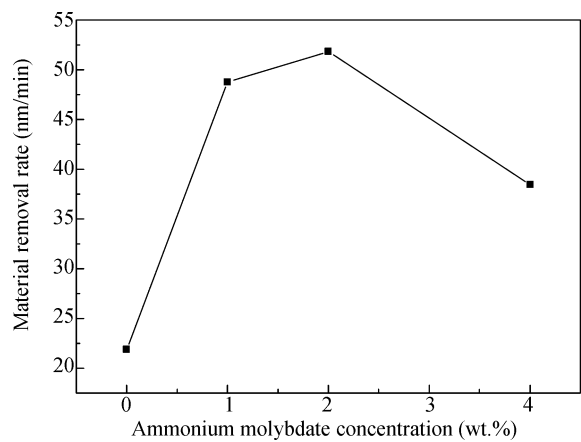

Fig. 3. MRR as a function of ammonium molybdate concentration.

the mean particle size increased sharply. This may be due to a decrease in the electrostatic repulsion force via ionic screening, which resulted in the agglomeration of the silica particles[8].

Figure 3 shows the MRR as a function of ammonium molybdate concentration. It was found that only 21.87 nm/min could be obtained using the baseline slurry (0 wt.% ammonium molybdate concentration). When the ammonium molybdate was added to the baseline slurry, the initial enhancement in the MRR up to 2 wt.% was followed by a significant decrease in the MRR at 4 wt.%. The highest MRR of 51.84 nm/min, which is twice as large as that of the baseline slurry, was achieved at a 2 wt.% ammonium molybdate concentration.

Figure 4 shows the RMS roughness as a function of ammonium molybdate concentration. When the ammonium molybdate was added to the baseline slurry, the RMS roughness decreased with increasing ammonium molybdate concentration up to 2 wt.%, after which it increased linearly up to 4 wt.%. To further investigate the surface features of glass substrates, typical AFM images of unpolished and polished surface were captured (see Fig. 5). The results mentioned above indicate that there exists an optimal ammonium molybdate concentration at 2 wt.% to obtain the highest MRR and the lowest RMS roughness within a particular polishing time. It was found that RMS roughness is inversely proportional to the MRR. This result may be explained as follows. The glass surface before polish-
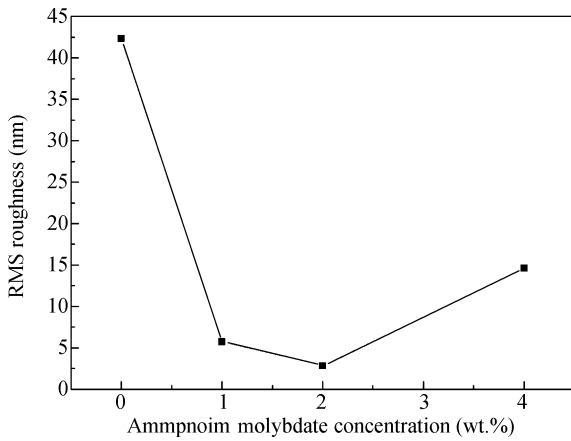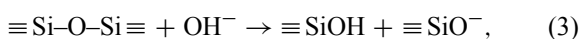
Fig. 4. RMS roughness as a function of ammonium molybdate concentration.

(a)

(b)

(c)

Fig. 5. Typical AFM images of surfaces that are unpolished (a) and polished by a silica-based slurry with (b) 0 and (c) 2 wt.% ammonium molybdate.

ing is very rough and the polishing time of 30 min is not enough to remove the surface damage layer shown by the AFM images in Fig. 5. In this case, the higher MRR results in a lower roughness. Prolonging the polishing time so as to remove the surface damage layer completely is the best way to reduce the RMS roughness. This will be studied in future work.

To further understand these results, the polishing mechanism was analyzed. Glass polishing in the basic silica based slurry is a chemical mechanical polishing process[1]. In general, CMP is explained by a combination of chemical and mechanical actions. The first is characterized by the chemical reaction between the sample material and the slurry liquid. The second is the action of friction between the abrasives and the polished surface. We will explain the results from the above two effects in terms of chemical reaction and coefficient of friction (COF), respectively.

In this study, the glass substrate polished in the experiment is Soda Lime glass. The structure of Soda Lime glass polished in this study is classified into two kinds: one is the continuous network, $\equiv$Si–O–Si$\equiv$, and the other is the collapsing structure, $\equiv$Si–O–Na (or terminal structure). When exposed to water, the glass reacts with water as shown in the follow reactions[1],

$$\equiv Si\text{–}O\text{–}Na + H_2O \rightarrow \ \equiv SiOH + Na^+ + OH^-, \quad (2)$$

$$\equiv Si\text{–}O\text{–}Si \equiv + OH^- \rightarrow \ \equiv SiOH + \equiv SiO^-, \quad (3)$$

$$\equiv SiO^- + H_2O \rightarrow \ \equiv SiOH + Na^+ + OH^-. \quad (4)$$

The Si–(OH) bonds are formed on the surface. This layer is softer than the glass, which facilitates its removal. Silica abrasive may provide mechanical grinding during the polishing. However, the abraded glass may remain at the interface, causing issues such as redeposition and increased surface roughness. When the ammonium molybdate is added into the baseline slurry, it can form a complex with the hydrolysis products of the glass substrate[9]. This complex reaction allows the hydrolysis products of glass to dissolve and hence be moved into the exit stream, which prevent their redeposition onto the glass substrate surface[9]. The initial enhancement in the MRR and the reduction in the RMS roughness up to 2 wt.% when the ammonium molybdate is added into the baseline slurry is ascribed
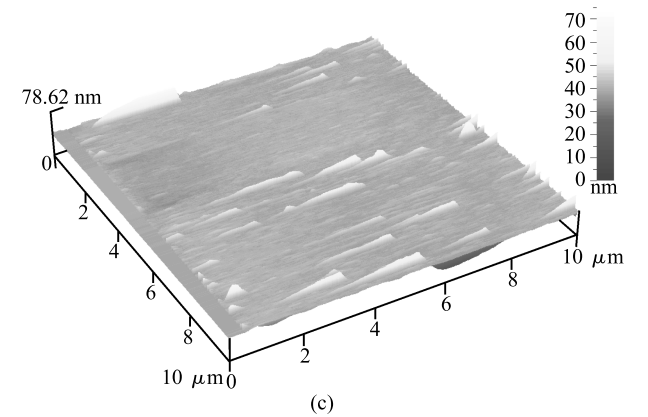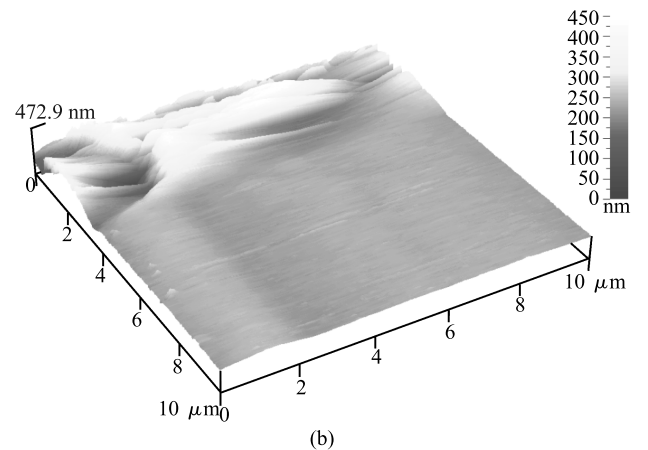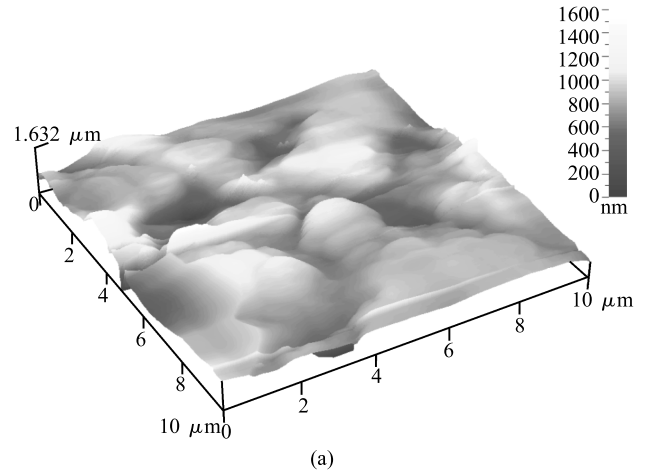
to the complexation of the hydrolysis products of glass with ammonium molybdate so as to prevent their redeposition onto the substrate surface. When the ammonium molybdate concentration reaches 4%, the MRR decreases sharply. This may be explained by the nonuniform contact between the glass surface and the agglomerated particles, which is confirmed by the particle size analysis, as shown in Fig. 2[8].

The study of the friction behavior during polishing is of great importance in evaluating this phenomenon with regard to the material removal mode, abrasive wear and surface quality[10]. Figure 6 shows the COF as a function of polishing
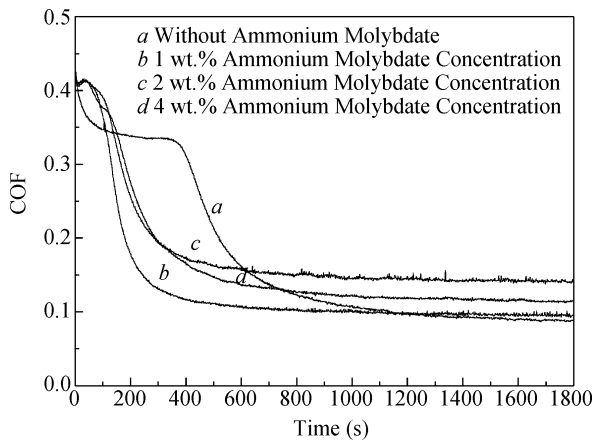
Fig. 6. COF as a function of polishing time for glass substrates polished by silica-based slurry with different ammonium molybdate concentrations.

time for glass substrates polished by a silica-based slurry with varying ammonium molybdate concentrations. The COF signal shoots up at the initial stage of polishing because the friction force between the wafer and the polishing pad, which is generated by the pressure and relative motion, overcomes the static friction force[11]. Then the COF decreases according to the polishing time in the first minutes and subsequently tends to become stable. The COF is known to be strongly dependent on the interfacial electrostatic interactions, dynamic surface conditions, properties of the opposing surfaces and the abrasive size, which all influence the contact area between the opposing surfaces[12]. In this study, the glass substrates were ground glass with many rough peaks (as shown in Fig. 4(a)), which were removed at the start of the polishing process with the high MRR[2]. The rough surface and high MRR may account for the high COF during the initial polishing process. With increased polishing time, the number of rough peaks decreased, which resulted in the decrease in RMS roughness, MRR and COF. When the rough peaks were completely removed, and consequently the contact area tended to remain constant, a stable COF was observed[10].

In addition, the stable COF values for the silica-based slurry were different according to the ammonium molybdate concentration: 2% > 4% > 1% > 0. This is in agreement with the trend of the MRR. From the above analysis, we can conclude that the COF is proportional to the MRR in this study.

4. Conclusions

In summary, we have investigated the effect of ammonium molybdate concentration on glass CMP performance. The addition of 2% ammonium molybdate showed the highest MRR and the best surface quality. These results revealed a mechanism in which ammonium molybdate reacted with the hydrolysis products of glass, preventing their redeposition onto the substrate, which enhanced the MRR and improved the surface quality of the glass substrate. This finding will be helpful in the application of silica based slurry in the field of glass CMP.

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