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Experimental Study on Cryogenic Polishing Single Silicon Wafer with Nano-sized Cerium Dioxide Powders

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Abstract. Cryogenic polishing single silicon wafer with nano-sized CeO_2 abrasives can be known as cryogenic fixed abrasives CMP (CFA-CMP). The abrasive slurry was made of nano-sized CeO_2 particles dispersed in de-ionized water with a surfactant and the polishing slurry froze to form cryogenic polishing pad. Then the polishing tests of the blanket silicon wafers in the presence of the cryogenic polishing pad containing the nano-particulates were carried out. The morphologies and surfaces roughness of the polished silicon wafers were observed and examined on an atomic force microscope (AFM). The results show that a super smooth surface with roughness of 0. 293 nm is obtained within 5000 nm× 5000 nm and the removal of material is dominated by plastic flowage.

Introduction

Integrated circuits (ICs) are built on semiconductor wafers. Over 90% of semiconductor wafers are silicon [1]. But the silicon wafers not only need to have very good flatness and low surface roughness but also have no surface damage and scratches. Silicon is a kind of hard brittle material and easy to fail in a way of wear-out-failure because of brittle fracture, so it is difficult to machine this kind of hard brittle material. Silicon wafers are polished currently by chemical mechanical polishing (CMP) mostly. CMP technique has been widely used in planarizing semiconductor wafers and attracted more and more attention from the researchers [2-4]. Ceria has been commonly used as an abrasive for glass polishing. It has the fasted polishing rate among those of SnO_2, TiO_2, ZrO_2, CrO_2, Al_2O_3, La_2O_3 and so on [5]. Recently, ceria slurry has also been used in the field of semiconductor CMP process for planarization of intermetal dielectrics [6, 7], and good polishing performance has been demonstrated.

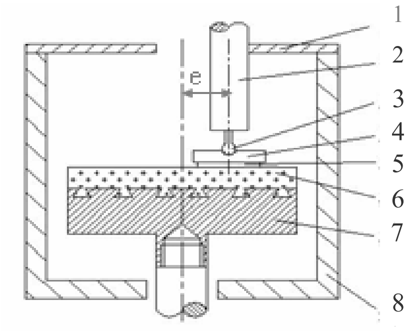
Some defects of the machined surface, such as residual stress, micro-cracks and surface damages, can be decreased in the cryogenic conditions [8-10]. In recent years, some polishing tests of blanket silicon wafers in the presence of the cryogenic polishing pad containing colloidal SiO_2 slurry were carried out and a smooth surface with an average roughness of 1.29 nm has been obtained [11]. However, few polishing tests with respect to the blanket silicon wafers with cryogenic polishing pad containing nano-sized ceria slurry have been carried out and the cryogenic polishing mechanisms have not been studied deeply in the field of semiconductor.

This paper aims to carry out some polishing tests with respect to the single silicon wafers in the presence of the cryogenic polishing pad containing nano-sized CeO_2 slurry and investigate the cryogenic polishing effect and mechanism.

Experimental

As Fig.1 shows, the CFA-CMP was carried out on a wafer polisher with an ice pad. During the polishing experiment, the wafer was mounted on an object carrier of 3 in. diameter. The applied pressure was controlled by an air cylinder. The down force pressure was kept at 0.05 MPa and the polisher rotated at 400 rpm. The eccentricity was kept at 10 mm and the polishing time was 60 min.

Single-crystal Si(100) wafer of 3 in. diameter was chosen in this study. The abrasive slurry was made of CeO_2 particles dispersed in de-ionized water with a surfactant. The particles used had a mean diameter of about 20 nm with a purity level of more than 99.9% (as shown in Fig.2). An organic polymer-type surfactant (0.05 wt %) was added to get a stable suspension. The concentration of CeO_2 was 1 wt %. The pH value (measured by PHS-3C at 21℃)of the slurry was fixed at 11.03 to get the most stable suspension. Then the polishing slurry froze in a die to form a cryogenic polishing pad, as shown in Fig.3. As comparison, the silicon wafer was prepared with conventional procedures as rough lapping with 305# and 303# silicon carbide, fine lapping with 302# silicon carbide and pre-polishing with 2.6 μm and 0.8 μm CeO_2 abrasives, respectively. The morphologies and surfaces roughness of the polished silicon wafers were observed and examined on an AFM (CSPM-4000). The AFM morphology of the pre-polished silicon wafer surface is shown in Fig.4. From Fig.4, it can be seen that the undulation of the pre-polished surface is bigger and there are some tubercles. The chemical reaction between CeO_2 and Si under alkaline condition was evaluated by using X-ray diffraction technique for phase identification.



1. Cover plate
2. Air cylinder
3. Pressure head
4. Object carrier
5. Workpiece
6. Ice
7. Die
8. Wall panel

Fig.1 Schematic diagram of cryogenic polishing apparatus

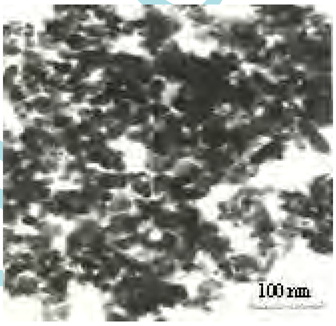


Fig.2 TEM micrograph of cerium dioxide powders

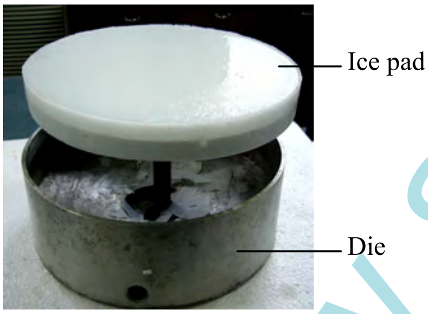


Fig.3 Cryogenic polishing pad

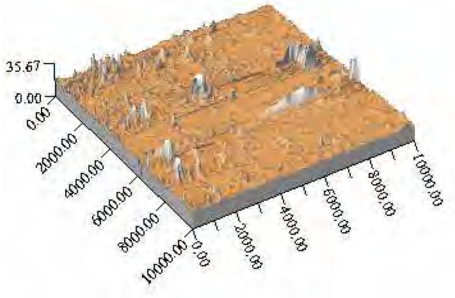


Fig.4 AFM morphology of pre-polished silicon wafer surface (within 10000 nm×10000 nm)

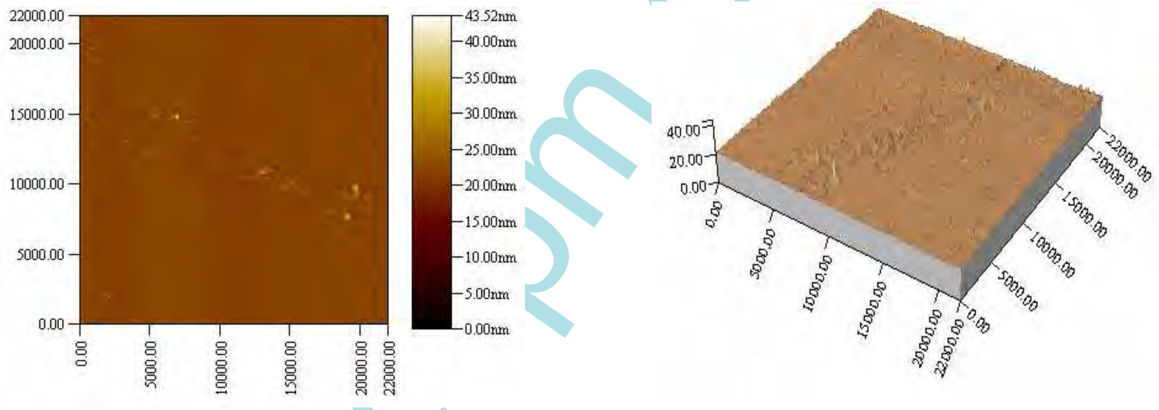
Experimental result and analysis

AFM Evaluation. The surface roughness of silicon wafer within different dimensions is shown in Table 1. As shown in Table 1, the surface roughness of silicon wafer polished with 20 nm CeO_2 particles is obviously smaller than that of pre-polished and a super smooth surface with an average roughness of 0. 293 nm is obtained within 5000 nm×5000 nm. The AFM morphologies of silicon wafer surface polished with nano-sized CeO_2 particles within 22000 nm ×22000 nm are shown in Fig.5. As shown in Fig.5, the undulation of polished surface is smaller and there are few tubercles. This super smooth surface benefited from the special cryogenic polishing mechanism.

Polishing Mechanism of CFA-CMP. When making cryogenic polishing pad, the bonding agent was de-ionized water and the abrasives were frozen into ice pad, so the ice pad can be known as cryogenic fixed abrasives polishing pad (CFA-PP). During the cryogenic polishing, though the temperature of the polishing pad was very low, the ambient temperature in the working area was about 3~5°C. And according to the theory of tribochemistry [12], high-temperature and high-pressure can be produced at the local contact point between the abrasives and the silicon wafer during the polishing. So, the temperature at the contact point can be greater than 0°C and there will be a thin liquid film between the polishing pad and silicon wafer after the superficial coat of the polishing pad thaws. With the polishing carries on unceasingly, the abrasives in the superficial coat of the polishing pad can pull off and the new ones can emerge continuously. Therefore, this CFA-PP has the ability of self-dressing. Another result of the high-temperature and high-pressure produced at the local contact point between the abrasives and the silicon wafer during the polishing is that it can cause a series of tribochemical reaction. Under alkaline condition, there will be a soft corrosion layer formed on the surface of the silicon wafer and then the soft corrosion layer will be removed by mechanical action of the abrasives, simultaneously, new surface will emerge. And this can make the whole chemical-mechanical reaction progress loop around.

Table 1 Surface roughness of silicon wafer within different dimensions

Surface states	5000 nm×5000 nm		10000 nm×10000 nm		22000 nm×22000 nm	
	R_a [nm]	*RMS* [nm]	R_a [nm]	*RMS* [nm]	R_a [nm]	*RMS* [nm]
Pre-polished	0.934	1.790	1.030	2.420	1.136	3.042
Polished with ceria slurry	0.293	0.406	0.390	0.744	0.396	0.669



(a) Two-dimensional pattern (b) Three-dimensional pattern

Fig. 5 AFM morphologies of blanket silicon wafer surface polished with nano-sized CeO_2 particles (within 22000 nm × 22000 nm)

Chemical Reaction. The pH value (measured at 21°C) of the polishing wastes was 10.22 and this means that chemical reaction occurred during CFA-CMP. The X-ray diffraction technique was applied in order to make clear the mechanism of the chemical reaction under CFA-CMP process. Fig.6 shows the X-ray diffraction patterns of a silicon wafer before and after chemical corrosion in the 20 nm CeO_2 slurry under alkaline condition. The concentration of CeO_2 was 1 wt % and the pH value (measured at 0°C) of the slurry was 10.95. The temperature of the slurry was 0°C and the time of chemical corrosion was 60 min. As shown in Fig. 6, the angle of the initial diffraction maximum of the silicon wafer does not change before and after chemical corrosion, however, there is a new diffraction peak at 69.47° after chemical corrosion. This indicates that there is some new substance formed on the surface of the wafer and the new substance may be the soft corrosion layer. Removal of silicon during CMP is explained by an attack of OH^- to silicon atoms catalyzing the corrosive reaction of H_2O resulting in cleavage of silicon bonds [13]. The chemical equation is as following:

$$Si + 2OH^- + H_2O \rightarrow SiO_3^{2-} + 2H_2 \uparrow \qquad (1)$$

If SiO_3^{2-} ion in the slurry can not be removed immediately, SiO_3^{2-} can hydrolyze according the following equation:

$$SiO_3^{2-} + 2H_2O \rightarrow H_2SiO_3 + 2OH^- \qquad (2)$$

The hydrolysis product H_2SiO_3 can partly polymerize into hydrated silica and simultaneously another part of H_2SiO_3 can ionize to form SiO_3^{2-} ion. In the end, the silicate colloid $\{[SiO_2]_m \cdot n\, SiO_3^{2-} \cdot 2\,(n-x)\, H^+\}^{2x-} \cdot 2xH^+$ can be formed. The silicate colloid covered the silicon wafer surface and is the main component of the soft corrosion layer. Otherwise, CeO_2 could be changed to oxygen deficient nonstoicheometric (Ce, Si) O_{2-x} compound because Ce cation has Ce^{4+} and Ce^{3+} while Si cation has only Si^{4-}. The tentative compound (Ce, Si) O_{2-x} could be crystalline [14]. The formation of silicate colloid $\{[SiO_2]_m \cdot n\, SiO_3^{2-} \cdot 2\,(n-x)\, H^+\}^{2x-} \cdot 2xH^+$ and amorphous Si-Ce-O in CFA-CMP process seems to be the key mechanism. So, the soft corrosion layer is composed of the silicate colloid $\{[SiO_2]_m \cdot n\, SiO_3^{2-} \cdot 2\,(n-x)\, H^+\}^{2x-} \cdot 2xH^+$ and the amorphous Si-Ce-O.

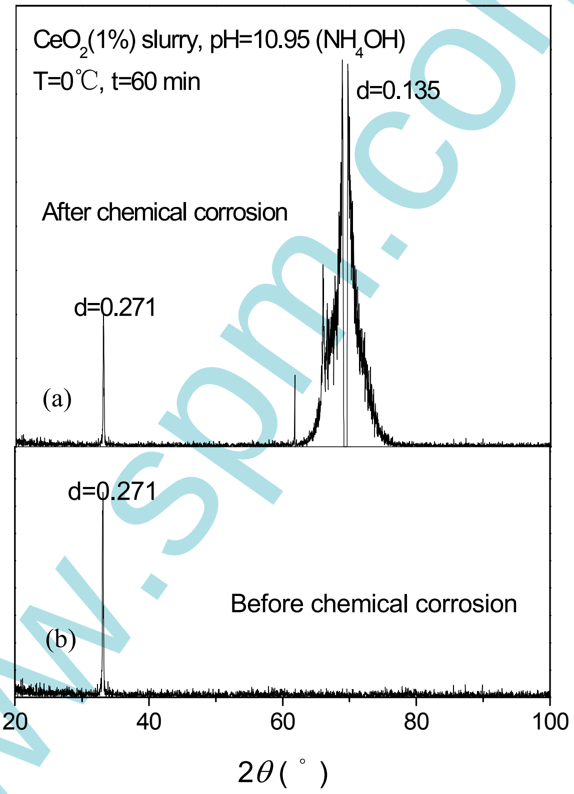


Fig.6 X-ray diffraction patterns of silicon wafer (a) before chemical corrosion (b) after chemical corrosion

Mechanical Action of the Abrasives. Fig.7 shows the model of CFA-CMP. If the thickness of the soft corrosion layer is σ, the depth a_0 that the nano particles embed the bulk of silicon wafer can be expressed as follows:

$$a_0 = a - \sigma \qquad (3)$$

Where a is the depth that the nano partiles embed the surface of the silicon wafer.

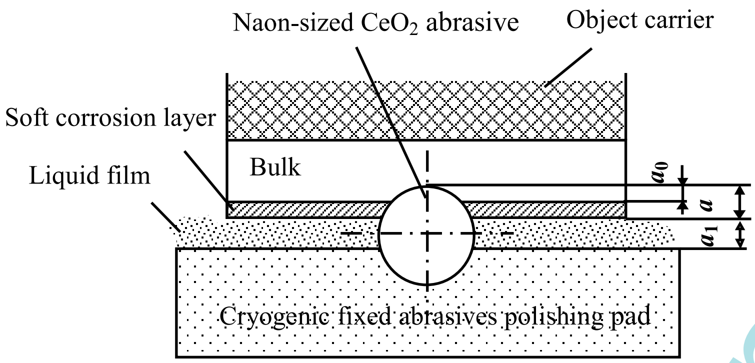


Fig.7 Model of material removal of CFA-CMP

From Eq. (3), we can see that the soft corrosion layer decreases the depth that the nano particles embed the bulk of silicon wafer. Otherwise, there are some polishing slurry between the polishing pad and silicon wafer after the superficial coat of the polishing pad thaws. So, during polishing, a stable thin liquid film can form because of the dynamic pressure produced by the stable rotation of the object carrier and the polishing pad. As shown in Fig. 7, assuming that the thickness of the liquid film is a_1, this film also has the effect of decreasing the depth that the nano particles embed the bulk of silicon wafer.

The transition from a brittle to a ductile mode during the machining of brittle materials is described in terms of energy balance between the strain energy and the surface energy [15]. It was found that there was a critical grain depth of cut for the brittle-to-ductile transition. For grain depths of cut below the threshold value, the material removal process was largely ductile. For the grain depths of cut above the threshold value, the material removal process was mostly ductile.

From the above analysis, we can see that when the abrasives are in the nano scale, the soft corrosion layer can obviously decrease the depth that the nano particles embed the bulk of silicon wafer, that is to say, the grain depth of cut decreases. And it is beneficial to processing in the ductile mode, decreasing the roughness of the polished surface and improving the polishing quality.

Conclusions

In this paper, the polishing tests of blanket silicon wafers with a cryogenic polishing pad containing the nano-ceria slurry were carried out to investigate the polishing effect and mechanism.

The following conclusions can be drawn:

1. Nano-sized powders of CeO_2 were collocated into polishing slurry and then the polishing slurry froze to form a cryogenic polishing pad. With the cryogenic polishing pad, a super smooth surface with an average roughness of 0.293 nm is obtained within 5000 nm×5000 nm.
2. Because the size of 20 nm CeO_2 is very small and there exists a soft corrosion layer and a stable thin liquid film between the silicon wafer and ice pad during polishing, the cutting depth of the abrasive decreases and the removal of material is dominated by plastic flowage.
3. The CFA-PP has the ability of self-dressing. The chemical corrosion and mechanical removal simultaneously exist during the cryogenic polishing of silicon wafer.

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