Study on polishing slurry of hydrogen peroxide-oxalic acid in CMP 304 stainless steel

Jianchun Weng[1, *], *Rongchuan* Lin[1], and *Xing* Rong[1]

[1]College of Mechanical and Energy Engineering, Jimei University, Xiamen 361021, China

Abstract. Stainless steel will become the substrate material of the flexible display, requirements of the flexible substrate in the surface quality and performance are very strict. Chemical mechanical polishing (CMP) is one of the most appropriate technologies to achieve the surface processing of ultra-thin stainless-steel flexible display substrate with ultra-smooth and damage-free. In this paper, the design of CMP slurry of 304 stainless steel on the hydrogen peroxide-oxalic acid type was proposed. Through experiment and analysis, the basic ingredients of CMP slurry was obtained. The research results showed that the hydrogen peroxide can increase the hydrophilicity of the stainless steel surface, and the Fenton type Haber-Weiss reaction can occur on the surface of the fresh metal substrate of stainless steel. The trivalent iron ions generated by the Fenton type reaction combined with oxygen to generate iron oxide and promoted the removal of the surface material. Under acidic conditions, the oxalic acid can decrease the stability of the oxide film on the stainless steel surface, promote the diffusion of oxygen into the metal interface, improve the oxygen reduction reaction, and increase the material removal rate. The results will provide an important reference for the next researching the CMP slurry of 304 stainless steel.

1 INTRODUCTION

Flexible display with ultra-thin, light weight, durable, large storage capacity, design freedom, flexible, winding and impact resistance and other properties [1-2], will become an important goal for the future development of display technology and widely used in industrial, civilian and military industries [3-4]. Flexible display huge market prospects, so that many countries and regions of research institutions and manufacturers into the research and application of flexible display technology [5-6], in recent years, many enterprises have introduced a foldable or bendable OLED screen [7].

Flexible display is a flexible material as substrate, the requirements on the surface quality and properties of the flexible substrate are very strict, the surface roughness must be less than 5 nm, waviness is less than 0.1 microns, high thermal stability, light weight, high strength thin, high flexibility and toughness, etc., therefore, the stainless steel material cost is low, will become the main future flexible large size display substrate materials[8-9]. The biggest problem of stainless steel as the substrate of flexible display is that the surface roughness is too large, which requires ultra-precision polishing of its surface. The processing quality and accuracy of ultra-thin stainless steel sheet will directly affect the performance of its devices[10]. At present, there is no technology for large-area (roll-to-roll) ultra-precision polishing of ultra-thin stainless-steel sheets. Therefore, how to efficiently obtain high quality and high precision in processing large-size flexible display substrates to meet the requirements of current and future flexible displays is an urgent matter for the flexible display industry[11].

Chemical mechanical polishing (CMP) technology is considered to be the best process method that can meet both surface roughness and surface smoothness requirements. It has become one of the most practical technologies for hard and brittle crystal materials to achieve the super-smooth and non-damage processing surface, and has been widely used in ultra-large-scale integrated circuits, semiconductor lighting and other fields [12]. Chemical mechanical polishing technology is probably the most suitable and fully applicable for high-efficiency ultra-precision machining of large ultra-thin stainless-steel flexible display substrate surfaces to obtain ultra-smooth and non-damaged machining surfaces.

Polishing slurry is an important component in chemical mechanical polishing. Its cost accounts for 60%~70% of the total cost of chemical mechanical polishing, so its quality determines the efficiency, surface quality and cost of chemical mechanical polishing. Oxidant and pH regulator are the important components in a chemical mechanical polishing slurry, which can promote the chemical reaction of the polished surface material, make the abrasives play the micro cutting function evenly and effectively, and improve the material removal. Therefore, it is urgent to study the chemical mechanical polishing slurry of stainless steel with environmental protection and high efficiency.

Therefore, in order to develop an environmentally friendly and efficient chemical mechanical polishing

* Corresponding author: gingerwjc@163.com

slurry for stainless steel, this paper proposes the design of hydrogen peroxide-oxalic acid type 304 stainless steel chemical mechanical polishing slurry, which provides theoretical and technical support for the researches of large-scale production, chemical mechanical polishing slurry and chemical mechanical polishing mechanism.

2 Experimental preparation and experimental parameters

All the chemical mechanical polishing experiments conducted in class 1000 clean room, the environment temperature control in 22°C, the resistivity of demonized water used in the experiment is 18.24 MΩ·cm. Samples used in chemical mechanical polishing experiment were a number of 50 mm diameters 304 stainless steel sheets. Before the experiment, its surface roughness Ra was 40-50 nm. The polishing experiment was carried out on a ZYP300 lapping and polishing machine made in Shenyang, and the type of polishing pad was Rode IC1000.

Polishing parameters selection. The rotational speed of polishing platen is set 60 r/min, the carrier speed is set for 60 r/min, the polishing pressure P is 2 psi, and the polishing time is set 15 min. Every time after polishing, conditioning the polishing pad and dressing time is for 15 min. In the process of polishing, the carrier along the arc reciprocating swing, swing range of 20 mm, oscillation frequency of 10 s, center distance of the object stage and pads is set to 80 mm.

Test instrument used in the experiment. Sartorius CP225D precision balance (0.01mg) was used to measure the sample weight before and after the polishing experiment, and then the material removal rate was calculated by calculation. 3D surface microscope (0.01nm vertical resolution) of Contour GT-K with BRUKER companies in the United States production used to measure the surface topography and the surface roughness of samples before and after polishing. The Lecia metallurgical microscope with DM2500M is used to measure the 2D original image of the surface before and after polishing. Using JNGX JL-1197 laser particle instrument tests the distribution of abrasive polishing and with pH (0.1) precision electronic testing pen test polishing slurry pH value.

Basic ingredients of polishing slurry. According to the results of the previous polishing slurry test and the material characteristics of 304 stainless steel, white corundum was selected as the abrasive for the polishing experiment, sodium native phosphate was selected as the dispersant, oxalic acid was used as the pH regulator, and hydrogen peroxide was used as the oxidant. The total volume of the polishing slurry was 250ml for the each chemical mechanical polishing experiment.

3 The experiment

3.1 Orthogonal experimental designs

According to the previous studies, the orthogonal test table without interaction was adopted to carry out the orthogonal experiment, which was repeated for three times. The experimental results were analyzed the significance of each component on the removal rate and surface roughness of 304 stainless steel materials through SAS software, and the optimal polishing slurry component was obtained comprehensively according to the single factor experiment results.

The factors to be determined in this orthogonal experiment include: particle size and content of white corundum, sodium hexametaphosphate, oxalic acid and hydrogen peroxide content. Four levels are selected for each factor, and the factor levels of the orthogonal experiment are shown in Table 1.

Table 1. Table of orthogonal test factors for hydrogen peroxide oxalic acid type polishing slurry.

Factor / The level of	a	b	c	d	e
	Particle size(μm)	Particle content (g)	Sodium hexameta phosphate (g)	Oxalicacid (g)	Hydrogen peroxide (g)
1	0.5	1.5	1	1	5
2	3.5	4.5	3	2	10
3	7	7.5	5	3	15
4	14	10.5	7	4	20

3.2 Orthogonal experimental table and experimental results

According to the number of factors, the horizontal orthogonal table L_{16} (4^5) with 5 factors and 4 factors ware selected. After the test, the material removal rate and surface roughness test data were recorded, and the experimental results were shown in Table 2 of the orthogonal test.

Table 2. Optimization test data of hydrogen peroxide oxalic acid type polishing slurry.

Factor / Number	a Particle size (μm)	b Amount of abrasive (g)	c Sodium hexameta phosphate (g)	d Oxalic acid (g)	e Hydrogen peroxide (g)	MRR (nm/min)	Roughness (μm)
1	0.5	1.5	1	1	5	60.19632	0.011
2	0.5	4.5	3	2	10	109.89687	0.012
3	0.5	7.5	5	3	15	136.75368	0.017
4	0.5	10.5	7	4	20	121.31873	0.017
5	3.5	1.5	3	3	20	129.65361	0.017
6	3.5	4.5	1	4	15	145.39726	0.018
7	3.5	7.5	7	1	10	149.71904	0.05
8	3.5	10.5	5	2	5	184.60204	0.03
9	7	1.5	5	4	10	145.08856	0.034
10	7	4.5	7	3	2	156.81912	0.05
11	7	7.5	1	2	20	140.14937	0.04
12	7	10.5	3	1	15	141.69287	0.023

13	14	1.5	7	2	15	148.79295	0.055
14	14	4.5	5	1	20	133.97539	0.036
15	14	7.5	3	4	5	162.37571	0.042
16	14	10.5	7	3	10	197.87610	0.101

3.3 Experimental results and analysis

3.3.1 The influence of various factors on material removal rate and surface roughness

According to the analysis of variance, factors a, b, c, d and e have a very significant impact on the material removal rate and surface roughness (because the Pr>F value of each factor is less than 0.01). The order of significance of each factor on material removal rate was: F (a) >F (b) >F (d) >F (e) >F (c); The influence degree of each factor on the material removal rate is the particle size, particle content, oxalic acid content, hydrogen peroxide content, sodium hevatophosphate content in descending order. The order of significance of each factor on surface roughness: F (a) >F (e) >F (c) >F (d) >F (b); The degree of influence of various factors on surface roughness is in descending order from the largest to the smallest, namely, particle size, hydrogen peroxide content, sodium hevatophosphate content, oxalic acid content and particle content.

3.3.2 The optimal combination of polishing slurry and polishing scheme

The optimized composition of the polishing slurry is shown in Table 3, and Table 4 is the verification test of the optimized polishing slurry. Figure 1 shows 2D and 3D diagrams of the surface topography of 304 stainless steel polished by optimized polishing slurry.

Table 3. Optimal polishing slurry obtained by orthogonal test.

Factor	a Particle size (μm)	b Grinding particle content (g)	c Sodium hexameta phosphate (g)	d Oxalic acid (g)	e Hydrogen peroxide (g)
Numerical	3.5	7.5	5	4	15

Table 4. Optimized mechanical polishing test results of polishing liquefaction.

Factor / Number	MRR(nm/min)	Ra
1	201.8794	0.018
2	205.9571	0.017
3	200.6874	0.015

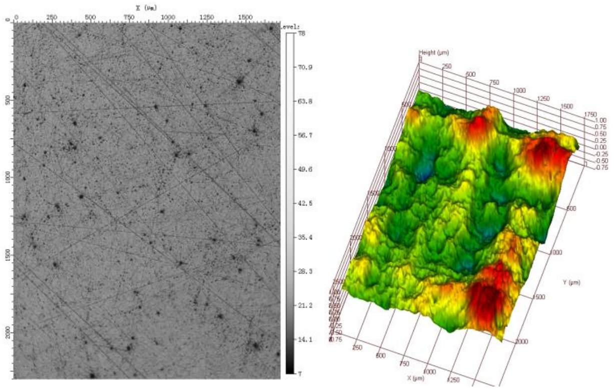

Figure 1. 2D and 3D diagrams of surface topography after polishing 304 stainless steel with optimized polishing slurry.

Figure 1 shows the surface morphology of 304 stainless steel after polishing with hydrogen peroxide oxalic acid polishing slurry. Based on the optimal ratio of polishing slurry, only the particle size was changed, and the polishing experiment was carried out under the same conditions to measure the material removal rate and surface roughness, and the polishing scheme of 304 stainless steel was obtained. See Table 5.

Table 5. Particle size selection scheme of hydrogen peroxide oxalic acid polishing slurry.

Particle diameter	30 (nm) Silica sol	50 (nm) Silica sol	W0.5 White fused alumina	W3.5 White fused alumina	W5 White fused alumina	W7 White fused alumina	W14 White fused alumina
MRR (nm/min)	71.86	90.60	126.75	201.88	212.37	145.39	171.57
Ra(μm)	0.007	0.009	0.017	0.018	0.023	0.038	0.040
Polishing stage	Semi finish polishing	Semi finish polishing	Rough polishing	Rough polishing	Rough polishing	Rough polishing	Rough polishing

4 Discuss

Oxalic acid ACTS as a pH regulator and hydrogen peroxide ACTS as an oxidant in the H_2O_2_oxalic acid chemical mechanical polishing slurry. When the oxalic acid content was 1.6%wt and hydrogen peroxide content was 6%wt, the material removal rate reached the maximum value. In chemical mechanical polishing, it is concluded that the addition of hydrogen peroxide can effectively improve the material removal rate.

(1) In chemical mechanical polishing, polishing interface can produce high temperature because of friction, this will increase the hydrophilicity on the surface of the stainless steel, under the action of hydrogen peroxide, this will increase the content of oxygen groups on the stainless steel surface. On the one hand, the hydrogen peroxide has the strong oxidizing, would that be to form a layer of dense oxide film on stainless steel surface [13], and it will be removed by the mechanical action of the particle. On the other hand, due to the presence of

oxygen in the polishing slurry, stainless steel will produce dissolved oxygen electrochemical corrosion[14], and the reaction formula is $Fe+1/2O_2+H2O \rightarrow Fe(OH)_2$.

(2) Oxalic acid is added into the polishing slurry to make the polishing slurry acidic. Under acidic conditions, due to the presence of H^+, on the one hand, the stability of the oxide film on the surface of stainless steel is reduced, which promotes the diffusion of oxygen to the metal interface and improves the oxygen reduction reaction; on the other hand, the hydrogen reduction reaction is increased, this is $2H_3O^++2e \rightarrow H_2\uparrow+2H_2O$, making the metal more soluble[15].

(3) Hydrogen peroxide, the oxidant in the polishing slurry, will have a Fenton-type Haber-Weiss reaction on the surface of the fresh metal matrix of stainless steel[16]. The decomposition of hydrogen peroxide will be accelerated, and the ferric ion generated by the reaction will combine with oxygen to form iron oxide. The main reaction mechanism is roughly as following:

$$Fe^{2+}+ H_2O_2 \rightarrow Fe^{3+}+HO\cdot+OH^+ \quad (1)$$

$$Fe^{2+}+ HO\cdot \rightarrow Fe^{3+}+ HO^- \quad (2)$$

$$H_2O_2 +HO\cdot \rightarrow HO_2\cdot+H_2O \quad (3)$$

$$Fe^{2+}+ HO_2\cdot \rightarrow Fe^{3+}+HO_2^- \quad (4)$$

$$Fe^{3+}+ HO_2\cdot \rightarrow Fe^{2+}+ H^+O_2 \quad (5)$$

$$Fe^{3+}+ HO_2^- \rightarrow Fe^{2+}+ HO_2\cdot \quad (6)$$

The iron oxide generated by the above reaction does not adhere firmly to the surface of the metal matrix, which is easy to fall off in the friction process and form particles. The metal matrix is exposed again, and the above process occurs repeatedly. The results show that the lower the pH of hydrogen peroxide polishing slurry, the more stable the oxidant hydrogen peroxide, the higher the material removal rate and the lower the surface roughness can be obtained.

5 Conclusion

To sum up, through a series of experiments, result analysis and discussion, the following conclusions are drawn:
(1) As a polishing slurry oxidant, the hydrogen peroxide can increase the hydrophilic of the stainless steel surface, increase the content of the stainless steel surface oxygen-containing groups, oxidize the surface of the stainless steel and formation of a layer of dense oxide film. And the existence of oxygen in the polishing slurry, will also make stainless steel produced dissolved oxygen electrochemical corrosion, promote the removal of materials.
(2) Hydrogen peroxide will produce Fenton-type Haber-Weiss reaction on the surface of the fresh metal matrix of stainless steel, and meanwhile, the ferric ion generated by the reaction will combine with oxygen to form iron oxide, promoting the material removal.
(3) When the pH value regulator of hydrogen peroxide based polishing slurry is oxalic acid, environmental protection requirements can be realized while adjusting the pH value. The lower the pH value of the polishing slurry, the greater the material removal rate.
(4) In acidic conditions, it will make the stainless steel surface oxidation film stability decline, promote oxygen to the metal interface diffusion and improve oxygen reduction reaction. Due to the presence of H^+, the hydrogen reduction reaction will increase, making the metal more soluble and promoting the material removal.
(5) Through orthogonal design and variance analysis The basic formula of H_2O_2-oxalic acid chemical mechanical polishing slurry for stainless steel was obtained. According to surface quality requirements of polishing, the selection of rough polishing and fine polishing process could be realized by changing the particle size.

The results of this paper provide an important reference for the further study of chemical mechanical polishing slurry of 304 stainless steel.

Acknowledgments

Natural Science Foundation of Fujian Province, China (2019J01709). Xiamen major science and technology projects (3502Z20191022).

References

1. Logothetidis S, Laskarakis A. Towards the optimization of materials and processes for flexible organic electronics devices[J]. The European Physical Journal Applied Physics, 2009,46(1): 12502(1-9).
2. Hwang Han Wook, Hong Seonghwan, Hwang Sang Soo, et al. Analysis of Recoverable Residual Image Characteristics of Flexible Organic Light-Emitting Diode Displays Using Polyimide Substrates[J]. IEEE Electron Device Letters, 2019,40(7):1108-1111.
3. Lee Seunghwan, Han Ju-Hwan, Lee Seong-Hyeon, et al. Review of Organic/ Inorganic Thin Film Encapsulation by Atomic Layer Deposition for a Flexible OLED Display, Journal of metals, 2019,71(1):197-211.
4. Bae S, Kim H, Lee Y, et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes [J]. Nature Nanotechnology, 2010, 5(8):574-578
5. Hong Kihyon, Yu Hak Ki, Lee IIIhwan, et al. Flexible top-emitting organic light emitting diodes with a functional dielectric reflector on a metal foil substrate, RSC Advances,2018,8(46): 26156-26160.
6. Someya T. Flexible electronics: Tiny lamps to illuminate the body [J]. Nature Materials, 2010, 9(11):879-880.
7. Xu zheng, song dandan, zhao su ling et al. Development and challenges of OLED, flexible, transparent display technology and organic light-

emitting materials. Modern display, 2009,101 (6) : 5-10

8. Sugimoto Akira, Ochi Hideo, Fujimure Soh, et al. Flexible OLED displays using plastic substrates [J]. IEEE J Sel Top Quantum Electron, 2004, 10(1): 107-114.
9. Bardsley J N. International OLED technology roadmap [J]. IEEE J Sel Top Quantum Electron, 2004, 10(1): 3-9.
10. Xie zhiyuan, Hung Liangsun, Zhu Furong. A flexible top-emitting organic light-emitting diode on steel foil[J]. Chem Phys Lett ,2003,381(5/6):691-696.
11. Liu haiyan. Performance and testing of glass substrates for tef-lcd [J]. Glass, 2009,36(1):22-24
12. Xiaokai Hu,Zhitang Song,Fei Qin,et al. Chemical mechanical polishing of stainless steel foil as flexible substrate. Applied Surface Science, 2012 ,258(15):5798-5802.
13. XIAO Xin, ZHONG Ping. Rapid pickling for stainless steel at room temperature, Electroplating & Finishing, 2005,24(1) 65-66.
14. Bao Qinai.The relationship between chloride ion and the corrosion of stainless steel in cooling water system,Industrial Water Treatment,2007,27(9) 1-6.
15. YE Chao, DU Nan, TIAN Wenming，et al. Effect of pH on Pitting Corrosion Process of 304 Stainless Steel in 3.5%NaCl Solution, Journal of Chinese Society for Corrosion and Protection, 2015, 35(1)38-43.
16. Wang Jihui, Gu Kali, Wuli. Surface Passivation Treatment and Tribological Properties of 1Cr18Ni9Ti Stainless Steel in Hydrogen Peroxide Solution, Tribology, 2009,29(1):18-26