Journal of The Electrochemical Society, **157** (6) H688-H691 (2010)
0013-4651/2010/157(6)/H688/4/$28.00 © The Electrochemical Society

Two-Step Chemical Mechanical Polishing of Sapphire Substrate

Zefang Zhang,[a,b,c,z] Weili Liu,[a,c,z] Zhitang Song,[a,c] and Xiaokai Hu[a,c]

[a]*State Key Laboratory of Functional Materials for Informatics, Laboratory of Nanotechnology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China*
[b]*Graduate School of the Chinese Academy of Sciences, Beijing 100049, China*
[c]*Shanghai Xinanna Electronic Science and Technology Company, Limited, Shanghai 201506, China*

Chemical mechanical polishing (CMP), as a widely used planarization technology, requires high removal rate and low surface roughness generally. However, it is difficult to meet these requirements in a single-step polishing process. To get an ultrasmooth surface of the sapphire substrate, we investigated a two-step CMP of the sapphire substrate using ultrafine α-alumina-based slurry and nanoscale silica-based slurry. Also, in situ coefficient of friction (COF) measurements were conducted. The results show that during the first-step polishing in the alumina-based slurry, the COF decreases with polishing time first and then tends to be a constant; a relatively high material removal rate was reached, and the root-mean-square (rms) roughness value of the polished surface can be decreased from 968.9–21.98 Å. In the second-step CMP, the nanoscale silica slurry was adopted; the COF increased in the first minute of polishing and then became stable too, and the rms roughness of the sapphire substrate surfaces can be further reduced to 6.83 Å by using the optimized process parameters. In addition, the CMP mechanism of sapphire using the above two slurries was deduced and documented preliminarily.
 [DOI: 10.1149/1.3410116]

Manuscript submitted July 20, 2009; revised manuscript received March 27, 2010. Published May 3, 2010.

Sapphire, composed of monocrystallized α-alumina, is an important ceramic material used widely in a range of applications such as optics, electronics, and temperature sensing.[1] For these applications, the surface roughness of the sapphire substrate is the key factor that influences its performance. In the sapphire manufacture process, fine surface machining and polishing for optoelectronic application may exceed 80% of the total cost.[1] Undoubtedly, the planarization machining is very important; however, the intrinsic nature of sapphire (great hardness and chemical inertness) poses great challenges to such machining.[2] Chemical mechanical polishing (CMP), which combines mechanical friction and chemical corrosion arising from the abrasives and chemical of slurries, respectively, has become an accepted planarization technology due to its high surface quality at a low cost and fast material removal rates (MRRs).[3]

Generally, one kind of slurry may not achieve desirable high polishing rate and low surface roughness through a single-step CMP. Therefore, a two-step CMP with different slurries has been investigated in several papers.[4-10] Typically, the first polishing step is carried out by a rigid polishing pad and slurry with a hard abrasive, whereas the second step is completed with a tender polishing pad and slurry with a soft abrasive. Lei et al.[7] studied the two-step CMP of a rigid disk substrate by the alumina-based slurry and silica-based slurry and obtained an atomic-scale surface. Darcangelo et al.[10] invented a two-step CMP process for glass substrate. In the first step, a conventional ceria abrasive was used to polish the glass to a surface finish below 10 Å. Then the surface quality is further improved by the combined action of surface corrosion by the alkali solution and removal of the continually forming hydrated surface layer by the spherical colloidal silica. There have been some studies on two-step CMP and the results show that it is an effective method to planarize semiconductor wafers, rigid disks, and glass substrates. However, there are no current studies for the two-step CMP of sapphire.

In this study, an ultrafine α-alumina-based slurry and a nanoscale silica-based slurry were prepared, and the two-step CMP of sapphire substrate in the two slurries was studied. During the CMP process, in situ coefficient of friction (COF) measurements were conducted.

Experimental

Preparation of α-alumina-based slurry.— The calcined α-alumina abrasives obtained from Shanghai Gona Powder Technology Co., Ltd. were irregularly shaped particles with an average diameter of 500 nm (as shown in Fig. 1) and a bulk density of 0.8 g/cm^3. The 5 wt % alumina powder and 0.5 wt % sodium hexametaphosphate, which act as a dispersant, were added to deionized (DI) water in a container under stirring. Then the solution pH was adjusted to 12 using 0.1 M potassium hydroxide solutions. Finally, the mixture was filtrated with a 20 μm pore strainer.

Preparation of silica-based slurry.— Macrogol 6000 (0.5 wt %), as a surfactant, was added to 5 wt % silica gel self-made with an average diameter of 50 nm (as shown in Fig. 2) in a container under stirring. Then the solution pH was adjusted to 12 using triethanolamine. Finally, the mixture was filtrated with a 1 μm pore strainer.

Polishing tests.— In this study, 2 in. sapphire wafers [(0001) oriented] were purchased commercially and double-side ground on a SPEEDFAM-16B-4M grinding equipment with boron carbide as abrasives. Then the sapphire wafers were polished using a CMP tester (CETR, CP-4). In addition, the CP-4 polisher is designed with online detector instruments such as acoustic, temperature, and COF. The polishing process parameters for the first and second steps such as pad rotation speed, wafer rotation speed, down force, slurry feed rate, polishing time, and polishing pads are summarized in Table I. To prevent alumina aging effects, the slurry was stirred magnetically during the first-step CMP process. After polishing, the substrate was

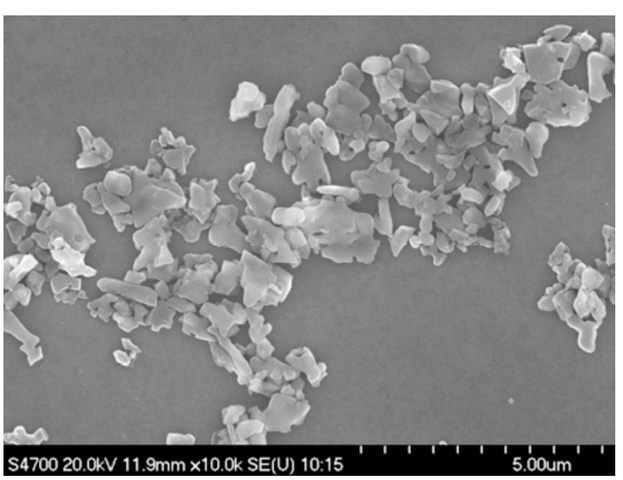

Figure 1. SEM image of alumina particles.

[z] E-mail: zfzhang@mail.sim.ac.cn, rabbitlwl@mail.sim.ac.cn

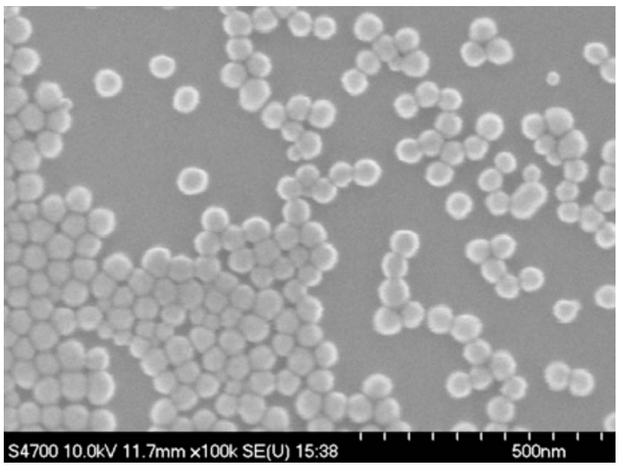

Figure 2. SEM image of silica particles.

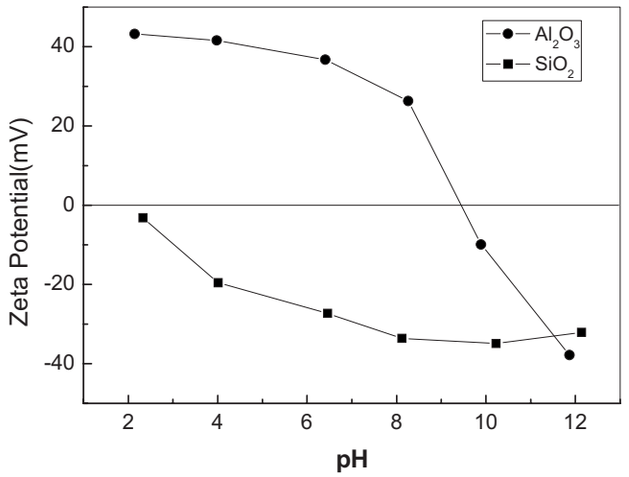

Figure 3. Zeta potentials of alumina and silica as a functional of pH values.

washed in an ultrasonic bath using a cleaning solution containing 1 wt % surfactant in DI water and then dried by N_2 gas.

Characterization methods.— The morphology of the abrasive particles was investigated by a Hitachi S-4700 field-emission-scanning electron microscope. The zeta potentials of the abrasive dispersing solution at different pH values were measured using a Particle Sizing System Nicomp 380. HCl/KOH was used to adjust the pH to the desired value. The weight of sapphire before and after polishing was measured by electron balance to calculate the MRR according to Eq. 1

$$\text{MRR} = \frac{10^7 \times \Delta m}{\rho \times 2.54^2 \times \pi \times t} \quad [1]$$

Here, Δm (g) is the mass variation in sapphire before and after polishing, t (min) is the polishing time, ρ is the density of sapphire, and MRR (nm/min) is the corresponding removal rate. The surface topography and root-mean-square (rms) roughness were measured by a Quesant Q-Scope 250 atomic force microscopy (AFM). The AFM operating mode was the contacting mode, and the scan area was 10×10 μm^2. The MRR and rms roughness is the average of 3 individual polishing tests.

Results and Discussion

Selection of pH value.— The pH value is an important influencing factor for the CMP performance. It plays a key role in the chemical component of the CMP process and may assist in stabilizing the slurries. The impact of pH on the sapphire polishing rate was studied by Zhu et al.[11] To study the pH effect, sapphire was polished using only pH adjusted DI water and pads in their study, where relative MRR increased as the pH was raised or lowered from neutral, and the highest removal rate was obtained near pH 12. The stability of abrasives at different pH values was characterized by the zeta potentials, and the results can be seen in Fig. 3. The absolute value of the zeta potentials for alumina and silica are more than 30 mV when the pH is about 12, which indicates that alumina and silica have good stability at or near pH 12. Therefore, we adjusted the slurry to pH 12.

Optimization of process parameters.— Many studies[12-14] have shown that the polishing parameters such as down pressure and rotation speed have an important influence on the CMP performance. In particular, for the second step, any little change in polishing parameters may have a strong effect on polished surface quality. We studied the influence of polishing pressure and rotation speed (both wafer and pad) on the MRR and rms roughness in the second step using a silica-based slurry, and the results can be seen in Fig. 4 and 5, respectively. During the change ranges of pressure and rotation speed in this study, the MRR increased with the increase in pressure or rotation speed. However, 5 psi and 100 rpm were adopted by us because the lowest surface roughness and moderate MRR were obtained.

COF analysis.— In situ friction force measurements have been used extensively to understand CMP mechanisms.[15-17] The friction force is known to be strongly dependent on interfacial electrostatic interactions, dynamic surface conditions, properties of the opposing

Table I. Process parameters of CMP processes.

Process conditions	The first step	The second step
Pad rotation speed (rpm)	100	100
Wafer rotation speed (rpm)	100	100
Down force (psi)	5	5
Slurry feed rate (mL/min)	100	100
Polishing time (min)	60	30
Polishing pads	Polyurethane pad (Shenyang Kejing Equipment Manufacturing Co., Ltd.)	Politex pad (Rohm and Hass)

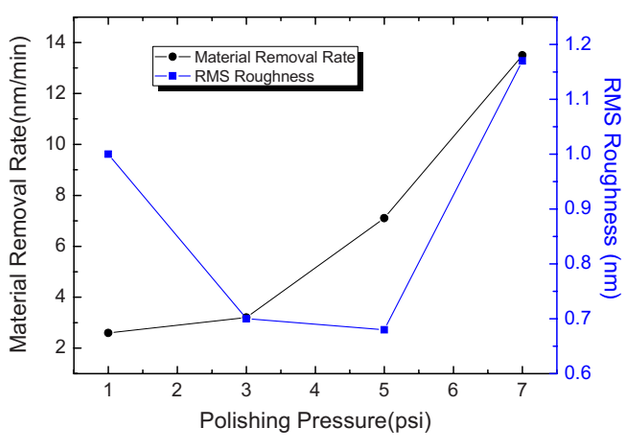

Figure 4. (Color online) Effect of polishing pressure on the MRR and rms roughness.

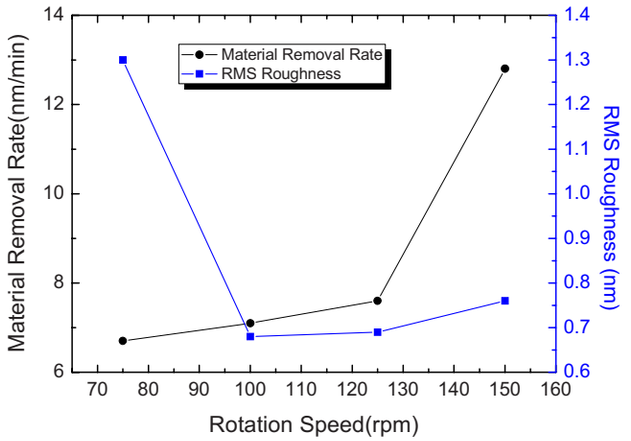

Figure 5. (Color online) Effect of rotation speed on the MRR and rms roughness.

surfaces, and the abrasive size, which all influence the contact area between the opposing surfaces.[18] The friction force is proportional to the normal load. The proportionality constant is the COF.[19] Figure 6 shows the COF as a function of polishing time for two steps. In the first step, the COF decreases sharply with the polishing time in the range of 0–500 s. However, there is no significant change in the COF when the time increases from 500 to 3600 s. In this study, the sapphire substrates polished were ground wafers and had many rough peaks (as shown in Fig. 7a). These rough peaks were first removed during the polishing process.[14] With the increasing polishing time, the number of rough peaks decreased, which results in the decrease in COF, as shown in Fig. 6. When the rough peaks are completely removed, the contact area tends to be a constant, which stabilizes the COF.[20] In the second step, the COF increases according to the polishing time in the first minute of polishing and then tends to be stable, which agrees with the results found by Belkhir et al.[20] The increase in the COF in the first minute is due either to the initial surface quality or to the first contact between the rough sample surface and the polishing pad.[20]

In addition, it is noticed that the COF in the second step is larger than that in the first step. This may be explained that the polishing pad used in the second step is the soft pad that induced the increase in contact area between the pad and surface of the sapphire substrate.

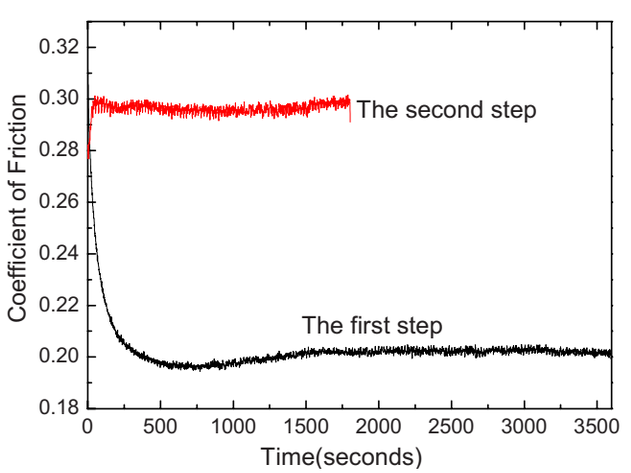

Figure 6. (Color online) COF as a functional of polishing time for two steps.

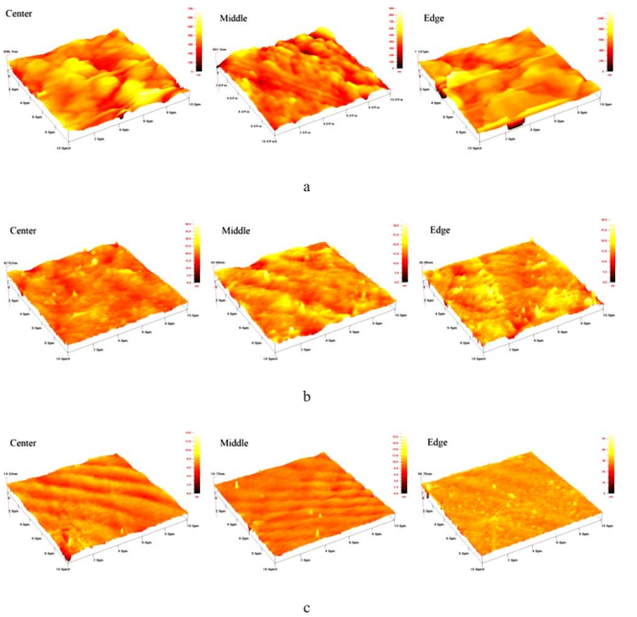

Figure 7. (Color online) Representative AFM images from center, middle, and edge of the sapphire in different CMP stages: (a) Before CMP, (b) after the first-step CMP, and (c) after the second-step CMP.

MRR and rms analysis.— The rms and MRR of sapphire substrates in different CMP stages are shown in Table II. It shows that the rms roughness value of the sapphire surface before polishing is very high. After the first-step CMP using an Al_2O_3 slurry, the rms value was decreased from 968.9 to 21.98 Å. Through the second-step CMP using a SiO_2 slurry by the optimized process parameters, the rms value can further be reduced to less than 1 nm. It means that the subnanometer precision sapphire surface has been obtained by using the two-step CMP.

The lower the Ra value is, the higher the surface planarization can be achieved. The higher the MRR is, the higher the polishing rates are.[6,21] An ideal CMP slurry or method is expected to reach the lowest surface roughness and the highest polishing rate. By comparing the two CMP processes, it is found that the first step gives higher MRR but poor surface quality, whereas the second step exhibits good surface quality but lower MRR. The first-step CMP using the prepared Al_2O_3 slurry is suitable for preliminary polishing to provide high polishing rate as well as full surface planarization, whereas the second-step CMP using the SiO_2 slurry is suitable for final polishing to provide a fine local planarization.[6] Therefore, by the combination of the two CMP steps with the two different slurries, the sapphire surface with subnanometer roughness can be achieved.

To further investigate the surface features of sapphire substrates, typical AFM images from the center, middle, and edge of the sapphire in different CMP stages are shown in Fig. 7. The sapphire substrate before CMP is ground sapphire and has many rough peaks (as shown in Fig. 7a). After the first-step CMP using the prepared Al_2O_3 slurry, the surface becomes smooth, but it is still rough with

Table II. RMS and MRR of sapphire substrates in different CMP stages.

	Before polishing	After the first-step CMP	After the second-step CMP
RMS (Å)	968.9	21.98	6.83
MRR (nm/min)		42.3	7.1

many microscratches. Further, through the second-step CMP using the nanoscale SiO_2 slurry, the surface becomes very smooth, and the number of microdefects including microscratches is further decreased. AFM analysis proves that the combination of two CMP steps with the two slurries can obtain an ultrasmooth sapphire substrate surface.

CMP mechanism.— The two kinds of slurry used in this study were composed of different abrasive particles with different shapes, hardness, and size, which result in separate removal rate and surface roughness. The Mohs hardness of α-alumina and silica are 7 and 9, respectively, and the sapphire has the same hardness as α-alumina. A hard abrasive can polish a soft material. Why can the soft silica polish a hard sapphire? This may be explained as follows.

The polishing process of sapphire using the prepared α-Al_2O_3-based slurry and SiO_2-based slurry have been considered as a CMP process, which is regarded as a combination of chemical and mechanical effects.[11,22-25] Many researchers have used several analytical techniques, including sputtered neutral mass spectrometry, metastable impact electron spectroscopy, thermal programmed desorption, low angle X-ray scattering, extended X-ray absorption fine structure, Fourier transform infrared (FTIR), AFM, and X-ray photoelectron spectroscopy (XPS) to study the surface modification of sapphire during the CMP process.[18] However, no technique or combination of techniques was found to unambiguously provide the composition, structure, and thickness information for a surface modification layer. Fortunately, XPS and FTIR conducted by Zhu et al.[11] showed that there are hydroxyls on the sapphire surface, and the AFM analysis of polished samples suggested that the hydration layer might be 1 nm thick. The following formulas offer some indication of the hydration layer

$$Al_2O_3 + H_2O \Leftrightarrow 2AlO(OH) \quad [2]$$

$$Al_2O_3 + 3H_2O \Leftrightarrow 2Al(OH)_3 \quad [3]$$

In the α-Al_2O_3-based slurry, α-Al_2O_3 can hydrate in a similar way to sapphire because they have the same crystal structure. When the two surfaces are brought into intimate contact under polishing pressure and shear, mutual adhesion occurs.[11] Further shear may allow the particle to "tear away" the bonded hydrated layers and even promote further removal by the sharp edge of the particle.[11] Simultaneously, perhaps due to the irregular shape and large size of alumina, a relatively high rms surface roughness was obtained.

There are three major proposed mechanisms for superpolishing sapphire using silica-based slurry. However, two of them may be used to explain the CMP process according to Zhu et al.'s study.[11] First, Namba et al.[22-24] proposed a pure mechanical wear mechanism at an atomic scale: The silica particles, moving with polishing fluid, collide with atoms from the sapphire surface; this collision causes an exchange of atoms by diffusion. During the next bombardment, the point defects produced are removed together with some surrounding substrate atoms. Second, Gutsche and Moody[25] reported that the polishing of silica is believed to follow a pure chemical reaction according to Eq. 4, and the reaction product is the aluminum silicate dehydrate. Meanwhile, the combination of two effects, the small size and round shape of silica, led to a good rms roughness

$$Al_2O_3 + 2SiO_2 + 2H_2O \rightarrow Al_2Si_2O_7 \cdot 2H_2O \quad [4]$$

Nevertheless, an online examination of the physical and chemical changes during the polishing process is lacking. The real CMP mechanism may be very complicated. More work needs to be done on these in the future.

Conclusions

The prepared α-alumina-based slurry and the nanoscale silica-based slurry are suitable for the preliminary polishing and the final polishing of sapphire substrates, respectively. After the two-step CMP using the two different slurries, the rms of the sapphire substrates can be decreased to 6.83 Å, and the AFM analysis shows that an ultrasmooth surface almost without microdefects has been achieved.

Acknowledgment

The work is sponsored by the National Integrate Circuit Research Program of China (no. 2009ZX02030 and no. 2009ZX02023), Programs from Science and Technology Council of Shanghai (no. 0952nm00200 and no. 08111100300), Shanghai Rising Star Program (no. 07QH14017), National Basic Research Program of China (no. 2007CB935400, no. 2010CB934300, and no. 2006CB302700), and National High Technology Development Program of China (2008AA031402).

Chinese Academy of Sciences assisted in meeting the publication costs of this article.

References

1. H. L. Zhu, L. A. Tessaroto, R. Sabia, V. A. Greenhut, M. Smith, and D. E. Niesz, *Appl. Surf. Sci.*, **236**, 120 (2004).
2. X. Hu, Z. Song, Z. Pan, W. Liu, and L. Wu, *Appl. Surf. Sci.*, **255**, 8230 (2009).
3. P. B. Zantye, A. Kumar, and A. K. Sikder, *Mater. Sci. Eng. R.*, **45**, 89 (2004).
4. Y. Ding, X. Zhang, and W. Gan, U.S. Pat. 2,007,264,827-A1 (2007).
5. M. S. Tsai, J. S. Lin, and B. T. Dai, *Proc. SPIE*, **3508**, 216 (1998).
6. H. Lei, H. Lu, P. Zhang, Z. Zhang, and B. Xiao, in *Proceedings of the 7th International Conference on Frontiers of Design and Manufacturing*, National Natural Science Foundation of China, p. 445 (2006).
7. H. Lei, J. B. Luo, and X. C. Lu, *Chin. J. Mech. Eng.*, **19**, 496 (2006).
8. Z. H. Lin, A. Yu, C. R. Hsu, and T. Tsai, U.S. Pat. 2,006,258,158-A1 (2006).
9. D. H. Min, U.S. Pat. 2,007,148,969-A1 (2007).
10. C. M. Darcangelo, R. Sabia, and H. J. Stevens, U.S. Pat. 6,322,425 (2001).
11. H. L. Zhu, D. E. Niesz, V. A. Greenhut, and R. Sabia, *J. Mater. Res.*, **20**, 504 (2005).
12. W. Cho, Y. Ahn, C. W. Baek, and Y. K. Kim, *Microelectron. Eng.*, **65**, 13 (2003).
13. M. Forsberg, *Microelectron. Eng.*, **77**, 319 (2005).
14. Z. F. Zhang and H. Lei, *Microelectron. Eng.*, **85**, 714 (2008).
15. W. Choi, U. Mahajan, S. M. Lee, J. Abiade, and R. K. Singh, *J. Electrochem. Soc.*, **151**, G185 (2004).
16. U. Mahajan, M. Bielmann, and R. K. Singh, *Electrochem. Solid-State Lett.*, **2**, 80 (1999).
17. U. Mahajan, M. Bielmann, and R. K. Singh, *Electrochem. Solid-State Lett.*, **2**, 46 (1999).
18. J. T. Abiade, W. Choi, and R. K. Singh, *J. Mater. Res.*, **20**, 1139 (2005).
19. H. Liang and D. R. Craven, *Tribology in Chemical-Mechanical Planarization*, p. 185, Taylor & Francis, Boca Raton, FL (2005).
20. N. Belkhir, D. Bouzid, and V. Herold, *Tribol. Lett.*, **33**, 55 (2009).
21. H. Lei and P. Z. Zhang, *Appl. Surf. Sci.*, **253**, 8754 (2007).
22. Y. Namba and H. Tsuwa, *CIRP Ann.*, **26**, 325 (1977).
23. Y. Namba and H. Tsuwa, *CIRP Ann.*, **27**, 511 (1978).
24. M. J. Bennett, J. J. Shaffer, Y. Shibano, and Y. Namba, *Appl. Opt.*, **26**, 696 (1987).
25. H. W. Gutsche and J. W. Moody, *J. Electrochem. Soc.*, **125**, 136 (1978).