Study on the Effect of Nano-SiO₂ in ULSI Silicon Substrate Chemical Mechanical Polishing Process

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Both process and mechanical of silicon substrate chemical mechanical polishing (CMP) are studied in detail, and the effects of experiments designed indicate that nano-SiO₂ grinding particles seem to be acted as catalyzer besides the grinding action during the CMP process. This is different from the traditional function. As a result, in the condition of low pH, the nano-SiO₂ slurry can be recycled. In the meanwhile, the removal rate can gain stability and pH value does not change obviously.

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1. INTRODUCTION

ULSI manufacturing technology develops rapidly to the higher integration, higher reliability, higher efficiency, and lower cost. Substrate area has been increasing. The wafers of 300-mm diameter have been produced in large scale. The development trend is 400 mm. Technical advances inspired the development of chemical mechanical polishing (CMP) for IC fabrication.

However, CMP has been widely recognized as the most promising technology for the planarization of multilayer structures in semiconductor manufacturing. In a typical CMP process, a wafer is rotated on its axis while being pressed face down by a carrier against a rotating polishing pad that is covered with slurry (Figure 1). A carrier film attaches the wafer to the carrier during the polishing. The relative motion of the wafer and pad, combined with the applied down force and chemical activity of the slurry, erodes features on the wafer. It is generally known that several process parameters including equipment and consumables (pad, backing film and slurry, etc.) can optimize and improve the CMP performance [1].

At present, for microelectronics development, it is key that the technology of lower roughness and lower cost in CMP processing. Chemical mechanical polishing process becomes the essential technique to achieve the sufficiently global and local planarization.

Chemical mechanical polishing (CMP) of single crystalline silicon (SCS) has been used for a long time in wafer manufacturing. At beginning, CMP of SCS is applied in thinning and it can create bondable surfaces in the manufactur-

ing of bonded silicon-on-insulator (SOI) materials. Recently, the use of SCS CMP for other applications has emerged. CMP of SCS has been used for thinning in the formation of vertical integrated circuits and in realization of high aspect ratio silicon microstructures. Now, in ULSI manufacturing, silicon substrate is chosen for using more than 80%. CMP has shown the ability to planarize selectively grown collectors in processing bipolar transistors. CMP has been employed to remove epitaxially overgrown silicon in order to create fully isolated SOI islands. These new applications clearly motivate a further understanding of the process. Even though CMP of SCS has been used for a long time, not that many investigations on the process have been published [2].

To fabricate devices with high integration, high reliability, the CMP under alkaline condition must be used [3–8]. Up to now, the function of nano-SiO₂ is generally regarded as machinery grind function [9–13]. But as a matter of fact, during the CMP, the chemical combination reaction exists between nano-SiO₂ and silicon substrate [14]. That reaction must be studied deeply, which is helpful to obtain silicon substrate with high DP, low roughness, and high efficiency.

2. EXPERIMENT

2.1. Experimental object and experiment

In this experiment, we used ϕ 15 mm N-type $\langle 111 \rangle$ and $\langle 100 \rangle$ orientation silica wafer ($\rho = 8 \sim 14 \Omega \cdot \text{cm}$).

Firstly, silicon wafers must be grinded and cleaned before polishing, and then put the wafers on the carriers of the

FIGURE 1: Typical CMP model.

SpeedFam I polisher. The polishing slurry used in the experiment is prepared with nano-SiO₂ colloid and kinds of chemical additives. Finally, the proper polishing pad and processing parameters are chosen to control polish process.

The slurry is silica sols contained oxidant, pH regulator, and other matters. The microtumble of SiO₂ particles acts on the wafer surface as mechanical grind, and the oxidant acts as chemical escharotics. Figure 2 shows the SEM of nano-SiO₂.

The CMP pad is made of a flexible microporous polyurethane material, which has elasticity and can be compressed. This peculiarity allows pad to absorb the slurry to contact with wafer sufficiently. In the experiment, Rodel CMP pad with groove is used.

Experiment

Measure the before-CMP thickness of wafers prepared above. With the same polisher and pad the wafer is polished. After polishing, the wafer should be cleaned, and then measure the post-CMP thickness.

Removal Rate ($R_r/\mu\text{m/h}$) = (before-CMP thickness—post-CMP thickness)/time.

2.2. Result and discussions

By the related CMP experiments containing the processing of same slurry ingredients, pad, and other parameters, changing the concentration of SiO₂, we achieved the relation curve of R_r versus concentration about Si(111), N-type material. Figure 3 shows the removal rate (R_r) of different SiO₂ concentration for polishing slurry.

From Figure 3, it is known that the removal rate is extremely low, just to be less than 1 μm per hour, when the alkaline aqueous solution without silica sols is used. But when we add 4/10000 silica sols to alkaline aqueous solution, CMP removal rate is improved quickly. When the concentration of SiO₂ rises to 20 wt%, namely, its concentration increases by 500 times, to our surprise, its removal rate has not obviously increased.

It is well known that SiO₂ plays a mechanical abrasive role during the silicon substrate CMP with alkali slurry. The reaction is [15]

That does not accord with the experiment fact. The presence of the silica sols influences the removal rate greatly. The

FIGURE 2: SiO₂ SEM. FIGURE 3: R_r versus concentration.

adding of 1/10000 silica sols can make the removal rate improve to 60–80 $\mu\text{m/h}$. Obviously, it is not only because silica sols improve the machinery effect of grind, but also the other influence.

To investigate further and to know the function of silica sols, we polish silicon wafer (N-type (100) and (111)) circularly at the same condition, and the effects are shown in Figures 4–7.

Figures 4–7 show that as slurry recycles for polishing,

- (1) pH drops to about 9.5 and reduces more than 1 pH value slowly from 10.90,
- (2) the removal rates of (111) and (100) wafer keep stable in 1.1 $\mu\text{m/min}$ and 1.4 $\mu\text{m/min}$.

But if its chemical reaction is followed (1) in the course of CMP, it will consume a large amount of alkali, which makes pH reduce quickly. For example, in the condition of pH = 10, pH should reduce rapidly during CMP and the removal

FIGURE 4: <100> Rr versus number.

FIGURE 6: <111> Rr versus number.

FIGURE 5: <100> pH versus number.

FIGURE 7: <111> pH versus number.

rate should be reduced rapidly. However, the fact is that pH changes slightly. So the reaction equation (1) is not the main reaction in experiment. There must be other reactions that be presumed as follows:

General reaction ((2) + (3)) is

Reaction (2) goes on the force and relative movement between the surfaces of the abrasive and the substrate. Thus, the chemical reaction produces SiO that seems to be extremely unstable and can be oxidized by oxygen of environment rapidly. Then SiO turns into steady SiO₂, and SiO₂ is grown into SiO₂ micelle, some SiO₂ or SiO₂ micelle top layer form a layer, which attracts some OH⁻ [16, 17] and makes pH reduce to some extent. Reactions (2) and (3) show the essence that SiO₂ accelerate chemical reaction and pH

changes little but reaction rate keep high for a long time. But the general reaction (4) shows that Si is oxidized to SiO₂. A large amount of SiO₂ in the slurry does catalysis at the beginning stage. The discovery of the reaction law above has meaningful guidance to CMP process. According to it, in Hebei University of technology, professor Liu Yuling invents a series of CMP polishing slurries with little particle size, fast removal rate, low roughness, and scale application.

3. CONCLUSIONS

This study is to investigate and verify the function of silica sols in the CMP processing. By the analysis of experiments, we draw the conclusion that SiO₂ gel particles take on effect as mechanical abrasive agent and as catalytic effect as well, and the subsurface damage of silicon wafer has not yet been found in experimental results and therefore the CMP process of silicon wafers by soft abrasives has great potential to be developed into a green or environment-friendly technology in IC fabrication.

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