8nd International Conference on Physical and Numerical Simulation of Materials Processing, ICPNS'16
Seattle Marriott Waterfront, Seattle, Washington, USA, October 14-17, 2016

Analysis on the Action of Oxidant in Chemical Mechanical Polishing of 304 Ultra-thin Stainless Steel

Su Jianxiu, Tian Feng, Li Yongfeng, Wang Zhankui, Fu Sufang
Henan Institute of Science and Technology, Xinxiang 453003, P. R. China

ABSTRACT

The ultra-thin stainless steel sheet will be used in flexible displays for substrate material. The application of the substrate requires its surface very smooth, no defects and damage free. Chemical mechanical polishing (CMP) has been considered as a practical and irreplaceable planarization technology in the ultra precision machining of the flexible display substrate. In chemical mechanical polishing of ultra-thin stainless steel, the oxidant of polishing slurry has an important influence on the material removal rate (MRR). In this paper, the influences of oxidant in slurry on MRR and surface roughness had been studied in CMP of ultra-thin 304 stainless steel based on alumina (Al_2O_3) abrasive. The research results show that the oxidant of the hydrogen peroxide and the oxalic acid have the interaction in CMP 304 stainless steel and when using the only one oxidant in polishing slurry, the hydrogen peroxide or oxalic acid, the MRR is less than the maximum. The oxalic acid can provide a strong acidic environment to ensure the stability of the hydrogen peroxide in polishing slurry and to improve the MRR in CMP 304 stainless steel. The research results can provide the reference for studying the slurry in CMP of ultra-thin stainless steel.

Keywords: Chemical mechanical polishing, Polishing slurry, Composite oxidant, Ultra-thin stainless steel, Material removal rate, Surface roughness

1. INTRODUCTION

In recent years, compared with LCD, OLED flat-panel display and plasma display, the advantages of flexible displays have become increasingly prominent, because of its ultra-thin, light weight, durable, large storage capacity, the design freedom, crooked, winded and impact resistance and other properties[1-2]. The flexible display technology has been gradually improving people's lives and communication method and significantly promoting the information visualization.

In the flexible display device, the flexible substrate is the basis of the research and development of flexible display [3-4]. Compared with the traditional glass and polymer substrate, the characteristics of metal substrate, such as high temperature resistance, good water resistance, oxygen resistance performance, low cost and easy to obtain, electrostatic effect, are outstanding, so it is currently used in flexible displays for substrate material [4-7]. The application of ultra-thin stainless steel sheet requires its surface very smooth, no defects and damage free. The processing quality and precision of ultra-thin stainless steel will directly affect the performance of the device [8].

Chemical mechanical polishing (CMP) has been considered as a practical and irreplaceable planarization technology in IC manufacturing. In recent years, some research and application have done in the ultra precision machining of the flexible display substrate. The schematic of CMP system sees Fig.1[9]. In the CMP process, the chemical reaction between chemical reagents in slurry and the material of wafer surface is conducted. The chemical reactant film is formed on the wafer surface and then is removed from the wafer surface by the abrasive particles in slurry. The new surface will emerge and the next CMP cycle begins. In this way, the surface material will be removed from the wafer surface by the combined action of chemical reagents and the abrasive particles. So the CMP slurry has important effect on the polishing efficiency and processing quality.

The CMP slurry consists of DI water, abrasive, pH regulator, oxidant, dispersant and other additives. In order to quickly form an oxide film weakened on the polishing surface in the process of CMP, oxidant is often added in the CMP slurry. The oxidant in the slurry can form the oxide film on the substrate surface and removed easily at the subsequent mechanical action. Combined with the chemical action of oxidant and the mechanical action of abrasive, the surface with high quality and global smooth can be achieved. So, the oxidant in slurry plays an important role in CMP process. In this paper, the influences of composite oxidant of the hydrogen peroxide and the oxalic acid in slurry on MRR and surface roughness have been studied in CMP of ultra-thin 304 stainless steel based on alumina (Al_2O_3) abrasive by experiment. The research results show that the oxidant of the hydrogen peroxide and the oxalic acid have the interaction in CMP 304 stainless steel. It can be obtained the maximum MRR in CMP 304 stainless steel using slurry with appropriate content of the hydrogen peroxide and the oxalic acid. The research results can provide the reference for studying the slurry in CMP of ultra-thin stainless steel.

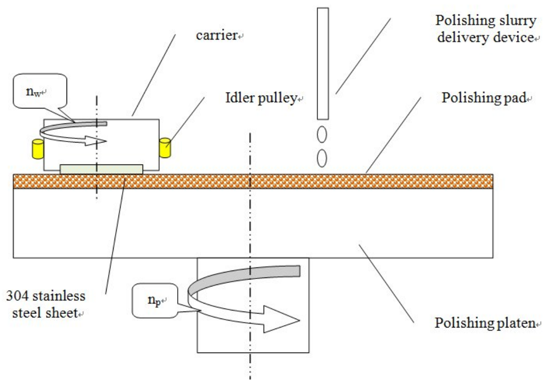

Fig.1 The schematic of CMP system

2. Experimental procedure

2.1 Experimental conditions and experimental parameters

The CMP experiments were conducted under different parameters and slurry on the CMP machine ZYP300 type produced by Shenyang. All the experiments are done in a clean room with Grade 1000 at the constant temperature of 22°C. Many ultra-thin stainless steel pieces of 60mm in diameter are used in the polishing experiments. Samples are bonded with paraffin on the carrier of stainless steel with Φ115mm in diameter. Each carrier sticks one ultra-thin stainless steel piece. The roughness of ultra-thin stainless steel surface before polishing is about *Ra*45nm, which is tested by SW1510MS 3D surface profiler produced by Taiwan. In the CMP experiments, the polyurethane pad is applied and conditioned for 10min before every polishing experiment with a diamond conditioner. The slurry is supplied at the flow rate of 15ml/min. The slurry 500ml can be made before each test. During the CMP process, the carrier has a reciprocating motion with a stroke of 20mm at the frequency of 10s and the centre distance between the pad and the wafer is set 80mm, the polishing pressure *P*=2psi, the carrier rotational speed n_w=60r/min, the platen rotational speed n_p=60r/min, the polishing time is 15min for each test. The Deionized (DI) water with the electrical resistivity 18.24MΩ•cm is used in the CMP experiments. The MRR can be calculated by weighing the weight of ultra-thin stainless steel piece on the high precision balance with the accuracy 0.01mg before and after CMP.

2.2 Slurry ingredient

According to the former research, the orthogonal design method and based on the composite oxidant of the hydrogen peroxide and the oxalic acid, the orthogonal design experiments of CMP had been conducted with alumina abrasive taking material removal rate (MRR) as the optimizing target. The basic slurry composition of CMP 304 stainless steel had been obtained, shown in Table 1. Then, according to the basic slurry composition, the influence of the slurry ingredients on material removal rate (MRR) and surface roughness had been done by changing a certain parameter.

Table 1 The basic slurry composition from orthogonal design experiments

Hydrogen peroxide	Oxalic acid	pH Value	Dispersant content	Active agent
4%	1.2%	2	1.2%	0.2%
Abrasive size (μm)	**Abrasive content**	**others**		
3.5	4.5% wt	DI water		

3. Experimental results and discussion

3.1 The influence of the oxidant type on MRR and surface roughness

In order to study the influence of the oxidant type on MRR and surface roughness, according to Table 1, four slurries had been made for study. The four slurries see table 2. The slurry 1, named S1, was the basic slurry composition from orthogonal design experiments, sees table 1. The slurry 2, named S2, was S1 without hydrogen peroxide, sees table 2. The slurry 3, named S3, was S1 without oxalic acid, sees table 3. The slurry 4, named S4, was only alumina abrasive and DI water, sees table 4. The experiment results using slurry 1 to slurry 4 are shown in the Fig.2 and 3, respectively. By the Fig.2 and Fig.3, the analysis results are as follows.

Table 2 The slurry S2

Abrasive content	Oxalic acid	pH Value	Dispersant content	Active agent
4.5% wt	1.2%	2	1.2%	0.2%
Abrasive size (μm)	**others**			
3.5	DI water			

Table 3 The slurry S3

Hydrogen peroxide	Abrasive content	pH Value	Dispersant content	Active agent
4%	4.5% wt	2	1.2%	0.2%
Abrasive size (μm)	**others**			
3.5	DI water			

Table4 The slurry S4

Abrasive size (μm)	Abrasive content	Dispersant content	others
3.5	4.5% wt	1.2%	DI water

By Fig.2, it can be seen that the MRR is the highest polishing with slurry S1 and the MRR is the lowest polishing with slurry S4. It is showed that oxidants have very important action in the material removal process of CMP. If there is not oxidant in slurry, the MRR will be very low. And using the only one oxidant, the hydrogen peroxide or oxalic acid, the MRR is less than the maximum. So it is also showed that the oxidant of hydrogen peroxide and oxalic acid have the interaction in CMP 304 stainless steel. By Fig.3, it is showed that it can be obtained the lowest of the surface roughness when polishing with slurry S1, but the difference of surface roughness is not much CMP using the four slurries, S1, S2, S3 and S4.

3.2 The influence of the content of oxalic acid on MRR and surface roughness

Based on the slurry S1, only to change the content of oxalic acid in the slurry S1, and several tests of CMP 304 stainless steel were conducted again. The experimental results are shown in Fig.4 and Fig.5.

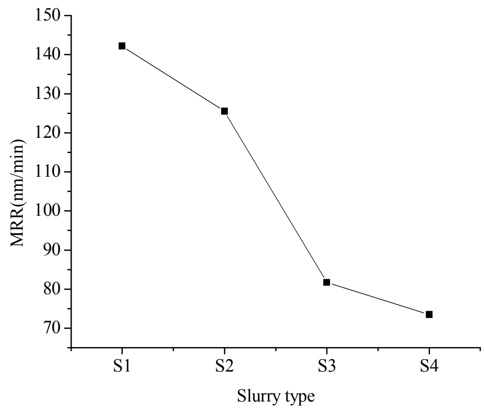

Fig. 2 MRR of the four slurries

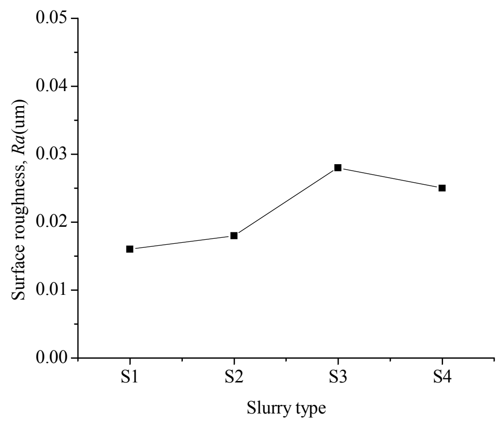

Fig. 3 Surface roughness after CMP using the four slurries

By Fig.4 and Fig.5, the results showed that with the decrease of the content of oxalic acid, the decrease of pH value in the polishing slurry, the MRR decreased with the decrease of the content of oxalic acid, but the changes of surface roughness are very small. Research shows that the hydrogen peroxide in weak acid and alkaline conditions shows instability and is rapid decomposed and when in strong acidic conditions of pH<3.5, the hydrogen peroxide is stable [10]. Because the oxalic acid is a strong acid, with the increase of the content of oxalic acid, it can provide a strong acidic environment to ensure the stability of the hydrogen peroxide and the hydrogen peroxide can play its role effectively. That is reason the MRR was the highest when the pH=2.

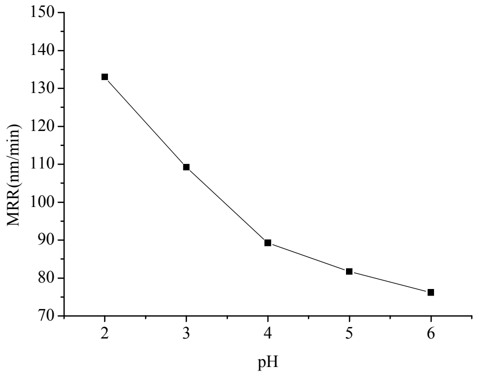

Fig. 4 MRR of the content of oxalic acid

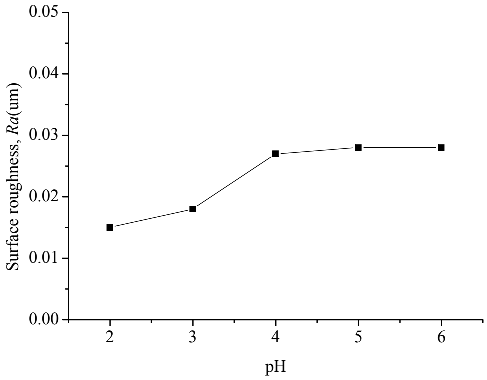

Fig. 5 Surface roughness of the content of oxalic acid

3.3 The influence of the content of the hydrogen peroxide on MRR and surface roughness

Also based on the slurry S1, only to change the content of the hydrogen peroxide in the slurry S1, and several tests of CMP 304 stainless steel were conducted again. The experimental results are shown in Fig.6 and Fig.7.

By Fig.6 and Fig.7, with the increase of the content of the hydrogen peroxide, the MRR increased gradually. When the content of the hydrogen peroxide increased a certain amount, the MRR reached a maximum value. After that, with the increase of the content of the hydrogen peroxide, the MRR decreased gradually. That is because that the hydrogen peroxide is a kind of strong oxidant, with the increase of the content of the hydrogen peroxide, the number of oxygen containing functional groups increases on the surface of stainless steel[11] and the chemical reaction can be effectively enhanced, so that the MRR increased. But when the content of hydrogen peroxide increases to a certain amount, and the hydrogen peroxide can react with the oxalic acid in polishing slurry, the reaction formula is $HOOCCOOH+H_2O_2 \rightarrow 2CO_2+2H_2O$. Which would lead to the descent of the content of the oxalic acid in polishing slurry, the pH values increased, the strong acidity of the slurry decreased, and the stability of the hydrogen peroxide becomes weak, so, the MRR decreased. But the change of the content of hydrogen peroxide has little effect on the surface roughness.

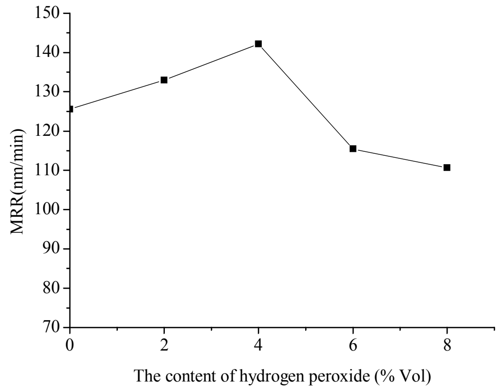

Fig.6 MRR of the content of hydrogen peroxide

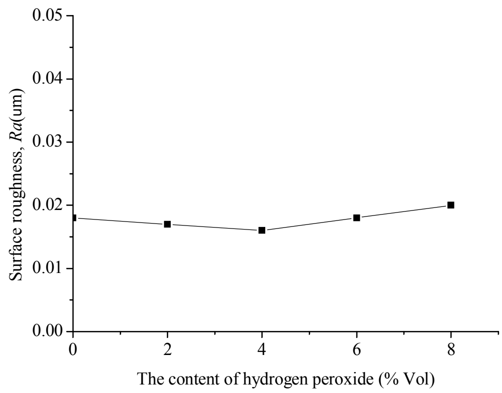

Fig.7 Surface roughness of the content of hydrogen peroxide

4. Conclusions

The influence of different oxidants on MRR in CMP 304 stainless steel is different. The oxidant of the hydrogen peroxide and the oxalic acid has the interaction in CMP 304 stainless steel. It can be obtained the maximum MRR in CMP 304 stainless steel using slurry with appropriate content of the hydrogen peroxide and the oxalic acid.

The hydrogen peroxide in weak acid and alkaline conditions shows instability. With the increase of the content of oxalic acid in polishing slurry, it can provide a strong acidic environment to ensure the stability of the hydrogen peroxide.

With the increase of the content of the hydrogen peroxide, the MRR increases. When the content of the hydrogen peroxide increases to a certain amount, the hydrogen peroxide can react with the oxalic acid in polishing slurry, the acidity of the slurry decreases, and the MRR decreases.

Acknowledgements

The authors acknowledge the financial support of the National Natural Science Foundation of China (No.51375149) and the Innovation Scientists and Technicians Troop Construction Projects of Henan Province.

REFERENCES

Logothetidis S., Laskarakis A (2009). Towards the optimization of materials and processes for flexible organic electronics devices. *The European Physical Journal Applied Physics*, 46 (1), 1-9.

Hanada T., Negishi T, Shiroishi I, et, al. (2010). Plastic substrate with gas barrier layer and transparent conductive oxide thin film for flexible displays. *Thin Solid Films*, 518 (11),3089-3092.

Sugimoto Akira, Ochi Hideo, Fujimure Soh, et al. (2004).Flexible OLED displays using plastic substrates', *IEEE J Sel Top Quanturn Electron*, 10(1),107-114.

Bardsley J. N. (2004).International OLED technology roadmap, *IEEE J Sel Top Quantum Electorn*, 10(1), (3-9).

Ye Ping. (2009). Flexible displays: broad prospects but challenges. *China Digital TV*, 61 (11),47-49.

Someya T. (2010).Flexible electronics: Tiny lamps to illuminate the body. *Nature Materials*, 9(11),879-880.

L. Haiyan. (2009).TFE-the performance of the LCD glass substrate and inspection.*Glass*,36(1),22-24.

X. Zhiyuan, H. Liangsun, Zh. Furong.(2003).A flexible top-emitting organic light-emitting diode on steel foil.*Chem Phys Lett* , 381(5/6).691-696.

Haifeng Ch. , Lijie M., Jianguo Y., et al. (2014).Study of the Slurry in CMP 304 Ultra-Thin Stainless Steel Surface. *Advanced Material Research*, 1027, 235-239

Zh. Qing,Y. Chao-yan,Y. Ke-na, et al.(2010).Study on Decomposition Rate and Stability of Hydrogen Peroxide. *Journal of Jiaxing University*,22(3).51-53.

X. Xin, Zh. Ping. (2005).Rapid pickling for stainless steel at room temperature. *Electroplating and Finishing*, 24(1),65-66.