Control Action of Temperature on ULSI Silicon Substrate CMP Removal Rate and Kinetics Process*

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Abstract: The kinetics process and control process of chemical mechanical high precision finishing for material surfaces were studied. According to the experiments, the seven kinetics process for chemical mechanical polishing (CMP) was generalized. Through investigating the CMP process of ULSI silicon substrate, we found that the chemical process was the CMP control process under the same mechanical action condition, which was determined by temperature. The key factor influencing the chemical reactions was effectively settled, which will be advantageous for improving the CMP removal rate for other materials.

Key words: chemical mechanical polishing; kinetics process; control process; silicon substrate; removal rate; polishing temperature

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1 Introduction

Traditional purely mechanical finishing techniques such as those utilizing diamond abrasives are complicated by the requirement of removing subsurface damage by using abrasives of continually decreasing size. The application of polishing in an environment that chemically reacts with the surface can eliminate subsurface damage and significantly increase surface quality. Such chemically assisted polishing has been dubbed "chemical mechanical polishing" or "chemical mechanical planarization" (CMP). Described generically as the process of smoothing and/or planing synergistically aided by combined chemical and mechanical effects, CMP has been widely and effectively applied to a variety of materials in the last two decades, including semiconductors, crystals, glasses, special metals, plastics, and computer disks. CMP is becoming popular because the advantages of CMP over other surface finishing techniques are great: little or no surface and subsurface damage, elimination of surface defects, high removal rates, high efficiency, and low cost. Furthermore, it has been confirmed that CMP is the best method for the global planarization of ULSI multilayer interconnections[1~4].

However, CMP is related to mechanics, hydrodynamics, physical chemistry, material tribology, and other subjects, and its kinetics process and control process are still not clear. The most basic polishing rate equation that has been widely used is Preston's equation[5,6], though there are various models for different aspects of a CMP process. The Preston equation, which predicts that the removal rate ($RR = \Delta h/\Delta t = K_p PV$), i.e., the decrease in thickness over time ($\Delta h/\Delta t$)[5,6], depends linearly on the downward wafer pressure P and the relative velocity between the pad and the wafer surface V, where K_p is the Preston's coefficient, which is a strong function of the other CMP parameters. The wide use of Preston's equation for CMP is surprising since it was obtained for polishing with hard pads and emphasized mechanical action for CMP processes. Chemical action is more complex and has a larger influence on CMP processes. It was found in our investigation that

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the removal rate in a CMP process is not simply the sum of mechanical and chemical action, but is $R \gg R_M + R_C$.

The whole process for CMP is the chemical mechanical complex process, i. e. the relative velocity between the pad and the wafer surface, stable pressure and temperature, certain pad and slurry with abrasive and additives[7~10]. How to confirm the kinetics process and find the kinetic control process is the key to improving the CMP removal rate and the material surface state.

2 Chemical mechanical polishing kinetics process

Research indicates that CMP is a complicated multiphase reaction process, e. g. ULSI silicon substrate polishing. Under the action of pressure, revolving, and mechanical abrasion, the reagent and reactant are more adjacent and react more readily. During the revolving, the energy of reactant particles increases, and there are more collisions between particles, and thus the particle proportion to activation energy is greater. During the CMP process, the main process is chemical reaction and diffusion in addition to the mechanical action of invariable pressure, velocity, pad, and abrasive. The slower process controls the removal rate. In order to ensure a better polishing effect, the mass transport process must be accelerated, which can lead to high smoothness, low damage, and a high rate, and achieve global planarization. Mass transport includes two aspects: First, the reactant must access the wafer surface in time, and the active component in the polishing slurry then reacts with the atoms of the wafer surface; The second is that the reaction product must be separated from the surface of the wafer rapidly, and the new surface must be exposed to the polishing slurry. How to accelerate the mass transport is then the key factor of the CMP process.

We investigated the CMP kinetic process thoroughly and generalized the seven steps as follows: (1) Reactant diffuses from main flow polishing slurry to unfinished wafer exterior surface; (2) Reactant diffuses from exterior surface to internal surface; (3) Reactant is adsorbed on unfinished wafer surface; (4) Chemical reaction occurs between reactant and unfinished material on surface, and resultant is formed; (5) Resultant desorbs from wafer surface; (6) Resultant diffuses from internal surface to exterior surface; and (7) Resultant diffuses from exterior surface to main flow polishing slurry.

In a balanced state, the rates of the seven steps are equal. The removal rate is controlled by the slowest process, for which resistance is the largest. Thus by decreasing the resistance of the slowest process, the total removal rate can be accelerated. If chemical reactive rate is slower, the total removal rate of the wafer is also slower. Furthermore, the surface degree of the finish is not good. On the contrary, even if the chemical reaction is very rapid, but desorption is very slow, the total removal rate is not good. Because resultants cannot be separated from the surface of the silicon immediately, the active component in the polishing slurry cannot expose and react with the atoms on the new surface of the wafer, thereby holding up the chemical reaction. In this research, we find if mechanical action is the control process, the roughness is higher; if chemical action is the control process, the roughness is lower. Enhancing mechanical action can improve smoothness, and enhancing chemical action can reduce damage to the layer.

3 Investigation of kinetics control process

In order to make clear the kinetics control process and the main factors influencing the process, we investigated the ULSI silicon substrate CMP.

3.1 Experimental procedure

In this experiment, we used 125mm n-type ⟨100⟩ and ⟨111⟩ orientation silicon wafers. The cycle time of group one is 10min and that of group two is 15min. The detailed parameters are shown in Table 1. The two groups' experimental data are shown in Tables 2 and 3. Figures 1 and 2 show the removal rate values of different circular times for the polishing slurry.

Table 1 CMP experimental detailed parameters

Experiment	Orientation	Pressure /(g/cm^2)	Slurry flow /(L/min)	T_{up}/℃	Unit type	Pad	Time
Group one	⟨100⟩	300	5.3~5.4	41	Speedfam -32BTAW	Rodel	15
Group two	⟨111⟩	300	5.3~5.4	43	Speedfam -32BTAW	Rodel	10

Table 2 CMP experimental data of group one

Slurry circular time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
T/℃	25	31	35	39	41	41	41	41	41	41	41	41	41	41	41
Removal rate /(μm/min)	0.45	0.79	1.09	1.27	1.42	1.55	1.41	1.45	1.48	1.42	1.49	1.35	1.51	1.60	1.52

Table 3 CMP experimental data of group two

Slurry circular time	1	2	3	4	5	6	7	8	9	10
T/℃	25	30	35	39	41	43	43	43	43	43
Removal rate /(μm/min)	0.35	0.59	0.78	0.91	1.02	1.09	1.18	1.15	1.19	1.17

3.2 Analysis and discussion

Figures 1 and 2 show the variation of the removal rate for different circular times for n-type ⟨100⟩ and ⟨111⟩ silicon wafer. From the figures we can see that the polishing removal rates are relatively lower under the initial condition. From Tables 1 and 2 we find that under the initial condition, the temperature is also lower. The key factor influencing this phenomenon is temperature. Under the same pressure and relative velocity action, temperature is the key factor to influence chemical action. That is to say, under the same mechanical action conditions, chemical action is the slower process, which is the key factor controlling the kinetics process. The Arrhenius equation $\left(V = K\exp\left(-\frac{E_a}{RT}\right)\right)$[11] reflects the rate of chemical action, where E_a is the reactive activation energy, R is the molar gas constant, T is the temperature, and K is the reactive characteristic constant.

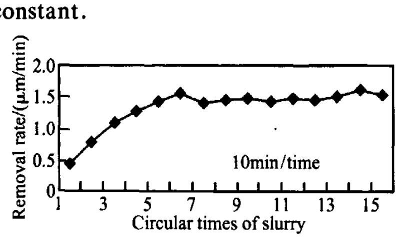

Fig. 1 Removal rate for different times in the first group experiment

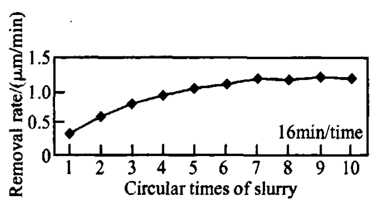

Fig. 2 Removal rate for different times in the second group experiment

Figure 3 shows the energy distribution curve of molecules. Here, ΔN is the number of molecules with energy $E \approx E + \Delta E$, N is the total number of molecules, and $\frac{\Delta N}{N\Delta E}$ is the ratio of molecules with energy $E \approx E + \Delta E$. E_0 is the lowest energy that activated molecules can have. The difference between the minimum energy of activated molecules and the average energy of the molecules is called the activation energy (E_a). That is to say, the lower the minimum energy of activated molecules is, the lower the activation energy E_a is. During the CMP process, with the function of pressure and spin, reactant molecules can be activated at lower energy as the temperature increases, which can lead to an increase in the total number of activated molecules. Then the position of the E_0 abscissa shifts left, which leads to a reduction in E_a. According to the Arrhenius equation, the rate of chemical action V will be accelerated clearly.

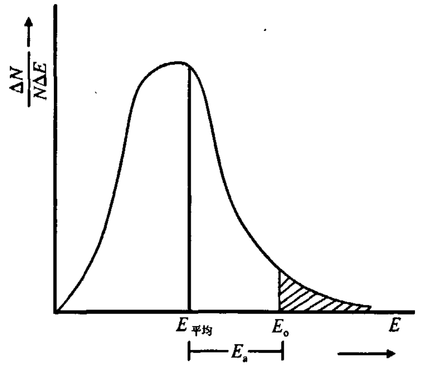

Fig. 3 Energy distribution curve of molecules

According to the above result that the chemical reaction process is the CMP control process under the same mechanical action condition, we can increase the temperature to accelerate the chemical reaction rate, which is advantageous to improve the substrate removal rate during the CMP process. This result has been used in the precision finishing of nucleus prohibitive explosive metal materials, cell battery substrates used in spaceflight, sapphire substrates, optics glass, computer hard disk substrates, and synthetic jewel using double frequency, and a good effect has been achieved.

3.3 Summary

In this paper, we investigated the CMP kinetics process and found that there were two main kinetics processes, which are the chemical reaction process and the diffusion process, in addition to the invariant mechanical action of pressure, spin and abrasive. The slower process controlled removal rate. In order to gain good polishing effect, we must accelerate the CMP mass transport process. According to the ULSI silicon substrate CMP experiment result, we also found that within round temperature range, the removal rate increased with temperature increasing, which indicated chemical action was influenced by temperature clearly and took control action for kinetics process under the condition invariant mechanical action. This result has been used on other substrate material precision finishing and gained good effect.

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温度对ULSI硅衬底化学机械抛光去除速率及动力学的控制*

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摘要：对材料表面化学机械高精密加工的动力学过程及控制过程进行了深入研究.根据大量实验总结出了CMP的七个动力学过程，在ULSI衬底单晶硅片的CMP研究过程中，确定了在相同机械作用条件下由温度引起的化学过程为CMP控制过程，对影响化学反应的关键因素进行了有效的优化，实现了多材料CMP速率的突破性提高.

关键词：化学机械抛光；动力学过程；控制过程；硅衬底；去除速率；抛光温度

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