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Chemical effect on the material removal rate in the CMP of silicon wafers

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ABSTRACT

This paper investigates the effects of oxidizer concentration, pH and slurry flow rate on the material removal rate (MRR) in chemo-mechanical polishing (CMP) of Si (1 0 0) wafers. The CMP was carried out in alkaline slurry using alumina and ceria particles with hydrogen peroxide. It was found that the applications of the two particle materials lead to very different results. When using the alumina particles, the MRR initially decreases with increasing the slurry pH value until pH = 9. Nevertheless, the application of the ceria particles increases the MRR before the pH of the slurry reaches 10. It was concluded that in the former, the effect was due to the particle agglomeration and the contact angle decrease of the oxidizer slurry with the wafer surface; whereas in the latter it was caused by the particle agglomeration and the modification of trivalent ceria ions. The influence of the slurry flow rate and oxidizer concentration, regardless of the particle type, was found to be similar—a higher flow rate or a higher oxidizer concentration brought about a greater MRR before reaching a plateau. Many of these were interpreted by an adhesive removal mechanism on the molecular scale.

1. Introduction

Due to its global planarization capability, chemo-mechanical polishing (CMP) is currently a main processing method in the fabrication of integrated circuits [1,2]. In a CMP process, a rotating wafer is pressed against a rotating polishing pad while slurry, comprising some chemical agents and abrasive particles, is fed into the wafer–pad interaction zone. The coupled chemical–mechanical interactions are believed to be responsible for the material removal in the polishing process [3]. However, some chemicals used in CMP are toxic, which increases production cost, creates disposal issues of the toxic chemicals, and causes pollution. A deep fundamental understanding of the chemical effects in CMP can provide some insight into the process optimization and reduce the usage of chemicals while maintaining a high removal rate.

Many processing factors can significantly influence a CMP process [4], such as properties of polishing pad, abrasive particles and chemical reagents. In the past years, much effort [5–7] has been placed to optimize the effect of mechanical parameters on polishing rate, including polishing pressure, speed, pad selection [8], abrasive size and concentration [9,10], etc. However, the improvement has been incremental and cannot meet the needs of fast growth of IC fabrication.

Although colloidal silica slurries have been widely used in the polishing of silicon wafers, the mechanisms of the material removal rate have not been properly understood yet. Meanwhile, this type of slurry contains lots of toxic chemicals [1,2,5]. Recently, two types of abrasives, Al_2O_3 and CeO_2, have received much attention in the CMP community due to their appropriate mechanical and chemical properties. Al_2O_3 abrasives have been used to perform damage-free polishing without using chemicals [11]. The investigation on silicon polishing using Al_2O_3 abrasives, de-ionized water and SUBA IV pad [12] showed that the material removal rate was low (~30 nm/min). On the other hand, ceria abrasives were applied to increase the polishing rate of SiO_2 wafers and optical glass because of the ceria's high chemical reactivity [13,14]. Song et al. [15] carried out the CeO_2 abrasives for silicon wafer polishing at a high platen speed (200 rpm). Nevertheless, the influence of oxidizers was not considered in their study. Furthermore, colloid abrasive SiO_2 is the commercially used slurry for silicon CMP, yet the surface quality in terms of material removal rate and chemical pollution after CMP are still a big concern [16]. Both experimental and theoretical studies [13–17] seem to have indicated that the chemical effects in CMP are dominated by the pH values of the slurry and oxidizer. Various oxidants such as H_2O_2, KIO_3 and $Fe(NO_3)_3$ have been used in the CMP of copper, tungsten, SiO_2 and optical glass [18,19]. Among these oxidizing agents, H_2O_2 is preferable since it forms harmless decomposition and by-products in the reaction. However, to our knowledge, very little has been done on the investigation into the CMP of silicon wafers using H_2O_2 with Al_2O_3 or CeO_2 abrasives.

While there are many factors that influence the quality of a CMP process, as briefly discussed above, the aim of this paper is to investigate the chemical effects of oxidizer concentration and pH value on the material removal rate in the CMP of silicon wafers. Two types

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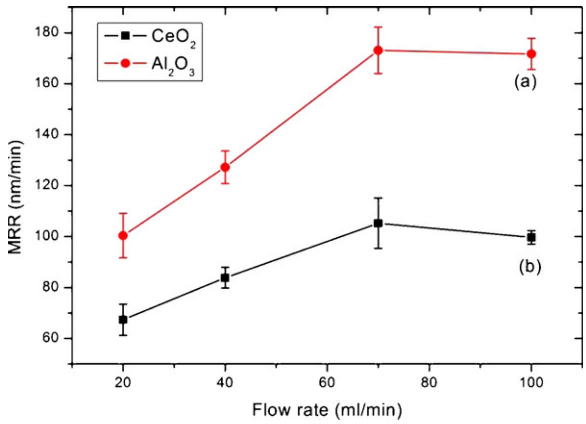

Fig. 1. Effect of slurry flow rate on *MRR*. Curve (a): slurry with Al_2O_3 abrasives, and curve (b): slurry with CeO_2 abrasives.

of abrasive materials, Al_2O_3 and CeO_2, will be used in the polishing slurries with an additive of H_2O_2. The influence of the slurry flow rate will be discussed, with an attempt to reduce the waste quantity of chemicals, such as oxidizers and pH chemicals. Although a desirable CMP process has both a high removal rate and good planarization, the degree of planarity was not considered in the present paper.

2. Experiment

The polishing experiments were conducted on commercially available (1 0 0) silicon wafers using a PM5 auto-lap precision lapping/polishing machine from Logitech Co. Two types of slurry were made in the laboratory. One contained Al_2O_3 abrasives (from Logitech Co.) and the other contained CeO_2 particles (from H.K. Yihel Trading Co.) of a normal diameter 50 nm. In both types of the slurry, de-ionized water and H_2O_2 (Analytically pure grade; from Sigma Co.) were used with the abrasive concentration of 2.5% Vol. NaOH and HCl were applied to adjust the pH value. To examine the slurry flow rate effect on the material removal rate, the slurry was delivered at variable flow rates from 20 to 100 ml/min. The sample size for the polishing tests was 20 mm × 15 mm. The polishing pad, of the diameter 300 mm, was Chemicloth Polishing Cloths, SKU:0CON-352 of Logitech made of urethane [8]. The wafer weight was measured before and after polishing to calculate the weight loss and material removal rate using a precision balance (resolution = 10^{-5} g, Sartφrius (BP 210D) Co.). Each test was repeated three times to verify the reproducibility of the experimental data. A UV/VIS/NIR spectrophotometry (Cary, 5E model) was used to obtain the transmittance spectra of ceria slurries in variable pH values and oxidizer concentrations at room temperature. The quartz analytical box for this purpose (optical prosperities, G380, Proscitech Co.) was made in house.

3. Results and discussion

3.1. The effect of flow rate on MRR

Fig. 1 shows the results using the polishing conditions of pressure = 20 kPa, oxidizer concentration = 0.4% Vol. and slurry pH value = 7. It is clear that the increase of the slurry flow rate promoted the polishing rate, regardless of the types of the abrasives used. This could be due to the increased wafer–abrasive interaction rate. However, when the slurry flow rate increased to a certain value (70 ml/min in the present case), the material removal rate became stable, indicating that the wafer–abrasive interaction had reached the maximum.

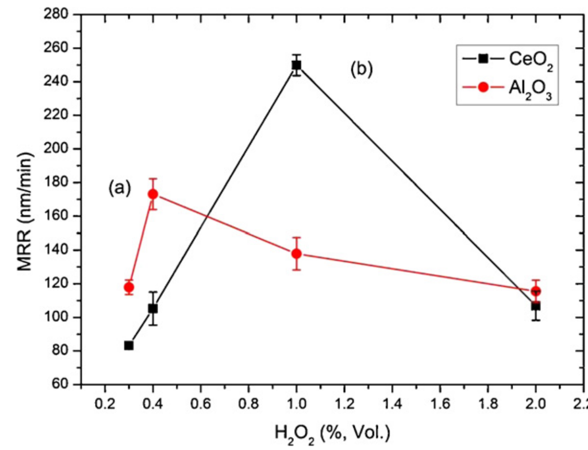

Fig. 2. Effect of oxidizer concentration on *MRR*.

The *MRR* with the Al_2O_3 slurry is much higher than with the CeO_2 slurry. This could be due to the aggregation of CeO_2 particles. In the absence of surfactant agents, the dispersion state of polishing slurry depends mainly on electrostatic means. The iso-electric point (IEP) of Al_2O_3 slurry pH is about 9–10 [20]. The agglomeration of Al_2O_3 slurry would not happen at pH = 7. However, the pH value of the slurry is around the IEP of CeO_2 (about 6–7) [21]. Thus in the case of CeO_2 abrasives, the electrostatic interaction of the particles becomes less repulsive. As a result, slurry agglomeration ensues, resulting in an increase in the size of an effective abrasive and, in turn, leading to a decrease in the number of effective abrasives (*N*) because the abrasive concentration in the slurry is a constant. A smaller *N* reduces *MRR*. Although a smaller *N* increases the force on an effective abrasive and thus its greater indentation or scratch depth (thus a larger *MRR*), *MRR* is more sensitive to the number of effective abrasives. Therefore, the more significant agglomeration of CeO_2 slurry leads to a smaller *MRR* compared with the case using Al_2O_3 slurry.

3.2. The effect of oxidizer concentration on MRR

Fig. 2 describes the variation of *MRR* with the oxidizer concentration (polishing conditions: pressure = 20 kPa, slurry flow rate = 70 ml/min, slurry pH = 7). Initially, the *MRR* is enhanced by the increase in oxidizer concentration. After reaching the maximum value, the *MRR* decreases. This is the same for both the CeO_2 and Al_2O_3 slurries, but the concentration points at the peaks of *MRR* are different, H_2O_2 = 0.4% Vol. in the case of the Al_2O_3 slurry and 1.0% Vol. when the CeO_2 slurry was used. The initial rise in the oxidizer concentration promotes the chemical reaction between Si and H_2O_2, forming soft chemical layers of silicon. At a lower oxidizer concentration, the fraction of reacted Si wafer surface is low. An addition of chemicals increases the fraction, leading to a higher *MRR*. After the saturation stage, more oxidizer concentration will not create more areas of reacted surface; *MRR* can no longer increase.

On the other hand, it is well known that the chemical reaction at a liquid and solid interface depends on their contact angle. A smaller contact angle accounts for a better interfacial wettability, which enhances the chemical reaction at the solid–liquid interface [22]. Using a contact angle meter (DIGIDROP, GBX, France), Lee et al. [16] investigated the relationship between contact angle and oxidizer (NaOH) concentration in silica slurry solution for the CMP of silicon wafers. They found that with the increase of oxidizer concentration, the contact angle would drop initially (thus an enhancement of chemical reaction and a higher *MRR*) but increase shortly (thus a reduced chemical reaction and *MRR*). This is in agreement with the