Study on Dispersant of Hydrogen Peroxide-Oxalic Acid Polishing Slurry in Chemical Mechanical Polishing of 304 Stainless Steel

Yongsheng Wang¹, Rui Xu², Yipu Wang², Zhankui Wang² and Jianxiu Su²,*

¹Zhumadian Technician College, Zhumadian, 463000, P.R.China
²School of Mechanical and Electrical Engineering, Henan Institute of Science and Technology, Xinxiang, 453003, P.R.China
* Corresponding author, dlutsu2004@126.com

Abstract. Flexible display has become a research hotspot for next-generation display technology. Stainless steel materials will become one of the main materials for flexible large-size display substrates, and chemical mechanical polishing (CMP) technology will be one of the most practical processing technologies to achieve super-smooth, non-destructive surface of stainless steel material. In this paper, through a series of experiments, the material removal rate and surface roughness of hydrogen peroxide oxidizer under different dispersants and different dispersant contents were studied. The results shown that when the content of dispersant sodium hexametaphosphate is 1.2% wt, the material removal was the largest, which was 146nm / min. the surface roughness after CMP was relatively low, Ra = 10nm. Sodium hexametaphosphate was selected as the dispersant of the solution. The research results provided a reference for further study of 304 stainless steel chemical mechanical polishing fluid.

1. Introduction
Flexible displays have ultra-thin, light weight, durable, large storage capacity, design freedom, flexibility, rewinding and impact resistance[1-2], which widely used in mobile phones, personal digital assistants PDA, notebook computers, trademarks, security identity documents, e-books, e-posters, car dashboards, sensors, environmental displays, medical, general lighting, robotic skin [3-4] and other industrial, civil and military industries. Due to the huge market prospect of flexible display, many research institutions and manufacturers in many countries and regions have invested in the research and application of flexible display technology [5-6]. In recent years, many companies have continuously introduced foldable or bendable OLED screens [7]. Flexible display is based on flexible materials, which have very strict requirements on surface quality and performance of flexible substrate. The surface roughness must be less than 5nm, waviness less than 0.1μm high thermal stability, light weight, high strength, ultra-thin, high flexibility and toughness. Therefore, stainless steel material has low cost and will become the main material of flexible large-scale display substrate in the future [8-9]. The quality and precision of ultra-thin stainless steel sheet processing will directly affect the performance of its devices [10]. When there are tiny defects on the surface of ultra-thin stainless steel, they will be inherited to epitaxial growth film and become the fatal defect of the device. Therefore, how to efficiently obtain high-quality, high-precision large-size flexible display substrates to meet the requirements of present and future flexible displays is an urgent task of the flexible display industry [11].

Many domestic and foreign scholars have conducted in-depth and extensive research on the polishing technology of stainless steel surfaces. The main polishing methods are: mechanical polishing,
chemical polishing, electrochemical polishing (also known as electric polishing or electrolytic polishing), and electrochemical mechanical polishing [12]. After mechanical polishing, chemical polishing, and electrochemical polishing, the surface roughness often fails to meet the requirements, and the damage layer is deep [13-14]. Stainless steel electrochemical mechanical polishing processing equipment is complicated, and it is difficult to control the surface quality due to the current flow characteristics [15]. Chemical mechanical polishing (CMP) technology is considered to be the best process method that can meet the requirements of surface roughness and surface flatness. It has become one of the most practical technologies for hard and brittle crystal materials to achieve super smooth and non-destructive processing of the surface, and has been widely used. It is applied to the fields of VLSI and semiconductor lighting [16]. Chemical mechanical polishing technology may be the most suitable, and it can be completely used in high-efficiency and ultra-precision processing of the surface of large-size ultra-thin stainless steel flexible display substrates to obtain ultra-smooth and non-damaged processing surfaces.

According to literatures, there are few literatures on chemical mechanical polishing of stainless steel. Literature [17-18] studies the influence of medium temperature of chemical mechanical polishing of stainless steel on polishing surface quality. Our research group [13-14] has carried out research on oxidant, polishing process and other aspects respectively. There are no other literature reports on ultra precision planarization of stainless steel by chemical mechanical polishing.

CMP slurry is an important component in chemical mechanical polishing. Its cost accounts for 60% - 70% of the total cost of chemical mechanical polishing. Its quality determines the efficiency, quality and the cost of chemical mechanical polishing. Dispersant is an important chemical component in the chemical mechanical polishing slurry, which is used to disperse the agglomerated abrasives, make the polishing slurry reach a certain viscosity, and make the removal rate of the polished surface material uniform. Therefore, it is an urgent task to study the environment-friendly and efficient chemical mechanical polishing slurry for stainless steel.

In order to develop an environment-friendly and efficient chemical mechanical polishing slurry for stainless steel, this paper studies the material removal rate and surface roughness of hydrogen peroxide oxidant under different dispersant and dispersant content through a series of experiments, and obtains the best dispersant and its optimum content, which provides a reference for further study of chemical mechanical polishing slurry for stainless steel.

2. Experimental Preparation and Experimental Parameters

2.1. Experimental Conditions

All CMP experiments were performed in a Class 1000 clean room, the ambient temperature was controlled at 22°C, and the resistivity of deionized water used in the experiments was 18.24MΩ • cm. The test samples were 304 stainless steel sheets with a diameter of φ50mm. After polished, the surface roughness Ra of each 304 stainless steel sheet was 40nm to 50nm. The polishing experiments were performed on a ZYP300 type polishing machine made in Shenyang.

Testing equipment used in the experiment. A Sartorius CP225D precision balance (accuracy 0.01mg) was used to measure the weight of the sample before and after the polishing experiment, and then the material removal rate was calculated by calculation. The Contour GT-K 3D surface microscope (vertical resolution 0.01nm) produced by the American company BRUKER was used to measure the surface roughness and surface morphology of the samples before and after polishing. The Leica DM2500M upright metallographic microscope was used to detect the original image of the 2D surface. The pH value of the polishing liquid was detected using a pH electronic test pen (accuracy 0.1).

2.2. Experimental Parameters

The rotational speed of the polishing disc is 60r/min, the rotational speed of the loading disc is 60r/min, the polishing pressure $P$ is 2psi, and the polishing time is 15min. After each polishing, the polishing pad is conditioned, and the conditioned time of polishing pad is 15min. In the middle, the
loading disc swings back and forth along an arc, the swing range is 20mm, the swing frequency is 10s, and the center distance between the loading disc and the polishing disc is set to 80mm.

2.3. Determination of Basic Composition of Polishing Slurry
According to the results of the previous orthogonal test of polishing slurry and the material characteristics of 304 stainless steel, white corundum was selected as the abrasive for polishing experiment, oxalic acid as the pH regulator and the hydrogen peroxide as the oxidant, the contents of their are shown in Table 1, and a total volume of 250ml of polishing slurry was prepared in each experiment.

Table 1. Composition and content of basic polishing slurry

| Factor          | pH | Abrasive size(μm) | Dispersant(g) | Oxidant (g) | Abrasive content(g) | Other          |
|-----------------|----|-------------------|---------------|-------------|---------------------|----------------|
| Value           | 4  | 3.5               | 3             | 5           | 4.5                 | Deionized water|

2.4. Selection of Dispersant Type
According to the literature, there are propanetriol, anhydrous ethylenediamine, triethylenediamine, pyridine and sodium hexametaphosphate that can be used as the dispersant of polishing slurry. Their characteristics are shown in Table 2. The five kinds of dispersants were selected in the hydrogen peroxide-oxalic acid type polishing slurry to study the best dispersant.

Table 2. Performance of various dispersants

| Name             | Molecular formula | Molecular weight | Proportion(20°C) | Viscosity(cst) |
|------------------|-------------------|------------------|-----------------|---------------|
| Pyridine         | C₅H₅N            | 79.1             | -               | -             |
| Hexametaphosphate| (NaPO₃)₆         | 611.77           | 2.484           | -             |
| Glycerol         | C₃H₈O₃           | 92.09            | 1.263           | 1412          |
| Triethylenediamine| C₃H₆N₃          | 103.1            | 0.96            | -             |
| Ethylenediamine  | C₄H₁₀N₂          | 60.1             | 0.899           | -             |

3. Experimental Results and Analysis
Fig.1 shows the experimental results of CMP using the hydrogen peroxide-oxalic acid type polishing slurry with various dispersants. It can be seen from the Fig.1 that when propanetriol, anhydrous ethylenediamine, triethylenediamine, pyridine and sodium hexametaphosphate are used as dispersants of the hydrogen peroxide-oxalic acid type polishing slurry, the material removal rate and surface roughness of CMP 304 stainless steel are affected under different concentrations.

It can be seen in Fig. 1 that when glycerin was used as a dispersant in a hydrogen peroxide-oxalic acid type polishing slurry, with the glycerol concentration increases, the material removal rate slightly increased, and the maximum material removal was reached 134 nm/min when the concentration reaches 1.2 wt%, after that, the material removal rate decreased slightly with the increase of glycerol content, and the surface roughness after polishing slightly changed up and down. When sodium hexametaphosphate was used as the dispersant in the hydrogen peroxide-oxalic acid type polishing slurry, the material removal rate also increased slightly with the increase of the concentration. When the concentration reached 1.2 wt%, it reached a maximum value of 146 nm/min. After that, the material removal rate decreased slightly with the increase of sodium hexametaphosphate content, and the surface roughness was the lowest at 1.2 wt% sodium hexametaphosphate content. This was because the sodium hexametaphosphate aqueous solution was acidic. The hydrosynthetic metaphosphoric acid intensified the corrosion of 304 stainless steel and improved the polishing rate. At the same time, its complexation was also beneficial to the polishing quality. With the increasing of the pyridine content, the material removal rate continued to decline significantly. When the content was 0.6 wt%, there was a maximum material removal rate of 80 nm/min, and the surface roughness after polishing slightly changed up and down. When triethylenediamine and anhydrous
Ethylene diamine were used as dispersants in the hydrogen peroxide oxalate polishing slurry, the change trend was basically the same. At the beginning, the material removal rate slightly increased with the increase of the content. When the content reached 1.8 wt%, the material removal rate reached the maximum value, which was 92 nm/min and 98 nm/min respectively. After that, the material removal rate obviously decreased with the increase of the content. Surface roughness is a slight change up and down after polishing. Fig. 2 (a) shows the surface morphology of 304 stainless steel after polishing with 1.2% wt hydrogen peroxide oxalate polishing slurry.

![Material removal rate and surface roughness](image)

**Figure 1.** Selection of hydrogen peroxide-oxalic acid type polishing liquid dispersant  
(a) Material removal rate, (b) Surface roughness

According to the above analysis, it can be seen from the figure that for the hydrogen peroxide oxalic acid polishing slurry, the material removal rate of propanetriol or sodium hexametaphosphate as the dispersant was much higher than that of the dispersant anhydrous ethylenediamine, triethylenediamine and pyridine. In the experimental dispersant, when the content of sodium hexametaphosphate was 1.2% wt, it had the largest material removal, which was 146 nm/min. At this time, the surface roughness after polishing was $R_a=10$ nm, which belonged to a low value at all experimental points (Fig. 1b). Therefore, sodium hexametaphosphate was selected as the dispersant of the hydrogen peroxide-oxalic acid type polishing slurry.

4. **Dispersion Analysis**

When sodium hexametaphosphate was added to the polishing slurry, it would hydrolyze to produce hexametaphosphate ion, which desorbed the adsorption force on the surface between the abrasives, and then it would be adsorbed on the positive electric area of the abrasive surface instead, which increased the hydrophilicity of the abrasive surface and promote the dispersion of the abrasives.
Studies have shown that sodium hexametaphosphate is a kind of polyphosphate (NaPO$_3$)$_n$ with indeterminate composition. Its degree of polymerization is $n=500$ to $10000$. Its anionic group has a high molecular weight, and the number of PO$_3$ groups is generally high as 30 to 90, forming a long chain, its tortuous connection between PO$_3^-$ can not only increase the negative ion repulsive force in the system, but also increase the steric repulsive force of the system, and improve the dispersion stability of the entire suspension.

![Figure 2](image)

**Figure 2.** Surface morphology of 304 stainless steel after CMP with hydrogen peroxide-oxalic acid type polishing slurry

The molecular formula of glycerol has three hydroxyl groups (-OH), which can be easily adsorbed on the surface of the abrasives, forming an adsorption layer on the surface of the abrasives to generate and strengthen the steric hindrance effect. In addition, the solubility between glycerol and water is very large enhancing the hydrophilicity of the abrasive surface, the hydration repulsion between abrasives can be significantly increased, effectively preventing the agglomeration of the abrasives themselves [19].

In the hydrogen peroxide-oxalic acid type polishing slurry, due to the strong oxidizing and electrochemical corrosion effects of the oxidizing agent hydrogen peroxide, it also reacts with the stainless steel base material to generate trivalent iron ion [20], which will be combined with oxygen to generate iron oxide, but glycerol easily reacts with hydrogen peroxide, reduces the oxidation of hydrogen peroxide in the polishing slurry, and reduces the material removal rate. Therefore, in the hydrogen peroxide-oxalic acid type polishing slurry, sodium hexametaphosphate has a higher material removal rate than glycerol.

5. **Conclusion**

In summary, through a series of experiments and results analysis, the following conclusions are drawn:

In a hydrogen peroxide-oxalic acid type polishing slurry, the dispersant glycerol easily reacts with hydrogen peroxide, which reduces the oxidation of hydrogen peroxide in the polishing slurry and reduces the material removal rate. Therefore, the material removal rate obtained by using glycerol as a dispersant is lower than that of sodium n-hexametaphosphate as a dispersant. The dispersant of sodium hexametaphosphate has the largest material removal rate when the content is 1.2% wt, which is 146nm/min. The surface roughness after polishing is $Ra=10nm$. So the sodium hexametaphosphate is selected as the dispersant of the hydrogen peroxide-oxalic acid type polishing slurry.

The research results in this paper provide important reference for the further study the chemical mechanical polishing slurry for 304 stainless steel.
6. Acknowledgements
The authors acknowledge the financial support of the National Natural Science Foundation of China (No.U1804142), Science and Technology Research Project of Henan Province (No.182102210303 and No.192102210058).

7. 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 [J]. 2009,46(1): 12502(1-9).
[2] Hanada T, Negishi T, Shiroishi I, et al. Plastic substrate with gas barrier layer and transparent conductive oxide thin film for flexible displays[J]. Thin Solid Films, 2010,518(11):3089-3092
[3] Ju S, Li J, Liu J, et al. Transparent active matrix organic light-emitting diode displays driven by nanowire transistor circuitry [J]. Nano Lett, 2008,8 (4):997-1004.
[4] Bae S, Kim H, Lee Y, et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes Nature Nanotechnology [J]. 2010, 5(8):574-578.
[5] Sekitani T, Nakajima H, Maeda H, et al. Stretchable active-matrix organic light-emitting diode display using printable elastic conductors [J]. Nature Materials, 2009,8(6):494-499.
[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 suling, et al: OLED, flexible, transparent display technology and development and challenges of organic light-emitting materials [J]. 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 Liang sun,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 test of glass substrate for tef-lcd [J]. Glass, 2009,36 (1): 22-24.
[12] Wang Yue, man Ruilin, Liang yonghuang. Research progress of stainless steel surface polishing technology, electroplating and environmental protection, 2012, 32 (2): 1-4.
[13] K.P. Han, J.L. Pang. Chemical Polishing for Stainless Steel. Journal of the Electrochemical Society of India [J]. 1996, 45 (1):50-52.
[14] H. Keping, F. Jingli. Study on chemical polishing for stainless steel. Transactions of the Institute of Metal Finishing [J]. 1998.76 (1):24-25.
[15] Yao Yingwu, Qiu Li, Zhao Chunmei, et al. Study on chemical polishing process of stainless steel Electroplating and finishing [J]. 2010,32 (9): 5-8.
[16] Xiaokai Hu,Zhitang Song,Fei Qin,et al. Chemical mechanical polishing of stainless steel foil as flexible substrate. Applied Surface Science[J]. 2012 ,258(15):5798-5802.
[17] Zheng Haifeng, Wei Xin, Xie Xiaozhu, et al. Temperature study of chemical mechanical polishing process of stainless steel substrate, diamond and abrasive tool engineering[J].2014, 34 (2): 20-24.
[18] Liu Yachuan, Gong Huangao, Zhang Keren. Study on the mechanism of sodium hexametaphosphate, Journal of Northeast Institute of technology [J].1993,14 (3): 231-235.
[19] Hong Lifu, Jin Xin. Preparation and modification of ultrafine silica, Journal of Beijing University of chemical technology [J].2004,31 (5): 69-72.
[20] Wang Jihui, Gu Kali, Wu Li, et al. Tribological properties of passivated 1Cr18Ni9Ti stainless steel in H2O2 aqueous solution. Journal of tribology [J]. 2009, 29 (1): 17-24.